

Identification of the thermal response of confined fluids to mechanical shear deformation

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BOOK OF ABSTRACTS

Annual European Rheology Conference 2022



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15th Annual European Rheology Conference VIII Iberian Meeting on Rheology

> Seville, Spain April 26-28, 2022

BOOK OF ABSTRACTS



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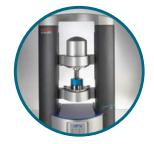


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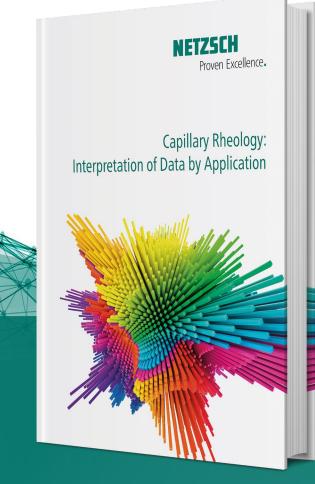
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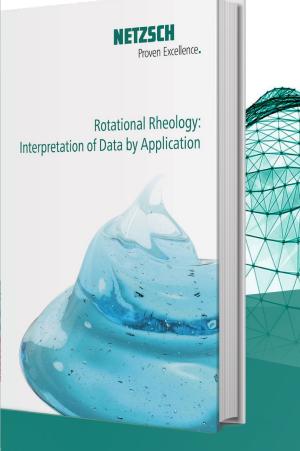
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Welcome to AERC 2022 in Seville

Dear participants of the joint Annual European Rheology Conference (AERC 2022) and the VIII Iberian Meeting on Rheology (IBEREO 2022), welcome to Spain and welcome to Seville. This is the second European Rheology Conference held in the city of Seville. The first one, the IVth European Rheology Conference, was held in 1994 and was an important step towards the foundation of the European Rheology Society in 1996.

As you know, the pandemic forced us to postpone the conference which was previously scheduled for April 2021. In addition, the threat of an uncontrolled expansion of the outbreak of COVID 19 infections has been present all this time. This has largely conditioned efforts to organize the conference.

We had to make a key decision about the format of the congress, at the height of the highest incidence of the virus in the last outbreak. We were committed to carrying out oral communications entirely in person, although conditioned by possible health restrictions. As for the poster communications, we opted for an asynchronous virtual format, with the aim of minimizing overcrowding, which has led us to cope with changes with respect to the AERCs prior to the pandemic.

We want to thank all the attendees for the enthusiasm shown in the conference and, especially, for the patience and effort made to adapt to all the constraints that have arisen.

The scientific program consists of 3 plenary lectures, 11 symposia for oral communications and more than 150 poster communications. Professor Jeffrey Morris, as the 2022 Weissenberg Awardee, will present the opening plenary lecture. The other two plenary lectures will be given by Professor Gareth McKinley and Professor Annie Colin. The 267 oral presentations, 14 of which are keynote lectures, have been distributed in 6 parallel sessions. Poster communications can be viewed asynchronously before or during the conference.

On behalf of the AERC2022 Organizing Committee, we would like to pay a special tribute to one of our colleagues and dear friends, Professor Lionel Choplin, who passed away unexpectedly in November 2021. In addition to his significant contributions to the field of rheology, Lionel actively contributed to the 4th ERC held in Seville in 1994, organizing the symposium on Industrial Rheology. Therefore, we would like to dedicate the symposium on rheology and industrial processing to honor the memory of Professor Lionel Choplin.

The AERC 2022 aims to cover all the fields where rheology is relevant for the advancement of scientific knowledge and technology. Ranging from the topics of more academic interest to a variety of industrial applications, it also seeks to contribute to tackling the issues of sustainable development and societal welfare, in consonance with the motto of the congress: Transdisciplinary Rheology, a bridge to sustainable progress and welfare.

We would like to express our gratitude to all the conference sponsors for helping us make this conference an outstanding event. In addition, we would like to pay special thanks to the organizers of the symposiums, for their generous and relevant work, as well as to all the participants who are undoubtedly contributing to make the AERC2022 a conference of great scientific success.

Welcome, enjoy the AERC 2022 Conference and your stay in Seville!

Antonio Guerrero and Teresa Cidade for the AERC 2022 Organizing Committee

ESR President Address

Dear Members of the European Society of Rheology,

with a great emotion I welcome you back to an in-person conference of the European Society of Rheology. The last years were characterized by the Covid-19 pandemic that first forced the rheology international community to postpone the International Congress on Rheology (ICR2020) for a few months and then to run it online.

As European Society of Rheology we also had to face the pandemic and indeed the 14th Annual Rheology Conference, first scheduled in Seville, became a virtual Conference in cyberspace (AERC2021). I am personally very grateful to the organizers of AERC 2021 (Roland Kadar and Mats Stading) for having made possible to keep the frequency of our annual meetings unchanged. The same gratitude is deserved to the organizers of the 15th Annual Rheology Conference for their prompt reaction to all the difficulties we faced and for their flexibility to modify the plans already organized so to meet the new requirements imposed by the Covid-19 pandemic in a way to allow us to meet again in-person.

Difficulties never come alone and indeed while I am writing this welcome letter, we are living a horrible war within Europe. We are not insensitive to this, and all our thoughts are addressed to people who are suffering, without distinction of nationality. We believe that the European community, whatever it may be, political or scientific, is founded on peace and so the European Society of Rheology firmly condemns war.

However, science is free, it makes people free, and freedom promotes peace. So,

welcome to Seville and to the Annual European Rheology Conference 2022 (AERC 2022)!

We are looking forward to an exciting scientific program, which will certainly keep us busy for the next days. We are eager of sharing ideas, of discussing of scientific topics and of networking among us. I am sure that AERC 2022 in Seville will be the best place where to do all these things in a quiet, friendly, and peaceful environment.

All this would not be possible without the enthusiastic and professional commitment of the local organizing committee, chaired by Antonio Guerrero and Teresa Cidade and composed of Jose Munoz Garcia, Jose María Franco, Pedro Partal, Felipe Cordobés, Anabela Raymundo, Carlos Bengoechea, Alberto Romero, Manuel Felix, and Luis Alfonso Trujillo. The session chairs, the exhibitors, the sponsors, and those who are working 'behind the scenes' were equally fundamental for the success of the conference.

I really thank you all very much!

Enjoy a very successful Annual European Rheology Conference 2022.

Mario Minale

President of the European Society of Rheology

Members of the Local Organizing Committee









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Emulsions, Foams and	Jan Vermant, Mario Minale and
Interfacial Rheology:	Teresa Sanz
Suspensions:	F. Galindo-Rosales, Francisco Rubio and Octavio Manero
Experimental Methods and New Advances in Rheometry:	Dimitris Vlassopoulos, Loic Hillou and Paula Moldenaers
Food Rheology:	Bettina Wolff, Isabel Sousa and M ^a Jesús Hernández
Industrial Rheology and Processing:	Francisco Martínez-Boza, María Graça Rasteiro and Patrick Anderson
Bio-rheology and Medicine:	Catarina R. Leal, Críspulo Gallegos and Mats Stading
Micro-, Nanofluidics and Microrheology:	Amy Shen, Anke Lidner and Juan Francisco Vega
Non-Newtonian Fluid Mechanics and Computational Rheology:	Baltasar Mena, Corneliu Balan and Miguel Nóbrega
Gels and Self Assembling Structures:	Domenico Gabriele, Joao Maia and Juan de Vicente
Polymer Solutions and Melts:	Antxon Santamaría, Evelyne Van Ruymbecke and Moshe Gottlieb
Solids, Glasses and Composites:	Alexandra Aulova, Nadia El-Kissi and Joamin Gonzalez-Gutierrez

Conference Program (I)

	Tuesday 26 th - Morning							
	Giralda I-II	Santa Cruz	Nervión	Prado	Arenal	Giralda VI-VII		
08:30	Opening (Giralda I-II)						08:30	
09:00	J. Morris (PL1) - Giralda I-II Rheology and fluid mechanics of concentrated suspensions						9:00	
10:00			Coffee	Break			10:00	
Chairs	Marco Ellero	Gareth Mckinley	Annie Colin	Catarina Leal	Mario Minale	Anke Lindner	Chairs	
10:30	NF1 - D. Nieto Simavilla Learning of constitutive equations for multiscale simulation of dilute polymeric solutions using a GENERIC-guided approach	GS1* - S. Jamali "Keynote Lecture Network physics and emergence of	SP1 - L. Kool Oscillatory compression of soft particles	BM1* - M. Rodriguez Hakim "Keynote Lecture	EI1 - E. Chatzigiannakis Studying droplet coalescence at different length-scales: from films to droplets	MN1 - A. Darras In vivo and in silico red blood cell lingering and partitioning in the microcirculation	10:30	
10:50	NF2 - N. Moreno Complex flow simulations of micros- tructured-fluids using a Lagrangian Heterogenous Multiscale Method	elasticity in colloidal gels: Mechanical perspective"	SP2 - J. Majesté Modelling extensional rheology of polyo- lefin based suspensions	The influence of saliva rheology on sheet formation and aerosolization"	SP2 - J. Majesté extensional rheology of polyo-	"Keynote Lecture Studying droplet coalescence at different length-scales: from films to droplets"	MN2 - J. Vega Tears for microrheology: Experimental study of artificial eyedrops	10:50
11:10	NF3 - C. Balan Is any logic behind the principles of the constitutive relations?	GS3 - F. Müller Influence of surface topography on the yielding of thermo-reversible colloidal gels	SP3 - F. Blanc Measurement of suspensions transient viscosity upon any change of shear direction thanks to a novel Cross-Rheo- meter apparatus	BM3 - C. Giacomin Hagfish slime behavior in particle-laden environments	E12 - L. Torres Interfacial viscoelastic properties and stability of emulsions	MN3 - V. Calabrese Alignment of colloidal rods in crowded environments	11:10	
11:30	NF4 - M. De Micco Machine-learning-based measurement of the relaxation time of viscoelastic fluids via particle ordering	GS4 - V. Garbin Tuning local microstructure of colloidal gels by ultrasound-activated deformable inclusions	SP16 - A. Fall Viscous dissipation in sheared unsaturated wet granular materials	BM4 - C. Wagner Viscosity of the intercellular liquid in Red Blood Cells	El3 - A. Majhi Coupling flow directions in emulsions with wall roughness	MN4 - Z. Li Dynamics of flexible Brownian filaments in 2D porous media	11:30	
11:50	NF5 - G. Giusteri Flow-type dependent rheologies and multiscale simulations	GS5 - T. Gibaud Interpenetration of fractal clusters drives elasticity in colloidal gels formed upon flow cessation	SP5 - E. Masghouni Shear and elongation rheology of filled polymers and their nano-structured multicomponent systems for ultra-high absorbance of EMR (electromagnetic radiation)	BM5 - U. Windberger Blood rheology in contact to biological surfaces	El5 - P. Capobianchi Shear rheology of a dilute ferrofluid emulsion: modelling and numerical simulation	MN5* - L. Casanellas "Keynote Lecture Microfluidic flow of vesicle prototissues	11:50	
12:10	NF6 - A. Colly Understanding instabilities for additive manufacturing in partially ordered system	GS6 - P. Lehéricey Probing plastic rearrangements in colloidal gels	SP6 - X. Chateau Contact and macroscopic ageing in colloidal suspensions	BM6 - C. Psevdos A monophasic blood flow model with slip for precise and accessible prediction of wall shear stresses in the microcircu- lation	El6 - C. Delgado-Sánchez Novel heat transfer fluid obtained by non-aqueous phase change emulsion	as a model for cellular tissues"	12:10	
12:30			Lu	nch			12:30	







Conference Program (II)

	Tuesday 26 th - Afternoon							
	Giralda I-II	Santa Cruz	Nervión	Prado	Arenal	Giralda VI-VII		
Chairs	Corneliu Balan	Joao Maia	Jeffrey Morris	Christian Wagner	Miguel Ángel Rubio	Juan Francisco Vega	Chairs	
13:50	NF7* - M. Graham "Keynote Lecture Elastoinertial turbulence via	GS7 - A. Poulesquen The gel/glass duality of weak colloidal gels	SPT - J. Ruiz-López Simulations of concentrated suspensions of rough parti-cles under boundary, mixed and full-film lubrication regimes	BM7 - M. Grassi Effect of cystic fibrosis sputum rheology on lungs drug delivery by inhalation	EI7 - O. Mileti Interfacial characterization and stability study of bituminous emulsions	MN7 - F. Bonacci Dynamics of semiflexible filamentsin oscillatory shear flows	13:50	
14:10	Tollmien-Schlichting instability"	GS8 - G. Camacho Villar Influence of particle size and magnetic field strength in the directed self-assembly under toggled fields	SP8 - M. Orsi Influence of coupled friction and adhe- sion on the rheology of non-Brownian suspensions	BM8 - M. Braunreuther In situ magnetic microrheology of airway mucus	El8 - E. Gilbert Controlling rheology of a solid emulsion with phase-changing droplets	MN8 - A. Jeyasountharan Microfluidic device to reduce multi-par- ticle string formation and self-assemble particles in microfluidic flow	14:10	
14:30	NF9 - R. Ghanbari Taylor-Couette stability modes of cellu- lose nanocrystals suspensions directly from birefringence patterns	GS10 - L. Hilliou Nonlinear elastic properties of gels made of different types of gelling carrageenan and their blends	SP9 - F. Balboa-Usabiaga Rheology of suspensions of star colloids	BM9 - R. Ferraro Cancer viscoelasticity: A dynamic compression assay for tumor spheroids characterization	EI9 - B. Medronho Microrheology of novel cellulose stabili- zed oil-in-water emulsions	MN9 - N. Burshtein Transport dynamics of microparticles in inertio-elastic vortex flows	14:30	
14:50	NF10 - K. Zinelis The fluid dynamics of dripping onto a substrate	GS11 - F. Dutertre Chitosan-based hydrogels: Influence of crosslinking strategy on rheological properties	SP10* - O. Volkova "Keynote Lecture Capillary and rotational flow of a	BM10 - A. Wierschem Studying the impact of microtubule polymerization affecting anti-cancer drugs on the cell mechanics with a monolayer rheometer	El10 - C. Guidolin Controlling foam ageing in viscoelastic media	MN10 - F. Del Giudice Controlled viscoelastic particle encapsulations in microfluidic devices	14:50	
15:10	NF11 - O. Manero Constitutive modeling for flowing mice- llar solutions: the structure factor	GS12 - M. Jiménez-Rosado Thermoresistant collagen/chitosan hydrogels for regenerative applications: Rheological and microstructural characterization	suspension of magnetic particles in the presence of discontinuous shear thickening"	BM11 - M. Hertaeg Jamming transition in biological tissues	EI11 - F. Lavergne Hallmarks of intermittent rearrange- ments in creep of liquid foams	MN11 - M. Villone Numerical study of the competitive effects of inertial and elastic forces on particle deformation and cross-streamli- ne migration in microfluidic flows	15:10	
15:30			Technical Exhibiti	on & Coffee Break			15:30	
Chairs	Natalie Germann	Nino Grizzuti	Philippe Coussot	Mario Grassi	Rosana Pasquino	Francesco Del Giudice	Chairs	
16:30	NF12 - R. Poole Generalised Newtonian fluid models in complex flows	GS13 - T. De Maeseneer The effect of temperature and particle size on the mechanical properties of particulate crosslinked gelatin-metha- cryloyl gels	SP12 - M. Trofa Numerical simulation of clogging in a microchannel with planar contraction	BM12* - S. Recktenwald "Keynote Lecture	El12 - T. Lenavetier Dissipative processes in an elementary foam	MN12 - T. Burghelea Dynamics of a single Newtonian droplet in a turbulent microscopic cross-slot flow of a shear thinning fluid	16:30	
16:50	NF13 - R. Hill The Oldroyd-A model	GS14 - L. Alves Controlling the gelation of cellulose-based systems: Macro- and microrheology studies	SP13 - J. Maia Microstructure and rheology of confined semi-dense and dense suspensions: Effect of confinement, flow rate and particle rigidity	Al-based microfluidic assessment of pa- thological red blood cell flow properties"	EI13 - P. Anderson Constitutive framework for rheologically complex interfaces with an application to elastoviscoplasticity	MN13 - J. Baué Role of the interfacial rheology on dro- plet dynamics in micro Hele-Shaw cell	16:50	
17:10	NF14 - S. Varchanis Shear-thinning and shear-thickening effects in the Oldroyd-B model	GS15 - S. Russo Spena Relations between rheology and processing properties in the 3D-printing of k-Carrageenan physical hydrogels	SP14 - E. Lemaire Impact of particle stiffness on non-Brownian suspension rheology	BM14 - C. Leal Rheology of bacterial cellulose wound dressing membranes	EI14 - M. De Corato Retraction of thin films coated by insoluble surfactants	MN14 - A. Cirillo Characterization of the elongational behavior of a viscoelastic fluid through a microfluidic approach	17:10	
17:30	NF15 - E. Southern Koopman with control for constitutive law identification	GS16 - A. Borrero-López Lignin as effective filler for enhancing cushioning properties of castor oil-based elastomers: Rheological and mechanical properties	SP15 - M. Minale Frequency dependent threshold for irre- versibility in non-Brownian suspensions	BM15 - S. Geisel Experimental challenges in characterizing the bulk rheology of bacterial biofilms	El21 - O. Laukkanen Shear and dilatational rheology of microgel monolayers at the oil-water interface: a comparison between ultra-low crosslinked and regularly crosslinked pNIPAM microgels	MN15 - M. Smith Machine learning boosts rapid microrheology with optical tweezer measurements	17:30	
	NF16 - D. Amoroso Numerical simulations of the stretching	SP4 - J. Carneiro Novel PDMS particle transparent sus-	SP27 - T. Voigtmann Yielding and history dependence in	BM16 - A. Ryl New criterion for assessing the potential	El16 - N. Di Spirito Bubble breaking dynamics	MN16 - R. Gupta	17:50	
17:50	and leveling flows of freestanding axisymmetric viscoelastic liquid films	pensions suitable for visualization and velocimetry experiments	fluidity models for glassy suspensions	of in situ gelling systems as injectable scaffolds	in complex fluids	Capillary flow of wormlike micellar gels		

Conference Program (III)

Wednesday 27 th - Morning							
	Giralda I-II	Santa Cruz	Nervión	Prado	Arenal	Giralda VI-VII	
08:30			• • • • • • • • • • • • • • • • • • • •	L2) - Giralda I-II lex fluids and soft solids using fractional calc	ulus		8:30
Chairs	Michael Graham	Juan De Vicente	Evelyn van Ruymbeke	Patrick Anderson	Dimitris Vlassopoulos	María Jesús Hernández	Chairs
09:30	NF17 - E. Rossi Simulations of thixo-viscoplastic flows around a cylinder using the Smoothed Particle Hydrodynamics method	GS17 - A. Leon-Cecilla Mechanical and microscopic characteri- zation of alginate hydrogels dehydrated under controlled stresses	SM1* - S. Costanzo "Keynote Lecture	IP1 - S. De Rosa Experiments and numerical simulations of the die swell pheno-menon of viscoe- lastic materials in 3D printing processes	EM1 - J. Sanders Rimming flow for measuring the complex viscosity $H^*(\Omega)$	FR1 - A. Ahlinder Utilising rheology in food 3D printing to achieve attractive meals for dysphagia patients	9:30
09:50	NF18 - S. Sneijders Simulating collisions of viscoelastic inhomogeneous droplets with smoothed particle hydrodynamics	GS18 - E. Guilbert Gelation of protein aggregate suspensions by salt diffusion	Strain hardening of unentangled polymer solutions in fast shear flows"	IP2 - M. Spanjaards Numerical study of the effect of thixotro- py on extrudate swell	EM2 - F. Del Giudice Rapid temperature-dependent rheolo- gical measurements of non-Newtonian solutions using a machine-learning aided microfluidic rheometer	FR2 - J. Santos Shear flow and microstructure of micro- fluidized pea fiber suspensions	9:50
10:10			Coffee	Break			10:10
Chairs	Michael Graham	Juan De Vicente	Antxon Santamaría	Patrick Anderson	Dimitris Vlassopoulos	María Jesús Hernández	Chairs
10:40	NF19 - C. Oishi Simulations of viscoelastic droplet-droplet collision	GS19 - S. Wojno Effect of sulfate content and counterion on phase transition of cellulose nano- crystal suspensions	SM3 - M. Zatloukal Measurement and modeling of uniaxial and planar exten-sional viscosities for various polymer melts in very fast flows	IP3 - M. Zare Entrainment of a viscoplastic fluid into a Newtonian fluid by a bubble crossing the interface between liquid layers	EM3 - T. Rüther A novel correction method for the shear rate in a couette rheometer	FR3* - A. Raymundo "Kevnote Lecture	10:40
11:00	NF20 - S. Bindgen Yielding mechanisms in capillary suspensions	GS20 - M. Tassieri What caging force cells feel in 3D hydro- gels: A rheological perspective	SM4 - O. Hassager Small-angle neutron scattering study of the structural relaxation of elongationally oriented, moderately stretched three- arm star polymers	IP4 - S. Varchanis Torsional instability of constant viscosity elastic liquid bridges	EM4 - K. Lennon A data-driven method for automated superposition of rheological data	Influence of rheology in 3D printing of protein based doughs"	11:00
11:20	NF21 - A. Pereira Maximum spreading of impacting Newtonian and viscoplastic drops: Highlighting controversial scaling laws through numerical simulations	GS21 - C. Wobill Influence of substrate composition and viscoelasticity on growth of filamentous fungi	SM5 - G. lanniruberto Modelling unentangled polymer melts in fast flows	IP5 - C. Georgantopoulos Understanding the sharkskin instability of filled rubber compounds: Investigating the influence of die geometry and filler dispersion	EM5 - J. Laeuger Polarized imaging: An essential tool for rheological investigations on complex fluids	FR5 - J. Zink Pre- and post-process evaluation of meat analogue texturability using high-pressure shear rheology and dynamic mechanical analysis	11:20
11:40	NF22 - K. Zografos The closed form Adaptive Length Scale model: Properties and performance for simple and complex flows	GS22 - M. Lopez-Lopez Rheological behavior of alginate-based magneto-polymer composites	SM6 - E. Gkolfi Investigating the structure-dynamics relation of star-shaped polymers in melts through atomistic molecular dynamics simulations	IP6 - M. Di Martino CFD characterization of the hollow-cone spray process: Newtonian and non-New- tonian fluids comparison	EM6 - M. Wilhelm Advanced combined rheometer setups to in-situ correlate molecular insights with mechanical properties	FR6 - N. Grizzuti Rheology-driven design of pizza gas foaming	11:40
12:00	NF23 - M. Krapez Soft blade coating of complex fluids	GS23 - S. Perez Robles Multiwave rheological tests to study thermogelation of HydroxyPropyl Methyl- Cellulose (HPMC) aqueous solutions	SM7 - V. Hirschberg Molecular origin of rheological properties of well-defined Polystyrene POM-POM model systems and comparison with well-defined PS combs and stars	IP7 - C. Gracia Fernández Rheological characterization of composi- tes used in 3D printing	EM7 - K. Amini High resolution Doppler Optical Coherence Tomographic (D-OCT) mea- surements of near-wall velocity profiles in duct flows of viscoelastic fluids	FR7 - I. Sousa Lupin and chickpea yoghurts, the importance of rheology measurements on product development	12:00
12:20			Lu	nch			12:20







Conference Program (IV)

	Wednesday 27 th - Afternoon							
	Giralda I-II	Santa Cruz	Nervión	Prado	Arenal	Giralda VI-VII		
Chairs	lan Frigaard	Manilo Tassieri	Ole Hassager	María Graça Rasteiro	Loic Hilliou	Isabel Sousa	Chairs	
13:40	NF24 - S. Sinha Disorder and non-linearity in immiscible two-phase flow in porous media		SM8 - C. Hannecart Tube-based modeling of stress relaxa- tion of bidisperse linear polymer blends in the linear regime of deformation	IP8 - I. Calafel Flexible PVC foams by 3D-printing: Rheological aspects	EM8* - D. Curtis "Keynote Lecture	FR8 - P. Mouraka Jamming of non-colloidal plant cell-wall particles: the role of packing, mechanical properties, and surface interactions	13:40	
14:00	NF25 - V. Niggel Imaging dense suspensions under shear	GS25 - Q. Sun Polymer induced liquid crystal phase behaviour of cellulose nanocrystal (CNC)	SM9 - S. Coombs Complex viscosity of star-branched macromolecules from analytical general rigid bead-rod theory	IP9 - P. Laure Identification of foaming parameters for polyurethane with the FOAMAT® device	Interconversion of parallel and orthogonal superposition rheometry data"	FR9 - R. Cardinaels Extensional stress-relaxation measu- rements on wheat flour dough – The key to finalizing the Fractional K-BKZ framework?	14:00	
14:20	NF26 - F. van Berlo Torsional fracture of viscoelastic liquid bridges	GS26 - D. Kogan Small and large amplitude oscillatory shear behavior of crosslinked polymeric system at the vicinity of the gel point	SM10 - V. lanniello Determination of molecular weight distri- bution of UHMWPE via solution rheology	IP10 - E. Peuvrel-Disdier Foamability of linear and branched polypropylenes by physical extrusion foaming - Input of the thermomechanical analysis of pressure drop in the die	EM10 - M. Hoffmann Coupled Rheo-Dielectric: In-situ investigation of the alignment of lamellar blockcopolymers	FR10 - M. Nunes Improving dough rheology using partially purified algae biomass	14:20	
14:40	NF27 - M. VIllalba Chehab Visualizing plug formation in cavities and apertures with a yield stress fluid	GS27 - R. Aguirresarobe Rheological implications of chemically dynamic polymer networks	SM11* - C. Ligoure "Keynote Lecture Competition between shear and biaxial extensional viscous dissipation in the	IP11 - T. Gibaud Mechanics and structure of carbon black gels under high-power ultrasound	EM11 - C. Misra Dichotomous behavior of stress and die- lectric relaxations in dense suspensions of swollen thermoreversible hydrogel microparticles	FR11 - G. Della Valle Rheological properties of artificial boluses of cereal foods enriched with legume proteins to quantify food-saliva interactions	14:40	
15:00	NF33 - K. Isukwem Stretching and breakup of falling viscoplastic sheets	GS28 - R. Pasquino Hardening phenomenon in wormlike micelles	expansion dynamics of polymeric liquid sheets"	IP12 - M. Staropoli Nanoscale investigation of the Payne effect in silica-filled rubbers through in-situ SAXS-rheological tests	EM12 - C. Marraffa Characterization of flow-induced soft particle glasses with a plane-plane rheo- meter and small-angle light scattering.	FR15 - D. Gabriele Functional bigels for food uses	15:00	
15:20						15:20		
				on a conce break			15:20	
Chairs	Baltasar Mena	Domenico Gabriele	Giovanni lanniruberto	Edith Peuvrel-Disdier	Manfred Wilhelm	Alberto Romero	Chairs	
16:20	Baltasar Mena NF29 - J. Cochran Slow fatigue and delayed sudden failure of amorphous and soft glassy materials in large amplitude oscillatory shear strain	Domenico Gabriele GS29 - D. Vlassopoulos How to tailor the nonlinear rheology of supramolecular assemblies by changing their environment			Manfred Wilhelm EM13 - A. Geffrault Shapes of 3D printed filaments of yield stress fluids	Alberto Romero BM17 - M. Cidade Injectable composite systems of ALG:- GG microparticles in pluronic hidrogels for bioactive cargo controlled delivery: Optimization of hydrogel composition based on rheological behavior		
	NF29 - J. Cochran Slow fatigue and delayed sudden failure of amorphous and soft glassy materials in large amplitude oscillatory shear	GS29 - D. Vlassopoulos How to tailor the nonlinear rheology of supramolecular assemblies by changing	Giovanni lanniruberto SM13 - M. Sattari Melt rupture and wall slip of metalloce- ne-catalyzed bimodal molecular weight distribution polyethylene under simple	Edith Peuvrel-Disdier	EM13 - A. Geffrault Shapes of 3D printed filaments of yield	BM17 - M. Cidade Injectable composite systems of ALG:- GG microparticles in pluronic hidrogels for bioactive cargo controlled delivery: Optimization of hydrogel composition	Chairs	
16:20	NF29 - J. Cochran Slow fatigue and delayed sudden failure of amorphous and soft glassy materials in large amplitude oscillatory shear strain NF30 - P. Edera Tuning internal stress distributions in soft	GS29 - D. Vlassopoulos How to tailor the nonlinear rheology of supramolecular assemblies by changing their environment GS30 - A. Huysecom Unravelling the network topology and elasticity of hydrophobically associating multiblock copolymers in aqueous solutions using a novel mechano-statistical	SM13 - M. Sattari Melt rupture and wall slip of metalloce- ne-catalyzed bimodal molecular weight distribution polyethylene under simple shear SM14 - S. Vervoort Assessment of a melt rheology approach to estimate composition in binary blends of linear low-density polyethylene (LLDPE) and low-density	Edith Peuvrel-Disdier IP13* - P. de Souza Mendes "Keynote Lecture Displacement of a yield strength material	EM13 - A. Geffrault Shapes of 3D printed filaments of yield stress fluids EM14 - M. Daneshi Flow onset mechanics of bubbles in	BM17 - M. Cidade Injectable composite systems of ALG:- GG microparticles in pluronic hidrogels for bioactive cargo controlled delivery: Optimization of hydrogel composition based on rheological behavior BM18 - J. Ferreira Shear-induced crystallization of a thera-	Chairs 16:20	
16:20	NF29 - J. Cochran Slow fatigue and delayed sudden failure of amorphous and soft glassy materials in large amplitude oscillatory shear strain NF30 - P. Edera Tuning internal stress distributions in soft particle glasses NF31 - A. Pourzahedi Flow onset for a single bubble in a yield-	GS29 - D. Vlassopoulos How to tailor the nonlinear rheology of supramolecular assemblies by changing their environment GS30 - A. Huysecom Unravelling the network topology and elasticity of hydrophobically associating multiblock copolymers in aqueous solutions using a novel mechano-statistical transient network model GS31 - G. Legrand Phase diagram and rheology of poly-	SM13 - M. Sattari Melt rupture and wall slip of metallocene-catalyzed bimodal molecular weight distribution polyethylene under simple shear SM14 - S. Vervoort Assessment of a melt rheology approach to estimate composition in binary blends of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) SM15 - S. Magalhães Intrinsic viscosity as a tool to study the effect of the extraction conditions on the	IP13* - P. de Souza Mendes "Keynote Lecture Displacement of a yield strength material in a radial Hele-Shaw cell" IP15 - N. Jaouadi Rheological and morphological investigation of poly (lactic acid)/polyamide 11 biosourced multiphase systems going from polymer blends to multi-micro-na-	EM13 - A. Geffrault Shapes of 3D printed filaments of yield stress fluids EM14 - M. Daneshi Flow onset mechanics of bubbles in yield stress fluids EM15 - M. Coppens Measuring the stress ratio and the corresponding wall friction coefficient	BM17 - M. Cidade Injectable composite systems of ALG:- GG microparticles in pluronic hidrogels for bioactive cargo controlled delivery: Optimization of hydrogel composition based on rheological behavior BM18 - J. Ferreira Shear-induced crystallization of a thera- peutic protein BM19 - V. Perez-Puyana Rheology as a key tool for the charac- terization of protein-based scaffolds for	16:20 16:40	

Conference Program (V)

	Thursday 28 th - Morning							
	Giralda I-II	Santa Cruz	Nervión	Prado	Arenal	Giralda VI-VII		
09:00	A. Colin (PL3) - Giralda I-II Rheological behavior of non-Brownian suspensions: towards a quantitative modeling							
Chairs	Paulo de Souza Mendez	Moshe Gottlieb	Octavio Manero	Alexandra Aulova	Paula Moldenaers	Olivia du Roure	Chairs	
10:00	IP17 - N. Baldino SAOS and LAOS tests response of modified bitumens with SBS supported by morphological characterization	SM17 - L. Brandfellner Interplay of molecular weight distribu- tion, drag reduction and degradation in shear for polyacrylamide	SP20 - C. Carotenuto Alteration of the water-soluble organic carbon induced by a simulated rainfall and its effect on natural slurries' rheology	SG1 - H. Winter Relaxation processes in partially arrested soft matter	EM17 - A. Rodriguez-Barroso Modeling and optimization of magnetic tweezers design	MN17* - G. D'Avino "Keynote Lecture Numerical simulations of viscoelas-	10:00	
10:20	IP18 - A. Neveu How does the rheology of lactose powders influence the pharmaceutical tablets weight consistency?	SM18 - A. André Linear viscoelasticity of unentangled and entangled linear supramolecular chains with sticky side groups	SP18 - J. López-Aguilar Effects of confinement-induced non-Newtonian lubrication forces on the rheology of a dense suspension	SG4 - H. Weingrill Powder rheological investigations of powder coatings in the fluidized state	EM18 - D. Tammaro Rheological characterization of microliter sized olefin block copolymers	tic particle ordering in a microfluidic channel"	10:20	
10:40			Coffee	Break			10:40	
Chairs	Paulo de Souza Mendez	Moshe Gottlieb	Octavio Manero	Helena Weingrill	Paula Moldenaers	Olivia du Roure	Chairs	
11:10	IP19 - F. Galindo-Rosales Influence of rheology and microscale on graphene-based inks in the gravure printing process	SM19* - F. Christakopoulos "Keynote Lecture ""Tying the knot"",	SP19 - O. Ranquet Rheology of artists' paints: Study of oil-based mock-up paints containing egg yolk proteins	SG3 - A. Izzet Probing the mechanical properties of a weakly jammed granular packing through acoustic wave propagation in weightlessness	EM19 - P. Heyer Measurement and visualization of slip in rubber flow	MN19 - F. García Daza Microrheology in anisotropic colloidal suspensions by dynamic Monte Carlo simulations	11:10	
11:30	IP20 - A. Tenorio-Alfonso Phototriggered curing of polyurethane adhesives based on o-nitrobenzyl-pro- tected pentanediol and cadaverine precursors	enhanced recycling through ultra-fast entangling across ultra-high molecular weight polyethylene interfaces"	SP17 - L. Gonzalez-Garcia Concentrated suspensions of conductive particles as electronic flowing leads	SG2 - S. Aime The yielding transition of soft glasses	EM20 - R. Hudson Stress-controlled optimally windowed chirp rheometry (∑-OWCh)	MN20 - A. Oseli Understanding carbon-nanotube network formation in polymer-based nanocomposites	11:30	
11:50	IP21 - J. Rodriguez Agudo Characterization of the frequency and temperature dependency of the complex Poisson's ratio by combining axial and torsional measurements in a single rheometer	SM21 - D. Parisi Associative properties of poly(vinyl alcohol) solutions	SP21 - R. Andrade The influence of hexagonal boron nitride nanostructures on the xanthan gum rheological behavior	SG5 - K. Cerdan Magnetorheological self-healing elastomers based on thermoreversible Diels-Alder networks	EM21 - T. Athanasiou Measurement of both normal stress differences using two partitions and piezoelectric sensor	MN21 - C. Oelschlaeger Imaging of the microstructure of Carbopol dispersions and correlation with their macroelasticity: a micro-and macrorheological study	11:50	
12:10	IP22 - M. Rasteiro Effects of poly(vinyl chloride) morpholo- gical properties on the rheology/aging of plastisols formulated using nonconven- tional plasticizers	SM22 - S. Coppola Rheology of associating and non-asso- ciating Ethylene-Propylene copolymers in lubricating hydrocarbon oils	SP22 - M. Zakhari Slip in soft permeable particles near a rigid wall	SG6 - D. Fauser Rheological characterization of humidity influences on thermoresponsive Shape Memory Polymers	EM22 - M. Khabazian Esfahani Quantifying simultaneous first normal stress and shear viscosity at high shear rates via capillary rheology for different LDPEs	MN22 - R. Biswas Investigating the micro-rheology of an aging colloidal clay suspension using an optical tweezer	12:10	
12:30			Lur	nch			12:30	







Conference Program (VI)

	Thursday 28 th - Afternoon								
	Giralda I-II	Santa Cruz	Nervión	Prado	Arenal	Giralda VI-VII			
Chairs	Modesto López-López	Martin Zatloukal	Francisco Galindo-Rosales	Joamin González	Mariana Rodriguez Hakim	Peter Fischer	Chairs		
13:50	GS33 - C. Boulet Ageing study of Bentonite, Attapulgite clays and their mixture	SM23 - R. Lyons On the synthesis and dynamics of polymer networks formed by dynamic covalent bonds and moving in a sticky polymer matrix	SP23* - L. Botto "Keynote Lecture Suspensions of plate-like particles	SG7 - M. Alonso-González Influence of biopolymeric fractions on rheological, mechanical and functional properties of rice bran-based bioplastics	El17 - K. Schwarzenberger Response of a surfactant- and parti- cle-laden bubble surface to asymmetric shear flow	MN23 - L. Noirez Identification of the thermal response of confined fluids to mechanical shear deformation	13:50		
14:10	GS34 - T. Bhattacharyya Ascertaining universal scaling behavior in a thermoresponsive polymeric system	SM24 - A. Gaillard What determines the drop size in sprays of polymer solutions?	with slip can display negative intrinsic viscosity"	SG8 - G. Della Valle Processing and mechanical behavior of extruded starch-protein composites	EI18 - D. Ashkenazi The effect of polymer chain flexibility on the interfacial viscoelasticity at the Air/ Water Interface	MN24 - S. Fernández-Silva Electrorheological characterization of vegetable oil and nanoparticles based ecolubricants	14:10		
14:30	GS35 - J. Ramirez Self-diffusion, rheology and network topology of star-shaped associative polymer gels studied by Molecular Dynamics simulations	SM25 - R. Miriyala A study on the thixotropic response of a filled polymer melt system	SP25 - M. Neukötter Instability analysis of suspensions with a polymer solution matrix	SG9 - S. Pashazadeh Extrusion instabilities in highly-filled wood fiber biocomposites	EI19 - P. Sánchez-Puga Nonlinear interfacial strain profiles and constant strain operation modes in the magnetic needle ISR	FR13 - L. Ramos Model gluten as near-critical gels	14:30		
14:50	GS36 - D. Schmidt Carbon-black assemblies in highly concentrated suspensions: Influence of the solvent polarity and solvent mixtures on the structure	SM26 - H. Fatahi Rheological study and phase change behavior of adipic acid as a PCM for thermal energy storage at 150 °C	SP26 - J. Lalieu Rheology of a particle-laden soap film	SG10 - G. Baeza Topology and dynamics: The two faces of the mechanical reinforcement in crystallizable polymers	El20 - D. Renggli Interfacial rheology of crowded phospho- lipid monolayers shows a fluid behaviour	FR14 - C. Leverrier Creation of plant particles weak gels through High Pressure Homogeneization (HPH) to limit sedimentation in juices	14:50		
15:10	GS37 - Y. Stergiou Viscous fingering in a non-Newto- nian liquid radial displacement by oppositely-charged surfactant-polymer interaction	SM27 - E. van Ruymbeke Dynamics and structure of metallo-su- pramolecular polymers based on telechelic precursors	SP28 - L. Hildebrand Pires da Cunha Settling dynamics of Brownian colloidal chains	SG11 - P. Bacova Dynamics and rheology in the vicinity of rough silica surfaces: Insight from the atomistic simulations	El4 - L. Trujillo-Cayado Rheological characterization and processing optimization of lemon oil nanoemulgels for the encapsulation of vitamin E	FR12 - P. Avallone Inverse quenching on gelatin solutions	15:10		
15:30			Coffee	Break			15:30		
Chairs	Jorge Ramírez	Evelyn van Ruymbeke	Ricardo Andrade	Guy Della Valle	Carlos Bengoechea	Teresa Cidade	Chairs		
16:00	NF28 - E. Missi Drag reduction assisted emulsification in cross-slot microchannel	SM28 - C. Coutouly ABA triblock copolymers as precursors for transient double networks with multiscale viscoelastic response	SP29 - M. Naccache Rheology of Amino-Functionalized Graphene Oxide Suspensions on Yield Stress Fluid	SG12 - D. Truzzolillo A cusp catastrophe model with disorder for the yielding transition of soft glasses	El22 - L. Gala Fingers formation and oscillatory Kelvin-Helmholtz instability in miscible fluids	FR16 - S. Simões Clean Label emulsions based on vege- table proteins	16:00		
16:20	NF34 - P. Moschopoulos Filament-stretching dynamics of elasto- viscoplastic materials	SM29 - H. Müller Polymer degradation and ageing of the poly(ethylene oxide) drag reduction refe- rence system in long-distance turbulent pipe flow	SP30 - A. Aubel Effects of a non ionic surfactant on the rheology of colloidal suspensions	SG13 - G. Arnold From stiff to soft: glass characterization with dynamic mechanical analysis (DMA) up to 950 °C	El23 - P. Palak Emergent patterns and stable interfaces during radial displacement of a viscoe- lastic fluid	FR17 - F. Martin Heat treatment of concentrated milk protein system affects viscosity and enzymatic coagulation properties	16:20		
16:40	NF35 - A. Ghazal Density unstable displacement of a Newtonian fluid by a viscoplastic fluid: Effect of buoyancy	SM30 - A. Foroozani Behbahani Dynamics and rheology of polymer melts via hierarchical atomistic and coarse-grained simulations	SP31 - M. Marchand Stress relaxations upon flow cessation in dense soft sphere packings	SG14 - A. Aulova Modelling creep behavior of PEEK at different temperatures using artificial neural networks	El24 - Y. El Omari Probing the elongational behaviour at interfaces of immiscible polymer systems using the dilational tensiometry: Effect of viscosity and temperature on the interfacial rheological properties	FR18 - M. Campos Assumpcao de Amarante Effect of acid precipitation on the gela- tion properties of quinoa protein isolate	16:40		
17:00	NF36 - S. Habibi Numerical study of particle suspensions in elastoviscoplastic (EVP) duct flows			SG15 - D. Strugova Linear viscoelasticity of PP/PS/MWCNTs composites: investigating of co-conti- nuous morphology evolution and filler network stability during steady shear	El25 - L. Esteban Heterogeneous viscoelastic fluids in porous media	FR19 - H. Hernández Rheology, texture, and chemical charac- terization of Halloumi cheese enriched with algae biomass	17:00		
17:20			Closing -	Giralda I-II			17:20		
17:40		End 17:40							

Contents

Tuesday Morning	1
Plenary Lectures	1
Non-Newtonian Fluid Mechanics and Computational Rheology	1
Gels and Self Assembling Structures	4
Suspensions	5
Bio-rheology and Medicine	8
Emulsions, Foams and Interfacial Rheology	10
Micro-, Nanofluidics and Microrheology	11
Tuesday Afternoon	15
Non-Newtonian Fluid Mechanics and Computational Rheology	15
Gels and Self Assembling Structures	18
Suspensions	21
Suspensions	22
Bio-rheology and Medicine	25
Emulsions, Foams and Interfacial Rheology	28
Micro-, Nanofluidics and Microrheology	32
Wednedsay Morning	37
Plenary Lectures	37
Non-Newtonian Fluid Mechanics and Computational Rheology	37
Gels and Self Assembling Structures	40
Polymer Solutions and Melts	43
Industrial Rheology and Processing	45
Experimental Methods and New Advances in Rheometry	47
Food Rheology	49
Wednesday Afternoon	53
Non-Newtonian Fluid Mechanics and Computational Rheology	53
Gels and Self Assembling Structures	56
Polymer Solutions and Melts	59
Industrial Rheology and Processing	61
Experimental Methods and New Advances in Rheometry	64
Food Rheology	67
Bio-rheology and Medicine	69
Thursday Morning	73
Plenary Lectures	
Industrial Rheology and Processing	
Polymer Solutions and Melts	76
Suspensions	78

i

Solids, Glasses and Composites	80
Experimental Methods and New Advances in Rheometry	82
Micro-, Nanofluidics and Microrheology	84
Thursday Afternoon	87
Gels and Self Assembling Structures	87
Non-Newtonian Fluid Mechanics and Computational Rheology	89
Polymer Solutions and Melts	90
Suspensions	93
Solids, Glasses and Composites	95
Emulsions, Foams and Interfacial Rheology	98
Micro-, Nanofluidics and Microrheology	102
Food Rheology	103
Poster Session	107
Section: Bio-rheology and Medicine (BM)	107
Section: Emulsions, Foams and Interfacial Rheology (EI)	110
Section: Experimental Methods and New Advances in Rheometry (EM)	114
Section: Food Rheology (FR)	117
Section: Gels and Self Assembling structures (GS)	124
Section: Industrial Rheology and Processing (IP)	127
Section: Micro-, Nanofluidics and Microrheology (MN)	132
Section: Non-Newtonian Fluid Mechanics and Computational Rheology (NF)	134
Section: Solids, Glasses and Composites (SG)	138
Section: Polymer Solutions and Melts (SM)	141
Section: Suspensions (SP)	145
Author Index	151
Paper Index	159

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Tuesday Morning

Symposium PL

Plenary Lectures

Weissenberg Lecture

Tuesday 9:00 Giralda 1-2 / Plenary Lectures

PL1

Rheology and fluid mechanics of concentrated suspensions

Jeffrey F. Morris

Levich Institute and Department of Chemical Engineering, CUNY City College of New York, New York, NY 10031, United States

Suspensions display a remarkably rich range of behavior. This is particularly true under conditions where the particles are concentrated, which rather arbitrarily we will say is particle volume fraction larger than 0.3. This includes rheological properties that vary extremely rapidly with shear rate, strong normal stresses, and the two-phase flow phenomenon of shear-induced migration. Because suspensions of spherical particles immersed in Newtonian liquid are simple and readily characterized, they provide the ideal ground for determining the fundamental basis for these behaviors. Considering experiment, discrete-particle simulations, and theory, I will trace efforts to understand nonlinear rheology in suspensions of "near-hard-sphere" suspensions, focusing on two topics: 1) particle pressure, including both its microstructural basis and impact on migration, and 2) DST and shear jamming in very dense suspensions. Because both phenomena can be linked to microstructural features, I will also discuss methods to describe, and in limited cases predict, the microstructure, from pair-particle correlations to percolated network structures.

Symposium NF

Non-Newtonian Fluid Mechanics and Computational Rheology

Organizers: Miguel Nóbrega, Baltasar Mena and Corneliu Balan

Tuesday 10:30 Giralda 1-2 / Track 1

NF1

Learning of constitutive equations for multiscale simulation of dilute polymeric solutions using a GENERIC-guided approach

David Nieto Simavilla¹, Pep Español², and Marco Ellero¹

¹Computational Fluid Dynamics, Basque Center for Applied Mathematics, Bilbao 48009, Spain; ²Universidad Nacional de Educación a Distancia, Madrid 28080, Spain

Polymer solutions display complex viscoelastic behaviour due to the orientation and stretching of chains. As a result, the simulation of polymer solutions requires a multiscale approach to avoid the high computational cost of resolving the materials' microscopic details. Viscoelasticity at the macroscopic level is included via a closure constitutive equation for the polymeric stress. A novel approach is to use Machine Learning (ML) to efficiently obtain the needed closure equations. However, arbitrary choices for the constitutive equation result in a black box connection between microscale and macroscale simulations. This approach works well for homogeneous flows and straightforward geometries, but problems can arise when simulating realistic flow processes at the macroscale.

We present a general data-driven constitutive learning approach guided by GENERIC, where the local chain conformation tensor c is sufficient to describe the rheology of the system. For our microscopic systems we use SDPD model particles with FENE springs to create chains that introduce viscoelasticity. In this physics guided approach the polymeric stress - as a function of the conformation tensor - is the only to-be-learned constitutive relation for the macroscopic simulations. On one hand, we show that in the miscrocopic simulation data the information rests on the polymeric entropy, a function of the eigenvalues of c alone. On the other hand, the evolution of the eigenvectors of c allows us to check the validity of an upper convected derivative in the reversible part of the evolution equation for c - an assumption often taken for granted. We discuss how to apply mix derivatives to introduce non-affine deformation as "slip". We find good agreement at low Weissenberg numbers between our simulation results and solutions for an Oldroyd-B fluid. Finally, we test our learning approach comparing microscopic and macroscopic Couette and Poiseuille flows.

Tuesday 10:50 Giralda 1-2 / Track 1

NF2

Complex flow simulations of microstructured-fluids using a Lagrangian Heterogenous Multiscale Method Nicolas Moreno and Marco Ellero

CFD-MS, Basque Center for Applied Mathematics, Bilbao, Spain

The rheological modelling of complex fluids such as colloidal suspensions, polymer solutions and multiphase flows poses significant challenges due to their inherent multiscale features. This requires novel methodologies able to capture relevant microscopic effects expanding over a wide range of spatial/temporal scales. Here, we introduce a fully-Lagrangian Heterogeneous Multiscale Method (LHMM) to model complex fluids undergoing arbitrary flow configurations. LHMM decomposes the problem in macro and micro scales, bypassing the requirement of constitutive relations. Microscopic simulations information determines the stresses of the macroscales whereas macroscopic kinematics define local microscopic boundary conditions. We use the Smoothed Dissipative Particle Dynamics (Espanol & Revenga, 2003) (SDPD) method to discretize the fluid both at macro- and microscales. Due to its compliance with the GENERIC framework and consistent scaling of thermal fluctuations the method can be applied under stochastic and deterministic conditions (Ellero & Espanol, 2018). At the microscales arbitrary boundary conditions (Moreno & Ellero, 2021) are adopted to simulate general mixed flows (shear, extensional and their combination). We validate the LHMM using different benchmark configurations for both Newtonian and non-Newtonian fluids. For complex fluids at microscale we model multiphase systems, polymer melts, and polymer solutions. The proposed thermodynamic-consistent methodology using Lagrangian discretizations at both scales provides a natural link between variations at a macroscale, whereas accounting for memory effects at microscales.

References:

Espanol, P., & Revenga, M. (2003). Smoothed dissipative particle dynamics. *Physical Review E*, 67(2), 026705.

Ellero, M., & Español, P. (2018). Everything you always wanted to know about SDPD?(? but were afraid to ask). *Applied Mathematics and Mechanics*, 39(1), 103-124.

Moreno, N., & Ellero, M. (2021). Arbitrary flow boundary conditions in smoothed dissipative particle dynamics: A generalized virtual rheometer. *Physics of Fluids*, 33(1), 012006.

Tuesday 11:10 Giralda 1-2 / Track 1

NF3

Is any logic behind the principles of the constitutive relations?

Corneliu Balan

Hydraulics, REOROM Laboratory, University Politehnica of Bucharest, Bucharest 060042, Romania

The theory of the constitutive relations, which describe the material behavior in the frame of continuum mechanics and thermodynamics, is based on some principles, e.g.: (i) Determinism, (ii) Fading memory, (iii) Local action, (iv) Objectivity/Frame Indifference, (v) Just setting. These principles are actually the postulates of the rheology, even if they are not always recognized or considered explicitly. The subject of axiomatic structure of rheology is not anymore in the focus of today scientific research, but the future seems to open again the interest on the topic once the artificial intelligence (AI) approaches are applied in materials modelling. AI procedures are based on languages and images recognitions techniques, which are implemented in computers by numerical codes created and organized accordingly to some logical structures. Any logical structure (generated by a human or artificial mind) is directly related to the past-history, a data base consists of sets of elements which are recomposed in a coherent picture. The paper presents a personal view on the roots of the axiomatic structure of the constitutive relations (applied to fluids). It is a historical perspective on the subject, in the context of the European scientific life in the first part of the XXth century. The analysis is mainly focused on the objectivity principle and its formulations by G.A.J. Jaumann (1863-1924), S. Zaremba (1863-1942), J.G. Oldroyd (1921-1982) and C. Truesdell (1919-2000). The research is also a scientific journey starting from Vienna University to Charlottenburg in Berlin and Sorbonne in Paris, with the end (or the beginning?) at Trinity College in Cambridge, UK. The guide I choose is Ludwig Wittgenstein (1889-1951), who published one hundred years ago Tractatus Logico-Philosophicus, a textbook in which I founded strange, unexpected, and subtle connections to the theory of constitutive relations.

Tuesday 11:30 Giralda 1-2 / Track 1

NF4

Machine-learning-based measurement of the relaxation time of viscoelastic fluids via particle ordering Maurizio De Micco. Massimiliano M. Villone, and Gaetano D'Avino

DICMaPI, University of Naples Federico II, Naples, Italy

The rheological characterization of complex fluids is of great importance in several applications. Among the rheological properties, relaxation time has a special relevance, as it provides a measure of fluid elasticity. Depending on the liquid, the relaxation time can vary over several orders of magnitude, from seconds to milliseconds. The latter is the case of aqueous solutions at low polymer concentration and biological fluids, where conventional rheometers fail to give accurate measurements and alternative techniques need to be developed. In this work, we present a non-intrusive method to measure the relaxation time of viscoelastic fluids in a microchannel by exploiting the phenomenon of "particle ordering" combined with a machine learning approach. Particles suspended in a viscoelastic medium flowing through a channel tend to migrate at the channel centreline and self-assemble in strings due to particle-particle hydrodynamic interactions. The ordering mechanism depends on the fluid relaxation time. Hence, we propose to measure this quantity from the distribution of the interparticle distances by using machine learning techniques. To prove the effectiveness of our approach, we generate "in silico" a dataset of interparticle distances by following the simulation procedure reported by D'Avino and Maffettone (D'Avino & Maffettone, 2020). The dataset is used as input for various machine learning algorithms, as support vector machines and random forests. Both classification and regression are carried out with high performances. In principle, the proposed approach can be used to measure other properties of fluids.

References:

D'Avino, G., & Maffettone, P. L. (2020). Numerical simulations on the dynamics of trains of particles in a viscoelastic fluid flowing in a microchannel. *Meccanica*, 55(2), 317-330.

Tuesday 11:50 Giralda 1-2 / Track 1

NF5

Flow-type dependent rheologies and multiscale simulations

Giulio G. Giusteri¹, Francesca Tedeschi¹, Leonid Yelash², and Maria Lukácová-Medvid'ová²

¹Department of Mathematics, University of Padua, Padua, Padua 35131, Italy; ²Institute of Mathematics, Johannes Gutenberg University of Mainz, Mainz, 55128, Germany

The importance of taking into consideration the dependence on the local flow type of the response of non-Newtonian fluids will be highlighted with particular reference to multiscale data-driven simulations. It is well known that polymeric fluids can display a nontrivial dependence of the viscosity on the flow type, to the point that shear thinning fluids may feature an increase of the viscosity with the extensional deformation rate. This is due to the different dynamics of the conformation of polymer chains when subjected to either pure extension or simple shear. Arguably, an intermediate behavior appears when the local flow is neither shear nor extension, but mixed. A framework to organize rheological data in mixed flows and reconstruct the stress tensor in a data-driven fashion (Giusteri & Seto, 2018) will be reviewed. When setting up multiscale simulation strategies it is very important to take into account the flow-type dependence in a consistent way (Tedeschi et al., 2022). The effects of this will be presented by discussing paradigmatic planar flows implied by data obtained with a FENE-type model for polymer chains.

References:

Giusteri, G. G. & Seto, R. (2018). A theoretical framework for steady-state rheometry in generic flow conditions. *Journal of Rheology*, 62(3), 713-723.

Tedeschi, F. et al. (2022). A multi-scale method for complex flows of non-Newtonian fluids, *Mathematics in Engineering*, 4(6), 1-22.

Tuesday 12:10 Giralda 1-2 / Track 1

NF₆

Understanding instabilities for additive manufacturing in partially ordered system

Arthur Colly¹, Christophe Marquette², Jean-Marc Frances³, and Edwin-Joffrey Courtial²

¹3d.FAB, Université Lyon1, ICBMS, UMR 5246; Elkem Silicones, Villeurbanne, Auvergne-Rhône-Alpes 69100, France; ²3d.FAB, Université Lyon1, ICBMS, UMR 5246, Villeurbanne, Auvergne-Rhône-Alpes 69100, France; ³Elkem Silicones, Saint-Fons, Auvergne-Rhône-Alpes 69192, France

Freeform 3D printing is an additive manufacturing technique enabling the 3D printing of soft materials with no or low yield stress (Colly et al., 2021). This widespread technique uses mostly fluid-based supports mediums describing yield stress behavior to embed the printed material during the process until its solidification. Many progresses were made in the last seven years by manufacturing many different materials regardless of their chemistry and with high shape complexity (Shiwarski et al., 2021). In this presentation, we present the additive manufacturing in a partially ordered system that uses solid particles as a support medium (Courtial et al., 2022). This unique support material fulfills the Freeform 3D printing requirement such as supporting the printed filament and self-repairing after its disruption by the printing head movements. Composite materials can be in-situ obtained or porous constructs if the powder support is removed. The success of this technique relies on the powder flowability properties but also on the printed material-powder bath physicochemical interactions and instabilities control. Powder shear tests are carried out to provide a quantitative description of the powder self-repairing property as well as the study of the granular Bond number. The understanding of the conditions for fluid intrusion into an array of solid particles is investigated across the viscoelastic properties of the extruded material, the contact angle but also instabilities described by the Bond and Galilei numbers (Boyce et al., 2016). Mechanical tests on the printed constructs are performed to quantify the effects of these conditions and instabilities.

References:

Colly, A., Marquette, C., & Courtial, E. J. (2021). Poloxamer/poly (ethylene glycol) self-healing hydrogel for high-precision freeform reversible embedding of suspended hydrogel. *Langmuir*, 37(14), 4154-4162.

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Symposium GS

Gels and Self Assembling Structures

Organizers: Joao Maia, Domenico Gabriele and Juan de Vicente

Tuesday 10:30 Santa Cruz / Track 2

Keynote

GS1

Network physics and emergence of elasticity in colloidal gels: Mechanical perspective

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Colloidal gels exhibit a range of rate- and time-dependent rheological behavior that are classified as thixotropic elaso-visco-plastic. This complex rheology arises from the colloidal phase dynamics, and specifically, the evolution of a particulate microstructure that forms due to attractive interactions between different particles. These forces result in thermoreversible bonds, which in turn result in space-spanning networks that govern the mechanics of colloidal gels. What is clear is that particle-level bonds give rise to clusters at the mesoscale, and that elasticity in these gels arises from a percolated network at the macroscale. Thus, understanding the physics of this particulate network is the key to controlling and designing gels with desirable properties. Thus, we borrow well-established concepts from network science to interrogate and characterize the particulate network in attractive colloidal gels. We associate each colloidal particle to a vertex, and each inter-particle bond to an edge; we then proceed to the analysis of the networks of bonds, completely unaware of the spatial coordination of the particles, and to reveal structural signatures both at local and global scales. We employ network science tools to identify colloidal clusters and coarse grain the network further. The cluster networks from gels of different energy potential show distinct features and a simple spring network made out of the clusters made was found to recover the mechanics of our colloidal gel, suggesting that the appropriate length scale for a network analysis is set by the cluster size rather than individual particles. Finally, we show that network resilience analysis made possible using a Girvan-Newman criterion shows similar features to those from the elasticity of the spring network when strength of attraction between colloids is varied.

Tuesday 11:10 Santa Cruz / Track 2

GS3

Influence of surface topography on the yielding of thermo-reversible colloidal gels

Florence J. Müller and Jan Vermant

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The microstructural and solid-liquid transition of colloidal gels has been intensively researched using various characterization methods in the past. In the present work we investigate the effect of surface topography on the yield stress and thixotropy. To this end, thermo-responsive octadecyl coated silica particles were synthesized in a controlled and reproducible manner using click-like chemistry to graft a stabilizing polymer layer around particles with concave, convex and no surface features. The thermo-responsive nature allows to delete the influence of mechanical history, as gelation can be induced by decreasing the temperature inside the measurement cell. This model system is utilized to compare the initial yielding behavior of colloidal gels with primary particles of different surface topographies. Rheological measurements show that surface roughness delays the structural yielding due to interlocking of the particles, in addition to influencing the thixotropy as roughness counteracts flow induced cluster densification.

Tuesday 11:30 Santa Cruz / Track 2

GS4

Tuning local microstructure of colloidal gels by ultrasound-activated deformable inclusions

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¹Delft University of Technology, Delft, The Netherlands; ²Université Gustave Eiffel - CNRS - ENPC, Champs sur Marne, France; ³IESL - FORTH, Heraklion, Greece

Today's advanced soft materials are not only precisely formulated, but also precisely structured, in order to confer them remarkable acoustical, biochemical, mechanical or optical properties. Physical processes allowing to produce a given microstructure, tune it or disrupt it, are particularly desirable. Applying oscillatory shear has recently been evidenced as a generic pathway to control and alter the microstructure of colloidal gels [1], which encompass a broad class of soft materials. In addition, applying oscillations in the ultrasound domain has been shown to disrupt and break instantaneously the microstructure of colloidal gels and suspensions in *rheoacoustic* materials [2]. We demonstrate a new approach to modify the microstructure of a model colloidal gel based on deformable inclusions, namely bubbles embedded in the material. We examine two different phenomena of bubble dynamics that apply a local strain to the surrounding material: dissolution due to mass transfer, with a characteristic strain rate of 10⁻³ s⁻¹; and volumetric oscillations driven by ultrasound, with a characteristic frequency of 10⁴ s⁻¹. In both cases, changes in the bubble radius apply an extensional, localised deformation onto the surrounding material [3], which can be used to modify the structure of the gel at the local scale. High-speed brightfield and laser confocal microscopy reveal that ultrasound-driven bubble dynamics produce a striking rearrangement of the gel particles into a microstructure with increased local ordering [4]. These observations open the way to local tuning of colloidal gels based on deformable inclusions controlled by external pressure fields.

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Moghimi, Jacob, Koumakis and Petekidis, *Soft Matter* 13, 2371-2383 (2017) Gibaud et al., *Phys Rev X* 10, 011028 (2020)

Saint-Michel and Garbin, *Curr Opin Colloid Interf Sci* 50, 101392 (2020) Saint-Michel, Petekidis and Garbin, arxiv:2112.07592 (2021)

Tuesday 11:50 Santa Cruz / Track 2

GS5

Interpenetration of fractal clusters drives elasticity in colloidal gels formed upon flow cessation

Thomas Gibaud

Physics, ENS de Lyon, Lyon, France

Colloidal gels are out of equilibrium soft solids composed of attractive Brownian particles that form a space-spanning network at low volume fractions. In such systems, it is admitted that the elasticity of the gels is imprinted in the network's structure. Using a peculiar protocol composed of a preshear followed by a flow cessation, we bring a colloidal dispersion from a fluid state to multiple metastable gel states. The final gel state keeps the memory of the preshear history and is selected by the preshear intensity. We observe that low preshear intensity induces the formation of more elastic gels. Having formed different gels from a single dispersion, we are uniquely positioned to explore the interplay between the gel's mechanical and structural properties. Coupling rheology to Small Angle X-ray Scattering (SAXS) experiments, we show that the gel is structured in fractal clusters that interpenetrate each other. The interpenetration is all the more important that the preshear intensity is low. Using a structure-based model, we demonstrate that this cluster interpenetration drives the gel elasticity. In situations such as 3D printing and molding or texture control, where flow rate and solidification are paramount parameters, our results open up a new perspective on the tunability of gel structure and mechanics without altering the product formulation.

Tuesday 12:10 Santa Cruz / Track 2

GS₆

Probing plastic rearrangements in colloidal gels

Pierre Lehéricey, Laura Stricker, Lucio Isa, and Jan Vermant

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A mechanistic understanding of yielding of colloidal gels is of both fundamental and practical interest, especially in view of the widespread use of these materials. The emergence of a yield stress is attributed to the formation of a percolated colloidal network. Only a few rheo-confocal studies focused on the microstructural evolution during yielding. However, due to their limited spatio-temporal resolution, these studies could, as yet, not provide a complete image of yielding at the colloidal network level. Using a homemade ultrafast rheo-confocal setup², we investigate the microstructure of a colloidal gel under shear scanning a 35 μ m x 20 μ m 3D voxel stack each second. Inspired by how structural rearrangements of particles trigger the yielding of colloidal glasses, we focus on the plastic rearrangements of particles of PMMA-g-PHSA in a model depletion gel under shear below or near the yield stress yielding. Image processing methods and particle tracking can be used to determine the local strain field stemming from plastic event and its propagation. We study the influence of the volume fraction and the depletion strength on such basic plastic events. We focus on the rearrangements before yielding, inspired by rheo-DLS experiments as precursors of yielding³, in order to assess their impact on the subsequent macroscopic yielding.

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- 3 : S. Aime et al., PNAS, 2018, 115

Symposium SP

Suspensions

Organizers: Francisco Rubio, Francisco Galindo-Rosales and Octavio Manero

Tuesday 10:30 Nervión / Track 3

SP1

Oscillatory compression of soft particles

Lars Kool¹, Anke Lindner¹, Kevin L. Galloway², and Paulo E. Arratia²

¹Laboratoire PMMH, ESPCI, Paris, France; ²Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA, United States

Granular materials are the second most handled material in industry, behind water. But despite their ubiquity in our daily lives, we still do not thoroughly understand how certain properties of their constituents (e.g., particle softness and compressibility) contribute to their macroscopic behavior. Here, we experimentally study the influence of individual particle softness on the compaction mechanics of the ensemble using a microfluidic model system. We developed a quasi-2D set-up to specifically probe particle softness and compressibility, based on the in-situ fabrication of PEGDA particles inside microfluidic channels, to create a multidisperse ensemble of frictionless particles (up to ~5000 particles). The advantage of this system lies in the possibility to precisely tune the mechanical particle properties while keeping particle roughness or interparticle friction constant. We have achieved Young's moduli ranging from 100 kPa to 10 MPa, and Poisson's ratio between 0.15 and 0.5. Using a pressure controller, we can apply an oscillating compressive force to the ensemble. Tracking the particles over time allows us to then study the macroscopic stress-strain response of the system, and link it to individual particle rheology, as numerical work predicts that the response

of a single particle can be extrapolated to the response of the ensemble. The relatively large deformations achieved in our experiments, up to $\epsilon = 0.25$, also allow us to reconstruct the micromechanical response, such as the packing fraction dependency of the coordination number $Z(\phi)$ and probability density function of interparticle forces, and compare our system to already existing experimental and numerical work.

Tuesday 10:50 Nervión / Track 3

SP2

Modelling extensional rheology of polyolefin based suspensions

Jean-Charles Majesté and Nanjunda Velu

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Polymers with a strain hardening behaviour under extensional flow is preferred for certain industrial processing techniques such as thermoforming, blow-molding, etc. Rigid inorganic fillers are commonly added to impart specific functional properties to polymers. Literature shows that addition of fillers modifies the nature of extensional flow. Depending upon the nature of the matrix, the composite melts show either a suppression in strain hardening or a strain softening behaviour in comparison to the matrix, posing difficulties in processing. However, the origin of the elongational thinning behaviour in composite melts is not fully understood yet. In this work, we investigate the effect of filler particles on the extensional rheological behaviour of polyolefins. We have studied the behavior or a filled linear matrix as well as a filled strain hardening one. The linear matrix used in this study is EPDM and for a strain hardening matrix, LDPE is used. For fillers, both fractal silica and micro sized silica beads have been chosen. Composites containing EPDM matrix show a strain softening behaviour whereas composites containing LDPE show only a suppression in strain hardening and not strain softening. Cross-linked EPDM-fractal silica composites show a complex extensional behaviour, with an initial strain softening followed by strain hardening at long times. To model the extensional behaviour of polymer composite melts, we first used the Leonov model for the EPDM-fractal silica system and discuss it's inherent drawbacks. To overcome these drawbacks, we attempt to develop a mean-field model that takes into account the complexity of local flows in the surrounding of the fillers. This model shows its ability to predict the extensional behaviour of all the systems under consideration, i.e. both linear matrix and strain hardening matrix with a reduced number of parameters.

Tuesday 11:10 Nervión / Track 3

SP3

Measurement of suspensions transient viscosity upon any change of shear direction thanks to a novel Cross-Rheometer apparatus

<u>Frédéric Blanc</u>¹, Camille Benarroche¹, Laurent Lobry¹, François Peters¹, Romain Mari², and Elisabeth Lemaire¹

Institut de Physique de Nice. CNRS, Université Côte d'Azur, Nice, France; ²Liphy. Université Grenoble Alpes, CNRS, Grenoble, France

It is now accepted that contact forces play a key role in the rheology of dense suspensions. Frictional contacts strongly increase the viscosity (Gallier et al., 2014). A striking feature of frictional suspensions is the transient viscosity behavior that happens when the shear direction is reversed. In such experiments the viscosity decreases after the shear reversal to a minimum where contacts vanish and increases again up to the steady value as frictional contacts re-build (Peters et al., 2016; Lin et al., 2015). This transient flow is related to the asymmetry of the shear-induced anisotropic microstructure of non-Brownian suspensions. So far, the effect of this anisotropy on the viscosity has only been characterized by reversing the shear direction although the particles organize in a 3D microstructure (Deboeuf et al., 2018) that has to be probed in any direction. It is therefore necessary to shear the suspension not only by reversing the direction of the flow but in all the directions perpendicular to the velocity gradient direction.

To this aim, we have developed a cross rheometry device that consists in two parallel horizontal plates moving one with respect to the other by means of two orthogonal translation stages. The displacement of these two stages allows the top plate to move in any direction relative to the bottom plate. The suspension, which is poured in a cup on the lower plate, can then be sheared in any direction. Stress measurements are performed by a force platform located below the lower plate which provides the force in the 3 directions. Knowing the shear force on the plate and its velocity, this device allows us to measure the transient shear viscosity upon any change of shear direction. We will present our results for a non-Brownian suspension with a volume fraction of 0.45.

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Tuesday 11:30 Nervión / Track 3

SP16

Viscous dissipation in sheared unsaturated wet granular materials

Abdoulaye Fall, Lhassan Amarsid, and Jean-Noël Roux

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We experimentally investigated the dense-flow rheology of unsaturated granular materials through experiments and discrete element simulations (DEM) of homogeneous, simple annular shear flows of frictional, cohesive, spherical particles. Herewith, we show that the rheology is essentially described by two dimensionless numbers: The reduced pressure P* comparing the cohesive to confining forces and the inertial number I, for a wide range of liquid content. Finally, we measure the effective friction coefficient and the solid fraction variation throughout the wet bed. From this, we show that, in the quasistatic regime, the Mohr-Coulomb yield criterion is a good approximation for large enough P*. The experimental results agree quantitatively with the numerical simulation ones, provided the intergranular friction coefficient μ is set to its physical value identified from dry material rheology. We also extend this investigation to the influence of the liquid viscosity on the the material rheology in the low liquid content. Away from the quasistatic limit, rheological properties are observed, for large enough liquid viscosities, to be essentially determined by the same viscous number as used to formulate constitutive laws in saturated, dense suspensions. In general, the form of a generalized constitutive laws in the presence of capillary cohesion and both inertial and viscous effects is discussed.

Tuesday 11:50 Nervión / Track 3

SP5

Shear and elongation rheology of filled polymers and their nano-structured multicomponent systems for ultrahigh absorbance of EMR (electromagnetic radiation)

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The present work comes within an ANR project dealing with the development of nanostructured polymeric composites with a high absorption of electromagnetic radiation. The strategy relies on tailoring their internal architecture leading to a morphological structuration with local electrical/magnetic properties through a nanolayer coextrusion and In-Mold Electronics process. In this regard, films containing conductive and/or magnetic fillers are investigated as support for Plastronic devices against electromagnetic pollution. The challenge is to obtain a 3D electrical/magnetic filler network with high orientation/ordered distribution. The chosen system for this work focuses on a PE matrix with different molecular architectures containing fillers of various dimensions and shapes to be coupled with amorphous high-Tg polymers, used as confining materials. Therefore, the filler compounds were obtained through the dilution of masterbatches using a new Extensional Mixing Element (EME) for improved dispersive mixing in twin-screw extrusion. In this talk, SAOS experiments were firstly performed in the molten state to correlate the viscoelastic properties to the percolation depending on the characteristics of the fillers. Specific attention is devoted to investigate the rheological behaviors in correlation with morphological properties (SEM, TEM) to be compared to the suspension models. Secondly, effects of flow were investigated in the nonlinear regime and in the transient regime that display less maturity in the rheology community, despite their importance for processing. Step and start-up shear and extensional properties were studied. The effect of the two flow kinematics and the characteristics of the fillers will be highlighted. Naturally, effects of strain rates or amplitudes (shear or elongation) on the alignment of particles or on their jamming and viscosity/elasticity ratios, were explored in order to predict the coextrusion and IME processing windows.

Tuesday 12:10 Nervión / Track 3

SP6

Contact and macroscopic ageing in colloidal suspensions

Francesco Bonacci¹, <u>Xavier Chateau</u>², Eric M. Furst³, Julie Goyon², and Anael Lemaitre²

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While the ageing behavior of dense suspensions or pastes at rest is almost exclusively attributed to structural dynamics, a set of experiments conducted on dense aqueous silica suspensions allowed us to identify another ageing process: contact-controlled ageing. To do so we have investigated the origin of shear modulus and yield strength ageing in dense aqueous silica suspensions at moderate ionic forces. We first showed by combining rheometry and confocal microscopy that the elastic modulus and yield stress of these suspensions at rest grow logarithmically with time while their structural evolution is rapidly arrested by the formation of thermally irreversible roll-resistant interparticle contacts. So these suspensions age in the absence of structural rearrangement. Then by performing three-point optical tweezer (OT) bending tests on particle rods, we showed that particle contacts resist rolling and yield by overcoming a rolling threshold. We also observed that both the rolling stiffness and rolling threshold grow logarithmically in time. By comparing the results of the measurements on the particle contact properties with the results of the rheometry tests, we were able to show that ageing of interparticle contacts governs both shear modulus ageing and yield stress ageing of these dense aqueous silica suspensions. We also identified simple constitutive relationships between contact-scale bending stiffness and rolling threshold, which transfer to macroscopic scale. This allowed us to propose a constitutive relationship between the macroscopic shear modulus and the yield strength of these silica suspensions that should be generic for an array of colloidal systems.

Symposium BM

Bio-rheology and Medicine

Organizers: Críspulo Gallegos, Mats Stading and Catarina R. Leal

Tuesday 10:30 Prado / Track 4

Keynote

BM1

The influence of saliva rheology on sheet formation and aerosolization

Mariana Rodriguez Hakim, Linard Räz, Laura Stricker, and Jan Vermant Department of Materials, ETH Zürich, Zürich, Zürich 8093, Switzerland

Some contagious diseases, such as COVID-19, spread primarily though the airborne transmission of aerosols and droplets that are produced upon sneezing, coughing, or speaking. The formation of these droplets and aerosols can occur both inside and outside of the respiratory tract. In the latter, the expelled saliva flattens into a sheet that can destabilize and break up into ligaments and droplets. The presence of macromolecular mucins in saliva influences the dynamics of aerosol generation and lifetime, since elasticity can (1) stabilize fluid sheets and filaments, (2) retard the onset of droplet formation, (3) affect the resulting aerosol size distribution, and (4) hinder the evaporation of individual droplets. Here, we report on several of these effects. We systematically replicate the aerosol formation process during sneezing using a custom-built impinging jet setup, in which the collision of two liquid jets forms a thin fluid sheet that can subsequently fragment into ligaments and droplets. This setup enables us to investigate a range of dynamic conditions, quantified by the dimensionless Deborah (De), Weber (We), and Reynolds (Re) numbers, which encompass those experienced in speaking or sneezing. We conduct experiments using saliva from different anonymous human donors, which exhibit significant variations in their stability and breakup, and find that the aerosolization propensity is correlated with higher ejecta velocities and lower saliva elasticities. Furthermore, we develop a physical model for the steady-state geometry, velocity, and stress distributions within viscoelastic sheets, which is numerically solved as a function of De, We, and Re. Our findings reveal a non-monotonic interplay between the dimensionless parameters which lead to extensional stress maxima and sheet size minima at specific values of De, We, and Re.

Tuesday 11:10 Prado / Track 4

BM3

Hagfish slime behavior in particle-laden environments

Caroline E. Giacomin¹, Dimitra Founta², Dimitris Vlassopoulos³, and Peter Fischer¹

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In humans, mucus can be found in the respiratory, gastrointestinal, and vaginal tracts. It forms the final barrier and gateway to particles reaching the epithelium which transfers particles into the human body. The structure of mucus is primarily composed of mucin, a glycosylated protein with negative charge. Mucus also contains water, proteins, lipids, salts, and cellular debris (Lock, 2018).

Hagfish (*Myxine glutinosa*) produce a mucosal network rapidly as a defense mechanism (Böni, 2018). Hagfish exudate can be harvested directly from the ventral slime glands of the hagfish yielding consistent, uncontaminated mucins. Mucins form a mesh-like structure and the conveyance of particles is limited by the mesh pore size and viscoelasticity of the network (Rementzi, 2019)(Lai, 2007). Depending on the surrounding environment, a mucus mesh preferentially absorbs different sizes of particles or particles with different surface charges (Bajka, 2015). Thus the ability of microbes, drugs, nutrients, pollutants, or other particles to reach the epithelium through mucus is dependent on their ability to be conveyed by said mucus (Lock, 2018).

To evaluate how mucus-particle interactions affect mucin networks, extensional and shear rheology, and light scattering are performed on particle-laden mucin networks. Further, water retention measurements are performed to elucidate which nanoparticles can macroscopically strengthen or weaken the mucus networks.

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Tuesday 11:30 Prado / Track 4

BM4

Viscosity of the intercellular liquid in Red Blood Cells

Christian Wagner, Thomas John, and Felix Maurer

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Red blood cells (RBCs) are known for their deformability, which allows them to squeeze through the smallest of capillaries. A quantitative comparison of simulations of RBC flow in capillaries with experimental results requires a set of cell membrane parameters as well as the viscosity ratio of the intercellular liquid (cytosol) and the outer liquid as blood plasma. The cytosol consists mainly of solved hemoglobin and some other proteins. We present a procedure to extract that cytosol from the RBCs to perform macroscopic rheology. Due to the extraction process, this cytosol is always contaminated with some buffer solution and the measured viscosity values vary greatly between different samples. However, by

simultaneously measuring the density of the samples accurately, we were able to establish a clear monotonic relationship between the densities and the viscosities of the samples. Furthermore, it is known that older blood cells have a slightly higher density than young cells due to water release. By centrifugation in density gradients (Percoll), we were able to determine the distribution function of the density for individual RBCs. Thus, using the above relation, we can determine the mean cytosol/plasma viscosity ratio, and even the distribution of this ratio for RBCs. The viscosity ratio was determined to be 15 with a width of \pm 1. This is significantly higher than the ratio of 5 previously used in many simulations.

Tuesday 11:50 Prado / Track 4

BM5

Blood rheology in contact to biological surfaces

<u>Ursula Windberger</u>¹, Sabrina Rohringer², Karl Schneider², Birgit Stoiber¹, Laurence Noirez³, and Günter Brenn⁴

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Liquid properties at the vicinity of an interface play a crucial role in multiple situations. The organization of the liquid near the interfaces, as well as the nature of the liquid/wall interactions, can dramatically impact the flow. It was proven that the nature of the test plate material in rheometry influences the behavior of simple liquids (1-3) as well as of blood plasma (4). These results lead us to hypothesize that also the blood - vessel wall interface will influence blood flow. To mimic physiological condition, we test and compare blood behaviour using conventional rheology (using steel boundary) and using borate glass plates coated with a fibrous collagen hydrogel and with endothelial cells (HUVEC) grown on it. Blood and plasma from healthy volunteers were tested in simple and oscillating shear flow at 0.3mm gap width, according to the microvascular scale. For measurements carried out on hydrogel-coated and uncoated glass plates, the mechanical equilibrium of the contained blood sample could almost be achieved and reveal an elastic response of the physiologic fluid with the storage modulus larger than the loss modulus (G'>G"). The measurement on steel plates exhibit lower moduli and an opposite behavior (G">G"), indicating the loss of contact to the test plate. The highest G'-value was obtained on hydrogel substrate followed by glass, HUVEC monolayers (here G'<G"), and steel. An extended yielding was observed for all coated surfaces. We conclude that the boundary surface conditions highly affect blood flow, and that conventional rheometry underestimates the role of vessel walls - either lined by cells or dissected - in flow resistance. Low flow velocities may play the most important role, as the fluid/substrate interactions are slower and thus facilitated, but high shear rates or deformations occur also in the vasculature.

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- 3: J Phys Chem Lett 2021, 12, 650-657.
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Tuesday 12:10 Prado / Track 4

BM₆

A monophasic blood flow model with slip for precise and accessible prediction of wall shear stresses in the microcirculation

<u>Christos Psevdos</u>, Kostas Giannokostas, Yiannis Dimakopoulos, and John Tsamopoulos Department of Chemical Engineering, University of Patras, Patras, Achaia 26504, Greece

Accurate simulation of 1D blood flow in microtubes has been made possible by the usage of biphasic models that account for the existence of a cell-free plasma layer adjacent to the walls. In this work, we present an application-focused approach by developing a monophasic model that retains the non-Newtonian rheological characteristics of blood while replacing the cell-free layer with a slip condition on the tube walls. Understandably, the purpose of this formulation is not to realistically simulate blood flow in microvessels, but rather to allow for quicker calculation of physiologically important quantities, such as the shear stress on vessel walls. This equivalency is achieved through the construction of a suitable explicit relationship for the slip parameter, which is calibrated via regression on the biphasic model results. Further investigation reveals that the monophasic model is able to closely follow the wall shear stress predictions of a biphasic model, exhibiting deviations below 2% of the expected value. This finding is reinforced by simulations on a vessel network, while also proving the notable reduction in computational time offered by the utilization of the monophasic model.

Symposium El

Emulsions, Foams and Interfacial Rheology

Organizers: Jan Vermant, Teresa Sanz and Mario Minale

Tuesday 10:30 Arenal / Track 5

EI1

Studying droplet coalescence at different length-scales: from films to droplets

Emmanouil Chatzigiannakis¹, Chen Yun², Rana Bachnak², Cari Dutcher², and Jan Vermant¹

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Droplet coalescence and the underlying dynamics of the separating film are some of the most important processes when it comes to emulsion stability. Although multiple techniques have been developed to study interactions between droplets, so far agreement between them has been at best observed only at a qualitative level. In this study we employ two recently developed techniques, i.e. the dynamic thin film balance (DTFB) and the hydrodynamic trap (HT) methods, to study the film drainage and the coalescence processes that are expected to take place in a o/w emulsion stabilized by an oil-soluble non-ionic surfactant. We show that a quantitative agreement between the different length-scales can be observed, as long as the experiments are well-controlled and the comparison is done at the same Capillary number. Using the DTFB we can gain insight in the processes that occur in the microscopic film level, but which affect the coalescence of droplets as studied in the HT. We thus address how variations in the collision angle, Marangoni-caused instabilities, and the possibility of contamination affect the distribution of coalescence times.

Tuesday 11:10 Arenal / Track 5

EI2

Interfacial viscoelastic properties and stability of emulsions

<u>Laura Torres</u>¹, Christine Dalmazzone¹, Isabelle Hénaut¹, and Jan Vermant²

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An emulsion is a system including at least two immiscible liquids where one is dispersed into another, mostly kinetically stabilized. These systems are common in foods, daily life products, biological systems, industrial processes, etc. An example of such an emulsion is produced water (PW), which is an oil in water emulsion, obtained after crude oil extraction and treatment. Depending on the application of emulsions, the involved industries are interested in either a high or a low stability. The first one is obtained by the addition of surface-active molecules (surfactants, proteins, amphiphilic molecules, etc.). Low stability, on the contrary, facilitates the separation of the phases and allows for instance wastewater (produced water) treatment. Coalesence is then readily obtained which leads to an easy separation. Often, the rate determining step in coalescence is thin film drainage. The influence of interfacial rheological stresses, occuring in the stress boundary condition, on the hydrodynamic film drainage has been pointed out, but the detailed influence of the interfacial rheological response is still not fully understood [1]. The aim of this work is to contribute to the experimental data and correlate this influence of interfacial rheology with macroscopic scale destabilization. The globular protein Bovine Serum Albumin (BSA) was chosen to study the impact of microscopic properties on emulsion stability because it leads neither to strong electrostatic repulsions nor to outspoken Marangoni effects. This system offers the opportunity to focus on interfacial viscoelastic properties. The microscopic scale study was carried out with a dynamic Thin Film Balance technique [2] to determine the drainage time, thickness at rupture and the mobility factor of thin films formed between two bubbles. Interfacial rheological properties of air-water and oil-water interfaces were measured with a Double Wall Ring (DWR) geometry, while the emulsion stability was assessed through the gas flotation technology used in wastewat

Tuesday 11:30 Arenal / Track 5

EI3

Coupling flow directions in emulsions with wall roughness

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Dense emulsions behave as a yield stress fluid, that has a critical stress above which the material starts to flow. Typically, the yield stress behaviour is captured in the Herschel-Bulkley model, which assumes a constant yield stress as material parameter. The microscopic origin of the yield stress is still under debate. It can be argued that flow in orthogonal directions simultaneously affect the yield stress and will make the yield stress either flow rate or field dependent. Therefore, it is important to understand how two orthogonal flows affect each other and how the Herschel-Bulkley equation can be generalised to explain such orthogonal flow situations. In this work, we show that wall patterning can be used to generate flow in two orthogonal directions that affect each other significantly. We induce secondary flows via shearing a common yield stress fluid in a rheometer using a concentric cylinder geometry with angled ridges. We image the flow fields by employing rheoMRI methods to show that flow directions in yield stress fluids are indeed significantly decoupled.

Tuesday 11:50 Arenal / Track 5

EI5

Shear rheology of a dilute ferrofluid emulsion: modelling and numerical simulation

Paolo Capobianchi¹, Michael McDougall², Marcello Lappa¹, Fernando T. Pinho³, and Monica Oliveira¹

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A stress model capable of predicting the rheological properties of a ferrofluid emulsion (i.e., an emulsion in which at least one of the two phases is a ferrofluid) subjected to the effect of a constant magnetic field has been developed adopting the approach detailed in Batchelor, J. Fluid Mech. 41, 545 - 570 (1970). Subsequently, the problem of a dilute emulsion made of ferrofluid drops surrounded by a non-magnetizable liquid subjected to the simultaneous effect of a shearing flow and a uniform magnetic field applied in the direction normal to the mean flow has been tackled through numerical simulations using a Volume of Fluid (VOF) approach. The numerical results have revealed that even upon the application of relatively small magnetic fields, the rheological properties of the emulsion can be significantly different from those determined in the absence of the magnetic field. Particularly, it has been observed an increase in the effective viscosity and a reversal of the sign of the two normal stress differences with respect to the case without magnetic field for those conditions where the magnetic force prevails over the shearing force. Comparisons between the results of our model with a direct integration of the viscous stress have provided an indication of the reliability of the model to predict the effective viscosity of the suspension. Moreover, the effective viscosity was found to behave as a monotonic increasing function of the applied magnetic field for a prescribed shearing flow. This latter circumstance allowed us to infer a simple constitutive equation describing the emulsion viscosity.

Tuesday 12:10 Arenal / Track 5

EI6

Novel heat transfer fluid obtained by non-aqueous phase change emulsion

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Thermal energy storage systems are widely used worldwide for efficient utilization and conservation of off-peak power, waste heat and intermittent energy sources, cleverly exploiting clean energy resources and decreasing energy consumption. An efficient, attractive and innovative method of storing thermal energy storage is latent heat storage. The so-called phase change materials (PCMs) can be added to conventional heat transfer fluids (HTFs), obtaining latent functionally thermal fluids that exhibit a higher specific heat storage capacity than conventional HTFs. One approach to obtain these systems is through phase change emulsions (PCMEs). The present work was aimed at formulating stable non-aqueous emulsions of a phase change material, stearic acid, with a melting peak temperature of 68-71°C and silicone oil in order to explore using such systems as novel PCMEs. Thus, the manufacture of these emulsions has been a complicated task due to the major difficulty in formulating stable non-aqueous emulsions, arising from the lack of data regarding the availability of suitable surfactants in such systems. Indeed, there is almost no research concerning non-aqueous PCMEs as latent functionally HTFs. A comprehensive investigation of the thermophysical properties of the emulsion, the viscous and viscoelastic behaviour, as well as their microstructure, was carried out. According to the results, the properties of the emulsion were greatly influenced not only by the amount of dispersed phase present in it but also by the speed of crystallization of this phase. As the temperature lowered, a well-developed three-dimensional network of crystalline structures interconnected with each other was formed as a consequence of the crystallization of the dispersed phase. Thus, the solid-like stearic acid deformable network would contribute to the enhancement of elastic and viscous properties.

Symposium MN

Micro-, Nanofluidics and Microrheology

Organizers: Anke Lidner, Juan Francisco Vega and Amy Shen

Tuesday 10:30 Giralda 6-7 / Track 6

MN1

In vivo and in silico red blood cell lingering and partitioning in the microcirculation

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Erythrocytes, also known as red blood cells, are the most abundant type of cells in the human body. Among the mechanical peculiarities of these cells are their specific shape and high flexibility. These properties are known to be critical for the cells to travel in the capillaries of our circulatory system, whose cross section is sometimes smaller than the erythrocytes diameter. It has also been shown recently that their flexibility can lead them to linger at bifurcations of the microcirculatory system. In this presentation, we discuss how to quantify the amplitude of this lingering. We applied this quantification to both *in vivo* measurements in the microcirculatory system of hamster and to numerical simulations. This reveals that the lingering competes with the classical Zweifach-Fung effect, which governs their partitioning through bifurcations of bigger vessels. More

accurately, we demonstrate a linear correlation between the lingering amplitude and deviations from the classical model of erythrocytes partitioning from the literature. This opens new interpretation to the hinderance of microcirculation by rigidified erythrocytes.

Tuesday 10:50 Giralda 6-7 / Track 6

MN2

Tears for microrheology: Experimental study of artificial eyedrops

Juan Francisco Vega¹, Mercedes Fernandez², Itxaso Calafel³, Martínez-Soroa Itziar⁴, Pérez Ane⁵, and Acera Arantxa⁶

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The rheological properties of different lubricating eyedrops applied for the medical treatment of dry-eye disease have been studied. At this first stage of the research the interest has been focused on hyaluronic acid-containing lubricant eyedrops. The viscoelastic properties of different formulations of hyaluronic acid-containing lubricant eyedrops have been determined by means of passive microrheology using nanoparticles as tracers. This technique is able to probe the local viscoelastic properties of soft materials, including biopolymers, by measuring the motion of these tracer nanoparticles embedded within them [1-3]. We have obtained the frequency dependence of the complex viscosity at T = 293 K of different commercial samples of artificial eyedrops. From the microrheological results, it has been possible to determine interesting properties of the biopolymeric solutions as the Newtonian viscosity and the shear thinning index by assuming the Cox-Merz rule. These two parameters are related to two main features of the solutions: the hydrodynamic size of the HA macromolecule and the HA concentration in the solution. In this work, it is demonstrated that passive micro-rheology is a very suitable technique to study the viscoelastic properties of artificial tears. However, to obtain a good result it is necessary to make an optimal selection of the tracer particles [4]. The results open the door for detailed studies of other systems, including natural tears of ophthalmic patients.

References:

- 1. P. Cicuta and A.M. Donald. Microrheology: a review of the method and applications. Soft Matter 3, 1449-1455 (2007)
- 2. W. Liu and C. Wu. Rheological study of soft matters: A review of microrheology and microrheometers. *Macromol. Chem. Phys.* 219(3):1700307 (2017)
- 3. K. Joyner, S. Yang, and G.A. Duncan. Microrheology for biomaterial design. APL Bioeng. 4, 041508 (2020)
- 4. A. Espasa-Valdepeñas, J.F. Vega, V. Cruz, J. Ramos, A.J. Mu"ller and J. Martinez-Salazar. Revisiting polymer-particle interaction in PEO solutions. *Langmuir* 37 (13)

Tuesday 11:10 Giralda 6-7 / Track 6

MN3

Alignment of colloidal rods in crowded environments

Vincenzo Calabrese, Stylianos Varchanis, Simon J. Haward, and Amy Q. Shen

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Understanding the flow and alignment of colloidal rods in crowded environments is pivotal for manufacturing structurally ordered materials in large-scale processing operations (e.g. fibre spinning). Unfortunately, the parameters controlling the flow-driven alignment of colloidal rods in crowded environments remain unclear. By coupling flow-induced birefringence and shear rheometry, we investigate the effect of two contrasting crowding agents at aligning rigid rod-like colloids under flow. We investigate the case where soluble polymers provide confinement to the colloidal rods (polymer-crowding) and analyse against a distinct case where colloidal rods restrain the motion of each other (self-crowding). We show that the colloidal rods probe the surrounding polymer fluid as a discrete medium rather than a continuum. The onset of flow-induced alignment of colloidal rods couples with the polymer relaxation time rather than the bulk viscosity as expected for a continuum fluid. At sufficiently strong shear rates, the colloidal rods' orientation to the flow follows a universal trend independent of the crowding type. Our results provide control parameters for the alignment of colloidal rods in crowded environments, which will be beneficial for the synthesis and design of anisotropic materials.

Tuesday 11:30 Giralda 6-7 / Track 6

MN4

Dynamics of flexible Brownian filaments in 2D porous media

<u>Zhibo Li</u>, Anke Lindner, and Olivia du Roure *ESPCI*, *PARIS*, *Île-de-France 75005*, *France*

Understanding the dynamics and morphological transitions of polymer chains in viscous flows is central to deciphering the rheological phenomena observed in polymer solutions, like shear thinning, normal stress differences, and viscoelastic instabilities. The flow of such suspensions through porous media plays a crucial role in various applications such as lab-on-chip analysis, enhanced oil recovery, membrane separation, and chromatography. Following our previous studies of the dynamics of elastic filaments in simple shear and strong compressional flow, we study morphological and orientational dynamics of actin filaments in regularly arranged porous media using a combination of microfluidics and fluorescence microscopy.

Porous media can be seen as the combination of many contraction-expansion domains resulting in flow with spatially alternating characteristics, some regions being dominated by shear and others by elongation/compression. Because of the repetition of the motif, in regularly arranged porous media, the deformation and the orientation of transported actin filaments show periodicity and history. The complex environment causes actin

filaments to show many distinct morphological dynamics. The filaments can not only buckle in two dimensions (2D) to form U-, S-, and W-shaped conformations, but can also be deformed in three dimensions (3D) to become folded, coiled or even helical. Some of the morphological transitions have already been observed and explained in previous studies, demonstrating that the elasto-viscous number, which compares viscous drag forces to elastic bending forces, controls the dynamics of the filament. The present work is a study of the distribution of morphologies and their transition as a function of the porous media geometry and the flow angle.

Tuesday 11:50 Giralda 6-7 / Track 6

Keynote

MN₅

Microfluidic flow of vesicle prototissues as a model for cellular tissues

Laura Casas-Ferrer, Majid Layachi, Gladys Massiera, and <u>Laura Casanellas</u> *Laboratoire Charles Coulomb, Université de Montpellier, Montpellier 34000, France*

The aim of this work is to characterize the flow of biomimetic tissues in microfluidic confinement, as a simplified model for cellular tissue flows observed in complex physiological problems. The prototissues have been conceived by the controlled assembly of giant unillamelar vesicles (GUV) and display tuneable mechanical properties and typical sizes [1]. Aspiration experiments are performed in microfluidic constrictions in order to test the role of GUV-GUV adhesion and aggregate size on the rheological response of the prototissue. In particular, our results show that depending on the aspect ratio between the prototissue and the constriction size the depicted flow behaviour is qualitatively differently. For sizes comparable to the channel constriction, prototissues slightly deform to pass through the constriction and elastically recover their initial shape after passage. For considerably larger sizes instead, a viscoelastic response is observed upon aspiration and almost no shape recovery is obtained after passage of the constriction. This irreversible deformation can be attributed to the rearrangements that take place at the vesicle level, which are dependent, in turn, on the degree of GUV-GUV adhesion [2].

References:

- [1] L. Casas-Ferrer, A. Brisson, G. Massiera and L. Casanellas, Design of vesicle prototissues as a model for cellular tissues. *Soft Matter*, 17, 5061 (2021).
- [2] I. Golovkova, L. Montel, F. Pan, E. Wandersman, A. M. Prevost, T. Bertrand and L-L. Pontani, Adhesion as a trigger of droplet polarization in flowing emulsions, *Soft Matter*, 17, 3820 (2021).

Tuesday Afternoon

Symposium NF

Non-Newtonian Fluid Mechanics and Computational Rheology

Organizers: Miguel Nóbrega, Baltasar Mena and Corneliu Balan

Tuesday 13:50 Giralda 1-2 / Track 1

Keynote

NF7

Elastoinertial turbulence via Tollmien-Schlichting instability

Ashwin Shekar, Richard J. Hommel, and Michael D. Graham

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Recent studies of channel and pipe flows of dilute polymer solutions at Reynolds numbers Re~1000-10000 have revealed a viscoelasticity-driven chaotic flow state denoted elastoinertial turbulence (EIT). Computations indicate that EIT displays tilted sheetike layers of polymer stretch with weak spanwise-oriented flow structures - a sharp contrast to the 3D quasistreamwise vortex structures that make up inertia-driven Newtonian turbulence. Direct simulations of two-dimensional channel flow of a FENE-P fluid have revealed the existence of a family of flows that is nonlinearly self-sustained by viscoelasticity with structure closely related to the classical Tollmien-Schlichting (TS) wave. At Reynolds number Re=3000, there is a solution branch with TS-wave structure but which is not connected to the Newtonian solution branch. At fixed Weissenberg number, Wi, and increasing Reynolds number from 3000-10000, this attractor goes from displaying a sheet of weak polymer stretch to an extended sheet of very large polymer stretch. This evolution arises from the coil-stretch transition when the local Weissenberg number at the hyperbolic stagnation point of the Kelvin cat's eye structure of the TS wave exceeds 1/2. At Re=10000, the Newtonian TS wave evolves continuously into the EIT state as Wi is increased from zero to about 13. The multilayer structure emerges through a "sheet-shedding" process by which the individual sheets break up to form the layered multisheet structure characteristic of EIT. Finally, having established the connection between the TS wave solution and EIT, we consider the question of how low in Reynolds number this solution family persists. At Wi=30, we find that the viscoelastic TS wave (EIT) solution family persists down to Re between below 200. These results may be related to observations of non-laminar flow in polymer solutions at Reynolds numbers below the Newtonian transition threshold.

Tuesday 14:30 Giralda 1-2 / Track 1

NF9

Taylor-Couette stability modes of cellulose nanocrystals suspensions directly from birefringence patterns Reza Ghanbari¹, Vahid Haghighat², Marianne Liebi³, Léo Mutschler¹, Kim Nygård⁴, Ann E. Terry², and Roland Kádár¹ Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg 41296, Sweden; ²CoSAXS beamline, MAX IV Laboratory, Lund University, Lund 22100, Sweden; ³Department of Physics, Chalmers University of Technology, Gothenburg 41296, Sweden; ⁴ForMAX beamline, MAX IV Laboratory, Lund University, Lund 22100, Sweden

Complex fluids and in particular, polymer solutions demonstrate rich flow transitions subjected to shear flows. Cellulose nanocrystals (CNCs) can self-assemble into liquid crystalline (LC) phases with distinctive birefringence patterns in the presence of shear flows. In this work and for the first time, our experiments point to unprecedented birefringence patterns of aqueous CNC suspensions in Taylor-Couette (TC) flow, where the squeezed fluid between two concentric cylinders is subjected to shear by the relative rotation of the cylinders. The setup is a custom-made TC visualization cell implemented on an Anton Paar MCR702 Multidrive in separate motor-transducer configuration. The visualization setup includes cross-polarized optical imaging making the supercritical flow patterns directly observable from the color patterns. This is in contrast to conventional TC setups whereby visualization additives are used to evidence flow instabilities. Thus, we examine flow transition sequences for biphasic CNC suspensions with increasing LC content. Our results are indicative of remarkable changes not only in the kinetics of flow transitions from primary azimuthal flow to secondary flow patterns such as Taylor Vortex Flow or high-order transitions at different CNC wt%, but also in the sequence of flow cascade, where exotic flow states emerge for counterrotating TC flows. On the one hand, our unique optical setup facilitates the detailed investigation of flow patterns towards the observation of birefringence fingerprints in TC flow. On the other hand, a strong insight is gained on how CNC nanorods and their self-assembled chiral nematic mesogens lead to different spatiotemporal features as the Reynolds and Elasticity numbers are altered through varying rotational velocities and the increase in CNC wt%, respectively. Our work sheds light on the role of self-assembly mechanisms in determining flow translations in LC polymers compared to their unfolded macromolecule counterparts.

Tuesday 14:50 Giralda 1-2 / Track 1

NF10

The fluid dynamics of dripping onto a substrate

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Extensional flows of complex fluids are important in many industrial applications, such as spraying & atomisation, as well as microfluidic-based drop deposition. Dripping-on-Substrate (DoS) is a conceptually-simple, but dynamically-complex, probe of the extensional rheology of low viscosity non-Newtonian fluids. It incorporates the capillary-driven thinning of a liquid bridge, produced by a single drop as it is dispensed from a syringe pump onto a solid substrate. By following the filament thinning process the extensional viscosity and relaxation time of the sample can be determined. Importantly, it allows experimentalists to measure the extensional properties of lower viscosity solutions than is possible with commercially-available capillary break-up extensional rheometers. Understanding the fluid mechanics behind the operation of DoS will allow us to optimise and extend the performance of this protocol. To achieve this we employ a computational rheology approach using adaptively-refined axisymmetric numerical simulations with the open-source Eulerian code, Basilisk. The volume-of-fluid technique is used to capture the moving interface, and the log-conformation transformation provides a stable and accurate solution of the viscoelastic constitutive equation. Here we focus on understanding the role of elasticity and finite chain extensibility on controlling the Elasto-Capillary (EC) regime, as well as the perturbative effects that gravity and the wetting of the solid substrate play in setting the evolution of the self-similar thinning and pinch-off dynamics. To illustrate the interplay of these different forces we construct a simple one-dimensional model that captures the initial rate of thinning, when the interplay of inertia and capillarity dominates and the structure of the transition region to the non-linear EC regime where the rapidly growing elastic stresses in the thread balance the capillary pressure as the filament thins towards breakup.

Tuesday 15:10 Giralda 1-2 / Track 1

NF11

Constitutive modeling for flowing micellar solutions: the structure factor

Octavio Manero

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Micellar solutions exhibit mechanical instabilities under flow, which may be increased by concentration fluctuations. Elastic stresses increase concentration fluctuations, which are experimentally observed by rheo-optical techniques, such as Rheo-SALS, depicting characteristic "butterfly" patterns. Scattering patterns provide information on the structure factor, arising from concentration fluctuations of the flowing solution. We describe experiments and models by which the structure factor can be calculated for these micellar solutions.

Tuesday 16:30 Giralda 1-2 / Track 1

NF12

Generalised Newtonian fluid models in complex flows

Robert J. Poole¹, Bayode Owolabi², Rishav Agrawal³, Jnandeep Talukdar⁴, and Chao-An Lin⁵

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Generalised Newtonian Fluid (GNF) models which assume that the viscosity of a non-Newtonian fluid can be modelled inelastically as a time-independent, i.e. instantaneous, scalar function of the rate of strain, are used frequently. Classical examples of such models include the power-law, Carreau and Cross models (plus many others). In general flows these models are simply a function of the magnitude of the strain rate tensor (the magnitude being related to the second principal invariant of this tensor). Strictly these models are restricted to steady, simply-shearing flows. Here we investigate the flow of such models - which retain the central idea of rather simple "inelastic" non-Newtonian fluid models - whilst attempting to move beyond the constraints of making such models simply a function of just the second invariant of the rate of strain tensor and potentially suitable for more general flows.

One approach has been to make the model a function of both the second and third invariants such that different viscosity behaviour can be predicted in shear and extension (Debbaut & Crochet, 1988). These models have been shown to be somewhat successful in predicting some well-known features of polymeric flows normally associated with elasticity/strong extensional viscosity effects. Here we investigate their suitability for modelling a rigid polymer (a xanthan gum) in turbulent channel flow and also for predicting enhanced pressure drop in laminar axisymmetric contraction flows.

References:

Debbaut, B., & Crochet, M. J. (1988). Extensional effects in complex flows. Journal of Non-Newtonian Fluid Mechanics, 30(2-3), 169-184.

Tuesday 16:50 Giralda 1-2 / Track 1

NF13

The Oldroyd-A model

Rebecca J. Hill¹, Mahdi Davoodi², and Robert J. Poole¹

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In his seminal paper Oldroyd (1950) laid down the general foundations for deriving invariant constitutive equations. Oldroyd discussed how there are an infinite number of possible sets of invariant equations of state which can be proposed for the Jeffreys-type model he used for illustrative

purposes. Oldroyd then illustrated two possible invariant forms of this model, one which he called case "A" - which used a lower convected derivative to make the Jeffreys model suitable for general flows - and case "B" which uses an upper convected derivative. Oldroyd then showed how, despite "at first sight these might appear to be trivially different generalizations", that in rotational Couette flow one model (the "Oldroyd-B") can give rise to the Weissenberg effect of rod climbing whilst the other, (the "Oldroyd-A") does not. This is because, despite both models exhibiting a constant shear viscosity, the Oldroyd-B model gives N_1 >0 and N_2 =0 whereas the Oldroyd-A gives N_1 =- N_2 . The Oldroyd-A model has remained essentially unstudied.

Interestingly, although fluids exhibiting N_1 =- N_2 do not seem (yet) to have been reported in the experimental literature, such behaviour has been predicted to occur theoretically for fluids exhibiting "sheet-like" or "film-fluid-like" behaviour such as foams or dense emulsions (Larson, 1997). Arguably, the Oldroyd-A model also represents the simplest model which can incorporate N_2 effects and allow issues due to elasticity to be "separated out" from those due to shear-thinning. Here we investigate the Oldroyd-A model in a range of duct flows, including axisymmetric pipe flow, partially full pipe flow and square duct flow, using both analytical and numerical means.

References:

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Tuesday 17:10 Giralda 1-2 / Track 1

NF14

Shear-thinning and shear-thickening effects in the Oldroyd-B model

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We present a comprehensive analytical and numerical study of shear-dominated flows of Oldroyd-B fluids, demonstrating that shear-thinning and shear-thickening effects can be predicted by the Oldroyd-B model. Starting from transient ideal Couette flow, we show that shear-thinning takes place when the shear rate is increased and shear-thickening when it is decreased. This happens because less work is required to increase the shear rate than to decrease it. Generalizing this observation to non-homogeneous steady flows, we show that reduced flow resistance is present around streamlines with increasing shear rate and increased flow resistance is present around streamlines with decreasing shear rate. We demonstrate this effect in smoothly converging or diverging Couette and Poiseuille flows. Finally, we show that the reduced flow resistance observed in the flow past a cylinder in a straight channel is caused by the contraction-expansion-like flow that takes place at the sides of the cylinder. Our findings are validated by a wide parametric analysis regarding the geometrical characteristics of the flow domains and the material parameters of the Oldroyd-B model.

Tuesday 17:30 Giralda 1-2 / Track 1

NF15

Koopman with control for constitutive law identification

Emily J. Southern and Eric E. Keaveny

Mathematics, Imperial College London, London, United Kingdom

Constitutive laws relate the stress in a material to its deformation. Determining the constitutive law experimentally typically involves subjecting the material to a prescribed deformation and measuring the force required to achieve it. Such experiments can often assume that the sample experiences homogenous shear and its response is linear. The decision on which constitutive law to fit to the resulting data is based on the rheologist's knowledge about the fluid in relation to the catalogue of standard models appearing in the literature. In this talk, we present an alternative approach based on the application of Koopman operator theory and Dynamic Mode Decomposition (DMD) in the context of control, which extracts material parameters that arise in stress-evolution equations of viscoelastic fluids directly from data. We will present results from various tests of the framework that highlight its accuracy in identifying material parameters. We will discuss how data should be chosen, but also demonstrate how data from multiple experiments can be combined to improve resolution. Finally, we will show that our approach provides a natural way to utilise data from the nonlinear regime and extends to higher-dimensional data sets where spatial data within a sample might be available.

Tuesday 17:50 Giralda 1-2 / Track 1

NF16

Numerical simulations of the stretching and leveling flows of freestanding axisymmetric viscoelastic liquid films

Davide Amoroso and Massimiliano M. Villone

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Freestanding liquid films play an important role in the field of multiphase systems, like foams and emulsions. Often, these are made of viscoelastic materials, thus the deformation history affects their stretching and leveling dynamics. The purpose of this work is to study the behavior of axisymmetric viscoelastic films through finite-element numerical simulations. In particular, two constitutive equations are considered, namely, the Oldroyd-B and Giesekus models. The circular films are subjected to a bi-axial extensional flow until a certain final radius, then they are left free to relax, thus to level their shape under the combined action of surface tension, elastic energy stored during the stretching phase, and viscous resistance. We perform a parametric study aiming at understanding the effects of the geometrical, physical, and operating parameters on the film stretching and leveling dynamics. Specifically, we investigate the interplaying effects of the height and radius of the film, of the viscosity and

relaxation time of the liquid, and of the strain rate imposed during the stretching phase. The effects of the operating parameters on the apparent equi-biaxial viscosity of the viscoelastic liquids are also studied.

Symposium GS

Gels and Self Assembling Structures

Organizers: Joao Maia, Domenico Gabriele and Juan de Vicente

Tuesday 13:50 Santa Cruz / Track 2

GS7

The gel/glass duality of weak colloidal gels

<u>Arnaud Poulesquen</u>¹, Bavand Keshavarz², Donatien Gomes Rrodigues¹, Michela Geri², Jean-Baptiste Champenois¹, Matthew G. Frith³, Jan Ilavsky³, Thibaut Divoux⁴, and Gareth H. McKinley²

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Alumino-silicate hydrogels are widely used in different industrial applications. These gels are simply made from a class of alumino-silicate materials known as zeolite precursors. Mixing two solutions of sodium aluminate and an alkali-silicate together initiates a series of condensation and bond-breaking reactions leading to a relatively rapid process of gel formation. The rheological behavior of the mature gels that form after gelation show interesting power law signatures in the linear viscoelastic regime over a wide range of timescales and frequencies. However, due to the rapidly mutating nature of these gels in the vicinity of the gelation point, little is known about the temporal evolution of the mechanical properties during the gelation/curing process. We use the Optimally Windowed Chirp (OWCh) technique to obtain the time- and frequency-resolved response from the material. This novel method enables us to reduce the mutation number of the system substantially and obtain fast and precise measurements. Parallel to mechanical spectroscopy we also study the structural evolution of these gels using time-resolved SAXS/WAXS measurements. Using these methods we can explore the mechanical/structural evolution of the gel over a wide range of time and length scales. We therefore construct the viscoelactic moduli of these weak colloidal gels over eight decades in material times by using the time-connectivity superposition principle. This protocol reveals the dual nature of the relaxation time spectrum with gel- and glass-like characteristics at large and small scales, respectively. These results enable us to understand connections between the structure and power-law rheology observed in the mature gel and more importantly provide an accurate spatio-temporal record of the timescales and elasticity of the evolving network.

Tuesday 14:10 Santa Cruz / Track 2

GS8

Influence of particle size and magnetic field strength in the directed self-assembly under toggled fields

<u>Guillermo Camacho Villar</u>, José Rafael Morillas Medina, Alejandro Rodriguez-Barroso, Óscar Martínez Cano, Matthew Terkel, and Juan de Vicente

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Magnetorheological (MR) fluids of interest in current applications are prepared by dispersion of magnetisable particles in (non-magnetic) liquid carriers. They exhibit a remarkable rheological change (so-called MR effect) upon the application of a magnetic field. The reason for this is the magnetic field-guided colloidal assembly of the dispersed magnetisable particles [1].

The self-assembly of magnetic colloids can be controlled through the field configuration (DC, AC or combinations) [2]. Understanding the underlying physical mechanism is crucial to enhance magnetorheology and successfully answer fundamental questions such as whether a limiting MR effect exists. Additionally, finding new routes to speed up the directed self-assembly is a hot topic today [3].

In this communication we construct a device that is capable to generate strong toggled magnetic fields and carry out carefully controlled experiments on magnetic latex particles of different size at a wide range of field frequencies. We show that the aggregation process is substantially accelerated when the magnetic field strength is increased for sufficiently small particles at the critical frequency. For Lambda ratios of the order of λ ~100 the classically reported two step aggregation process [4] becomes a single one scaling with ~t^{-0.4}.

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Acknowledgements:

This work was supported by MICINN PID2019-104883GB-I00 project, Junta de Andalucía P18-FR-2465 and A-FQM-396-UGR20 projects and European Regional Development Fund (ERDF). G.C. acknowledges FPU20/04357 fellowship. J.R.M. acknowledges European Union's Horizon 2020 research and innovation program under the Marie Sklodowska-Curie Grant (EFST)-H2020-MSCA-IF-2020 (Grant 101030666).

Tuesday 14:30 Santa Cruz / Track 2

GS10

Nonlinear elastic properties of gels made of different types of gelling carrageenan and their blends

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Gelling carrageenans are additives used extensively in the food industry, but the structure-elastic relationships in the gel network are still to be clearly established [1]. This contribution focuses on the insufficient rationalization of carrageenan gel elasticity by models which take on board mechanically relevant structural features. After introducing selected linear and nonlinear elastic models, preliminary results comparing such models to structural and rheological data are presented. In particular, the concentration scaling of the strain hardening exhibited by iota-carrageenan and hybrid-carrageenans with different chemical structure is discussed. In addition, the nonlinear elastic properties of blends of kappa- and iotacarrageenan are systematically compared with those of hybrid-carrageenan gels exhibiting equivalent disaccharide contents.

[1] Loic Hilliou, Structure-Elastic Properties relationships in Gelling Carrageenans (2021), Polymers, 13: 4120. DOI: 10.3390/polym13234120.

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Santa Cruz / Track 2 14:50

GS11

Chitosan-based hydrogels: Influence of crosslinking strategy on rheological properties Fabien Dutertre

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The thiol-ene click chemistry is a versatile methodology widely used to form bio-hydrogel by crosslinking polysaccharides. In this opportunity, chitosan-based macrogels were prepared through thiol-ene reactions. First, the chitosan (CS) was functionalized with a vinyl group (CS-ene) or thiol groups (CS-SH). Then, two crosslinking strategies (photochemically and thermochemically activated) were compared: (1) CS-ene with CS-SH and (2) CS-ene cross-linked with di(ethylene glycol)-bis(thiol) (dEG-(SH)₂). The first strategy, where the crosslinking reaction occurs between two functionalized macromolecules and intra-chains crosslinking reactions are avoided ("no loop"), leads to the formation of weak gels. In this case, rheology displays a critical gel point (G' ~ G" ~ $\omega^{0.5}$) and the cross-linking density estimated by NMR slightly depends on the substitution degree of pentenoate-modified CS. The second strategy, where the functionalized chitosan (CS-ene) is crosslinked by reaction with a small dithiol molecule (dEG-(SH)₂), provided stronger gels with a faster diffusion of the dEG-(SH)₂ during the network formation, which strengthen the gel modulus. The last strategy is the most efficient methodology for the macrogel synthesis, despite that the "loop" formation cannot be fully avoided. Finally, both methodologies were transposed at the microscale through inverse emulsion to attempt to synthesize chitosan-based microgel.

16:10 Santa Cruz / Track 2

GS12

Thermoresistant collagen/chitosan hydrogels for regenerative applications: Rheological and microstructural characterization

Mercedes Jiménez-Rosado, Pablo Sánchez-Cid, Antonio Guerrero, Alberto Romero, and Víctor Perez-Puyana Chemical Engineering, Universidad de Sevilla, Sevilla, Spain

Hydrogels are considered excellent biomaterials for soft tissue regeneration. In this way, different biopolymers have been evaluated to form hydrogels. Furthermore, the combination of different biopolymers could improve the properties of these hydrogels, combining the high biocompatibility of biopolymers such as collagen (CG) with the good thermomechanical resistance of others such as chitosan (CS). Nevertheless, all the CG/CH combinations studied so far to obtain hydrogels require a chemical crosslinking to generate or promote their network structure, which typically complicates hydrogel processing and compromise their cytotoxicity. In this way, the main objective of this work was the use of physical crosslinking to obtain a hybrid CG/CS hydrogel. However, to tackle the formation of physically structured hybrid hydrogels with suitable rheological behavior, various physical changes may be necessary (i.e. temperature drop or pH change). Thus, the sequence of processing stages can be regarded as critical to achieving the desired properties of the hydrogel and, therefore, must be evaluated and optimized. Rheology has been selected as a key methodology to evaluate the thermomechanical properties of CH/CS hydrogels by using small amplitude oscillatory shear tests. In addition, hydrogel microstructure has also been studied by scanning electron microscopy. The main results showed that the sequence of processing steps can be used to tailor the rheological and microstructural properties of the hybrid hydrogels CG/CS highlighting the dominant role of either of the two biopolymers. It can be concluded that there is a synergy between collagen and chitosan that improved the properties of hydrogels, showing good thermomechanical resistance that could enhance their potential use in regenerative applications.

Tuesday 16:30 Santa Cruz / Track 2

GS13

The effect of temperature and particle size on the mechanical properties of particulate crosslinked gelatinmethacryloyl gels

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Crosslinked gelatin-methacryloyl is an excellent candidate for tissue engineering purposes due to its excellent biocompatibility and easily tunable mechanical properties. It is a chemically modified natural polymer that undergoes UV-induced crosslinking in the presence of a photo-initiator. The latter induces chemical crosslinks in addition to the physical crosslinks inherent to gelatin. These physical crosslinks are present below a temperature of 35 $^{\circ}$ C as single α -helices or triple helices depending on the chain conformation and thermal preparation conditions. A triple helix consists of three individual helices which are all in trans-conformation, whereas an α -helix can be in trans- or cis-conformation. To design a stable scaffold material that maintains its mechanical properties inside the human body, rheological characterization at physiological conditions are of great importance. Here, crosslinked gelatin-methacryloyl is used in powder form of which the powder particles swell upon addition of water. The rheological properties of three distinct gel materials, which are chemically identical but differ in particle characteristics, are studied at temperatures ranging from just below room temperature to elevated temperatures encountered inside the human body. The absolute values of the elastic moduli are related to the swell behaviour of the particles which is particle size dependent. This swell behavior has been investigated by laser diffraction and light microscopy at multiple temperatures. Furthermore, the gels show a decrease in modulus at elevated temperature related to the loss of physical crosslinks. Upon cooling, the modulus of certain gels is not restored. The (ir)reversibility of the reduced modulus can be correlated to the swell behaviour of the particles and conformation of the gelatin chains. The latter has been characterized as a function of temperature by circular dichroism, FTIR-spectroscopy, and NMR-spectroscopy.

Tuesday 16:50 Santa Cruz / Track 2

GS14

Controlling the gelation of cellulose-based systems: Macro- and microrheology studies

<u>Luís Alves</u>¹, Rasteiro Maria¹, Gamelas José¹, Magalhães Solange¹, Coelho Natacha², Alexandra Filipe², Bruno Medronho², Filipe Antunes¹, Björn Lindman³, Daniel Topgaard⁴, and Yeshayahu Talmon⁵

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Cellulose-based systems can form gels in a wide range of concentrations and/or conditions. Gelation of the suspensions or solutions can be induced or delayed according to the needs. For example, gelation of cellulose dissolved in alkali solutions, being a relevant issue with impact on the stability and processability of the solutions, is still poorly understood. The gelation of these systems can be delayed or even avoided by the addition of selected additives, such as urea. On the other hand, cellulose dissolved in concentrated acidic aqueous solvents form extremely viscous solutions; increasing the temperature leads to a gradual transition from an anisotropic-to-isotropic phase, as suggested by a loss of birefringence in optical microscopy. Cellulose-derivatives can change the rheology of plant culture media and impact plant shoot growth. Finally, the rheology of suspensions of TEMPO oxidised nanofibrils can be tuned by changing the physical-chemical conditions and gelation can be induced, facilitating the preparation of cellulose nanofibrils based films. Gelation and phase transitions were studied by different techniques, ranging from rheometry and microrheology to electron and optical microscopy, and NMR spectroscopy. An excellent agreement between the different techniques was found, especially between optical microrheology and conventional mechanical rheometry. Keywords: Aggregation, Cellulose; Hydrogels, Rheological properties; Solutions; Suspensions.

Tuesday 17:10 Santa Cruz / Track 2

GS15

Relations between rheology and processing properties in the 3D-printing of k-Carrageenan physical hydrogels Simona Russo Spena, Daniele Tammaro, and Nino Grizzuti

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Additive manufacturing, commonly known also as 3D-printing or rapid prototyping, has been introduced since the late 1980s and offers a new paradigm for engineering design and manufacturing, as it allows to fabricate very complex structures. In particular, 3D-printing of hydrogels is a very popular method to produce scaffolds to be used in tissue engineering and other biomedical applications. When printing a thermo-reversible physical hydrogel, a delicate balance between thermal and flow parameters exists. The characteristic times of the sol-gel transition, regulated by a well-defined thermal history, must be compared and optimized with respect to the characteristic times of the printing process. In this work we propose a thermo-rheological approach to the 3D-printing of physical hydrogels. In particular, a low-cost desktop 3D-printer for thermoplastic polymers was suitably modified to print a 1.5% wt solution of k-Carrageenan. The thermal behaviour of the printer was determined by performing experimental measurements of the temperature time evolution during the different processing steps, from solution loading to the extrusion of the incoming gel to the final solidification stage. In parallel, linear viscoelastic oscillatory shear measurements were performed in an Anton Paar MC702 rheometer under thermal histories as close as possible to those previously measured in the printing process. The comparison between the rheological results and the quality of printing under different thermal histories is presented and discussed, highlighting the main relations between rheological and processing behaviour, which help in the assessment and optimization of the printing conditions.

Tuesday 17:30 Santa Cruz / Track 2

GS16

Lignin as effective filler for enhancing cushioning properties of castor oil-based elastomers: Rheological and mechanical properties

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In this study, lignin was proposed as an effective filler for castor oil-based polyurethane elastomers in order to improve mechanical properties. Different lignin and HDI concentrations have been tested and evaluated. For comparison, a reference sample (only castor oil and HDI) (COPE) was also prepared. Considering the rheological properties, the addition of lignin hinders the elastic properties, as COPE showed a more elastic behaviour compared to other polyurethanes with similar HDI content. Lignin addition produces maximum values of linear viscoelasticity functions at 8%. For a lower lignin content, an excessive crosslinking achieved during the lignin functionalization previous step compromises further the compatibilization with castor oil. For a higher lignin content, the too-high lignin/HDI ratio reduces the free-HDI available to react with castor oil during the second step, again diminishing the viscoelastic functions. As expected, an increase in HDI concentration strengthened the viscoelastic response, as a higher crosslinked network was achieved. The mechanical performance of the polyurethane elastomers was tested from compressive and tensile points of view. The high elastic behaviour observed for COPE was also associated to certain embrittlement, as observed by the low compressive and tensile stresses and strains at failure. By lignin addition instead, superior mechanical properties were generally observed. A small addition of lignin (4%) raised elongation and compression at break. When lignin concentration was doubled, outstanding strains were still observed and stresses were also exceptionally improved. Increasing HDI concentration led to high stresses at failure, but compromising the strains achieved. The dynamic properties of the optimum formulation were also evaluated. Overall, this study demonstrates the suitability of lignin to act as filler to perform castor oil-based polyurethane elastomers for a wide variety of applications.

Symposium SP

Suspensions

Tuesday 17:50 Santa Cruz / Track 2

SP4

Novel PDMS particle transparent suspensions suitable for visualization and velocimetry experiments

João Carneiro, Joana Ferreira, João Miranda, and João Moreira de Campos

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Optical visualization and velocimetry measurement techniques, such as Laser Doppler Velocimetry (LDV) and Particle Image Velocimetry (PIV), are frequently used in experimental fluid mechanics to study particulate fluids or dilute suspensions. For highly concentrated particle suspensions, the suspensions need to be transparent, otherwise the light diffraction dampens the optical measurement techniques. In order to obtain a transparent suspension, the refractive index of both the solid and liquid components must match. Suspension turbidity has long been a problem, and the availability of transparent suspensions is scarce (Wiederseiner, et al., 2011). This study reports the generation of a transparent suspension with variable rheology and great optical properties. The particulate matter comprises of sub 10 µm spherical silicone Polydimethylsiloxane/silicone (PDMS) particles, which is a widely used commercially available material. PDMS is transparent, low-cost, biocompatible and non-toxic polymer, and has been traditionally used as a material for catheters, drainage tubing, insulation for pacemakers, membrane oxygenators, among others, and widely used to manufacture microfluidic channels and vascular phantoms (Mata et al., 2005). Due to the low refractive index of PDMS, it is a very attractive material to produce suspensions to be handled in experiments involving visualization and velocimetry techniques In this study, the flow field of suspensions comprised by a DMSO Dimethyl sulfoxide (DMSO)/water base fluid and PDMS particles, up to 20% (w/w), are successfully investigated in microchannels by Particle Image Velocimetry (PIV) exhibiting negligible light diffraction.

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Symposium SP

Suspensions

Organizers: Francisco Rubio, Francisco Galindo-Rosales and Octavio Manero

Tuesday 13:50 Nervión / Track 3

SP7

Simulations of concentrated suspensions of rough particles under boundary, mixed and full-film lubrication regimes

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The rheology of concentrated suspensions of particles is complex and typically exhibits a shear-thickening behavior. Despite the recent interest arisen, the causes of the shear-thickening remain unclear. Frictional contacts have been able to explain the discontinuous shear thickening (DST) in theoretical and simulation works (Mari et al., 2014) Surprisingly, the interparticle friction coefficient is considered to be a constant in most simulations and theoretical works reported to date despite the fact that tribological experiments demonstrate that the friction coefficient can not only be constant (boundary regime) but also decrease (mixed regime) or even increase (full-film lubrication regime), depending on the normal force and the relative velocity of the particles. When two particles are subjected to a large normal force and/or the relative velocity is small, i.e. the boundary lubrication (BL), the particles get in contact and the friction coefficient is constant in good agreement with previous publications. However, when the interparticle normal forces are small and/or the relative velocities are large, the interstitial fluid is entrained in the contact. This regime can be described in terms of the so-called Elasto-Hydrodynamic Lubrication (EHL) theory. Interestingly, the transition (i.e. mixed lubrication) between the BL regime and the EHL regime is governed by the particles' roughnesses (de Vicente et al., 2005). In this communication, particle-level simulations of suspensions of hard spheres were carried out using short-range lubrication based on Prasanna Kumar et al. (2021) and roughness-dependent frictional forces describing the full Stribeck curve and spanning from the BL to the EHL regime (de Vicente et al., 2005). Suspensions with different particle's roughness were simulated to show that the particle roughness is a key factor in the shear-thickening; for sufficiently rough particles the suspension exhibits shear-thickening while for sufficiently smooth particles the DST disappears.

Tuesday 14:10 Nervión / Track 3

SP8

Influence of coupled friction and adhesion on the rheology of non-Brownian suspensions

Michel Orsi, Laurent Lobry, and François Peters

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In the last decade, many experimental and numerical studies have evidenced the prominent role played by the contact interactions between particles in the rheological properties of non-Brownian suspensions (Mari et al., 2014; Gallier et al., 2014), including shear-thinning behaviour in suspensions of rigid particles (Lobry et al., 2019) or discontinuous shear-thickening (Mari et al., 2014). It is now well known that the value of the friction coefficient between particles has a major influence on the jamming solid volume fraction Φ_m of non-Brownian suspensions, which has been found in the approximate range [0.55, 0.64] for rigid particles.

Recent experiments (Gilbert, D. et al.) concerning suspensions of soft particles have shown that, depending on the material rigidity, Φ_m could decrease down to values as low as 0.40. Such a low value cannot be explained by friction only, and it has been proposed that adhesion between particles together with friction may be responsible for this behaviour and for the shear-thinning behaviour that is also observed.

The present work aims at understanding the influence of adhesion between particles on the rheological properties of suspensions using particle scale simulations. The influence of friction and adhesion on the usual material functions (shear viscosity, normal stress differences, contact stresses) is studied. In particular, adhesion is shown to result in a strong decrease of the jamming volume fraction in frictional suspensions. Finally, the pair distribution function is computed, shedding light on the particular shear-induced microstructure that underlies the rheology of such adhesive suspensions.

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SP9

Tuesday 14:30 Nervión / Track 3

Rheology of suspensions of star colloids

Florencio Balboa-Usabiaga and Marco Ellero

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Most rheological studies on colloidal suspensions assume colloids with simple shapes such as spheres or ellipsoids. However, complex shaped colloids can now be employed thanks to the advances in the controlled synthesis of microparticles (Sacanna and Pine (2011), Bourrianne et al. (2020)). Here, we report a numerical investigation, using the rigid multiblob method (Balboa Usabiaga et al. (2016), Sprinkle et al. (2017)), on the rheology of suspensions of star colloids. Our star colloids are rigid particles with long and slender appendages connected to a central core. We show that the specific form of the colloids have a profound effect on the viscosity. In particular, colloids with curved arms and "hooks" can entangle with their neighbors and form long lived clusters. Such clusters control the viscosity, the structure and the rheology of the suspension. Contrary to the case of spherical colloids we observe that these effects are very strong even at moderate volumes fraction over a wide range of Péclet numbers.

Funding: "la Caixa" Foundation (ID 100010434), fellowship LCF/BQ/PI20/11760014, and from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 847648.

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Tuesday 14:50 Nervión / Track 3

Keynote

SP10

Capillary and rotational flow of a suspension of magnetic particles in the presence of discontinuous shear thickening

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The rheology of suspensions showing discontinuous shear thickening (DST) is well documented in conventional rheometer with rotating tools, but their study in capillary flow is still lacking. We present results obtained in a homemade capillary rheometer working in an imposed pressure regime for a suspension made of submicronic iron particles (Bossis et al., 2021). We show that the shape of the experimental curve giving the volume flow rate versus the wall stress in a capillary can be qualitatively reproduced from the curve stress-shear rate obtained in rotational geometry at imposed stress but instead of a sharp decrease of the volume flow rate observed at a critical stress, this transposition predicts a progressive decrease in flow rate. The Wyart-Cates theory is used to reproduce the stress-shear rate curve obtained in rotational geometry and then applied to predict the volume flow rate at imposed pressure. The theoretical curve predicts a total stop of the flow at high stress, whereas experimentally it remains constant. We propose a modification of the theory which, by taking into account the relaxation of the frictional contacts in the absence of shear rate, well predicts the high stress behavior. We also hypothesized that the DST transition propagates immediately inside the capillary, once the wall shear stress has reached its critical value: $\tau(R) = \tau_c$, even if the internal shear stress $\tau(r < R)$ is below the critical one. In this way the whole experimental curve can be well reproduced by the modified W-C model. Some preliminary results concerning the effect of a magnetic field on the DST transition in capillaries will also be presented. Besides an analysis of shear induced migration in Poiseuille flow and of its effect on the volume flow rate indicates that there should not be a noticeable modification of the concentration inside the capillary for these highly concentrated suspensions.

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Tuesday 16:30 Nervión / Track 3

SP12

Numerical simulation of clogging in a microchannel with planar contraction

Marco Trofa, Gaetano D'Avino, and Pier Luca Maffettone

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Clogging is the mechanism that interrupts the flow in confined geometries due to the complete blockage of the channel cross-section. It represents a critical issue in the processing of particle suspensions for both industrial and biological applications, and it is particularly relevant in microfluidics and membrane technology due to the high particle confinement and the difficult device cleaning. Although numerous experimental and numerical studies have been carried out to understand the mechanism governing this complex multiscale phenomenon, the picture is not yet clear and many questions remain, especially at the particle level. In this regard, numerical simulations represent a useful investigation tool since they provide a direct insight to quantities not easily accessible from experiments. In this contribution a detailed CFD-DEM (Computational Fluid Dynamics - Discrete Element Method) simulation study on the clogging mechanism in a microchannel with planar contraction is carried out. Both constant

flow rate and constant pressure drop conditions are investigated, highlighting the effect of flow conditions, particle volume fraction, cohesion forces, and contraction angle. The onset of clogging conditions is discussed.

Tuesday 16:50 Nervión / Track 3

SP13

Microstructure and rheology of confined semi-dense and dense suspensions: Effect of confinement, flow rate and particle rigidity

Joao Maia¹, Erika Barcelos¹, Shaghayegh Khani¹, Arman Boromand¹, Fellipe Oliveira², and Monica Naccahe³

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Suspensions have been extensively studied over the past decades and continue to be the focus of many works. A particular application in which suspensions have been increasingly explored is in confined systems. Although some attempts have been made at addressing confinement in suspensions, a systematic study evolving the combined effects of confinement, flow rate and particle rigidity in concentrated suspensions is still lacking. In this work, Core-Modified Dissipative Particle Dynamics is employed to model semi-dense and dense suspensions under confinement. The walls as well as the solvent are represented as traditional DPD particles which interact center-to-center by soft potentials. Colloidal particles, on the other hand, are modelled as Core-Modified particles, having a rigid core and a soft shell and the interactions are driven by a semi-hard potential. Colloidal particles interactions take place by means of a core force, responsible to tune the rigidity, and a lubrication force, representative of the short-range hydrodynamic interactions. Since the interactions between wall and the particles are soft, penetration may occur, which is undesirable, so a Machine Learning model was used to determine the interaction parameters that minimize wall penetration by the solve and colloidal particles. The effect of flow rate, confinement and particle rigidity were systematically studied in semi-dense and dense suspensions in a pressure driven flow. Rigid particle suspensions are more viscous and have a slower motion compared to the soft ones. Different microstructures and particles arrangement were observed depending on the values of the parameters adopted, with confinement being the most important factor driving particle migration and optimal confinement value existing for the formation of a percolating network, which is a necessary condition for discontinuous shear-thickening.

Tuesday 17:10 Nervión / Track 3

SP14

Impact of particle stiffness on non-Brownian suspension rheology

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We attempt to identify the impact of particle stiffness on the shear-thinning behavior exhibited by frictional and adhesive non-Brownian suspensions. To this aim, we compare the rheological behavior of suspensions whose particles have different Young's moduli. The stiffest particles are Soda-lime glass beads with a Young modulus of 70 GPa. The two other kinds of particles are made of polydimethylsiloxane and have been manufactured using a homemade millifluidic device that allowed us to produce batches of sparsely polydisperse particles with tunable Young modulus: 1.8 MPa for the softest ones and 15 MPa for the stiffest. We show that the observed shear-thinning is mainly caused by the presence of adhesive forces between particles. For each of the three suspensions, the shear-thinning behavior is described by the variation of the jamming volume fraction, ϕ_m , with stress, σ , and the results are interpreted in the light of the model proposed by Richards et al. (2020). We show that the magnitude of variation of ϕ_m with σ is greater the lower the particle stiffness. More precisely, in the adhesive regime, decreasing the particle stiffness leads to a significant decrease in the value of the jamming fraction while, as predicted by the JKR theory, the characteristic adhesion stress, σ_a , does not vary with stiffness. We finally show that, for stresses much higher than σ_a , the suspensions behave like usual frictional suspensions with a viscosity controlled by both the particle volume fraction and the value of the interparticle friction coefficient. Finally, we examine the impact of the stiffness when the particles are stabilized by an electric double layer and when they are no longer in contact.

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Richards, J. A., Guy, B. M., Blanco, E., Hermes, M., Poy, G., & Poon, W. C. (2020). The role of friction in the yielding of adhesive non-Brownian suspensions. *Journal of Rheology*, 64(2), 405-412.

Tuesday 17:30 Nervión / Track 3

SP15

Frequency dependent threshold for irreversibility in non-Brownian suspensions

Raffaella Martone, Johanna Vargas Clavijo, Simona Molitierno, Claudia Carotenuto, and Mario Minale Department of Engineering, University of Campania Luigi Vanvitelli, Aversa, Caserta 81031, Italy

It was experimentally shown that the response of a non-Brownian Newtonian suspension to a time sweep oscillatory shear (OS) can be frequency dependent (Martone et al. 2020 J Rheol 64:1075), despite the classical Stokesian dynamics model predicts rate independence. The addition of a van der Waals (vdW) attractive force, negligible with respect to the other forces acting on the system, preserves the Newtonian (rate independence) behaviour in steady shear, and introduces the rate dependence in OS (Ge et al 2021 Phys Rev Fluids 6:L101301). The vdW force is able to mediate the morphology evolution in OS such that both the regime complex viscosity and its time evolution resulted frequency dependent. The new model predictions were in good agreement with the experiments. Ge et al. (2021) also proved numerically the existence of a critical strain amplitude, marking a threshold for irreversibility, that depends on the frequency and the particle volume fraction. For strain amplitudes larger than this critical value the system entered the reversible adsorbing state where particles self-distribute to avoid collisions, for values smaller than it, the behaviour is irreversible with particles forming clusters where they keep colliding.

We experimental investigated the existence of this frequency dependent critical strain amplitude by running time sweep OS at different frequencies and amplitudes. We followed the transients until the regime and interpolated the data with the hyperbolic/exponential decay $(exp[-t/\tau]/t^n)$ characteristic of critical phenomena. We focused both on the complex viscosity and its elastic component, η^n , and proved the existence of a frequency dependent transition to irreversibility where the regime η^n is larger than the steady preshear one, indicating a particle colliding state. The non-Brownian suspension elasticity is indeed only caused by particle collisions. The investigated suspension is made of hollow glass spheres suspended in a Newtonian PIB at 40% volume fraction.

Thursday 17:50 Nervión / Track 3

SP27

Yielding and history dependence in fluidity models for glassy suspensions

Thomas Voigtmann and Stephan Domann

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The transient rheological response of glass-forming fluids is quite rich because the slow structural relaxation time interferes with the imposed time scales of the flow. It is thus a challenge to establish constitutive equations that are both accurate enough such that they capture a large set of the observed phenomenology, and yet simple enough to be readily solved in combination with the laws of continuum mechanics. Furthermore, the empirical description of the different modes of deformation triggered by different flow geometries, suffers from the fact that many studies on soft materials focus on simple shear.

The integration-through transients (ITT) formalism has established integral constitutive equations (ICE) that, combined with mode-coupling theory closure schemes, give a good qualitative account of the nonlinear rheology of glass-forming suspensions. Yet, ICE are notoriously difficult to solve in combination with the (differential) Navier Stokes equations.

We discuss constitutive equations that are in-between microscopical correctness (inspired by ITT) and numerical feasibility. The CE take the form of generalized Maxwell-type fluidity models that take into account the non-linear effect of strong flow on the stress and fluidity relaxation time scales during non-stationary deformation. In particular, we will address the yielding and creep of nonlinear viscoelastic materials under various deformation geometries, and the role of compressibility in different local measures of the deformation field.

Symposium BM

Bio-rheology and Medicine

Organizers: Críspulo Gallegos, Mats Stading and Catarina R. Leal

Tuesday 13:50 Prado / Track 4

BM7

Effect of cystic fibrosis sputum rheology on lungs drug delivery by inhalation

Michela Abrami¹, Massimo Maschio², Massimo Conese³, Marco Confalonieri⁴, Francesco Salton⁴, Fabio Gerin⁵, Barbara Dapas⁵, Rossella Farra⁵, Alessandra Adrover⁶, Gesmi Milcovich⁷, Claudia Fornasier⁵, Alice Biasin¹, Gabriele Grassi⁵, and Mario Grassi¹

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Cystic Fibrosis (CF), one of the most common lethal genetic diseases in people of Caucasian origin, causes a severe increase of mucus viscosity (due to water loss) in many organs, mainly the airways. As a consequence, increased viscosity impairs muco-ciliary clearance determining sputum (pathological mucus) stagnation, thus promoting bacterial lung infections. In the case of drugs administered by inhalation (usually, mucolytics, anti-inflammatory and antibiotics), the structure of the Airway Surface Liquid (ASL) lining the walls of the bronchial tree requires an in-depth understanding in order to improve the efficacy of the drugs. Indeed, ASL is composed by a thin inner water-like serous fluid named periciliary layer, where cells cilia beat, and by a thicker outer non-Newtonian viscoelastic fluid representing the Mucus Layer (ML). In particular, ML, is a heterogeneous medium made up of mainly physical cross-linked polymeric regions, embedded in a less viscous water-like fluid. Although drug transport inside ASL can depend on different factors, drug diffusion is one of the most important. Thus, the estimation of the drug diffusion coefficient (D) is a key factor: at this purpose the Lustig-Peppas model for not swelling systems represents an effective tool. Indeed, this model refers to both the network mesh size and the volume fraction of the solid (polymeric) network permeating the ML. Interestingly, based on the Flory, Chui and Schurz theories, it is possible to express D directly as a function of the ML shear modulus (G). Thus, assuming that ASL rheological properties are similar to those of sputum, it is possible evaluating D and the kinetics of drug penetration inside ASL. Therefore, this work provided to measure CF sputum G by fitting the generalized Maxwell model to frequency sweep data, to evaluate D and to simulate drug diffusion through the ASL layer by means of Fick's equation

Tuesday 14:10 Prado / Track 4

BM8

In situ magnetic microrheology of airway mucus

Margaret Braunreuther and Gerald G. Fuller

Chemical Engineering, Stanford University, Stanford, CA 94305, United States

Effective mucociliary clearance is vital for healthy airway function, as mucus acts as a primary defense against foreign particles and infectious agents. Cystic Fibrosis (CF) is a genetic disease that is characterized by hindered ion transport in airway epithelial cells. As a result, the mucus secreted by these cells becomes dehydrated, forming thick stratified layers. This change in mucus properties can severely impair mucociliary clearance, leading to airway obstruction, chronic infection, and inflammatory lung damage. Recent studies have found evidence that cilia function in the presence of secreted mucus is dependent on the genotype of the cell layer. It is well known that CF mucus exhibits viscosities orders of magnitude greater than those of healthy mucus. However, thus far it has not been feasible to measure mucus properties on live cells as it is produced by the epithelial cell layer. A new instrument, the "Magnetic Live Cell Rheometer", recently developed by the Fuller group has been adapted to examine mucus rheology *in situ* via magnetic microrheology. Human airway epithelial cells (HAECs) are grown in 2D air-liquid interface (ALI) cultures. During rheological experiments, we maintain cells at ALI, using micron scale magnetic microwires to probe the properties of the mucus as a function of distance from the cell layer. We apply and remove a magnetic force and track microwire displacement to determine the compliance and viscosity of healthy and diseased mucus on the respective HAEC cultures. We then test rheological response to the application of existing mucoactive agents to establish correlation with clinical response and assess the impact of genetic variants. With this method, we demonstrate the ability to study mucus rheology in a physiologically relevant environment, examine phenotypic differences in mucus rheology, and rapidly test drugs on mucociliary mechanics.

Tuesday 14:30 Prado / Track 4

BM9

Cancer viscoelasticity: A dynamic compression assay for tumor spheroids characterization

Rosalia Ferraro, Vincenzo Pepe, and Sergio Caserta

DICMAPI, Università degli Studi di Napoli Federico II, Napoli, Italy

Cancer is a complex, heterogeneous and multifactorial disease, that is a leading healthcare problem worldwide. Several experimental and clinical studies of malignant neoplasms indicate that invasive growth and metastasis are the main manifestations of tumour progression, strongly influenced by the microenvironment (Ferraro, under review), in particular mechanical stresses. Deep biomechanical differences between healthy and tumoral tissues exist, in fact, malignant transformations are associated with significant changes in the cytoskeleton structure and cell-cell interactions. Understanding the mechanical behaviour and cellular organization is not easy; a novel approach is based on the analysis of living tissues as bio-soft matter, based on typical rheological models traditionally developed for non-bio complex fluids (polymers, surfactants, foams, etc.) (Steinberg, 1963). Our work is focused on the development and validation of an innovative methodology to measure the role of external (bio) mechanical stimuli on the capacity of tumours to invade the surrounding healthy tissue, using a 3D model of not-vascularised tumour: cell spheroid. Tumoral spheroids are tightly bound cellular aggregates that tend to form when cells are growth in a nonadherent environment. To measure the mechanical response of the system, we applied a dynamic compression to the spheroids. Shape evolution of spheroids under controlled compression was modelled using standard springs and dampers rheological models available in the literature in order to estimate viscosity and elastic modulus of the system, quantifying the cell adhesion and invasive potential of different types of tumour.

Tuesday 14:50 Prado / Track 4

BM10

Studying the impact of microtubule polymerization affecting anti-cancer drugs on the cell mechanics with a monolayer rheometer

Suhyang Lee¹, Dong-hee Jung¹, Santanu K. Basu², Khawaja M. Bashir¹, Man-Gi Cho¹, and <u>Andreas Wierschem²</u>
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Microtubules are an important part of the cytoskeleton. Together with actin filaments and intermediate filaments, they govern the mechanical properties of eukaryotic cells. We modify the polymerization level of the microtubules using different anti-cancer drugs and detect the impact on the cell mechanics. To this end, we studied the linear viscoelastic response of a large number of cells in a monolayer with a narrow-gap rheometer and analyzed the impact of various factors such as gap width, normal force and drug concentration on amplitude sweeps. We carried out this study with MCF-7 and HeLa cells using paclitaxel to enhance the polymerization level and vinblastine to decrease it. Since the drugs are cytotoxic in mitosis at high concentration levels, we used hydroxyurea to arrest the division cycle of the cells in the S phase.

Tuesday 15:10 Prado / Track 4

BM11

Jamming transition in biological tissues

Michael J. Hertaeg¹, Suzanne Fielding¹, and Dapeng Bi²

¹Physics, Durham University, Durham, United Kingdom; ²Physics, Northeastern University, Boston, MA, United States

The collective motion of cells in tissues is an important feature in many biological processes, including wound healing, cancer development and morphogenesis. These processes require active rearrangements over long times while maintaining overall mechanical integrity. Recent work spanning many types of cells [1] has identified solid-like to liquid-like transitions which resemble the glass or jamming transition that is well studied in non-biological particulate systems. However, transitions in cell structures occur at packing fractions equal to unity, implying a different mechanism compared to simple particulate systems. Previous experimental and theoretical work has identified key factors that relate to tissue

rigidity. These include cell shape, which is determined by a competition between cell-cell adhesion and cortical tension. Also, many cells can produce active forces through swimming or crawling that were also found to influence rigidity [2].

Vertex models, where confluent cells are represented with a tiling of polygons defined by vertex positions have commonly been used in previous studies on tissue mechanics [3]. Here, we study the stress response of an active vertex model over large shear strains to elucidate the onset of rigidity transitions in living tissue. The relationship with strain rate, cell shape and activity are determined and new mechanisms responsible for observed tissue behaviour are proposed.

References:

- [1] Fredberg, J., Mitchel, J., Kim, J., & Park, J. (2016). Unjamming and cell shape in the asthmatic airway epithelium. *The FASEB Journal*, 30(S1).
- [2] Bi, D., Yang, X., Marchetti, M. and Manning, M., 2016. Motility-Driven Glass and Jamming Transitions in Biological Tissues. *Physical Review X*, 6(2).
- [3] Nagai, T., & Honda, H. (2001). A dynamic cell model for the formation of epithelial tissues. Philosophical Magazine B, 81(7).

Tuesday 16:30 Prado / Track 4

Keynote

BM12

AI-based microfluidic assessment of pathological red blood cell flow properties

Steffen M. Recktenwald¹, Greta Simionato², Marcelle Lopez³, Lars Kaestner⁴, Stephan Quint³, and Christian Wagner¹

¹Department of Experimental Physics, Saarland University, Saarbrücken 66123, Germany; ²Institute for Clinical and Experimental Surgery, Saarland University, Homburg 66424, Germany; ³Cysmic GmbH, Saarbruecken 66123, Germany; ⁴Theoretical Medicine and Biosciences, Saarland University, Homburg 66424, Germany

One of the most intriguing features of red blood cells (RBCs) is their high deformability that determines microvascular blood flow. The flexibility of healthy RBCs allows them to adapt their shape dynamically to the flow conditions. Their shape is a highly sensitive parameter for both intrinsic cell properties and external influences and plays a crucial role in proper blood circulation. In this study, we examine the effect of pathological changes on the capillary flow behavior and morphology of RBCs on a single-cell level. Therefore, cells from COVID-19 patients are pumped through microfluidic channels with dimensions similar to the RBC size covering a broad velocity range. These microfluidic experiments are combined with a neural network approach to enable a rapid and robust classification of healthy and pathological RBC shapes in flow. Here, we find that COVID-19 patients exhibit drastically altered RBC shapes, and we show how these pathological cell shapes affect the RBC flow properties. Further, we demonstrate that an exchange of the surrounding plasma medium can result in a recovery of RBC shapes and lead to an improvement of capillary flow. Our study aims to understand the influence of diseases on RBC morphology and flow behavior and showcases the application of RBC shape transitions as a biomarker for hematological diagnostics and patient treatment.

Tuesday 17:10 Prado / Track 4

BM14

Rheology of bacterial cellulose wound dressing membranes

<u>Catarina R. Leal</u>¹, Gonçalo Cavaco², João Saraiva³, Raquel Portela², Rita G. Sobral², and Pedro L. Almeida¹

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Wound healing process involves a series of complex biological processes that can be slow and lead to chronic inflammation, particularly serious in burn patients with additional systemic impairments. Progresses have been made lately in the development of therapeutic approaches for skin damage treatment, although further work is still needed to improve wound healing and recovery. This work focuses on a wound dressing that prevents skin dehydration and bacterial infection based on bacterial cellulose (BC) produced by Komagataeibacter rhaeticus. The secreted extracellular cellulose can be easily isolated in the form of fibers with high purity, and under static cultivation conditions a BC-biofilm of varying thickness is obtained [1]. We produced hydrated membranes, using BC micro and nano fibers, that mimick the skin barrier function. To increase the water retention capacity after the first de-hydration, we performed ex-situ chemical modifications by crosslinking unmodified BC hydrogels with two different crosslinkers: Citric Acid (CA) and Epichlorohydrin (ECH). The viscoelastic properties of BC, BC-CA and BC-ECH membranes, were evaluated at 25 °C and 37 °C. The tests were performed in amplitude and frequency sweep modes, where storage (G') and loss (G") moduli were measured as function of strain and angular frequency, respectively. Temperature sensitivity was mainly observed in BC-CA and BC-ECH membranes, showing lower G' and G" values at 37 °C. BC membranes did not changed their viscoelastic response. Regarding the crosslinking agent, the ECH appears to be more effective than the CA. These results are discussed regarding the characterisation of the morphology and texture, water retention capacity, mechanical and antibacterial properties of BC membranes.

References:

 $[1]\ R.\ Portela\ et\ al., \textit{Microbial Biotechnology},\ 2019,\ 12(4),\ 586-610.$

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Tuesday 17:30 Prado / Track 4 **BM15**

Experimental challenges in characterizing the bulk rheology of bacterial biofilms

Steffen Geisel¹, Eleonora Secchi², and Jan Vermant¹

¹Laboratory of Soft Materials, ETH Zurich, Zurich 8093, Switzerland; ²Institute of Environmental Engineering, ETH Zurich, Zurich 8093, Switzerland

Bacterial biofilms are formed by communities of microorganisms that are encased by a matrix consisting of self-produced, hydrated extracellular polymeric substances [1]. Biofilm formation is observed in many microorganisms and provides a protected mode of growth that infers resistance to antibiotics or the host's immune system. Consequently, mechanical removal is often necessary but aggravated by the biofilm's complex, viscoelastic response [2]. Furthermore, the mechanical behaviour of biofilm also plays a role in the spreading, dispersal and subsequent colonization of new surfaces. Therefore, the characterization of the mechanical behaviour of biofilms plays a crucial role in controlling and combating biofilms in the industrial and medical environment.

The mechanical signature of the biofilm is known to be viscoelastic and highly variable depending, among others, on flow conditions during growth, age of the biofilm or ultimately the measurement setup [3]. We performed in-situ rheological measurements of Bacillus subtilis biofilms grown on the rheometer under well-controlled conditions relevant to many biofilms' habitats. We investigated how the shear stress during growth influences biofilm mechanics and compared these results to techniques commonly used in literature. This work helps us understand how different growth and measurement conditions contribute to the large variability of mechanical properties reported in the biofilm literature.

References:

- [1] Flemming et al., The perfect slime. IWA Publishing, London, 2017
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17:50 Prado / Track 4 Tuesday

BM16

New criterion for assessing the potential of in situ gelling systems as injectable scaffolds Anna Ryl and Piotr Owczarz

Department of Chemical Engineering, Lodz University of Technology, Lodz 93-005, Poland

In situ gelling systems are promising solutions in biomedical engineering as systems supporting the processes of treatment and regeneration of damaged tissues. During minimally invasive injection application, due to the flow at high shear rates, changes in the conformation of polymer molecules may occur and, consequently, affect the conditions of thermoinduced sol-gel phase transition, including the risk of spilling the sol before the actual gelation. This effect has not been studied and discussed so far.

As an experimental material, chitosan (CS) and hydroxypropyl cellulose (HPC) sols were used, which were injected with hypodermic needles (14G-25G) or sheared directly in the rheometer measuring system in the range of the shear rate $\gamma = 200 - 15,000 \text{ 1/s}$. The sol-gel phase transition conditions at 37 °C were determined using rheometric and turbidimetric techniques. The effect of the short-term shear interval on the thixotropic properties was determined using the three-interval thixotropic test (3ITT) coupled with the small-angle light scattering analysis (Rheo-SALS).

It was found that the use of low, in relation to injection, shear rates accelerate the gelation, its increase extends the gelation time; applying the highest shear rates may significantly slow down (HPC) or accelerate (CS) gelation. The latter effect is particularly interesting due to the significant reduction of the gelation time when using small needles, which will further reduce patient discomfort during application. Noteworthy is the correlation between the deformation parameter determined during the 3ITT with the gelation time versus the shear rate observed during the injection. Finally, an interpretation of the influence of an intensive shear field on the conformation of the molecules on a molecular scale was proposed, indicating a shear-induced progressive disruption of polymer aggregates [1].

[1] Ryl A. & Owczarz P. (2021) Int. Journal of Molecular Sciences, 22(24), 13208.

Symposium El

Emulsions, Foams and Interfacial Rheology

Organizers: Jan Vermant, Teresa Sanz and Mario Minale

13:50 Arenal / Track 5 Tuesday

EI7

Interfacial characterization and stability study of bituminous emulsions

Olga Mileti¹, Noemi Baldino¹, Ylenia Marchesano¹, Francesca R. Lupi¹, Domenico Gabriele¹, and Massimo Paolini² ¹DIMES, University of Calabria, Rende, Italy; ²Valli Zabban S.p.A., Bologna, Italy

Emulsions are widely used in different applications, food, medical and petroleum industry. In particular, in road asphalt construction, bituminous emulsions are considered a green, friendly-environment and cost-effective alternative. As for all emulsions, also in bituminous ones, stability is a key parameter, depending on several factors, such as the choice of the emulsifier and the quantity to be used, the water solution pH and the bitumen/water ratio. Rapid-setting (RS) bituminous emulsions are particularly reactive and their reactivity is determined by their components, in particular by the amount and type of emulsifier. The use of biodegradable emulsifiers, also derived from the food industry, is a new goal of the bitumen industry, to make the process more sustainable. Then to study new materials to be used, the interfacial tension is an important tool to investigate the surfactant power of the chosen components and additives. Otherwise, the control of the stability is basic. So, the focus of this work is to investigate the interfacial activity of several surfactants and to study the stability and flow properties of the respective emulsions. The interfacial analysis was performed by the pendant drop tensiometer at different pH values and with several surfactants. The adsorption isotherms and the relative kinetic information were obtained. The interfacial effect was correlated to the bulk properties of the bituminous emulsions prepared with a 50/70 bitumen, in naturally and acidified ambient. The emulsion viscosities were obtained at different temperatures and the stability was monitored by optical observation, turbidimetry and zeta potential measurements. All results were compared with the industrial one.

Tuesday 14:10 Arenal / Track 5

EI8

Controlling rheology of a solid emulsion with phase-changing droplets

Elina Gilbert, Anniina Salonen, and Christophe Poulard

LPS, Université Paris-Saclay, Orsay, France

Classic viscoelastic systems show correlated storage and loss moduli. To try and decouple them, we study "solid emulsions" with a crosslinked continuous phase. Emulsions rheological properties depend on both the continuous and the dispersed phase, as well as the interface between them. Thus, by encapsulating the liquid dispersed phase in a solid elastic matrix, we can create a composite material with tunable rheological properties [1]. The chosen dispersed phase in our "solid emulsion" can solidify at room temperature. This phase change is used to vary the moduli of the dispersed phase. Previous theoretical work has shown that for liquid inclusions we can expect to see different rheological responses depending on the continuous and dispersed phase moduli, the size of the droplets in the matrix and the volume fraction of dispersed phase [2, 3]. However, when the inclusions are solid, the complex modulus should only depend on the continuous phase and volume fraction [4]. We first show the feasibility of a composite system whose storage and loss moduli can be controlled independently, and study the mechanisms for such a decorrelation. For our system, we have observed a decoupling of the storage and loss moduli in the rheological response for liquid insertions in the matrix. When the droplets are solid, we observe however a deviation from the expected behavior solely controlled by the matrix and the volume fraction, that we investigate through rheology and compression-decompression experiments.

References:

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Tuesday 14:30 Arenal / Track 5

EI9

Microrheology of novel cellulose stabilized oil-in-water emulsions

Bruno Medronho^{1,2}, Carolina Costa², Anabela Romano¹, Björn Lindman³, Hakan Edlund², and Magnus Norgren²

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Diffusing wave spectroscopy (DWS) is a powerful optical technique suitable to investigate turbid samples in a nondestructive and reproducible way, providing information on the static and dynamic properties of the system. This includes the relative displacement of emulsion droplets over time and changes in the viscoelastic properties. Here, novel and promising cellulose-based oil-in-water (O/W) emulsions were prepared and studied, for the first time, by DWS. Cellulose plays the role of a novel eco-friendly emulsifying agent. The hydrolysis time of cellulose was observed to affect the average size of the emulsion droplets and their stability; the longer the hydrolysis time, the more dispersed and stable the emulsions were found to be. Additionally, a good complementarity between the microrheology (DWS) and macrorheology (mechanical rheometer) data was found. Our work suggests that DWS is a highly attractive method to investigate the stability, aging and microrheology properties of cellulose-based emulsions, providing valuable insights on their microstructure. This technique is thus highly appealing for the characterization and design of novel emulsion formulations.

Tuesday 14:50 Arenal / Track 5

EI10

Controlling foam ageing in viscoelastic media

Chiara Guidolin¹, Jonatan Mac Intyre², Antti Puisto², Emmanuelle Rio¹, and Anniina Salonen¹

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Foams are dispersions of gas bubbles in a continuous medium. Their typical cellular structure lends them lightness and peculiar mechanical properties that are exploited in many industrial applications. However, liquid foams are not stable, as a competition between different mechanisms can alter their internal structure over time. Drainage, coalescence and coarsening can be a strong limitation in industrial processes, as they slowly lead to an irreversible foam damage. The desired longevity of a foam clearly depends on the specific applications, that still call for a thorough understanding of foam stability. We study how the mechanical properties of the continuous phase impact on the coarsening process, in conditions where drainage and coalescence can both be neglected. We control the mechanical properties by using concentrated oil-in-water emulsions as the continuous phase of foams. In fact, at sufficiently high droplet concentrations, emulsions show an elastic behavior, thanks to the storage of interfacial energy from drop deformations. As this elasticity increases with droplet concentration, we can vary the elasticity of the foam continuous phase by simply adjusting the emulsion oil fraction. We study foamed emulsion coarsening in quasi-2D foam systems, which allow to follow the

bubble pattern evolution over time through imaging experiments. We show that the elasticity of the continuous phase strongly influences the ripening of foamed emulsions, leading to reduced bubble growth rates. Moreover, we show that increasing the emulsion elasticity deeply affects the foam structure, with the appearance of unrelaxed bubble patterns. The results can lead to a more efficient control of the foam structure and stability.

Tuesday 15:10 Arenal / Track 5

EI11

Hallmarks of intermittent rearrangements in creep of liquid foams

François A. Lavergne and Véronique Trappe

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Liquid foams are soft jammed materials that constantly reconfigure due to coarsening-induced intermittent bubble rearrangements. Under a small applied stress, rearrangements lead to a slow power-law creep deformation at early times, which is followed by a constant creep rate at long time, reminiscent of normal viscous fluids. Here, we use optical microscopy to identify the rearrangements involved in these two regimes. We find that at short timescales, newly rearranged zones appear in different regions of the sample, with volumes distributed according to the same power-law as the creep rate. At the crossover to viscous relaxation timescales, rearrangements start occurring mostly in previously rearranged zones, while about 50% of the total volume still remains unchanged. As we find that the power-law strain is recovered when the stress is released, we conclude that the early-time rearrangement dynamics correlates with reversible contributions to creep, while the recurrence of events at the same location relates to dissipation.

Tuesday 16:30 Arenal / Track 5

EI12

Dissipative processes in an elementary foam

Théo Lenavetier¹, Raphaël Poryles¹, Adrien Bussonnière², Emmanuel Schaub¹, and Isabelle Cantat¹

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In many consumer goods and industrial processes, liquid foams are notably used for their viscoelastic behaviour. Given that their liquid matrices are Newtonian fluids with viscosities lower by several orders of magnitude, their strong dissipative properties are surprising, and recent advances have shown that they may originate from a very localised zone near the junctions between the foam films. To further investigate the different mechanisms involved there, we designed a special frame allowing us to create and observe three soap films connected together with a meniscus. We can control the lengths of the films using three synchronized motors to explore different geometries of deformation. We monitor the film velocity by photobleaching a fluorescent dye, the thickness profile of our films with a spectral camera and the tension in the films by tracking the meniscus position. We also track the size of the meniscus using the fluorescence of our soap solution and a ray tracing-based criterium. Thus, the whole setup allows us to quantify both the exchanges of interface and volume between the films. Looking at various geometries of deformation, we witness that the viscoelastic response of a single soap film strongly depends on the coupling with the neighbours.

Tuesday 16:50 Arenal / Track 5

EI13

Constitutive framework for rheologically complex interfaces with an application to elastoviscoplasticity

Mick A. Carrozza, Markus Hütter, Martien A. Hulsen, and Patrick D. Anderson

Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

Interfaces with a sufficiently dense microstructure can yield because of network breakdown during flow, being an origin of plastic deformation in emulsions and foams. In this talk we will discuss our continuum constitutive framework for isotropic non-linear viscoelastic sharp interfaces with an application to elastoviscoplasticity [1]. The framework uses a multiplicative split between the elastic and plastic parts of the deformation and presents general constitutive modelling choices for the (relation between the) extra interfacial stress tensor and plastic surface rate-of-deformation tensor. It also provides a clear separation between interfacial shear and dilatation, as well as conditions for inherent thermodynamic consistency. Predictions of the elastoviscoplastic model in steady interfacial shear and dilatational flow have been investigated numerically. Qualitative agreement with interfacial rheometry results from the literature has been found. That is, a predominantly elastic response is obtained at small deformations, with a transition to primarily plastic flow at high stress levels. Besides, strain softening and eventually a plastic plateau occur upon further deformation beyond the yield point in shear. In dilatation on the other hand, the model predicts a decreasing stress without a plateau upon deformation beyond yielding. The predictions for the interfacial yield stress and strain, and (the relative strength of) the overshoot are studied for various choices of the parameters in the model.

References

[1] M.A. Carrozza, M. Hütter, M.A. Hulsen, P.D. Anderson. Constitutive framework for rheologically complex interfaces with an application to elastoviscoplasticity. *Journal of Non-Newtonian Fluid Mechanics*. Accepted for publication.

Tuesday 17:10 Arenal / Track 5

EI14

Retraction of thin films coated by insoluble surfactants

Marco De Corato¹, Daniele Tammaro², Pier Luca Maffettone², and Norberto Fueyo¹

¹Aragon Institute of Engineering Research, University of Zaragoza, Zaragoza, Spain; ²Dipartimento di Ingegneria Chimica, University of Naples Federico II, Naples, Italy

We investigate the effects of insoluble surfactants on the retraction of a circular thin film of liquid that is punctured at its centre. We assume that the surface pressure of the liquid-gas interface is related to the number density of surfactants through a linear equation of state, which is characterized by a single parameter: the Gibbs dilation modulus. To solve the governing equations and track the deformation of the domain, we use the finite element method with an Arbitrary Lagrangian-Eulerian approach where the film surface is sharp. Our simulations show that the surface elasticity introduced by the surfactants slows down the retraction and introduces oscillations at early times. In agreement with previous experiments and theoretical analysis, we find that the presence of surfactants introduces perturbations of the film thickness over progressively larger distances as the surface elasticity increases. The surface perturbations travel faster than the retracting edge of the film at a speed proportional to the Gibbs modulus. For large values of the Gibbs modulus, the interface behaviour approaches that of an incompressible two-dimensional solid. These results represent a first step towards the understanding of the breakup of films and filaments with complex surface rheological properties.

Tuesday 17:30 Arenal / Track 5

EI21

Shear and dilatational rheology of microgel monolayers at the oil-water interface: a comparison between ultralow crosslinked and regularly crosslinked pNIPAM microgels

Olli-Ville Laukkanen, Maximilian M. Schmidt, Colin Weyer, and Walter Richtering Institute of Physical Chemistry, RWTH Aachen University, Aachen 52074, Germany

Particle-laden fluid interfaces play a crucial role in a wide range of multiphase systems present in industrial and biological processes. For example, the use of smart emulsifying agents such as stimuli-responsive microgels allows controlled inversion or breaking of the system by mild changes in external conditions [1]. Poly-N-isopropylacrylamide (pNIPAM)-based microgels possess a volume phase transition temperature (VPTT) of about 32 °C, meaning that these microgels are swollen (deswollen) below (above) this temperature. The properties of pNIPAM microgels can also be tuned by varying their crosslink density; with decreasing crosslink density their conformation and behavior at fluid interfaces approach those of flexible macromolecules [2]. We investigate the interfacial shear and dilatational rheology of ultra-low crosslinked (ULC) and regularly crosslinked (5 mol% BIS) pNIPAM microgels at the decane-water interface. The interfacial shear properties are measured as a function of surface pressure (i.e. monolayer compression state) and correlated with the two-dimensional phase behavior of the microgels. Oscillating drop measurements reveal a distinct maximum in the dilatational storage modulus of ULC microgel monolayers around VPTT, whereas monolayers of regularly crosslinked microgels do not exhibit such a feature. Moreover, oscillating barrier measurements demonstrate dilatational strain softening in loosely packed monolayers, while dilatational strain hardening is observed in densely packed monolayers. These findings highlight the tunable viscoelastic response of microgel monolayers confined to oil-water interfaces and their relevance in various industrial applications.

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- [2] Scotti, A., et al. Nature communications. 2019, 10, 1418.

Tuesday 17:50 Arenal / Track 5

EI16

Bubble breaking dynamics in complex fluids

Nicola Antonio Di Spirito, Shadi Mirzaagha, Ernesto Di Maio, Rossana Pasquino, and Nino Grizzuti DICMaPI, University of Naples Federico II, Naples, Italy

In this work we analyzed bubbles breaking and hole opening velocity of non-Newtonian fluids. Novel and tricky experiments on hole opening dynamics of different non-Newtonian fluids with various rheological behaviors were performed by using a home-made apparatus equipped with a fast camera capable of acquiring images at a speed of 20000 frames/s. The analysis of complex bubbles breaking was achieved by measuring the hole radius as a function of time, and, as such, the resulting hole opening velocity. With the aim of establishing a general approach on the bubble dynamics, the experiments were analyzed through a dimensionless approach, to discern the role of viscous, elastic, surface tension and inertial forces on the opening velocity, depending on the nature of the specific fluid of interest. A set of new equations for the computation of the film retracting velocity was used. A good agreement between the experimental data and the mathematical derivation for the opening velocity was found.

Symposium MN

Micro-, Nanofluidics and Microrheology

Organizers: Anke Lidner, Juan Francisco Vega and Amy Shen

Tuesday 13:50 Giralda 6-7 / Track 6

MN7

Dynamics of semiflexible filaments in oscillatory shear flows

<u>Francesco Bonacci</u>¹, Brato Chakrabarti², David Saintillan³, Olivia du Roure¹, and Anke Lindner¹

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Understanding the conformational dynamics of flexible fibers in time-dependent flows is of key importance for the characterization of complex biological phenomena, the control of polymer-based material properties during processing, and for the development of new lab-on-chip technologies. Here, we combine microfluidic experiments using actin filaments and computational modeling to study the dynamics of flexible Brownian fibers submitted to oscillatory forcing. We show that, unlike time-invariant shear flows, where the emergence of morphological transitions is essentially governed by a single dimensionless parameter, μ , that compares the relative importance of viscous to elastic restoring forces, the addition of an independent timescale in the problem makes way for a variety of unexplored deformation dynamics. This timescale, which is captured by a new dimensionless number $\rho = \gamma_m T$ comparing the maximum shear rate γ_m to the oscillation period T, controls the amplitude and frequency of filament motion and thus its orientation θ_0 at the begin of every cycle. This is in sharp contrast with a constant shear, where filament tumbling always starts from a flow-aligned state $\theta_0 \approx 0$ and is triggered by thermally induced orientational fluctuations. By investigating single half periods, we indeed find that, in addition to μ , the deformation modes and amplitudes strongly depend on ρ and θ_0 . In very strong flows, both parameters cause jointly the emergence of novel higher order buckling modes, but can also combine to bring about complete suppression of such instabilities. In particular, we show that strong deformations are only reached for sufficiently large ρ and initial angles close to the flow direction. We finally investigate the asymptotic behavior over many periods by characterizing global attractors of filament orientation and associated morphologies.

Tuesday 14:10 Giralda 6-7 / Track 6

MN8

Microfluidic device to reduce multi-particle string formation and self-assemble particles in microfluidic flow Anoshanth Jeyasountharan and Francesco Del Giudice

Chemical Engineering, Swansea University, Swansea SA1 8EN, United Kingdom

The occurrence of multi-particle strings, i.e. doublets in a microfluidic system, is a limitation for employing microfluidics in biomedical applications such as flow cytometry, which requires isolated particle/cell trains for end-point analysis and limits deterministic encapsulation of particles/cells in droplets for drug delivery systems. Herein, we designed a novel microfluidic device with rotated triangle structures to reduce and break particle doublets based on fluid velocity variations. We suspended 20-micron particles at mass concentrations equal to 0.2 and 0.3 wt % and 45-micron particles at 0.7 wt % in 0.2 wt % Xanthan Gum to analyse particle flow. We found that a significant fraction of particle doublets was reduced in the device after flowing through sixteen rotated triangle structures. Next, we studied the viscoelasticity-induced self-assembly of 20 and 45 micron particles in a glass capillary attached to the end of the device directly after the last rotated triangle. Progressive self-assembly of both 20 and 45 micron particles was observed along the length of the glass capillary from 5 cm to 25 cm. Self-assembly of particles with minimal multi-particle string i.e. doublet occurrence provides great opportunities to implement such microfluidic devices in fields such as biomedical engineering, material science and beyond.

Tuesday 14:30 Giralda 6-7 / Track 6

MN9

Transport dynamics of microparticles in inertio-elastic vortex flows

Noa Burshtein¹, Arash A. Banaei², Marine Aulnette¹, Simon J. Haward³, Amy Q. Shen³, Luca Brandt², and Anke Lindner¹ [ESPCI, Paris, Ile de France 95005, France; ²Royal Institute of Technology, Stockholm, Sweden; ³Micro Bio Nanofluidics Unit, Okinawa Institute of Science and Technology, Okinawa, Japan

Particulate matter is common in biological and environmental flows and is used in numerous industrial and pharmaceutical applications. A particle's motion and flow dynamics are strongly affected by its interactions with the flow structure. For example, under Poiseuille flows, spherical microparticles will find equilibrium positions that can be further tuned with their surrounding viscoelastic fluids. While under turbulent flow conditions, depending on their properties, particles will preferentially concentrate at specific regions of the flow field. However, the transport dynamics of microparticles in a simplified unstable flow regime, such as a single vortex, remains to be explored. Here we focus on the response of neutrally buoyant spherical particles to a steady vortical flow field, in both Newtonian and weakly elastic fluids. For this purpose, we use a microfluidic cross-slot geometry to generate a well-characterized, three-dimensional flow instability that displays as a stationary streamwise vortex at moderate Reynolds number ($Re = \rho Uw/\eta \sim 50$, where U is the flow velocity, $w = 1100~\mu m$ is the channel's width, ρ and η are the fluid's density and viscosity, respectively). Our experimental results, supported by numerical simulations, show that as the diameter of the spherical particles is increased from 20 to 140 μm , the particles are progressively expelled from the vortex core. This trend is further enhanced when the fluid's elasticity is slightly increased. Currently, we are also investigating the dynamics of microfibers in a vortical flow field. Initial observations indicate that

fibers can rotate, and either follow or diverge from the vortical streamlines, depending on the fiber length, initial orientation and position in the flow field. This work provides a fundamental contribution to the study of particle-flow interactions and for the improvement of particle sorting and transport techniques with possible environmental, industrial and pharmaceutical applications.

Tuesday 14:50 Giralda 6-7 / Track 6

MN10

Controlled viscoelastic particle encapsulations in microfluidic devices

Keshvad Shahrivar and Francesco Del Giudice

Chemical Engineering, Swansea University, Swansea SA1 8EN, United Kingdom

The encapsulation of particles in droplets using microfluidic devices finds application across several fields ranging from biomedical engineering to materials science. The encapsulation process, however, is often affected by poor single encapsulation efficiency, quantified by the Poisson statistics, with droplets containing more than one particle or with several empty droplets. We here demonstrate that aqueous solutions of viscoelastic liquids enable controlled single particle encapsulation in microfluidic devices having either T-junction or flow-focusing geometry, with a single encapsulation efficiency up to 2-fold larger than the one predicted by the Poisson statistics. We achieved such results by employing and designing modular microfluidic devices made of a first channel to achieve particle ordering with a constant frequency of particles approaching the encapsulation area, followed by the encapsulation device. We first present the scaling for both droplet formation and frequency, and we then discuss the single encapsulation data. We also demonstrated co-encapsulation of particles coming from two different streams with efficiency up to 2-folds larger than the stochastic value.

Tuesday 15:10 Giralda 6-7 / Track 6

MN11

Numerical study of the competitive effects of inertial and elastic forces on particle deformation and cross-streamline migration in microfluidic flows

Giancarlo Esposito¹, Salvatore Romano², Martien A. Hulsen³, Gaetano D'Avino², and Massimiliano M. Villone²

¹University of Patras, Patras, Greece; ²University of Naples Federico II, Naples, Italy; ³Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

The flow dynamics of suspensions in microfluidic channels depend on the interplay among several parameters, such as the flow rate and the rheology of the fluid, wall effects, inertial effects, and particle deformability. The manipulation of such parameters can allow to control the trajectories of the particles, thus achieving their focusing and/or sorting. In particular, the three dimensionless parameters characterizing the dynamics of a soft solid particle in a Newtonian liquid undergoing Poiseuille flow in a straight channel are the confinement ratio ß, comparing the size of the particle and that of the channel, the Reynolds number Re, measuring the relative weight of the liquid inertial and viscous forces, and the elastic capillary number Cae, quantifying the relative importance of the liquid viscous stress and particle elastic stress. When inertia is negligible, a neutrally buoyant deformable particle displaces toward the centerline of the channel [1]. Outside the Stokes regime, given ß, the cross-streamline migration and final equilibrium position of a deformable particle in the channel cross-section depend on the interplay between inertial and elastic forces, namely, on Re and Cae. In the recent years, elasto-inertial microfluidics is emerging as a powerful tool to achieve efficient particle focusing and/or sorting by proper tuning of the geometrical and process parameters [2], with important applications in the diagnostic field. In this study, we investigate the dynamics of deformable particles suspended in Newtonian liquids undergoing pressure-driven flow at non-negligible inertia in microfluidic channels to understand the mutual, and competing, effects of fluid inertia and particle elasticity on particle cross-streamline migration. Our analysis is carried out by means of fully three-dimensional finite-element direct numerical simulations.

References:

[1] M.M. Villone and P.L. Maffettone, Rheol. Acta 58:109 (2019) [2] D. Stoecklein and D. Di Carlo, Anal. Chem. 91:296 (2018)

Tuesday 16:30 Giralda 6-7 / Track 6

MN12

Dynamics of a single Newtonian droplet in a turbulent microscopic cross-slot flow of a shear thinning fluid

Yongbin Ji¹, Elia Missi², Jérôme Bellettre², Agnés Montillet³, Patrizio Massoli⁴, and <u>Teo Burghelea²</u>

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An experimental characterization of the dynamics of a single Newtonian droplet within a non-Newtonian fluid in a cross-slot microchannel is presented. The dynamics of the droplet are quantitatively assessed by high-speed video imaging which allows one to measure the statistics of droplet sizes and shapes and to describe droplet breakup process. To assess the role of non-Newtonian shear thinning behavior on the droplet dynamics, xanthan solutions with various concentrations (0.05% - 0.2%) have been used as a continuous phase. The imposed flow rates are of the order of mL/min which are substantially higher than those used in conventional droplet-based microfluidics which renders the flow inertially unstable and, for the highest flow rates investigated, inertially turbulent. The experimental results indicate that the specific swirl motion observed at the impact of the two fluid streams in the cross-slot micro-channel increases the probability for droplets of getting trapped within the collision region. The oscillatory dynamics of the droplet shape within the trapping region is gradually inhibited when the shear thinning effects are gradually increased. The shear thinning rheology of the aqueous phase equally influences the breakup dynamics of the droplet. At intermediate Reynolds number the shear thinning behavior leads to the formation of very thin and long filaments. A decrease of the characteristic breakup time of droplet is observed when the polymer concentration increases. As the Reynolds number is increased and the flow turns turbulent, the shear-thinning effects

delay the droplet breakup process. A full phase diagram of the dynamical modes observed by varying both the Reynolds number and the rheology of the continuous phase is presented.

Tuesday 16:50 Giralda 6-7 / Track 6

MN13

Role of the interfacial rheology on droplet dynamics in micro Hele-Shaw cell

Jacques-Teïva Baué, Isabelle Cantat, and Marie-Caroline Jullien

Institut de Physique de Rennes, Université de Rennes 1, Rennes, France

The development of droplet-based microfluidics addresses the question of predicting the velocity of these droplets when they are pushed by a carrier phase. In this work we focus on non-wetting droplets, i.e. there is a lubrication film between the droplet interface and the channel wall. These droplets are squeezed between the channel walls, i.e. they adopt a pancake-like shape. It is well known that the dynamics of droplets depend strongly on the physicochemical properties of the solutions, in particular on the solubility of the surfactant that is used. Typically, an accumulation of surfactant at a stagnation point of the interface can generate Marangoni stresses, leading to an increased dissipation in the lubrication film, and thus to a decrease in droplet velocity. We report experimental studies on the dynamics of droplets in a microfluidic Hele-Shaw cavity, by investigating the impact of the solubility of the used surfactants on their velocity. Surprinsingly, we observe that dependind on the chemistry, the droplet velocity either increases or decreases with the radius. We show that the relevant parameter for this transition is the carbon chain length of the ionic surfactants we used. In order to investigate the local signature of the surfactant along the lubrication film, we have set up a Reflection Interference Contrast Microscopy (RICM) device with which the thickness of the lubrication films can be measured. Able to reconstruct the topography of the droplet/external phase interface, the local properties of the interface can be extracted. The lubrication film appears to be thicker than the ones obtained by the classical models done by the sliding, rolling and stress-free boundary conditions.

Tuesday 17:10 Giralda 6-7 / Track 6

MN14

Characterization of the elongational behavior of a viscoelastic fluid through a microfluidic approach Andrea Iginio Cirillo^{1,2}, Giovanna Tomaiuolo^{3,2}, and Stefano Guido^{3,2}

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The presence of elongational fluxes characterizes several industrial applications involving viscoelastic fluids. Key examples can be found in food dough processing, polymer fibers' spinning and in the manufacturing of pressure sensitive adhesives. Characterizing the elongational behavior of a material is thus essential to predict and improve its performances to finally achieve a better optimization of its processing. The elongational properties of a material are commonly studied via specific extensional rheometers such as the Extensional Viscosity Fixture and the CaBER whose application, however, is limited to mildly and highly viscous fluids. An interesting solution for the investigation of low viscosity fluids is represented by microfluidics, the science and technology of low volumes - down to 10-9 *l* - processed in micro-confined environments like micrometric capillaries. In this work, two microfluidic techniques were adopted to investigate the elongational properties of different viscoelastic fluids characterized by a stringy behavior, namely the propensity to form filaments when stretched. In detail, the extensional viscosity of each fluid was evaluated by employing a flow focusing cross-shaped microchannel, where the sample undergoes an elongational deformation thanks to the stretching exerted by the lateral flow of a second immiscible fluid. The generation and evolution of the sample's thread were therefore analyzed according to the methodology proposed by Arratia et al. (Arratia et al., 2008). Owing to the presence of two immiscible phases, the interfacial tension between the fluids (not present in the literature) was measured adopting the microfluidic approach developed by D'Apolito et al. (D'Apolito et al., 2018).

Tuesday 17:30 Giralda 6-7 / Track 6

MN15

Machine learning boosts rapid microrheology with optical tweezer measurements

Matthew G. Smith, Jack Radford, Graham M. Gibson, Daniele Faccio, and Manlio Tassieri University of Glasgow, Glasgow G12 8LT, United Kingdom

Since their first appearance in the 1970s, optical tweezers have been successfully exploited for a variety of applications throughout the natural sciences, revolutionising the field of microsensing. In particular, they have been adopted as exceptional sensitive transducers (i.e., able to resolve pN forces and nm displacements, with temporal resolution down to a few microseconds) for developing novel microrheology methods for measuring the rheology of complex fluids having very feeble viscoelastic properties. However, when similar approaches are considered for rheological studies of living systems such as cells, there exist some issues related to the 'time-scales' involved during the measurements that preclude the determination of the viscoelastic properties of such systems (Tassieri, 2015). In this work, we present a machine learning algorithm that uses feature extraction on only one second of trajectory of an optically trapped particle to determine the viscosity of Newtonian fluids; yet returning viscosity values carrying an error of ~10%, which is on average four times smaller than those obtained from conventional analytical methods applied to the same data. We envisage that the proposed ML algorithm will revolutionise the field of microrheology with optical tweezer by substantially reducing the measurement time from tens of minutes to a few seconds; thus allowing their use for the rheological characterization of living systems.

References

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MN16

Tuesday 17:50 Giralda 6-7 / Track 6

Capillary flow of wormlike micellar gels

Ronak R. Gupta¹, Masoud Daneshi², Ian A. Frigaard^{1,2}, and Gwynn J. Elfring¹

¹Mechanical Engineering, University of British Columbia, Vancouver, British Columbia V6T1Z4, Canada; ²Department of Mathematics, University of British Columbia, Vancouver, BC V6T1Z2, Canada

Wormlike micellar solutions formed by long-chained zwitterionic surfactants show gel-like rheology at room temperature and have recently been found to exhibit other complex rheological features. We study the capillary flow of these wormlike micellar gels to uncover rheological fingerprints on a canonical flow scenario and quantify pressure drop for a range of flow rates to see if micelles undergo a structural transition that reflects on the viscosity-shear rate scaling. We also use optical coherence tomography based velocimetry to quantify velocity profiles and wall-slip. Our experiments shed light on the fluid dynamics of wormlike micelles and other complex fluids in simple geometries.

Wednedsay Morning

Symposium PL

Plenary Lectures

Wednesday 8:30 Giralda 1-2 / Plenary Lectures

PL2

Compact and accurate descriptions of complex fluids and soft solids using fractional calculus Gareth H. McKinley

Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Many soft materials including foods, consumer products & biopolymer gels are characterized by multi-scale microstructures and exhibit power-law responses in canonical experiments such as SAOS and creep. It is difficult to describe the material response of such systems quantitatively within the classical framework of springs & dashpots - which give rise to Maxwell-Debye exponential responses. Instead, empirical functions and subjective metrics such as 'firmness', 'thickness' etc. are often used to describe and compare material responses. I will show that the language of fractional calculus and the concept of a 'spring-pot' element provides a useful framework that is especially well-suited for modeling and quantifying the rheological response of power-law-like viscoelastic materials. We illustrate the general utility of this approach using fractional differential forms of the Maxwell, Kelvin-Voigt and Zener models. We then use these models to quantify viscoelastic responses of a range of soft materials including gluten and milk protein gels, cheese, polymer melts, hydrogen-bonded networks, colloidal pastes, as well as complex interfaces. The fractional exponents that characterize the dynamic material response can also be connected directly with scaling exponents from microstructural models such as the SGR model and the fractal dimensions of the underlying microstructure. This fractional framework can also be extended to the nonlinear domain by evaluating the corresponding continuous spectrum and integrating the fractional kernel into familiar Wagner/K-BKZ formulations with a generalized damping function. Using this integral fractional framework and carefully considering the asymptotic limits of small & large deformation rates we develop general expressions for the rate-dependent viscosity of a fractional viscoelastic fluid. This analysis also provides a systematic understanding of why familiar rheological heuristics such as the Cox-Merz rule and the Gleissle mirror relation often, but not always, work so well!

Symposium NF

Non-Newtonian Fluid Mechanics and Computational Rheology

Organizers: Miguel Nóbrega, Baltasar Mena and Corneliu Balan

Wednesday 9:30 Giralda 1-2 / Track 1

NF17

Simulations of thixo-viscoplastic flows around a cylinder using the Smoothed Particle Hydrodynamics method Emanuele Rossi¹, Imanol Garcia de Beristain¹, J. Esteban López-Aguilar², Adolfo Vazquez-Quesada³, and Marco Ellero¹ Computational Mathemathics - CFD Modellling and Simulation, Basque Center for Applied Mathematics, Bilbao, Spain; ²Facultad de Química, Departamento de Ingeniería Química, Universidad Nacional Autónoma de México, Ciudad de México, Mexico; ³Departamento de Física y Matemáticas, Universidad de Alcalá, Madrid, Spain

Thixotropic materials are complex fluids exhibiting transient viscous response upon application/removal of a finite shear flow (Mewis & Wagner, 2012). Thixotropic effects are present in many different systems and applications, from food products to plastics and semi-liquid metals, such as molten aluminium. In this work we present a first attempt to simulate the rheological properties of thixo-viscoplastic flows using a Smoothed Particle Hydrodynamic (SPH) method (Vázquez-Quesada et al., 2019). A 2D setup is used in this study to validate the model. The computational domain is represented by a circular cylinder placed at the center of a channel surrounded by a fluid moving with a constant velocity applied on the top and bottom boundaries.

We use the viscoplastic Papanastasiou model (Papanastasiou, 1987), which describes materials that combine solid-like to fluid-like features: at low stress, these materials do not flow, behaving as a rigid body, while they have a fluid-like response for high stresses. In order to assess accuracy, SPH results for yielded/unyielded regions at different Bingham numbers are compared with independent simulations using a Finite Volume Method solver, named RheoTool, based on OpenFOAM. In order to simulate viscoplastic-thixotropic flows, the Papanastasiou model was extended using an additional coupled evolution equation for a microstructure parameter (Le-Cao et al., 2020) which was used to analyse the modified flow properties.

References:

Mewis, J., & Wagner, N. J. (2012). Colloidal suspension rheology. Cambridge university press.

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Papanastasiou, T. C. (1987). Flows of materials with yield. Journal of Rheology, 31(5), 385-404.85-404.

Le-Cao, K., Phan-Thien, N., Mai-Duy, N., Ooi, S. K., Lee, A. C., & Khoo, B. C. (2020). A microstructure model for viscoelastic-thixotropic fluids. Physics of Fluids, 32(12), 123106

Wednesday 9:50 Giralda 1-2 / Track 1 NF18

Simulating collisions of viscoelastic inhomogeneous droplets with smoothed particle hydrodynamics

Stephan Sneijders and Johan T. Padding

Department of Process and Energy, Delft University of Technology, Delft, The Netherlands

Spray drying is a widely adopted technology in industry to turn solutions and suspensions into dry powders. In a spray dryer, a liquid feed mixture is forced through a nozzle at the top of a drying chamber, forming a spray of many small droplets suspended in hot dry air. As the droplets fall down in this hot dry air, the solvent gradually evaporates and the solute or solids concentration at the droplet surface increases forming a radial concentration gradient. Experiments show that the concentrations typically observed in such a process can have a strong influence on the rheological properties of the fluid: some industrial mixtures remain Newtonian even at higher concentrations, with the Newtonian viscosity increasing as a function of concentration, while others start showing viscoelastic behavior as concentration increases. Even in the simplest case of a fluid that exhibits Newtonian behavior over the whole relevant range of concentrations, the resulting gradient in viscosity affects the mechanics observed in collisions between droplets. The effects are possibly even more complex when the material exhibits viscoelastic rheology. In our work we use smoothed particle hydrodynamics (SPH) to investigate droplet collisions of droplets with a radial distribution of rheological properties. First, we examine the effects of Newtonian droplets with viscosity as a function of radial position. Second, we investigate droplets with viscoelastic properties varying along the radial direction. In order to simulate viscoelastic behavior with SPH we have implemented responsive particle dynamics (RaPiD); a method which proved fruitful in Brownian-dynamics-based methods. The RaPiD method has some free parameters which have to be calibrated in advance. These parameters are calibrated by performing small amplitude oscillatory shear simulations with the SPH method and matching the results with rheological benchmark experiments.

Wednesday 10:40 Giralda 1-2 / Track 1

NF19

Simulations of viscoelastic droplet-droplet collision

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We have numerically investigated the binary collision of viscoelastic drops by using a Front-tracking/Marker-And-Cell methodology. The numerical scheme is validated with shear-thinning fluids under surface tension effects. After, we have solved the droplet-droplet dynamics for viscoelastic constitutive models of Oldroyd-B and Phan-Thien-Tanner (PTT). In order to describe our main finding, maps of outcomes as functions of the dimensionless numbers that govern the problem are provided. The simulations describe the bouncing, coalescence, and separation outcomes varying the Weber number as well as Weissenberg number. Our findings suggest that surface tension and elasticity act to maintain the integrity of the merged drop and avoid separation.

Wednesday 11:00 Giralda 1-2 / Track 1

NF20

Yielding mechanisms in capillary suspensions

Sebastian Bindgen¹, Rudolf Weeber², Georg Rempfer², Christian Holm², and Erin Koos¹

¹Chemical Engineering Department, KU Leuven, Leuven 3001, Belgium; ²Institute for Computational Physics, University of Stuttgart, Stuttgart 70569, Germany

Capillary suspensions (Koos & Willenbacher, 2011) are a soft matter system that offer an attractive processing route to adjust the bulk properties of suspensions. They consist of particles and two immiscible liquid phases where the particles are connected via liquid bridges to form a sample spanning network. Previous in-vitro experiments have shown that multiple configurations are possible depending on the physico-chemical properties of the constitutive components (Bindgen et al., 2020). Apart from preliminary results in continuous shear flow (Bindgen et al., 2021), a description of the yielding mechanism, however, has not yet been established.

In our study, we describe changes with increasing oscillatory amplitude using the MD simulation package Espresso together with Lees-Edwards boundary conditions (Yang et al., 2021). In order to model the yielding behavior of networks formed by capillary forces, we first preform a particle network based on attractive forces computed via a toroidal bridge model (Megias-Alguacil & Gauckler, 2009) in static conditions. As forces act on particle surfaces rather than the center of particles, our model allows us to capture rigid body dynamics to include contact line pinning. The bulk fluid is modeled using the lattice Boltzmann technique.

We show that the linear regime of capillary suspensions ends far below deformations that introduce bond breaking whereas the yield point is mostly controlled by the network collapse. This collapse behavior is dominated by the amount of fluid present in the capillary bridges connecting particles. Bond reformation during shearing further influences the dynamic properties of capillary suspensions.

These results have clear implications for industrial processes and networks with other attractive interactions.

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Wednesday 11:20 Giralda 1-2 / Track 1

NF21

Maximum spreading of impacting Newtonian and viscoplastic drops: Highlighting controversial scaling laws through numerical simulations

Anselmo Pereira¹, Elie Hachem², and Rudy Valette³

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The impact of drops on solid and free liquid surfaces represents a crucial topic in interfacial hydrodynamics and soft matter rheology directly related to extremely important environmental and industrial situations, such as pesticides deposition, inkjet printing, coating, motor jets, ceramic beads and non-spherical particles production, as well as encapsulation processes. Interestingly, despite the considerable number of studies devoted to this topic, its most fundamental question remains opened: what is the maximum diameter attained by an impacting drop? In this connection, controversial theoretical arguments and scaling laws have been proposed. In the present work, we highlight this long-standing problem within fluid mechanics through finite element-based numerical simulations combined with an adaptive variational multi-scale and a Level-Set method for two materials (air, and Newtonian/viscoplastic drop). Thanks to kinematic and energy budget analyses that take into account a wide range of impact velocities and rheological properties, we show that the maximum spreading of Newtonian and viscoplastic drops impacting on solid or liquid surfaces is simply governed by the conservation of kinetic energy into surface, viscous dissipation, plastic and/or pressure/gravitational energies. This energy transfer process gives rise to a number of spreading regimes expressed by scaling laws related to the Weber number, the Reynolds number, the Bingham number and the Froude number. The scaling laws, however, are highly dependent on the interfacial interactions between the drop and the impacted surface. Lastly, comparisons between our numerical results and experimental ones available in the literature indicate that, for most situations of practical interest, all energy terms mentioned above are important, which elucidates the origins of the controversial debate concerning the spreading scaling laws.

Wednesday 11:40 Giralda 1-2 / Track 1

NF22

The closed form Adaptive Length Scale model: Properties and performance for simple and complex flows Konstantinos Zografos¹, Alexandre M. Afonso², and Robert J. Poole³

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In this paper we employ the closed form of the Adaptive Length Scale (ALS-C) model (Ghosh et al., 2002) and investigate its characteristics and potential use in numerical studies of dilute polymer solutions in general flows. The ALS-C model was inspired by the ability of a Kramers chain to capture important properties of dilute polymer solutions in rapidly varying extensional flows, such as coil-stretch hysteresis. The introduction of two variable extensibility parameters which adapt to the flow changes together with a shear-controlling parameter, modify the developed stresses and allow for a new range of responses. The ALS-C can be considered as a generalised version of the Finitely Extensible Nonlinear Elastic model that follows the Peterlin approximation. In proposing the model it was hoped that it would be capable of predicting the enhanced pressure drop observed in many flows of dilute polymeric solutions, but this hypothesis has never been tested in complex flows.

The ALS-C model has not been yet considered in flows outside of simple homogeneous shear or extension and specifically not in any general computational fluid dynamics (CFD) simulations. We have implemented the model into an in-house CFD solver appropriate for viscoelastic fluids (Oliveira et al, 1998), which employs the log-conformation approach (Afonso et al., 2009) within a finite-volume methodology. Here, we present the new set of equations that need to be solved together with a modified approach that enhances the computational speed for evaluating the instantaneous changes in the adaptive length scale as a result of the instantaneous changes in the flow field (Zografos et al., 2021). The response of the model is illustrated initially for standard rheological and steady-state shear flows and then is followed by its performance in flows within a range of complex geometries.

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Wednesday 12:00 Giralda 1-2 / Track 1

NF23

Soft blade coating of complex fluids

Marion Krapez¹, Anais Gauthier¹, Jean-Baptiste Boitte², Christophe Kusina², Odile Aubrun², Jean-François Joanny^{3,4}, and Annie Colin¹

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The spreading of complex fluids is a key process in the industry. Classic examples are the coating of paint or protective layer, cream and make-up application on the skin, and the fabrication of paper. In all these situations the fluids are non-Newtonian due to the presence of polymers or/and particles, resulting in more complex rheological behavior under shear. Here, we consider the spreading of polymer solutions with an elastic blade that deforms during the coating (similarly to a brush, a finger, or a rubber squeegee). Using complex fluids with well-chosen rheological properties, we disentangle the effects of shear viscosity, shear thinning, and normal stresses over the characteristics of the deposited film and the coating process. We reveal two counterintuitive results: it takes more energy to spread a volume of a shear thinning fluid than a volume of a Newtonian fluid in a given time. Second, the first normal stress difference, which usually leads to remarkable behaviors such as the swelling of jets during extrusion or the rise of the fluid on a rotating rod, has a strikingly negligible effect here, due to the coating geometry. We combine experiments, a numerical model, and a scaling analysis to evidence and explain these observations.

Symposium GS

Gels and Self Assembling Structures

Organizers: Joao Maia, Domenico Gabriele and Juan de Vicente

Wednesday 9:30 Santa Cruz / Track 2

GS17

Mechanical and microscopic characterization of alginate hydrogels dehydrated under controlled stresses

Alberto Leon-Cecilla¹, Cristina Gila-Vilchez¹, Juan D. G. Duran¹, Luis Álvarez de Cienfuegos², and Modesto T. Lopez-Lopez¹

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Orgánica, Universidad de Granada, Granada, Granada 18071, Spain

The research into designing and manufacturing of anisotropic materials has undergone significant development due to the potential applications of these materials in fields such as biomedicine or tissue engineering. The control of its mechanical properties and microstructure is crucial to obtain safe and biocompatible materials which are capable of imitating natural tissues. Today, one of the most widely used materials for these applications are polymeric hydrogels, defined as three-dimensional cross-linked hydrophilic polymeric network capable of retaining water within them. These materials are characterized by their high water content (greater than 90% by volume), biocompatibility, soft consistency and modifiable mechanical properties. In this work, we have studied and compared the effect of dehydration on sodium alginate gels of two different molecular weights. During dehydration processes, we have controlled the water loss by applying two different mechanical stresses, compression or traction, as well as the time during which we applied these stress. These controlled dehydration processes result in a permanent reorganization in the internal structure of the gels and an increase in the polymer concentration, which results in the creation of new bonds between the polymeric fibres and the generation of an internal anisotropy in the material. Moreover, if we adjust the molecular weight of alginate, the stress applied and the time of dehydration, we can control the mechanical properties and the degree of anisotropy in the hydrogel. This allows us to obtain materials with the appropriate mechanical and microstructure properties for their possible biomedical applications.

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Wednesday 9:50 Santa Cruz / Track 2

GS18

Gelation of protein aggregate suspensions by salt diffusion

Emilie Guilbert¹, Clément De Loubens¹, Alice Vilotte², and Hugues Bodiguel²

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We investigate the gelification between a calcium solution and a suspension of nanometric globular protein aggregates obtained by heat aggregation of a beta-lactoglobulin solution. A capillary is filled with this suspension of aggregates at mass fractions below its gel point and then brought into contact with a drop of calcium at different concentrations. Observation under the microscope highlights gelation kinetics that follow classical diffusion-reaction laws, with a short-time regime limited by the reaction, and a long-time regime limited by the diffusion. Unexpectedly, the gelation mechanism also induces a solvent flow from the aggregate suspension to the calcium solution. We explain this phenomenon by the difference in chemical potentials between the aggregate suspension and the calcium solution. However, by analogy with osmotic phenomena, this

flow, characterised by the tracking of micrometric particles, seems to suggest that the forming gel acts as a semi-permeable membrane for calcium ions.

Wednesday 10:40 Santa Cruz / Track 2

GS19

Effect of sulfate content and counterion on phase transition of cellulose nanocrystal suspensions

Sylwia Wojno¹, Amit Sonker², Gunnar Westman², and Roland Kádár¹

¹Department of Industrial and Materials Science, Division of, Chalmers University of Technology, Gothenburg, Sweden;

Cellulose nanocrystals (CNC) show significant potential for many applications, either as material on its own or as renewable reinforcement in polymers. Additionally, CNC properties can be tailored by changing sulfate content and/or counterions. The degree of sulfation affects the hierarchical ordering in CNC suspensions, which in turn can self-assemble into nematic and chiral nematic structures, exhibiting birefringence above a critical concentration. In this work, we explore the effects of two different sulfate degrees and six different counterions (H⁺, Li⁺, Na⁺, K⁺, triethanolamine (TEtA), triethylamine (TEyA), within 4 wt% CNC. We focus on the effects thereof on CNC phase transitions through rheo-PLI (polarized light imaging) and nonlinear oscillatory shear (Fourier-Transform Rheology and stress decomposition). We note that all suspensions at 4 wt% exhibit liquid crystalline (LC) phase, which was identified based on birefringence, steady shear, linear viscoelastic oscillatory shear data and polarized optical microscopy (POM). The addition of a different counterion than H⁺ decreases steady shear viscosity. From a nonlinear rheological point of view, oscillatory shear of CNC suspensions in the nonlinear regime generates higher harmonic contributions in the shear stress response. The nonlinear material response expressed by the third relative higher harmonic of the shear stress shows that suspensions with counterion different than H⁺, exhibit a unique three-scaling region behaviour. All suspensions show nonlinear intra-cycle strain stiffening behaviour (S>0), with weak angular frequency dependence. A significant difference at the transition from intra-cycle shear thickening (T>0) to intracycle shear thinning (T<0) between LC concentrations of untreated CNC (CNC-SO3H) and suspensions with grafted different counterions was recorded

Wednesday 11:00 Santa Cruz / Track 2

GS20

What caging force cells feel in 3D hydrogels: A rheological perspective

<u>Manlio Tassieri</u>, Giuseppe Ciccone, Oana Dobre, Graham M. Gibson, Jose M. Rey, Cristina Gonzalez-Garcia, Massimo Vassalli, and Manuel Salmeron-Sanchez

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It has been established that the mechanical properties of hydrogels control the fate of (stem) cells. However, despite its importance, a one-to-one correspondence between gels' stiffness and cell behaviour is still missing from literature. In this work, the viscoelastic properties of poly(ethylene-glycol) (PEG)-based hydrogels are investigated by means of rheological measurements performed at different length scales. The outcomes of this work reveal that PEG-based hydrogels show significant stiffening when subjected to a compressional deformation, implying that conventional bulk rheology measurements may overestimate the stiffness of hydrogels by up to an order of magnitude. It is hypothesised that this apparent stiffening is caused by an induced "tensional state" of the gel network, due to the application of a compressional normal force during sample loading. Moreover, it is shown that the actual stiffness of the hydrogels is instead accurately determined by means of both passive-video-particle-tracking (PVPT) microrheology and nanoindentation measurements, which are inherently performed at the cell's length scale and in absence of any externally applied force in the case of PVPT. These results underpin a methodology for measuring hydrogels' linear viscoelastic properties that are representative of the mechanical constraints perceived by cells in 3D hydrogel cultures.

Wednesday 11:20 Santa Cruz / Track 2

GS21

Influence of substrate composition and viscoelasticity on growth of filamentous fungi

Ciatta Wobill¹, Patrick Rühs², and Peter Fischer¹

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Filamentous fungi have an important function in generation of various enzymes, primary and secondary metabolites used in the food and pharmaceutical industry. Furthermore, they have been traditionally used for food fermentation products and their components, such as mycoprotein, used for meat alternatives [1]. More recently, fungi and its mycelium are also being used to produce material that could replace medical constituents, plastics or used as building material [1-3]. By fine-tuning the material to fungal requirements, novel materials can be produced. The fungal mycelium, made of hyphae, is a highly branched network spreading into the host material to absorb nutrients necessary for growth [3,4]. Material characteristics such as pH, nutrient content, and growth conditions like temperature, humidity and gas concentration lead to varying fungal growth patterns and vigor [1,4]. To investigate the influence of host material and its rheological properties on fungal growth, assays are performed and set into relation to viscoelastic properties of the culture material measured with rheology. Confocal microscopy gives insight on the growth behavior on a micro-level. We could show that by increasing storage and loss moduli in gelled culture media, growth velocity can be decreased significantly. Whereas in flexible gel or non-gelled media fungi increase the surface area by penetrating mycelial surface into the culture media.

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²Department of Chemistry and Chemical Engineering, Division o, Chalmers University of Technology, Gothenburg, Sweden

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Wednesday 11:40 Santa Cruz / Track 2

GS22

Rheological behavior of alginate-based magneto-polymer composites

Mariem M. Abrougui¹, Cristina Gila-Vilchez², William R. Suarez-Fernandez², Francisco J. Vazquez-Perez², Luis Álvarez de Cienfuegos³, Juan D. G. Duran², and Modesto T. Lopez-Lopez²

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Magneto-polymer composites consist of dispersions of magnetic particles in polymeric systems and combine the elasticity of polymers with the magnetic character of the dispersed particles. This interesting feature allows actuation by noncontact magnetic forces and remote control of the properties of magneto-polymer composites, and it is the base of many applications, including magnetic soft actuators. In this work we review our recent results on the rheological characterization of novel alginate-based magneto-polymer composites. In the absence of cross-linking, for medium molecular weight (120,000-190,000 g/mol) sodium alginate, dispersions of iron particles in polymer solutions behaved as liquid-like materials, but for large molecular weight (up to 600,000 g/mol) sodium alginate a transition to gel-like behavior (storage modulus larger than loss modulus) took place at a polymer concentration of 7% w/v. Addition of calcium ions to the solutions of polymers induced cross-linking that resulted in gel-like behavior even for medium molecular weight sodium alginate at low concentration. We investigated the role of iron particle concentration in the rheological properties of these gels. We also investigated samples containing rod-like and platelet-like magnetic composites instead of spherical iron particles. For this aim, we used sepiolite and bentonite clays as core support on which we deposited magnetite nanoparticles by an in-situ process of synthesis. In addition, we studied the rheological properties of all these magneto-polymer composites under the application of magnetic field and found a strong magnetorheological effect. A comparison between the magnetorheological effect developed by these systems was finally performed.

Wednesday 12:00 Santa Cruz / Track 2

GS23

Multiwave rheological tests to study thermogelation of HydroxyPropyl MethylCellulose (HPMC) aqueous solutions

Saray Perez Robles, Claudia Carotenuto, and Mario Minale

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The hydroxypropyl methylcellulose (HPMC) is a cellulose ether extensively used for coatings, films, membranes, drilling, pharmaceuticals, cosmetics, and foods due to its capacity to give boil-out control, avoid bursting, retain moisture, and improve the volume and texture of different fluids. HPMC hydrates in cold water and transforms into a gel upon heating. The thermogelation process is reversible; thus, the gel reverts to the sol state upon cooling. In the HPMC, the cellulose hydroxyl groups (three per anhydroglucose unit, AGU) are replaced by either methoxy or hydroxypropyl units. The degree of substitution (DS) identifies the average number of methyl groups, and the molar substitution (MS) represents the hydroxypropyl average content per AGU. The quantity and position of the substituents may affect the thermogelation. During a heating ramp, HPMC aqueous solutions show a smooth decrease of the storage (G') and loss moduli (G"), followed by an abrupt fall and a subsequent increase of both moduli, with G' overcoming G". Furthermore, in the sol-gel transition, an evolution of the microstructure occurs in time also at a constant temperature. Hence, the dynamic spectra taken during a frequency sweep test run either by increasing or decreasing the frequency are unavoidably affected by the microstructure evolution. We propose multiwave testing as a more accurate strategy for investigating thermogelation. The thermal ramp multiwave test allows obtaining isochronal frequency spectra at each temperature to follow exhaustively the microstructure evolution with time. As result, we successfully revise the viscoelastic moduli behaviour of HPMC aqueous solutions using the multiwave method, reinterpreted the frequency effect on different DS and MS HPMC samples, and obtained new hints of the microstructure evolution during the thermogelation.

Symposium SM

Polymer Solutions and Melts

Organizers: Antxon Santamaría, Evelyne Van Ruymbecke and Moshe Gottlieb

Wednesday 9:30 Nervión / Track 3

Keynote

SM₁

Strain hardening of unentangled polymer solutions in fast shear flows

<u>Salvatore Costanzo</u>, Vincenzo Ianniello, Rossana Pasquino, Nino Grizzuti, Giovanni Ianniruberto, and Giuseppe Marrucci *University of Naples Federico II, DICMaPI, Napoli, Italy*

We investigate the linear and nonlinear shear flow properties of unentangled linear polystyrene solutions with the same fractional number Z of entanglements of a polystyrene melt. The latter has a molecular weight equal to 30 kDa. The solutions are made by dissolving long polystyrene chains (from 126 kDa to 1000 kDa) in oligostyrene with molecular weight equal to 2 kDa. The volume fraction of long polystyrene in solution is decreased with increasing molecular weight, in order to keep Z constant. While the fractional number of entanglements remains unchanged, the maximum extensibility of the chain increases upon dilution. The linear viscoelastic spectra of the solutions are well described by the Rouse model incorporating glassy relaxation modes. As expected, the Rouse modulus decreases, and the longest Rouse time increases, by decreasing the volume fraction of the long chain. The combination of low elastic modulus and long relaxation time, coupled with the use of a cone-and-partitioned plate fixture, allows to attain values of the Rouse Weissenberg number larger than 3000. As a result of such strong flows, chains are stretched close to their maximum. With strong stretch, strain hardening of the transient shear viscosity is clearly observed. In the strain hardening regime, axial force transducer overload is rapidly approached. Before overload occurs, normal stress data indicate that the second normal stress difference is virtually zero. Brownian dynamics simulations based on Rouse chains incorporating finite extensibility are shown to be suitable to describe the macroscopic rheological behaviour of the solutions.

Wednesday 10:40 Nervión / Track 3

SM3

Measurement and modeling of uniaxial and planar extensional viscosities for various polymer melts in very fast flows

Martin Zatloukal and Jiri Drabek

Polymer Centre, Faculty of Technology, Tomas Bata University in Zlín, Zlín 76001, Czech Republic

In order to optimize and develop new polymeric materials for advanced polymer processing, it is necessary to know their rheological behavior, especially during uniaxial and planar stretching. However, conventional rheology tools do not allow the flow behavior of polymers to be evaluated under the conditions typical for very fast flows. In this work, novel rectangle and circular orifice (zero-length) dies have been utilized for temperature-strain rate dependent planar and uniaxial extensional viscosity measurements for various polymer melts by using Cogswell and Gibson methodologies and the capability of different constitutive equations to describe the measured experimental data has been tested. Specific attention was paid to recently proposed frame-invariant Generalized Newtonian Fluid constitutive equation [Zatloukal, M., Drabek, J. (2021) Physics of Fluids, 33 (8), art. no. 083106], which uses basic rheological and molecular parameters. For the first time, the monomeric friction coefficient for fully aligned chains was determined for PP using a high-strain-rate limiting value of uniaxial extensional viscosity. As the friction coefficient for the PP melts control flow induced crystallization and extensional rheology at high extensional rates, the results obtained are assumed to be valuable not only with regard to fundamental understanding of polymer physics and development/validation of advanced constitutive equations, but also with respect to understanding stability of non-Newtonian flows in advanced polymer processing, such as, for example, optimized production of polymer membranes for energy storage membranes via cast film process or filtration membranes prepared by the meltblown process used, for example, in production of face masks.

Acknowledgments: The authors wish to acknowledge the Czech Science Foundation (Grant No. 21-09174S) for the financial support.

Wednesday 11:00 Nervión / Track 3

SM4

Small-angle neutron scattering study of the structural relaxation of elongationally oriented, moderately stretched three-arm star polymers

Kell Mortensen¹, Anine L. Borger¹, Jacob J. Kirkensgaard¹, Qian Huang², <u>Ole Hassager</u>³, and Kristoffer Almdal⁴

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We present structural relaxation studies of a polystyrene star polymer after cessation of high-rate extensional flow. During the steady-state flow, the scattering pattern shows two sets of independent correlations peaks, reflecting the structure of a polymer confined in a fully oriented three-armed tube. Upon cessation of flow, the relaxation constitutes three distinct regimes. In a first regime, the perpendicular correlation peaks disappear, signifying disruption of the virtual tube. In a second regime, broad scattering arcs emerge, reflecting relaxation from highly aligned chains to more relaxed, still anisotropic form. New entanglements dominate the last relaxation regime where the scattering pattern evolves to a successively elliptical and circular pattern, reflecting relaxation via reptation.

Wednesday 11:20 Nervión / Track 3

Modelling unentangled polymer melts in fast flows

Giovanni Ianniruberto¹, Hongwei Liu¹, Antonio Brasiello², and Giuseppe Marrucci¹

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It has been thought for a long time that unentangled polymer melts are well described by the Rouse model, provided finite extensibility (FENE) corrections are included. In recent times, however, further corrections appeared indispensable in fast flows. Both experiments and nonequilibrium molecular dynamics (NEMD) simulations of uniaxial extensional flows revealed that the extensional viscosity does not approach the expected plateau value predicted by FENE models because of flow-induced co-alignment of the Kuhn segments of the polymer molecules, and the consequent reduction of the monomeric friction coefficient [1]. Finally, the link between the monomeric friction coefficient and the random forces due to thermal motion, known as fluctuation-dissipation theorem, does not necessarily hold true away from equilibrium [2]. We here take advantage of the rich set of data obtained by Xu et al. [3] with NEMD simulations of several Kremer-Grest melts in fast steady shear flows to try and reproduce them by suitable Brownian dynamics simulations, with the aim of understanding the role of the nonlinear mechanisms mentioned above. Indeed, the data of Xu et al. include not only the viscosity and the first normal stress difference, but also the second normal stress difference is present in unentangled melts, and that the ratio to the first normal stress difference is virtually the same than that of entangled melts. Even more surprisingly, and differently from entangled melts, the normal stress ratio in the unentangled case remains essentially constant with increasing shear rate, possibly because of flow-induced excluded volume interactions.

References:

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- 3. Xu et al. Journal of Chemical Physics 2014, 140, 174902.

Wednesday 11:40 Nervión / Track 3

SM₆

SM5

Investigating the structure-dynamics relation of star-shaped polymers in melts through atomistic molecular dynamics simulations

Eirini Gkolfi¹, Petra Bacova², Laurence G. Hawke³, and Vagelis Harmandaris¹

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Star polymers are used as model systems for more complex architectures as their dynamical behavior can be tuned from linear-like to coloidal-like by adjusting the number of arms. An important characteristic related to the dynamical response of the star-like polymers is their penetrability. A recent experimental evidence suggests that penetrability may depend not only on the number of arms but also on their internal packing. In this work, we perform atomistic molecular dynamics (MD) simulations of non-entangled poly(ethylene oxide) (PEO) and polystyrene (PS) stars in melts. These two dissimilar polymers differ in flexibility and glass transition temperature. By varying the number of arms (functionality) as our main parameter, we aim to alter their mutual penetration and adjust the local packing. In addition to our previous structural analysis, we use two approaches to probe the dynamics with respect to the functionality. Firstly we measure segmental displacement along the arm and analyze the observed tendencies by confronting our results with the continuous Rouse model adapted for star-like architectures. Deviations from the ideal theoretical Rouse model are detected, attributed mostly to the intramolecular dynamical gradient originating from the multi-arm star-like architecture. The second approach involves the implementation of a challenging grid-based algorithm for the estimation of the free volume in the system. Results are related to the internal packing of the molecules and the permeability of the material. Our results provide information complementary to the experimental techniques or more generic models and can thus contribute to a better understanding of structure-dynamics relation in materials with branch-like architectures, such as those used in all-polymer nanocomposites or nanostructured electrolytes.

Wednesday 12:00 Nervión / Track 3

SM7

Molecular origin of rheological properties of well-defined Polystyrene POM-POM model systems and comparison with well-defined PS combs and stars

Valerian H. Hirschberg, Max G. Schußmann, Marie-Christin Röpert, and Manfred Wilhelm

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The correlation of molecular and rheological properties is one of the key challenges of polymer science. A series of Polystyrene (PS) based model systems with a well-defined POM-POM topology is synthesized by a newly proposed combination of anionic polymerization technique and grafting-onto method to correlate molecular and rheological and mechanical properties. The influence of the three main topological parameters, (I) the molecular weight of the backbone between the two stars / POMs, $M_{W,BB}$, (II) the number of side chains per POM, n_{SC} , and (III) their molecular weight, $M_{W,SC}$, is investigated. Shear and extensional rheological data of these POM-POMs were investigated in the framework of zero shear viscosity, η_0 , and strain hardening factor (SHF) and correlated with the molecular structure. Experiments revealed, that $M_{W,SC}$ below three times the entanglement molecular weight, $3M_e$, has little influence on the η_0 , compared with the linear backbone, resulting in a maximum η_0 decreases by over a factor of 1000 compared to a linear chain with the same M_W . For high $M_{W,SC}$, in the terminal regime, G' and G'' are parallel with a constant slope of around 0.6. In extensional rheology, for POM-POM PS with $M_{W,SC}$ around $1M_e$, and an entangled backbone (two distinct rubber plateaus in the mastercurve), the highest strain hardening with a SHF above 200 could be observed. The results are compared with model

PS combs and stars, as well as with rheological models, such as the MSF and the POM-POM model and topology-property predictions from literature.

Symposium IP

Industrial Rheology and Processing

Organizers: María Graça Rasteiro, Francisco Martínez-Boza and Patrick Anderson

Wednesday 9:30 Prado / Track 4

IP1

Experiments and numerical simulations of the die swell phenomenon of viscoelastic materials in 3D printing processes

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Extrudate swelling is a well-known phenomenon occurring in extrusion processes where the material expands once it exits the die. This phenomenon, due to the existence of normal stresses in polymeric liquids, alters the extrudate cross-section shape as compared to the die profile. For this reason, a deep understanding of the swelling phenomenon is needed to properly design the die cross-section to obtain the desired extrudate shape. In the present work, we carry out experiments and numerical simulations to investigate the extrudate swelling phenomenon in a 3D printing process of a molten polylactic acid flowing in a converging die. The simulations are performed through the software RheoTool where the Volume-Of-Fluid method is used to compute the evolution of the fluid-air interface. The polymeric liquid is modelled by a multimode Giesekus constitutive equation with parameters obtained by fitting the fluid rheology. The simulation results are compared with experimental data, analysing both the die swell ratio and the shape of the material exiting the die. The effect of the flow rate, temperature, and die geometry on the extrudate cross-section profile is investigated.

Wednesday 9:50 Prado / Track 4

IP2

Numerical study of the effect of thixotropy on extrudate swell

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The extrusion of highly filled elastomers is widely used in the automotive industry. In this paper, we numerically study the effect of thixotropy on 2D planar extrudate swell for constant and fluctuating flow rates, as well as the effect of thixotropy on the swell behavior of a 3D rectangular extrudate for a constant flowrate. To this end, we used the Finite Element Method. The state of the network structure in the material is described using a kinetic equation for a structure parameter. Rate and stress-controlled models for this kinetic equation are compared. The effect of thixotropy on extrudate swell is studied by varying the damage and recovery parameters in these models. It was found that thixotropy in general decreases extrudate swell. The stress-controlled approach always predicts a larger swell ratio compared to the rate-controlled approach for the Weissenberg numbers studied in this work. When the damage parameter in the models is increased, a less viscous fluid layer appears near the die wall, which decreases the swell ratio to a value lower than the Newtonian swell ratio. Upon further increasing the damage parameter, the high viscosity core layer becomes very small, leading to an increase in the swell ratio compared to smaller damage parameters, approaching the Newtonian value. The existence of a low-viscosity outer layer and a high-viscosity core in the die have a pronounced effect on the swell ratio for thixotropic fluids. https://doi.org/10.3390/polym13244383

Wednesday 10:40 Prado / Track 4

IP3

Entrainment of a viscoplastic fluid into a Newtonian fluid by a bubble crossing the interface between liquid layers

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A remediation strategy for mined tailings is to return these tailings to a mined-out pit and cap them with water. In the case of Base Mine Lake in the oil sands region of Alberta, the tailings form a layer that has been characterised rheologically as a yield stress fluid [1]. The water cap is sufficiently deep that wind-driven resuspension of tailings into the water cap is limited and turbidity is decreasing with time, thereby improving water quality [2]. However, the methanogenesis of residual hydrocarbons in the tailings layer generates methane bubbles that rise through the tailings into the water column. Field observations and laboratory experiments suggest that as these bubbles enter the water cap they entrain tailings that contribute to the turbidity of the water cap [3,4].

Here the dynamics of isolated bubbles crossing the horizontal interface separating miscible viscoplastic and Newtonian liquids is studied computationally. The objective is to quantify the controlling effect of the rheology of the lower fluid layer (in particular its yield stress) on the entrainment. We have also studied the effect of other controlling physical parameters such as inertia, surface tension, and the density and viscosity

contrast between the two liquids. The yield stress has been found to limit the amount of entrainment. We have also analyzed the topology of the interface between two liquid layers and how it relates to the entrainment directly. Another interesting phenomenon we explored is how isolated bubbles may trap at the interface due to yield or capillary blockage. Our results elucidate a possible physical mechanism causing the continuous release of bubbles from mud layers.

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Wednesday 11:00 Prado / Track 4

IP4

Torsional instability of constant viscosity elastic liquid bridges

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Micro Bio Nanofluidics Unit, Okinawa Institute of Science and Technology, Okinawa, Japan

By experiment and simulation, we report that viscoelastic liquid bridges made of constant viscosity elastic liquids, aka Boger fluids, can be effectively destabilized by torsion. Under torsion, the deformation of the liquid bridge depends on the competition between elastocapillarity and torsion-induced normal stress effects. When the elastocapillary effect dominates, the liquid bridge undergoes elastocapillary instability and thins into a cylindrical thread, whose length increases and whose radius decays exponentially over time. When the torsion-induced normal stress effect dominates, the liquid bridge deforms in a way similar to edge fracture, a flow instability characterized by the sudden indentation of the fluid's free surface when a viscoelastic fluid is sheared at above a critical deformation rate. The vertical component of the normal stress causes the upper and lower portions of the liquid bridge to approach each other, and the radial component of the normal stress results in the liquid bridge thinning more quickly than under elastocapillarity. Whether such quick thinning continues until the bridge breaks depends on both the liquid bridge configuration and the level of torsion applied.

Wednesday 11:20 Prado / Track 4

IP5

Understanding the sharkskin instability of filled rubber compounds: Investigating the influence of die geometry and filler dispersion

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Rubber compounds filled with silica manifest extrusion flow instabilities [1,2] at the die exit of extrusion lines, usually sharkskin. Within this study the extrusion flow instabilities of the compounds are investigated as a function of die geometry, round capillary and rectangular slit dies,[3,4] and filler dispersion. This study uses the Inn et al., [5] analytical model which correlates the spatial characteristic wavelength (λ) of the extrusion flow instabilities with the ratio of extensional (Y_s) and shear stress (σ_x) of the extrudate at the die exit region. Thus, correlations between the extrusion performance and the molecular properties (relaxation time, amount of filler and dispersion agent) of the compounds are presented. In addition, a recently proposed geometry-dependent [6,7] model is used to predict the spatial characteristic wavelength (λ) of the extrusion flow instabilities of the rubber compounds from a round capillary die to a rectangular slit die and vice versa.

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Wednesday 11:40 Prado / Track 4

IP6

CFD characterization of the hollow-cone spray process: Newtonian and non-Newtonian fluids comparison Massimiliano Di Martino¹, Deepak Ahirwal², and Pier Luca Maffettone³

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The atomization of a bulk liquid into tiny droplets, dispersed in a gaseous medium, is a complex multiphase process not yet fully understood. Nowadays, the SARS-CoV-2 global pandemic emphasizes the current interest in investigating the key aspects that determine the performance of small-scale cleaning sprayers for the surface disinfection. From this perspective, the characterization of the atomization process turns out to be crucial for a comprehensive product design study. As many applications require wide spray pattern, some devices are used to expand the output liquid against the contracting surface tension forces. This is the case of the pressure-swirl atomizer, where the swirl flow leads the liquid sheet to

exhibit a distinctive hollow-cone shape. The configuration of the atomizer and the properties of the multiphase system affect the spray morphology and the droplets/ligaments distribution. Aim of the work is to investigate through the computational fluid dynamics (CFD) the stability of the gasliquid interface produced by a swirling liquid injection at short and long distances from the nozzle outlet. By implementing the Volume Of Fluid (VOF) and the Volume Of Fluid To Discrete Phase Model (VOF-to-DPM) methods, we show transient studies in which the liquid-gas interactions and the further propagation of droplets are resolved within and outside the nozzle geometry, simultaneously. As the viscosity is known to be a relevant parameter in fluid formulation, we consider Newtonian and non-Newtonian rheologies for their ubiquitous presence in detergent or sanitation fluids. We highlight the relevance of non-Newtonian dispensed liquids by analyzing the influence of rheological parameters on the hollow-cone spray performance. Furthermore, we compare the Newtonian and non-Newtonian primary atomization in terms of spray pattern and drops propagation from the nozzle outlet to a wall located further from the primary breakup region.

Wednesday 12:00 Prado / Track 4

IP7

Rheological characterization of composites used in 3 D printing

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The operating principle of fused deposition modeling (FDM) is highly similar to conventional polymer extrusion. In this case, a thermoplastic-based filament is driven by a system of small wheels, towards an extrusion head. There it is heated to exceed its melting temperature to be extruded through a small diameter nozzle that has movement in two axes: horizontal and vertical. The molten filament is deposited on a platform, describing a previously established trajectory and cooling and solidifying as it advances, due to the contrast of temperatures. Once said trajectory is completed, the process is repeated, depositing the filament on the previous layer, adhering to the already solidified polymer. In this way, the final 3D piece is created by adding layers in the Z direction. It is clear that the rheological study of the materials to be printed is key when it comes to obtaining correct properties both during the printing process and the final product. In this work, ABS and ABS with carbon fiber will be rheologically characterized.

Symposium EM

Experimental Methods and New Advances in Rheometry

Organizers: Loic Hillou, Paula Moldenaers and Dimitris Vlassopoulos

Wednesday 9:30 Arenal / Track 5

EM1

Rimming flow for measuring the complex viscosity $\eta^*(\Omega)$

Jurgen Sanders

Jurgen Sanders, Vila Nova de Gaia 4430-192, Portugal

Measuring the shape, amplitude and phase, of the liquid free surface in rimming flow inside a rotating horizontal cylinder can determine the complex viscosity $\eta^*(\Omega)$ of a linear viscoelastic liquid. The surface shape can be measurement by reflection of light with a light source and a focusing screen outside of the cylinder. This allows a complete thermal isolation of the sample. First measurements of η^* with a prototype rimming flow device have been performed for an STP motor additive in a frequency range of 3 to 10 rads/sec and a viscosity range of $\eta' = 4$ to 12 Pa·s, $\eta'' = 1$ to 3 Pa·s. The cylinder had an inner diameter of 64 m. Measurements were taken at filling levels between 36% to 84%. Results are promising and provide an opportunity to determine $\eta^*(\Omega)$ independently from traditional stress/strain methods. Further developments may be refining the experimental apparatus, testing with different liquids, comparing results from different methods, and a more detailed study of the onset of flow instabilities when slowing down the rotation speed of the cylinder.

Wednesday 9:50 Arenal / Track 5

EM2

Rapid temperature-dependent rheological measurements of non-Newtonian solutions using a machine-learning aided microfluidic rheometer

Francesco Del Giudice¹ and Claire M. Barnes²

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Microfluidic rheometry is considered to be a potential alternative to conventional rheometry for the rheological characterization of viscoelastic solutions having relatively low viscoelastic properties. We here introduce a microfluidic rheometer for rapid simultaneous measurement of shear-viscosity and longest relaxation time of non-Newtonian solutions at different temperatures. At variance with previous technologies, our microfluidic rheometer provides a very short turnaround time of around 2 minutes or less thanks to the implementation of a machine-learning algorithm. We validated our platform on several aqueous solutions of polyethylene oxide. We also performed measurements on hyaluronic acid solutions in the clinical range for joint grade assessment. We observed a monotonic behaviour with the concentration for both rheological properties, thus speculating their use as potential rheo-markers, i.e., rheological biomarkers, across several disease states, where different

concentrations of proteins in the biofluid are related to distinct health conditions. Finally, we also designed a simple Matlab application to quickly derive the rheological parameters from microfluidic measurements performed with our experimental setup.

Wednesday 10:40 Arenal / Track 5

EM3

A novel correction method for the shear rate in a couette rheometer

Torben N. Rüther, Steffen Jesinghausen, and Hans-Joachim Schmid

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When measuring substances in a coaxial system, the shear stress distribution can be directly derived from the momentum equilibrium but the determination of the shear rate is a bit more complicated as the flow law must be known beforehand. However, it is paradox that actually the shear rate has to be determined in order to reveal the flow law. Therefore, the shear rate is calculated as apparent shear rate assuming a Newtonian flow law and has to be corrected afterwards. Already existing approaches for solving this problem show some weaknesses in terms of accuracy or usability. For example, the correction method of Schümmer is easy to use but comparatively imprecise. More precise methods, like the correction of Krieger und Elrod use the first and second derivative of the measured values, what may lead to considerable evaluation and accuracy difficulties. For the novel approach to determine the true shear rate presented here, it is only necessary to be able to represent the rotational speed as a function of the shear stress (both on the inner cylinder). This can be achieved easily with the help of a polynomial of any degree supplemented with a sum of any number of power functions if more accuracy is needed $(2 \cdot \omega = \sum_{i=1}^{N} \{a_i \cdot \tau^i\} + \sum_{k=1}^{M} \{b_k \tau^c_k\}$). The coefficients a_i and b_k can now be adjusted via a simple conversion (the exponents i and c_k remain the same) to calculate the shear rate directly using the resulting function. The implementation of the correction is therefore much easier than for comparable methods. The accuracy is only depending on the adjustment of the polynomial-power-fits to the measured values. The presentation will cover the theoretical derivation and the practical applicability will be demonstrated correcting simulated results and real tests in comparison to already entrenched correction methods.

Wednesday 11:00 Arenal / Track 5

EM4

A data-driven method for automated superposition of rheological data

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The superposition of data sets with internal parameteric self-similarity is a longstanding and widespread technique for the analysis of many types of experimental data across the physical sciences. For rheologists, the most familiar application is time-temperature superposition. Typically, this superposition is performed manually, or more recently by using one of a few automated algorithms [1]. However, these methods are often heuristic, are prone to user bias via manual data shifting or parameterization, and lack a native framework for handling uncertainty in both the data and the resulting model of the superposed data. In this work, we develop a data-driven, non-parametric method for superposing experimental data with arbitrary coordinate transformations, which employs Gaussian process regression to learn statistical models for the experimental data, and then maximum *a posteriori* estimation to optimally superpose data sets. This statistical framework is robust to experimental noise, and automatically produces uncertainty estimates for the learned coordinate transformations. Moreover, it is distinguished from black-box machine learning in its interpretability -- specifically, it produces a model that is not only predictive, but may itself be interrogated to gain insight into the system under study. We demonstrate these salient features of our method through its application to multiple data sets characterizing the rheology of soft materials, and in each case our method replicates results obtained by other techniques but with reduced bias and added uncertainty estimates. This method enables a standardized, statistical treatment of self-similar material data across a broad range of fields, producing interpretable and predictive data-driven models that may inform applications such as materials classification, design, and discovery.

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Wednesday 11:20 Arenal / Track 5

EM5

Polarized imaging: An essential tool for rheological investigations on complex fluids

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Simultaneous use of rheological and optical techniques, i.e. of rheo-optical methods, is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids. Most rheo-optical techniques, such as small-angle light scattering, microscopy or spectroscopy methods are monitoring the sample only at a small specific spot. In contrast with a rheo polarized imaging techniques called SIPLI (shear induced polarization light imaging) the whole plate is observed and the birefringence can be displayed over the full range of shear rates within one single experiment. SIPLI combines a visualization technique with measurements of local stresses through the detection of the birefringence. By employing parallel-plate geometries, different shear rates are present throughout the sample, from a maximum shear rate at the edge of the sample to a zero shear rate in the center of the plate. Polarized imaging is the ideal tool for following shear induced orientation, crystallization or phase transitions in all complex fluids as long as they have some optical transparency. SIPLI has been used successfully for liquid crystals, polymer melts, block copolymers, nano-crystalline cellulose, hydrogels, clay suspensions, among other materials. An extra benefit of the sample visualization is the avoidance of measurement artefacts due to the easy detection of, for example, edge effects, shear banding and air bubbles.

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Wednesday 11:40 Arenal / Track 5

EM₆

Advanced combined rheometer setups to in-situ correlate molecular insights with mechanical properties

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Molecular understanding of mechanical properties over a broad length and time scale is crucial to develop advanced materials. Our research aims to design unique combined rheometer setups that can monitor molecular observables, such as molecular dynamics or chemical functional groups, during in-situ measurements of mechanical responses, enabling unique correlations of molecular with macroscopic properties. We developed a unique combination of rheology and low-field time domain NMR (TD-NMR) by implementing a compact 25 MHz NMR magnet into a DHR-3 rheometer. This RheoNMR device can quantify segmental motion of polymer chains via transverse relaxation (T2) measurements while simultaneously perform advanced rheological protocols. We applied this device in rubber science to test whether varying vulcanization procedures of natural rubbers impact the molecular structure of the polysulfidic crosslinks. At a same elastic shear modulus of 0.2 MPa, we find that rubbers produced by efficient vulcanization (i.e., high ratio of accelerator to sulfur) exhibit 50 % higher T2 rates compared to conventional vulcanization procedures (i.e., low ratio of accelerator to sulfur), indicating that during efficient vulcanization predominantly rigid mono-sulfidic crosslinks are formed that reduce the conformational flexibility of polymer chains. The formation of this rigid nanostructure has to be considered for applications where fracture resistance is essential. The RheoNMR device was further used in hydrogel synthesis to study the impact of crosslinker concentration (DC) during the aqueous copolymerization of acrylic acid and methylenebis(acrylamide) crosslinker. The inverse correlation of the elastic shear modulus with T2 relaxation times reveals a pronounced molecular rigidity for higher DC at early gelation times, indicating the formation of inelastic, rigid domains such as crosslinking clusters, reducing thereby crosslinking efficiency. A further outlook on unique Rheo-Dielectric and Rheo-IR combinations will be demonstrated as well

Wednesday 12:00 Arenal / Track 5

EM7

$\label{thm:continuous} \begin{tabular}{ll} High resolution Doppler Optical Coherence Tomographic (D-OCT) measurements of near-wall velocity profiles in duct flows of viscoelastic fluids \\ \end{tabular}$

<u>Kasra Amini</u>, Krishne Gowda. V, Shahriar Habibi, Outi Tammisola, and Fredrik Lundell *FLOW*, *Dept. of Engineering Mechanics, KTH Royal Institute of Technology, Stockholm, Sweden*

Considering the non-linear nature of viscosity-based interactions in non-Newtonian fluid flows, alongside their relatively large, entangled compounds, the observed dynamics near solid walls are counter-intuitive compared to the Newtonian fluid mechanics. These aberrations might be in terms of emergence of slip on the wall as functions of fluid type and surface treatments, and/or other deviations from the pre-established velocity profile near the surface. In this work Doppler Optical Coherence Tomography (D-OCT) has been used to measure the flow velocity in the near-wall region in a Viscoelastic Fluid (VEF). As the conventional optical measurement techniques such as PIV and LDV are not accurate near the surface, and since the study of velocity profiles in near-wall regions rely on high spatial resolutions not easily accessible with other methods such as HWA, added by the opacity of many non-Newtonian fluids, where most of the listed methods fail to function, D-OCT has been chosen to provide a tomographic field measurement with the resolutions as high as ~3 µm. Aqueous solutions of Polyacrylamide based anionic polymer, plus Rhodamine for contrast required by OCT, has been used as the VEF in concentrations of 170, 210, 250, 290, and 340 ppm, to investigate the effects of elasticity. The manuscript presents rheological measurements of the used VEFs. The flow setup is a 90mm-long duct of 2×6.5 mm² cross section fed by a syringe pump and drained into atmospheric conditions. The flow rates have been set to 1.0, 1.4, 1.8, 2.2, 2.6, and 3.0 ml/min, corresponding to bulk velocities in the range of 1.28 to 3.85 mm/s. The velocity profiles are reported for the central regions of the longer side of the duct targeting a 2D profile. The curves are compared with the Newtonian case and an analytical solution presented in the paper. The results further demonstrate the potential of OCT as a technique to study near-wall phenomena and flow-surface interactions in the flows of non-Newtonian fluids.

Symposium FR

Food Rheology

Organizers: Bettina Wolff, Isabel de Sousa and Ma Jesús Hernández

Wednesday 9:30 Giralda 6-7 / Track 6

FR1

Utilising rheology in food 3D printing to achieve attractive meals for dysphagia patients

Astrid Ahlinder, Evelina Höglund, and Mats Stading

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Dysphagia, swallowing difficulties, affects 10-30% of the worldwide population above 65 years. For dysphagia patients, swallowed food, bolus, risks entering the windpipe and lungs leading to pneumonia. Therefore the rheology and texture of the bolus is critical for these patients (Stading, 2021). There are rheologically modified foods, called timbales, commercially available for dysphagia patients. So far, the nutritional and rheological properties of the timbales have been the main concern and they are mostly available in simple shapes and colours with limited resemblance of the original food. Even if timbales have high nutritional value, many dysphagia patients lose interest in consuming food and

therefore suffer of ill health. This work has aimed to increase the attractiveness of these products by coupling direct extrusion additive manufacturing, commonly known as 3D printing, with rheology to achieve shapes of timbales more reminiscent of the original food item (Ahlinder et al., 2021). Rheology is a given tool for understanding how a material behaves throughout the 3D printing process and how processing parameters need to be adapted to it (Aho et al., 2019). Processing parameters need to be adapted to both the flow through the syringe and the deposition onto the build plate. Using advanced 3D scanning of the food items of interest, computer aided design (CAD) files were generated and texturized food was used to create timbales with realistic shapes through 3D printing. The commercially available Foodini 3D food-grade printer was used.

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Wednesday 9:50 Giralda 6-7 / Track 6

FR2

Shear flow and microstructure of microfluidized pea fiber suspensions

<u>Jenifer Santos</u>¹, Luis A. Trujillo-Cayado¹, Carmen Gálvez², María del Carmen Garcia¹, and José Muñoz²

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Dietary fibers have been defined as carbohydrate polymers with ten or more monomeric units, which are not hydrolyzed by endogenous enzymes in the small intestine of humans. Pea fibers are considered as non-allergenic and has positive effects on abnormal glycemic activities and intestinal control. This type of fiber has a low amount of carbohydrates, making it ideal for incorporation into food products. Interestingly, the properties of the fibers are influenced by the processing. Morales-Medina (2020) stated that microfluidization yielded progressive reduction of particle with increasing energy-input in pea hull suspensions. In this work, the influence of number of passes using a microfluidizer at 25000 psi on the rheology of a suspension containing 2 wt% pea fiber is studied. Microfluidization causes a reduction in the size of the fiber particles. The corresponding increase in surface area results in more stable pea fiber suspensions which show gel-like rheological properties regardless of the number of passes, as also reported for suspensions of microfluidized citrus peel fibers (Bruno et al, 2021). The storage modulus and yield point increase with the number of passes. These properties seem to be clearly related to the particle size distribution. The microstructure of pea fiber suspensions has been analyzed before and after start-up at the inception of shear tests. This work contributes to the study of shear flow of microfluidized pea fiber suspensions in connection with their microstructure, which is of paramount importance for their handling properties.

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Morales-Medina, R.; Dong, D.; Schalow, S. & Drusch, S. (2020). Impact of microfluidization on the microstructure and functional properties of pea hull fibre. *Food Hydrocolloids*, 103, 105660.

Wednesday 10:40 Giralda 6-7 / Track 6 Keynote

FR3

Influence of rheology in 3D printing of protein based doughs

Estefanía Álvarez-Castillo¹, Sonia Oliveira², Carlos Bengoechea¹, <u>Anabela Raymundo</u>², Isabel Sousa², and Antonio Guerrero¹ Chemical Engineering, Universidad de Sevilla, Sevilla, Spain; ²LEAF-Linking Landscape, Environment, Agriculture and Food, Universidade de Lisboa, Lisbon, Portugal

The interest in 3D printing polymer processing is increasing strongly in recent decades. Its customizing potential allows its application in a great variety of fields, such as food or biomedicine. The present study aimed at the determination of the main rheological properties required for proper 3D-printing performance of protein-based doughs plasticized by glycerol. The protein sources selected (blood plasma, pea and soy) are obtained as by-products or biowastes from the food industry in order to contribute to the reduction of the negative environmental impact associated with their disposal. The printability of doughs with different porcine plasma protein (PPP) contents (from 40 to 50 wt.%) was initially assessed on rheological terms. Also, the rheology of composite materials was studied when a fraction of PPP was replaced by either a soy protein isolate (SPI) or a pea protein concentrate (PPC), keeping the total biopolymer content constant (45 wt. %) within the formulation. The development of printability maps for specific rheological properties, such as viscosity or viscoelastic moduli, highlighted the importance of controlling the rheological properties of doughs for an efficient 3D printing process. Additionally, all printable doughs displayed similar textural profiles. Eventually, formulations that resulted in 3D-printed materials that managed to reproduce the desired pattern were selected for further analysis. Thus, the high water uptake of these 3D printed materials was used to introduce certain minerals (magnesium, iron) and antioxidant compounds (astaxanthin) and then assess their potential as functional snacks through two additional steps (removal of the plasticizer through immersion, and a subsequent lyophilization stage). Both mineral content and bioactivity were enhanced through immersion of the 3D-printed materials in aqueous solutions of magnesium glutamate, iron lactate or astaxanthin.

Wednesday 11:20 Giralda 6-7 / Track 6

FR5

Pre- and post-process evaluation of meat analogue texturability using high-pressure shear rheology and dynamic mechanical analysis

Joël Zink and Erich J. Windhab

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Plant-based meat analogues are gaining increased interest from both the food industry and academia. One of the main drives is the general public's awareness of the overexploitation of natural resources and their impact on climate change. Such meat analogues can be produced using a high-moisture extrusion process. For this, protein isolates or concentrates are mixed with water in a twin-screw extruder, heated up to the gelation point of the main protein fractions to obtain a melt that is subsequently solidified in a cooling die. The last step, the cooling in the die is crucial to the final texture of the product. The laminar flow profile of the hot liquid protein melt forms a parabolic flow inducing the formation of fibrous protein strands that confer unidirectional tear-ability to the meat analogue product resembling the texture of cooked chicken breast, pulled pork or fish filets. The so textured meat-like products are more appealing to today's consumer than less texturized products like tofu or mould-based products. Nevertheless, it is still not possible to assess whether a given formulation can be texturized to a satisfying degree and which processing parameters are optimal without performing trials with the manufacturing equipment. These trials are highly time and cost-intensive and conducted using a trial-and-error approach. Moreover, the evaluation methods for the quality of the product are usually limited to qualitative perception rather than being based on methods yielding quantitative results. This study gives insights into how high-pressure shear rheology can be used to investigate the texturability of meat analogue formulations prior to pilot or industry scale trials. Furthermore, it is demonstrated that the textural anisotropy of the product can be quantitatively measured using dynamic mechanical analysis.

Wednesday 11:40 Giralda 6-7 / Track 6

FR₆

Rheology-driven design of pizza gas foaming

Pietro R. Avallone, Paolo Iaccarino, <u>Nino Grizzuti</u>, Rossana Pasquino, and Ernesto Di Maio *DICMaPI*, *University of Naples Federico II*, *Naples*, *Italy*

Bread and pizza are very common aerated baked products mainly composed of water, flour and yeast. Taste, texture and aroma, not to mention aesthetics, are the reasons why air is incorporated in such products. They are leavened by yeast, a bio-chemical blowing agent releasing carbon dioxide as a product of a fermentation reaction, during the so-called proofing step. Leavening is a rather slow process that may take up to several hours. Furthermore, yeast can generate intolerance, determining digestive or more severe allergy-related issues. In this work we investigate the production of a yeast free-pizza by gas foaming and the use of rheology to guide the process design. The novel process relies on the use of a gaseous blowing agent and a pressure program to form and stabilize bubbles during baking, avoiding the use of yeast and the associated lengthy leavening stage. The evolution of the dough structure during baking has been studied by a rheological characterization at leavening and baking conditions. These experimental pieces of information have been used to evaluate the time available for blowing agent sorption under pressure during early baking stage, and to guide the pressure release during the final baking, in order to achieve an optimally foamed pizza.

Wednesday 12:00 Giralda 6-7 / Track 6

FR7

Lupin and chickpea yoghurts, the importance of rheology measurements on product development

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The demand for alternatives to dairy products, other than soy, is steeply increasing. The objective of this study was to find an alternative to dairy and soy yoghurts, by using lupin and chickpea seeds, nutritionally balanced and sustainable European crops with positive impacts on health. Rheology is our first tool to product development as it reveals the internal structure that determines the texture and mouthfeel of the products, essential to consumer acceptance. A beverage based on these legumes was produced (Lopes et al., 2020) and then yoghurt was made using commercial soy yoghurt as inoculum. Parameters as temperature, incubation time and proportion of soy yoghurt added were tested. Rheology measurements were then carried out on the final yoghurts, the dynamic moduli G' and G" as well as the viscosity were determined. The aim was to find the best conditions for the production of yoghurts based on lupin and chickpea. With the results of the frequency sweep, we could conclude on the optimal processing to have a firm yoghurt. Concerning the yoghurt starter concentration, 10%, was the best concentration, as this corresponded to a maximum of plateau modulus. The optimal temperature of incubation was 40°C, which corresponded to the optimal temperature for the growth of LAB (lactic acid bacteria). Finally, concerning the time of incubation, 12 hours was the best duration. The tests at 20 and 8°C highlighted the importance of cooling the yoghurts. Indeed, the values at 20°C were always lower than those at 8°C as cooling helps the gel to form and reinforces structure with intermolecular bridging. The results of viscosity showed that this is not the best test to reveal and differentiate the internal structure of this material. Finally, the lupin yoghurts studied were more structured than the ones from chickpea, due to a higher content on protein in the matrix, being these the most similar in consistency to commercial soy yoghurts.

References:

Lopes, M., Pierrepont, C., Duarte, C. M., Filipe, A., Medronho, B., & Sousa, I. (2020). Legume beverages from chickpea and lupin, as new milk alternatives. *Foods*, 9(10), 1458.

Wednesday Afternoon

Symposium NF

Non-Newtonian Fluid Mechanics and Computational Rheology

Organizers: Miguel Nóbrega, Baltasar Mena and Corneliu Balan

Wednesday 13:40 Giralda 1-2 / Track 1

NF24

Disorder and non-linearity in immiscible two-phase flow in porous media

Santanu Sinha, Subhadeep Roy, and Alex Hansen

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Two-phase flow of immiscible fluids in porous media exhibits non-linear power-law type relationship between the total flow-rate and pressure drop in the steady state similar to the rheology of a non-Newtonian fluid (Sinha et al., 2017). This non-linearity appears in a regime where viscous forces compete with capillary forces and undergoes a crossover to a linear regime when increasing the pressure drop. Different experimental and numerical studies have reported different values for the exponent related to this power law (Zhang et al., 2021). Theories have suggested that the non-linearity is an outcome of the disorder in the pore-space properties, such as the pore sizes and wettabilities. To investigate about this in detail, we studied systematically how the disorder in the pore-radii controls the effective rheology of two-phase flow in a porous medium. With analytical derivations using capillary bundle model and numerical simulations using dynamic pore-network model, we measured the exponent related to the non-linearity and the crossover pressure drop while varying the shape and span of the disorder distribution (Roy et al., 2021). In case of a capillary bundle when the pores do not interact to each other, we find that the non-linear exponent is equal to 3/2 irrespective of the distribution type. For a pore network where the pores are connected to each other, we find that the shape of the distribution alters the exponent continuously within a range whereas the width of the distribution controls the crossover pressure drop.

References:

Sinha et al. (2017). Effective rheology of two-phase flow in three-dimensional porous media: experiment and simulation. *Transport in porous media*, 119(1), 77-94.

Zhang, Y., Bijeljic, B., Gao, Y., Lin, Q., & Blunt, M. J. (2021). Quantification of nonlinear multiphase flow in porous media. *Geophysical Research Letters*, 48(5), e2020GL090477.

Roy, S., Sinha, S., & Hansen, A. (2021). Role of pore-size distribution on effective rheology of two-phase flow in porous media. Frontiers in water. In press

Wednesday 14:00 Giralda 1-2 / Track 1

NF25

Imaging dense suspensions under shear

imaging dense suspensions under snear

Vincent Niggel, Pierre Lehéricey, Jan Vermant, and Lucio Isa

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Dense suspensions of colloids can show different non-linear rheological responses, including shear thickening, which is a general phenomenon whereby the viscosity of dense suspensions increases at high shear. This response can both cause problems in industrial processes, like the mixing of dense pastes (Paul et al., 2004), but can also lead to the development of interesting materials for shock-absorption applications (Soutrenon & Michaud, 2014). To influence this behavior, different factors can be tailored, such as the modification of the roughness of the particles, the type of suspending medium or even the surface chemistry of the particles. However, a detailed microscopic insight on the origin of shear thickening is still incomplete. For a long time, it was believed that the increase in viscosity was the sole result of the formation of particle clusters held together by hydrodynamic forces. More recently, evidence has been gained to support the presence of networks of contacts between particles under shear (Morris, 2020). Last year, the observation of the force chain network was reported (Pradeep et al., 2020), but a live visualization of those microscopic contacts, and of their effect on the overall flow, still remains elusive. Our goal is to use rough particles with tailored surfaces to disclose the presence of relative sliding and rotation at the contact points between particles under high shear and help form a bridge between the well-characterized bulk rheological response and the emerging investigation of particle tribology, also providing new elements to inform numerical simulations.

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Paul, E. L., Atiemo-Obeng, V. A., & Kresta, S. M.(Eds.).(2004). *Handbook of Industrial Mixing: Science and Practice*. Wiley. https://doi.org/10.1002/0471451452

Soutrenon, M., & Michaud, V. (2014). Impact properties of shear thickening fluid impregnated foams. *Smart Materials and Structures*, 23(3), 035022.

Morris, J. F. (2020). Shear thickening of concentrated suspensions: Recent developments and relation to other phenomena. *Annual Review of Fluid Mechanics*, 52, 121-144.

Pradeep, S., Nabizadeh, M., Jacob, A. R., Jamali, S., & Hsiao, L. C. (2021). Jamming distance dictates colloidal shear thickening. *Physical Review Letters*, 127(15), 158002.

Wednesday 14:20 Giralda 1-2 / Track 1

NF26

Torsional fracture of viscoelastic liquid bridges

San To Chan¹, <u>Frank P. A. van Berlo</u>², Hammad A. Faizi³, Atsushi Matsumoto¹, Simon J. Haward¹, Patrick D. Anderson², and Amy Q. Shen¹

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Short liquid bridges are stable under the action of surface tension. In applications like electronic packaging, food engineering, and additive manufacturing, this poses challenges to the clean and fast dispensing of viscoelastic fluids. Here, we investigate how viscoelastic liquid bridges can be destabilized by torsion. By combining high-speed imaging and numerical simulation, we show that concave surfaces of liquid bridges can localize shear, in turn localizing normal stresses and making the surface more concave. Such positive feedback creates an indent, which propagates toward the center and leads to breakup of the liquid bridge. The indent formation mechanism closely resembles edge fracture, an often undesired viscoelastic flow instability characterized by the sudden indentation of the fluid's free surface when the fluid is subjected to shear. By applying torsion, even short, capillary stable liquid bridges can be broken in the order of 1 s. This may lead to the development of dispensing protocols that reduce substrate contamination by the satellite droplets and long capillary tails formed by capillary retraction, which is the current mainstream industrial method for destabilizing viscoelastic liquid bridges.

Wednesday 14:40 Giralda 1-2 / Track 1

NF27

Visualizing plug formation in cavities and apertures with a yield stress fluid

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In this work we visualize, experimentally, the flow of Carbopol gels in both cavities and apertures to gain insight into fouling mechanisms during cross-flow filtration. In the first phase of this work, we characterize the flow over a cavity using optical coherence tomography, a geometry representing the simplest case of a blocked cross-flow filtration aperture. We measure the size and shape of the plugged zone as a function of Bingham and Weissenberg numbers and note, crucially, a fore-aft asymmetry in the plug that scales with the product of the Bingham and Weissenberg numbers. A similar trend was observed with a 2D numerical simulation using an Augmented-Lagrangian method. In the second phase of this investigation, we measure the local flow field of Carbopol gels in a cross-flow filtration aperture using confocal microscopy. Both suction (filtration) and blowing (flow-reversal) cases were considered and characterized the flow states where the apertures become blocked. Interestingly, we found that near the point of complete aperture blockage, the shape of the plug depends upon the history of the flow, i.e. whether plug-formation is approached from either decreasing suction or blowing velocities. These results suggest a hysteresis near the yielding point. Further investigation is needed to explain this behaviour.

Wednesday 15:00 Giralda 1-2 / Track 1

NF33

Stretching and breakup of falling viscoplastic sheets

Kindness C. Isukwem, Elie Hachem, Rudy Valette, and Anselmo Pereira

PSL Research University, Sophia-Antipolis, France

The breakup can be seen as the final stage of a continuous fluid flow. This breakup of a continuous fluid sheet, that was initially stable into satellites (or not) is a vital process that impacts many industrial operations, typically applications for which there is a struggle between clean and fast dispensation of the fluids. The breakup of a fluid sheet is driven primarily by capillarity which is resisted by inertia property of the sheet. Despite numerous studies and the invaluable industrial applications of fluid sheet breakup, the physics is still largely unknown (whether for Newtonian or non-Newtonian fluids); for instance, one important question arising from preliminary investigations for this work, is whether we can predict/model the breakup profile of a fluid, considering physical forces acting on the process. This work aims to highlight the physical mechanisms driving fluid sheet breakup especially under viscoplastic flow conditions, and finally correlate the final breakup profile of the fluid sheet to these important physical parameters. We investigate the stretching and subsequent breakup of falling viscoplastic sheets attached to two parallel plates and surrounded by air. Our study is conducted through a mixed approach combining two-dimensional numerical simulations, energy budget analyses and scaling laws. The numerical results are based on an adaptive variational multi-scale method for multiphase flows. We choose to focus on the Bingham model for the viscoplastic material. Thanks to such examinations, different stretching and breakup regimes are stressed: inertio-gravitational (IG); viscoplasto-gravitational (VPG); and inertio-capillary (IC). These regimes are linked with the dimensionless numbers driving the problem, which in turn, are also correlated to the appearance of satellite objects following the viscoplastic sheet rupture. Keywords: falling viscoplastic sheet; Bingham material; stretching and breakup; multiphase flow; 2D numerical simulation.

Wednesday 16:20 Giralda 1-2 / Track 1

NF29

Slow fatigue and delayed sudden failure of amorphous and soft glassy materials in large amplitude oscillatory shear strain

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We study large amplitude oscillatory shear strain within the soft glassy rheology model of amorphous materials and yield stress fluids. In some regimes of strain amplitude and degree of sample annealing (duration of ageing) prior to the shear being applied, we uncover a process of slow fatigue, starting from an initially solid-like state, which can occur over several thousand cycles, before the sample then abruptly yields plastically. We observe two distinct mechanisms for yielding. In one of these the sample remains homogeneous as it yields. In the other, the yielding process is closely associated with a shear banding instability that leads to the formation of heterogeneous shear. For parameter values corresponding to the crossover between these two regimes, the yielding event can be difficult to predict, with a very broad spectrum of number of cycles to yielding according to initial randomness in the initial condition.

Wednesday 16:40 Giralda 1-2 / Track 1

NF30

Tuning internal stress distributions in soft particle glasses

Paolo Edera, Bruno F. Di Dio, Stefano Aime, and Michel Cloitre

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Soft materials have the capacity to store mechanical stresses when they solidify after flow cessation [Mohan et al, J. Rheol. 59, 63 (2015)]. Internal stresses imprint mechanical memory inside materials, which is at the origin of the spontaneous motion occurring without forced flow in colloidal glasses and biological materials and determines their long term behavior. Two important manifestations of internal stresses are the dependence of the mechanical properties on the shear direction and physical aging. These phenomena can adversely affect the physical characterization of soft materials and are vital for process design. They are also crucial from a fundamental perspective because they contain information on the microstructural evolution of materials both at rest and under shear. Controlling the internal stresses distribution and preparing soft materials close to mechanical equilibrium is thus an outstanding challenge. Here we address this question for the case of soft particle glasses (SPGs) made of microgels packed at high volume fraction above jamming. We characterize the internal stress distribution by the asymmetry, which is at the origin of a directional bias in the mechanical properties, and the standard deviation, which corresponds to the mechanical energy responsible for physical aging. We propose a protocol based on a sequence of forced oscillations at constant stress amplitude close to the yield stress, which prepares the SPGs in a reproducible state with a symmetrical distribution of internal stress, yielding no directional bias. The mechanical energy and the extent of aging is controlled by the duration of the oscillatory stress application. Our results can be understood qualitatively in terms of the out-of-equilibrium microstructure of SPGs and are well reproduced by a simple elastoplastic model. Preliminary results using other types of yield stress materials support the generality of our findings.

Wednesday 17:00 Giralda 1-2 / Track 1

NF31

Flow onset for a single bubble in a yield-stress fluid

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We use computational methods to determine the minimal yield-stress required to hold static a buoyant bubble in a yield-stress liquid. Static bubbles in viscoplastic fluids occur in many industrial settings. In the oil sands industry, the by-products of the extraction of bitumen from oil sands are stored in tailings ponds over many decades. Pond slurries, known as Fluid Fine Tailings and Mature Fine Tailings (FFT/MFT) are complex suspensions rheologically characterised as thixotropic yield-stress fluids. Anaerobic micro-organisms within the fluid form both carbon dioxide and methane. The objectives of this research are to understand how bubbles may be trapped in the different layers (FFT, MFT) within the pond. Trapping happens due to the yield-stress of the pond fluids. The underlying research motivation is environmental, i.e. emissions estimation and control.

Computations have been conducted using both Augmented Lagrangian and FISTA (fast iterative shrinkage-thresholding algorithm) methods, both of which are able to capture zero strain rates reliably in unyielded regions. Coupled with the adaptive meshing methods, these capture the yield surfaces well. The static limit is governed by the bubble shape, surface tension, buoyancy and yield-stress. For a given bubble geometry, bubbles are static if the fluid yield-stress is above a critical limit. We study families of bubble shapes to understand the characteristic effects of aspect ratio and curvature in both 2D planar and axisymmetric settings. For these families we explore the relative effects of surface tension and buoyancy on flow onset. These results help us obtain new insight into understanding bubble stoppage criteria in viscoplastic fluids.

Acknowledgement: This research was made possible by funding from NSERC and COSIA/IOSI (project numbers CRDPJ 537806-18 and IOSI Project #2018-10).

Wednesday 17:20 Giralda 1-2 / Track 1

Rising cloud of bubbles in a yield-stress fluid

Emad Chaparian¹ and Ian A. Frigaard²

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Gas emissions from tailings ponds is one of the environmental challenges of oil sands production. In a stratified pond, the fine fluid tailings (FFT) forms a layer which does not appear to consolidate significantly over timescales of 10-100 years. The bulk rheology of this layer exhibits a yield stress [1]. The yield stress both contributes to the slow consolidation and can trap bubbles that result from biodegradation. Hence, here we study the conditions for bubbles to be statically buoyant in a yield-stress fluid without any motion. The key parameter is the yield number $Y=t_y/(??gl)$ which represents the ratio of the yield stress to the buoyancy stress (l is the volumetric radius of the bubble). The goal is to compute the critical yield number Y_c for clouds of bubbles. In [2] we computed Y_c for a single bubble with different shapes for a wide range of surface tensions: if $Y<Y?_c$ then the bubble rises and if $Y=Y?_c$ then the yield stress suppresses the flow and makes the bubble static. We have previously demonstrated that particles which are close enough can form clusters in a yield-stress fluid and move together, which can tremendously increase Y_c in a suspension [3]. Here, the aim is to shed light on how multiple bubbles feel their neighbors and interact, and hence to evaluate Y_c for a suspension (or cloud) of bubbles as a function of volume fraction? We perform computations in a periodic box with randomized positions of the monodispersed circular bubbles. A large number of realizations are investigated to obtain statistically converged results. The results show that Y_c (?) increases with the volume fraction as a larger volume of gas should be brought to halt and also the interaction of bubbles triggers the cloud motion. The contributions of each are investigated [4].

References:

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- [2] Pourzahedi et al., accepted for publication in J. Fluid Mech. (2021)
- [3] Chaparian et al., Phys. Fluids 30, 033101 (2018).
- [4] Chaparian, Frigaard, J. Fluid Mech. 927, R3 (2021).

Symposium GS

Gels and Self Assembling Structures

Organizers: Joao Maia, Domenico Gabriele and Juan de Vicente

Wednesday 14:00 Santa Cruz / Track 2

GS25

NF32

Polymer induced liquid crystal phase behaviour of cellulose nanocrystal (CNC)

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Cellulose nanocrystal (CNC) is a promising sustainable material receiving notable attention in fabricating functional hybrid material. The rod-like shape and negative charge enable its rich colloidal behavior such as liquid crystalline phase and hydrogel formation mediated by different additives. [1,2] We present our recent advances on the effect of depletion induced attraction on CNC self-assembly by polymer addition. Non-absorbing 20 and 200 kDa polyethelene glycol (PEG) were added in CNC water suspensions. Different techniques such as polarized light microscopy (PLM), atomic force microscopy (AFM), rheology, and small angle X-ray scattering (SAXS) were used to elucidate the transient phase behavior. Pure CNC suspension shows highly ordered structure, with tactoid nucleation, growth and mergence microscopically, and eventually presents macroscopic phase separation. Three typical liquid crystal shear rheology regimes are observed. Structural developments have been further investigated by the evolution of scattering correlation peaks, which correspond to CNC interparticle distances within and between nematic planes. The 20 kDa addition induces slight attractive depletion force. Tactoid growth has been confined with characteristic correlation peak ratio preserved. The whole system turned into fully nematic phase macroscopically. With the 200 kDa PEG addition, attractive force becomes predominant. CNC self-assembly is suppressed and a hydrogel forms. Interference colors are present accompanied by significantly enhanced mechanical strength and clear Cox-Merz rule deviation. Thus, depletion induced attraction force has the potential in enabling fine-tuning of CNC self-assembly and phase behavior with adjustable mechanical strength and optical activity.

References:

- [1] Parker RM et al. The self-assembly of cellulose nanocrystals: Hierarchical design of visual appearance. Advanced Materials (2018).
- [2] Bertsch P et al. Ion-induced formation of nanocrystalline cellulose colloidal glasses containing nematic domains. Langmuir (2019)

Wednesday 14:20 Santa Cruz / Track 2

GS26

Small and large amplitude oscillatory shear behavior of crosslinked polymeric system at the vicinity of the gel point

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Non-linear rheology and particularly medium and large amplitude oscillatory shear (MAOS and LAOS) have gained considerable attention in the last decade [1]. Yet, little attention has been devoted to the non-linear behavior of crosslinked systems and more specifically, the evolution of non-linear rheological properties at the different stages of the crosslinking process. Poly (vinyl alcohol) (PVA) hydrogels can be formed by chemical crosslinking with glutaraldehyde. Reaction induced evolution of viscoelasticity during gelation of semi-dilute PVA in aqueous dispersions was studied through rheological measurements in the linear and non-linear domains. The work primarily focuses on the characteristics of the MAOS and LAOS behavior near the critical gel point.

1. Rogers S (2018) Large amplitude oscillatory shear: Simple to describe, hard to interpret. Phys Today 71:34-40

Wednesday 14:40 Santa Cruz / Track 2

GS27

Rheological implications of chemically dynamic polymer networks

Robert Aguirresarobe, Mercedes Fernandez, and Antxon Santamaria

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Traditional thermoset materials have been used for centuries, from natural rubber to the most recent epoxy formulations. The reason behind this interest is the enhanced performance in terms of mechanical and thermal properties in comparison with the thermoplastic counterparts. However, due to their cross-linked network structure, they present several drawbacks in terms of manufacturing and recyclability. Indeed, once the polymer network is formed, it is not possible to melt or solubilize the material without degrading the structure. Recently, a new concept has been established to overcome these limitations. This concept is based on the incorporation of active elements capable to undergo reversible or "dynamic" reactions upon stimulation(Kloxin, Scott, Adzima, & Bowman, 2010). This new class of materials, known as dynamic polymer networks or covalent adaptable networks (CANs), can potentially merge the most appealing characteristics of two worlds: The enhanced performance of thermosets and the processability and recyclability of thermoplastics. Dynamic polymer networks are classified into two main groups according to the chemical reactions that occur in the material(Aguirresarobe et al., 2021). On the one hand, dissociative networks present chemical groups capable to split into two stable parts that, upon stimulation, can recombine to the original structure. Therefore, such structures can be broken and reformed on demand. On the other hand, the active groups present in associative networks introduce the dynamic features through a reaction intermediate. Thus, dynamic nature relies on a network rearrangement without breaking the polymer structure. In this work, we discuss the rheological implications of introducing dynamic structures into polymers. Thus, a series of polyurethane networks have been synthesized using different dynamic monomers. In addition, the influence of the polymer structure itself in the dynamic characteristics of the network.

Wednesday 15:00 Santa Cruz / Track 2

GS28

Hardening phenomenon in wormlike micelles

Rossana Pasquino, Salvatore Costanzo, Giovanni Ianniruberto, Marrucci Giuseppe, and Nino Grizzuti DICMaPI, University of Naples Federico II, Naples, Italy

We report shear startup data on solutions of two branched wormlike micelles, differing only in concentration and type of two binding aromatic sodium salts. The surfactant molecule is Cetylpiridinium Chloride, at a fixed concentration (100mM). Sodium Salycilate and Diclofenac Sodium are used as binding salts, at two different concentrations, 68mM Sodium Salycilate and 52mM Diclofenac. Their linear viscoelastic response is very similar, with a significant mean number of entanglements per chain. The systems show the typical response of a wormlike micellar solution, with terminal behavior at low frequencies, a well-defined cross-over and a plateau region. In nonlinear regime, surprisingly, the systems behave differently. In shear start-up flow, more specifically, the solution containing Sodium Sacylate shows flow instabilities and strain hardening phenomena, whereas the solution containing Diclofenac does not. The latter, although branched, behave similarly to ordinary linear polymers in fast shear flows, exhibiting pronounced overshoots as well as tiny undershoots in transient shear viscosity, before approaching the steady state. This has been also proved by successfully comparing data with predictions of a constitutive equation, recently adopted both for ordinary entangled polymers and linear wormlike micelles. Concerning the Sodium Salycilate sample, a possible mechanism for the onset of flow singularities is suggested and discussed in view of a modified rubber network theory, specifically developed for micellar networks. We speculate that the type of salt and its packing effectiveness at the micellar interface are crucial for the dynamics of the wormlike micelles.

Wednesday 16:20 Santa Cruz / Track 2

GS29

$How \ to \ tailor \ the \ nonlinear \ rheology \ of \ supramolecular \ assemblies \ by \ changing \ their \ environment$

Emmanouil Vereroudakis¹ and <u>Dimitris Vlassopoulos</u>²

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Whereas the self-assembly of hydrogen-bonding motifs in apolar solvents is known and has been used widely, the role of the environment (temperature, humidity, pressure) had not been an issue of concern. Recently, it was demonstrated the humidity substantially affects (seeps-up) the linear viscoelastic response of supramolecular polymers, while fragmental evidence of similar effects on the nonlinear rheology was presented. The exact role of water molecules on the self-assembly remains debatable and two different mechanisms have been put forth, chain

scission and "co-polymerization". It is possible that the exact mechanism depends on the type of the motif and the conformation of the self-assembled supramolecules. However, in either case the net rheological result is the faster dynamics. With this background, we present here a systematic investigation of the nonlinear shear rheology of two different supramolecular polymer solutions under conditions of controlled temperature and humidity. We focus on step-rate (stress growth function) and step-strain (stress relaxation) tests and examine the stability over time, thixotropy and the validity of the Cox-Merz rule. Since temperature affects the environmental humidity, the two parameters are interrelated. In fact, changing the temperature affects the supramolecular conformation and this turns out to be a crucial factor controlling the emergence of shear strain hardening. Hence, the external environment mediates the nonlinear rheological response of supramolecular polymers.

Work in collaboration with L. Bouteiller, A. Louhichi, N. van Zee, E. W. Meijer.

Wednesday 16:40 Santa Cruz / Track 2

GS30

Unravelling the network topology and elasticity of hydrophobically associating multiblock copolymers in aqueous solutions using a novel mechano-statistical transient network model

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The micellar assemblies formed by hydrophobically associating block copolymers in selective solvents are often employed as multifunctional interaction nodes in physical polymer gels. Hydrophilic blocks capped by two hydrophobic blocks have the potential to bridge two different micellar cores which are in close proximity, thereby forming a sample-spanning network. Whereas most studies use telechelic triblock copolymers with hydrophobic end groups, our study focuses on alternating PEO-PPO multiblock copolymers with multiple hydrophobic PPO blocks distributed along the chain, giving rise to a multitude of possible chain configurations. Therefore, in this contribution we adopt a combinatorics approach to extend and generalize the mechano-statistical transient network model originally developed by Annable for telechelic triblock copolymers [1,2] to more general alternating multiblock copolymers. By using knowledge about the spatial distribution of the micellar nodes, as inferred from Small-Angle X-ray Scattering, the model allows us to translate microscopic changes in the micellar network topology to macroscopic rheological behavior. Interestingly, the model predictions of elasticity as a function of concentration show excellent agreement with experimental rheological data. The evolution of the high-frequency plateau modulus and hence the elasticity can be linked to a change in the network topology from loop-dominated with low-functional crosslinking nodes at low concentrations to bridge-dominated with highly functional crosslinking nodes at higher concentrations. A thorough understanding of the network topology and its effect on the rheological properties of the network will pave the way for the development of transient networks with custom-made elasticity and relaxation dynamics.

References:

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Wednesday 17:00 Santa Cruz / Track 2

GS31

Phase diagram and rheology of polymer-carbon black aqueous suspensions

Gauthier Legrand, Sébastien Manneville, and Thibaut Divoux

Laboratoire de Physique ENS de Lyon, Lyon, France

Carbon Black (CB) colloidal particles are combustion residues commonly used in industry for their mechanical and electrical properties in a wide range of applications such as inks, tire strengthening, and flow batteries. When dispersed in mineral oil, these particles aggregate under the effect of Van der Waals interactions and form a gel, *i.e.*, a percolated network even at very low mass fractions, of the order of 0.1%. These gels behave as viscoelastic solids at rest and flow like viscous liquids beyond a critical stress, or under the effect of large deformations. The rheological properties of these gels have been extensively studied and offer the image of a rheopectic material, whose microstructure at rest is strongly dependent on the shear history.

Here we report on the rheological properties of aqueous suspensions of carbon black. The dispersion in water of these hydrophobic particles is made possible by adding a cellulose ether, namely carboxymethylcellulose (CMC). This gum is commonly used as a resin in ion chromatography and as a food additive. First, we will discuss the behavior of these CB-CMC aqueous suspensions through a phase diagram in the (% wt. CB, % wt. CMC) plane, which exhibits four prominent behaviors: phase demixion, viscoelastic liquid, viscoelastic solid and brittle paste. In this study we mainly focus on the viscoelastic solid properties. Unlike dispersions of CB in oil, a critical mass fraction of CB, of the order of 5 to 10%, is necessary to obtain a viscoelastic solid. Moreover, two asymptotic behaviors are observed above this critical mass fraction of CB depending on whether the amount of CMC in solution is larger than the overlap concentration of the polymer solution C^* . Comparing suspensions at 8% wt. CB, we observe that for $C > C^*$, the behavior of the mixture is dominated by the colloids.

Key words: Carbon Black, Cellulose, Phase diagram, Yield stress fluid, Viscoelasticity

Symposium SM

Polymer Solutions and Melts

Organizers: Antxon Santamaría, Evelyne Van Ruymbecke and Moshe Gottlieb

Wednesday 13:40 Nervión / Track 3

SM8

Tube-based modeling of stress relaxation of bidisperse linear polymer blends in the linear regime of deformation

Céline Hannecart^{1,2}, Christian Clasen², and Evelyne van Ruymbeke¹

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While tube-based models succeed in predicting the stress relaxation of monodisperse linear polymer melts of various chemistries and entanglement states in the linear regime of deformation, approaches to predict the relaxation of blends with either a high [1] or a low [2] molecular weight matrix within the same model usually fail. Although these approaches consider the existence of a thin tube (representing all entanglements along the polymer chain) in a fatter one (representing self-entanglements), they use two different mechanisms to describe the stress relaxation of the fatter tube. The first model [1] considers the fatter tube to relax through the thin tube motion, while the second model [2] considers it to relax thanks to constraint-release events. In this work, we propose to combine both mechanisms in the tube model (as was done by Shivokhin et al. (2014) for star/linear blends in a slip-spring model) to describe the stress relaxation of various bidisperse linear polymer blends with a wide range of compositions, and validate this approach on different chemistry sets. To this end, we first use the approach proposed by Watanabe et al. (2020) to model the stress relaxation of un-self-entangled samples through a Constraint Release Rouse process and find the characteristic time of this process. We then show for dielectric and viscoelastic data from literature that both the mechanisms from Read et al. (2012) and from van Ruymbeke et al. (2014) are necessary to model the relaxation of bidisperse blends, and finally develop a tube-based model able to predict the relaxation of a wide set of bidisperse blends.

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Wednesday 14:00 Nervión / Track 3

SM9

Complex viscosity of star-branched macromolecules from analytical general rigid bead-rod theory

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Chemical Engineering, Queen's University, Kingston, Ontario K7L1C3, Canada

The complex viscosity of planar star-branched polymers has been derived from general rigid bead-rod theory, but only for singly-beaded arms. Here, we explore the respective roles of branch functionality, arm length and non-planar arrangements, analytically from general rigid bead-rod theory. For non-planar, we include polyhedral, both regular and irregular. Further, for all structures, we compare with and without the central bead. We fit the theory to complex viscosity measurements on polybutadiene solutions, one quadrafunctional star-branched, the other unbranched, of the same molecular weight (Mw=200,000 g/gmol). We learn that when general rigid bead-rod theory is applied to quadrafunctional polybutadiene, a slightly irregular center-beaded tetrahedron of interior angle 134° is required (with 1,360,000 g/gmol per bead) to describe its complex viscosity behaviour.

Wednesday 14:20 Nervión / Track 3

SM10

Determination of molecular weight distribution of UHMWPE via solution rheology

<u>Vincenzo Ianniello</u>¹, Salvatore Costanzo¹, Rossana Pasquino¹, Giovanni Ianniruberto¹, Theo A. Tervoort², and Nino Grizzuti¹

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We investigate the linear shear rheology of ultra high molecular weight polyethylene (UHMWPE) solutions with the aim of extrapolating the molecular weight distribution of the pure melt. The UHMWPE is dissolved in oligo-ethylene [1] to avoid issues related to unfavourable interactions with the solvent in the concentrated regime. To prepare the solutions, the UHMWPE, the solvent and a fixed amount of antioxidants are mixed by means of a co-rotating twin screws micro-compounder [2]. All prepared solutions are within the concentrated regime, as confirmed by the scaling laws of the main rheological parameters (plateau modulus, relaxation time, zero-shear viscosity) upon concentration. We adopt a heuristic approach based on a time-concentration superposition principle to extrapolate the linear viscoelastic behaviour of the pure melt over many decades of angular frequency, eventually attaining the terminal relaxation regime. The latter is difficult to achieve by direct measurements in the molten state because of experimental issues, such as polymer degradation at high temperature. The viscoelastic spectrum of the melt is used to obtain the molecular weight distribution according to the time-dependent diffusion/double reptation model by van Ruymbeke et al. [3]. The model allows to determine the molecular weight distribution starting from the linear rheological behaviour of either a melt or a solution [4]. The MWD evaluated with our approach compares favourably with data obtained from gel permeation chromatography on the UHMWPE melt.

References:

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- [2] A. Brem et al., Macromolecules, 53, 5957-5970, 2020;
- [3] E. van Ruymbeke et al., Journal of Non-Newtonian Fluid Mechanic, 105, 153-175, 2002;
- [4] K. Chaudhuri and A.K. Lele, Journal of Rheology, 64, 1-12, 2020.

Wednesday 14:40 Nervión / Track 3

Keynote

SM11

Competition between shear and biaxial extensional viscous dissipation in the expansion dynamics of polymeric liquid sheets

Ameur Louhichi¹, Carole-Ann Charles¹, Dimitris Vlassopoulos², Laurence Ramos¹, and <u>Christian Ligoure</u>¹ *Laboratoire Charles Coulomb, Université de Montpellier, MONTPELLIER 34095, France; ²IESL, FORTH, Heraklion GR-711 10, Greece*

When a drop of fluid hits a small solid target of comparable size, it expands radially until reaching a maximum diameter and subsequently recedes. In this work, we show that the expansion process of liquid sheets is controlled by a combination of shear (on the target) and biaxial extensional (in the air) deformations. We propose an approach toward a rational description of the phenomenon for Newtonian and polymeric fluids by evaluating the viscous dissipation due to shear and extensional deformations, yielding a prediction of the maximum expansion factor of the sheet as a function of the relevant viscosity. For Newtonian systems, biaxial extensional and shear viscous dissipation are of the same order of magnitude. On the contrary, for thinning solutions of supramolecular polymers, shear dissipation is negligible compared to biaxial extensional dissipation and the biaxial thinning extensional viscosity is the appropriate quantity to describe the maximum expansion of the sheets. Moreover, we show that the rate-dependent biaxial extensional viscosities deduced from drop impact experiments are in good quantitative agreement with previous experimental data and theoretical predictions for various viscoelastic liquids.

Wednesday 16:20 Nervión / Track 3

SM13

Melt rupture and wall slip of metallocene-catalyzed bimodal molecular weight distribution polyethylene under simple shear

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Apparent slip occurs in the flow of linear polyethylene melts over a high surface energy wall changing both the velocity profile and the stress. The slip behavior of bimodal molecular weight distribution (MWD) resins has found to be different from that of unimodal resins and is not yet fully understood. There is a systematic change in MWD of the four resins that are used in this study which make it possible to study the effect of short and long chains on the slip behaviour. The no-slip behavior was measured using a stress-controlled rotational rheometer by conducting small amplitude oscillatory shear (SAOS) tests at 190 °C in the frequency range of 0.01-500 rad/s and assuming the Cox-Merz relationship. A sliding plate rheometer (SPR) was used to study the slip behaviour of bimodal polyethylene resins in simple shear. The SPR tests were conducted at 190 °C and various nominal shear rates to measure the shear stress in the presence of slip. The results show that slip occurs over a broad range of stress. The amount of short chains strongly affects the slip behaviour of these materials. The higher the short chain content, the lower is the stress at which slip is observed in our experiments. The presence of short chains affects the slip behaviour at all stresses within the transition region before strong slip is fully developed. In the stress region where strong slip is fully developed, the slip behaviour is independent of MWD. During the slip experiments it became obvious that melt rupture was also occurring and therefore we visually studied this aspect of the flow behavior using a glass plate as the stationary plate. The time to rupture at various stresses was also determined from the transient stress curves. The visual studies show that all materials undergo melt rupture after slipping. The amount of short chains also significantly affects the stress at which melt rupture happens in the experiments.

Wednesday 16:40 Nervión / Track 3

SM14

Assessment of a melt rheology approach to estimate composition in binary blends of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE)

<u>Sylvie Vervoort</u>¹, Luca Martinetti², Jaap den Doelder^{1,3}, Teresa P. Karjala⁴, Keran Lu⁴, John P. O'Brien⁴, Christopher M. Thurber², Tom Collins², and Robert L. Sammler²

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Blown films are often composed of blends of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE). The linear chains of the LLDPE component enhance the film solid-state performance while the nonlinear chains of the LDPE component enhance the blown-film fabrication performance. The compromise between melt fabrication and final film performance is governed by the LDPE amount in the blend. Often, LDPE is added as a minor component to improve processability while keeping mechanical performance of the film high. The feasibility of using a melt rheology approach to assess the LDPE level in LLDPE/LDPE blends will be discussed. The approach focuses on the ability of the long-chain branches in LDPE to enhance strain-hardening during uniaxial extensional flow. The extensional strain hardening ratio (SHR) is shown

to correlate with LDPE level in the blend for the selected set of LLDPEs and LDPEs. The observed trend is (i) monotonic, (ii) approximately linear, and (iii) with a slope that depends primarily on the LDPE component.

Wednesday 17:00 Nervión / Track 3

SM15

Intrinsic viscosity as a tool to study the effect of the extraction conditions on the molecular weight of lignin Solange Magalhães¹, Luís Alves¹, José Gamelas¹, Bruno Medronho², Maria da Graça Carvalho¹, and Maria da Graca Rasteiro¹ CIEPQPF - Chemical Eng. Department, University of Coimbra, Coimbra, Portugal; ²Universidade do Algarve, Faro, Portugal

The average molecular weight of polymers can be estimated from various ways. A simple approach to estimate the average molecular weight of a polymer is studying the intrinsic viscosity $[\eta]$ and calculating the molecular weight average, MW [1]. The Mark-Houwink relation give us the average molecular MW and is widely applied to a perfectly monodispersed polymer of relatively low molecular weight. In the case of the lignin, a by-product from the separation of different components of plant biomass, the size and structure of this kind of compound can substantially differ from native lignin [2]. These two factors, molecular complexity and structural diversity, led us to study the relationship between intrinsic viscosity and molecular weight, where besides changing the original raw material from which lignin was extraxted, we have also changed the extraction conditions (time and temperature), the ratios between the different extraction agents. It was concluded that, in general, only the extraction conditions significantly influence the average weighted molecular weight, that is the dependence of viscosity on polymer concentration, being visible even in the colour of the extracted lignin. Generally, with the increase in temperature and extraction time, the MW decreases, due to the depolymerization of lignin. The depolymerized lignins can present different colours both in the dried state and in solution. Typically, the lower the MW, the darker the dried lignin powder and solution are.

References:

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- [2] Nadda A, Sharma S (2020) Lignin Biosynthesis and Transformation for Industrial Applications

Wednesday 17:20 Nervión / Track 3

SM16

Tube model predictions accounting for flow induce disentanglement and tumbling

<u>Laurence G. Hawke¹</u>, Christina Pyromali², Dimitris Vlassopoulos², and Evelyne van Ruymbeke³

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Nonequilibrium Molecular Dynamics (NEMD) Simulations suggest that, at fast shear, flow induced disentangled (FID) and chain tumbling are important mechanisms in monodisperse melts of linear chains (Sefiddashti et al., Macromolecules, 52, 8124, 2019). Classical tube models omit these mechanisms (Graham et al., J. Rheol, 47, 1171, 2003). Refined tube models account either for flow induced disentanglement (Desai & Larson, J. Rheol, 58, 255, 2014) or tumbling (Costanzo et al., Macromolecules, 49, 3925, 2016). Here, we incorporate the semi-phenomenological tumbling formalism of Costanzo et al. in the Desai-Larson model which accounts for FID as well as for friction reduction. We compare model predictions against NEMD outcomes and experimental polystyrene data. We find that, for shear rates exceeding the inverse entanglement time, friction reduction is important to reproduce the NEMD data reasonably. Concerning the comparison with the measurements, it turns out that friction reduction is not essential since the achieved shear rates do not exceed the inverse entanglement time. The main outcome is that even with FID and tumbling included, a single mode tube model cannot fully reproduce all measurements.

Symposium IP

Industrial Rheology and Processing

Organizers: María Graça Rasteiro, Francisco Martínez-Boza and Patrick Anderson

Wednesday 13:40 Prado / Track 4

IP8

Flexible PVC foams by 3D-printing: Rheological aspects

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Use of polymeric foam in today's technology grows exponentially throughout the world. Their lightweights, superior insulating abilities, excellent strength/weight ratios, energy absorbing performance and comfort features make them especially attractive in several areas such as furniture, transportation or packaging. Poly(vinyl chloride), PVC, foams in particular are of great importance due to their versatility. The possibility of incorporating different amounts of plasticiser makes it possible to obtain both rigid and flexible PVC foams. In this sense, PVC plastisols have been extensively studied (1). However, there are few studies related to lower plasticiser contents, and none related to the use of these formulations in new processing techniques such as 3D printing. Foamable materials bring about a new challenge for additive manufacturing, since they provide the possibility of generating new-dual pore complex geometries via a one step-process combining gas foaming and 3D modelling. Recently, some attempts have been done with PLA (2) but no one focused on PVC. This work explores the possibility of controlling the cellular architecture of flexible and foamable PVC formulations obtained by 3D printing. The evaluation of the rheological properties of the melt at printing/foaming

temperatures, as well as the analysis of the foaming kinetics will allow us to predict the cellular architecture of the deposited filament. This knowledge combined with the print design parameters, will allow a rigorous control of the cellular structure of the printed part, and, therefore, the control of the final density and mechanical properties of the system.

References:

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- (2) Choi, W. J., Hwang, K. S., Kwon, H. J., Lee, C., Kim, C. H., Kim, T. H., and Lee, J. Y. (2020). Rapid development of dual porous poly (lactic acid) foam using fused deposition modeling (FDM) 3D printing for medical scaffold application. *Materials Science and Engineering: C*, 110. 110693.

Wednesday 14:00 Prado / Track 4

IP9

Identification of foaming parameters for polyurethane with the FOAMAT® device

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A key problem in the modeling of polyurethane foaming is the determination of relevant physical parameters for the viscosity, the gas expansion and the curing rate. Indeed, it is difficult to measure the chemical kinetics parameters as well as the viscosity of industrial polyurethane formulations (polyol-isocyanate-water mixture) because the time scales of gas production and polyurethane crosslinking are very short and hardly compatible with the installation of the sample in characterization devices such as DSC and parallel plates rheometer.

A FOAMAT® system has been developed to get these experimental data but the relationship between measurements and rheochemical parameters has not been clearly established.

In our approach an analytical model of the foaming process is developed in the cylindrical FOAMAT® geometry which allows identifying the parameters of the curing and gas production kinetics equations, as well as the viscosity. As a consequence, one exhibits new modeling equations [2] for polyurethane foaming which can be fully identified with this FOAMAT® device.

This analytical model is based on a set of simplifying hypotheses which validity is checked using the finite element computation software REM3D® dedicated to foaming modelling and applicable for injection-molding processing. Furthermore, an analysis of the influence of viscosity modeling on foaming simulation has been performed.

References:

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[2] Raimbault, C, Laure, P, François, G, et al. Foaming parameter identification of polyurethane using FOAMAT® device. *Polym Eng Sci.* 2021; 61: 1243- 1256. https://doi.org/10.1002/pen.25676

Key-Words: Polyurethane, Foam, FOAMAT® experiments, Foaming and Curing Kinetics, Rheology, Modelling

Wednesday 14:20 Prado / Track 4

IP10

Foamability of linear and branched polypropylenes by physical extrusion foaming - Input of the thermomechanical analysis of pressure drop in the die

Carlos Sandino¹, Edith Peuvrel-Disdier¹, Jean-François Agassant¹, Séverine A.E. Boyer¹, Patrice Laure^{1,2}, Geoffrey Hibert³, and Yves Trolez³

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This study aims to better understand the polypropylene (PP) foamability by physical extrusion foaming comparing branched chains with strain hardening versus linear ones. Trials were conducted in a single screw extrusion equipped with a gear pump for the gas dissolution step (same extrusion parameters, 1wt% CO2) and a static mixer cooler allowing to decrease the melt temperature before the final die (referred as foaming temperature). The effect of decreasing the foaming temperature on the PP foamability was analyzed. The foam density of branched PP varies from high to low values while decreasing the foaming temperature. This foamability transition coincides with an increase of the pressure drop in the die. As reported, branched PPs depict a better foamability than linear grades. As the pressure drop in the die is responsible of the polymer foaming, a thermomechanical analysis of the polymer flow was conducted to better understand the foamability transition. The pressure drop was calculated in the die using dedicated analytical expressions for the converging and capillary parts and a power law for the viscosity curve. Calculated pressures are lower than the measured values. The discrepancy is interpreted as an additional contribution due to the elongational flow in the converging channel, which can be estimated. The pressure drop variation with the foaming temperature follows an Arrhenius dependence in the case of linear grades. In the case of branched grades, the Arrhenius dependence is valid for large foaming temperatures but a large discrepancy is reported for low foaming temperatures. Two phenomena (presence of strain hardening for branched PP and/or of crystallization) can be at the origin of this discrepancy. These hypotheses will be examined and discussed for the different polymer grades in order to clarify the physical scenario for the foaming process.

IP11

Wednesday 14:40 Prado / Track 4

Mechanics and structure of carbon black gels under high-power ultrasound

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A colloidal gel forms as attractive colloidal particlesdispersed in a fluid aggregate into a space-spanning network. Gels behave like soft elastic solids at rest and easily flow upon application of mild external stresses including shear, compression, gravity or vibrations. Those properties are of prime importance for applications to material design and industrial processes in construction materials like cement, in food science, as well as in ink-jet printing or flow-cell batteries. In practice, however, applying a mechanical strain or stress in order to disrupt the gel at will is far from ideal as it involves stirring devices such as pumps, motors or other rotating tools that may not be compatible with applications. In particular, in industrial lines dedicated to particle fabrication, gels may form in the process and clog the production pipe. In such a case, the production must be stopped and the pipe cleaned. Using high-power ultrasound could be very useful to fluidize the gels ex-situ, without dismounting the line. Here, the effects of high-power ultrasound on the carbon black gel are demonstrated using two experiments: rheology coupled to ultrasound to test for the gel mechanical response and a time resolved ultra small-angle X-ray scattering experiment (TRUSAXS) coupled to ultrasound to test for structural changes within the gel. We show that high-power ultrasound above a critical amplitude leads to a complex viscoelastic transient response of the gels within a few seconds: a softening of its storage modulus accompanied by a strong overshoot in its loss modulus. Under high-power ultrasound, the gel displays a viscoelastic spectrum with glass-like features and a significant decrease in its yield strain. Those effects are attributed to the formation of intermittent micro-cracks in the bulk of the gel as evidenced by TRUSAXS. Provided that the shear rate is not large enough to fully fluidize the sample, high-power ultrasound also facilitates the flow of the gel.

Wednesday 15:00 Prado / Track 4

IP12

Nanoscale investigation of the Payne effect in silica-filled rubbers through in-situ SAXS-rheological tests

Mariapaola Staropoli¹, Dominik Gerstner², Benoit Duez², Michael Sztucki³, Guido Vehres⁴, Aurel Radulescu⁴, Thomann Jean-Sébastien¹, Stephan Westermann¹, and Wim Pyckhout-Hintzen⁴

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This contribution deals with the structural and rheological properties of a silica filler network within an industrial elastomeric compound. Time-resolved ultra-small x-ray scattering (USAXS) patterns have been collected under the effect of a periodic deformation with variable dynamic amplitudes applied in-situ by means of a home-built DMA (Dynamic Mechanical Analysis) rheometer. The in-situ configuration allows the correlation between the structural evolution of the filler clusters under large-amplitude oscillatory extension (LAOE), detected by x-ray scattering, and the dynamic-mechanical stress-strain response. This specific combination of scattering and rheological methods allows a simultaneous identification of the induced structural changes on a microscopic level and the macroscopic mechanical properties. This contribution introduces a mathematical scattering model that provides a quantitative description of the filler network evolution under the effect of a dynamic deformation. With the aim of addressing the Payne effect and the underlying structural modifications correlated to intra- and inter-filler-aggregate effects, all rubbers were pre-conditioned to suppress stress softening related to the Mullins effect. 2D scattering images as well as the corresponding averaged intensities reveal a re-arrangement of the filler clusters along the direction of the applied dynamic sinusoidal deformation. From the structural study of the filler, a jamming/de-jamming transition between the filler clusters is identified as one contributor to non-linear viscoelastic behavior of the rubber and associated with structural arrest of the dynamics by the percolation of rigid fillers. The dynamic stress response of the full composite shows an onset of non-linear behavior, and odd and even higher harmonics of the fundamental excitation frequency are evidenced.

Wednesday 16:20 Prado / Track 4

Keynote

IP13

Displacement of a yield strength material in a radial Hele-Shaw cell

Behbood Abedi, Lara S. Berghe, Bruno S. Fonseca, Rafael M. Oliveira, and <u>Paulo R. de Souza Mendes</u> *Mechanical Engineering, PUC-Rio, Rio de Janeiro, RJ 22451-900, Brazil*

The growth of viscous fingers in the displacement of a yield strength material confined between the plates of a radial Hele-Shaw cell is investigated. We have built a cell whose diameter is three orders of magnitude greater than the gap width. The apparatus is filled with a Carpobol® solution and then air is injected to start the radial displacement process. The high aspect ratio of the Hele-Shaw cell facilitates formation and visualization of interfacial patterns up to late stages of the instability evolution. Using a mobile camera directly placed above the top plate, we performed a comprehensive investigation about the effects of gap size, injection rate, wettability and dynamic yield strength on the morphology of the air-gel interface. Among other findings, we observed residuals of unyielded Carbopol solution arrested on the surface wall. The morphology of these residuals can be either thin layers or isolated blobs, depending on the values of the governing parameters. This phenomenon renders non-uniform the effective gap of the displacing fluid, generating three dimensional effects and causing secondary instabilities which were found to be related to the presence or absence of wall slip.

Wednesday 17:00 Prado / Track 4

IP15

Rheological and morphological investigation of poly (lactic acid)/polyamide 11 biosourced multiphase systems going from polymer blends to multi-micro-nanolayers

Nour Jaouadi¹, Khalid Lamnawar¹, Abderrahim Maazouz¹, and Mohamed Jaziri²

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The objective of this study is to gain a deep understanding of the Micro-nano-structuration of biosourced polymers multiphase systems based on polylactide (PLA) and polyamide 11 (PA11). Generally, PLA cannot challenge regular commodity polymers due to its weak thermo-mechanical properties and its poor elongation properties. Firstly, we present a promising route to overcome these drawbacks in order to enhance the processability of PLA blending with other ductile biopolymers such as PA11, as well as mixing PLA/PA11 with a chain extender, Joncryl ADR-4368, containing reactive epoxy functions. To attain our objectives, different blending approaches were used. The effects of those strategies on the morphology and rheology properties were investigated. Results showed that a "self compatibilization" between PLA and PA11 chains can occur but it was found to be insufficient. The role of Joncryl as a compatibilizer for the PLA/PA11 system has been demonstrated by the significant decrease of particle size and interfacial tension as well as the improvement of ductile properties. Moreover, a new relaxation peak appeared in the relaxation spectrum, indicating the generation of a copolymer at the polymer-polymer interface. Secondly, the obtained blends were structured by the innovative coextrusion process allowing the in-situ evolution of their morphology by confinement. Hence, the work is in progress to investigate their morphological, rheological and mechanical properties.

Wednesday 17:20 Prado / Track 4

IP16

Rheological behaviour of green thickened matrices obtained from natural deep eutectic solvents (NADEs) and lignocellulose

Esperanza Cortés-Triviño¹, Juan Cubero-Cardoso², Concepción Valencia¹, Juan Urbano², and José M. Franco¹

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Over the last century, the Principles of Green Chemistry have been the focus of attention in most of the industrial sectors, thus increasing the interest in using environmentally friendly raw materials from renewable resources to replace petroleum-based products (Perona et al., 2020). For instance, the use of vegetable oils and bio-based thickening materials has been a breakthrough as an alternative to traditional products in the lubricant field (Cortés-Triviño et al., 2018; Zainal et al., 2018). However, they showed some limitations in some of their performance properties, such as viscosity index or thermal resistance, requiring to apply chemical modifications to improve them (McNutt & He, 2016). In this work, natural deep eutectic solvents (NADEs) containing hydroxyl groups in their chemical structure were used as alternative to vegetable oils in the production of novel structured formulations. Thus, the influence of their chemical nature, which was modified by varying the number of hydroxyl groups in the hydrogen bond donor (HBD) compound, on the viscous flow properties was investigated. NADEs were synthetized by mixing citric acid and different HBDs, i.e. glycerol, xylitol, and sucrose, obtaining supramolecular structures at room temperature with remarkable viscosity and tunable properties. Besides, a lignocellulose residue was epoxidized to be used as a thickening agent for NADEs by fostering the chemical crosslinking between the HBD hydroxyl groups and the epoxy groups of the lignin-based material. The effect of NADEs properties and lignocellulosic thickener concentration was evaluated from a rheological point of view. A variety of green thickened matrices with rheological responses from liquid-like to gel-like were obtained, having potential applications in different industrial sectors.

Symposium EM

Experimental Methods and New Advances in Rheometry

Organizers: Loic Hillou, Paula Moldenaers and Dimitris Vlassopoulos

Wednesday 13:40 Arenal / Track 5

Keynote

EM8

Interconversion of parallel and orthogonal superposition rheometry data

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Superposition rheometry, in which small amplitude oscillatory perturbations around a non-equilibrium flow condition are used to probe flow induced microstructural changes, can be implemented in either orthogonal or parallel configurations. Orthogonal superposition data (in terms of the orthogonal 'storage' and 'loss' moduli), are often interpreted as per their linear viscoelastic counterparts. However, the complexity of the flow in parallel superposition experiments means that the parameters characterising the oscillatory response are more difficult to interpret. Consequently, the use of a comparison of the moduli measured in orthogonal directions is rarely seen in the literature as a measure of flow induced anisotropy. To facilitate such a comparison, the authors have recently published a series of papers that consider the problem of interconversion between orthogonal and parallel superposition data. If possible, such an interconversion facilitates a valid comparison of the parallel and orthogonal superposition moduli. In this presentation, we will consider how interconversion can be undertaken using some well-known constitutive equations via discrete relaxation spectra with interesting properties before applying the models to the study of worm like micelles.

Wednesday 14:20 Arenal / Track 5

EM10

Coupled Rheo-Dielectric: In-situ investigation of the alignment of lamellar blockcopolymers

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The coupling of rheology and broadband dielectric spectroscopy (Rheo-Dielectric) allows us to investigate the dynamics of materials in a very broad time (e.g. 10^{-2} to 10^{6} Hz) and length-scale (e.g. local to chain motions). Our unique Rheo-Dielectric setup enables us to investigate the orientation of lamellar polystyrene and polyisoprene blockcopolymers by large amplitude oscillatory shear (LAOS). For this, the dielectric normal mode of 1,4-cis-polyisoprene is used to probe the macroscopic orientation process in-situ. The development of the overall orientation can be observed by the time evolution of the dielectric loss modulus (ϵ "(t)). Furthermore, the time evolution of the dielectric loss modulus can be correlated with the mechanical nonlinear parameter (13/1)(t). The final orientation of the blockcopolymers as predicted from ϵ " (t) is proven by small-angle X-Ray scattering (SAXS), where either a parallel, perpendicular, or biaxial (parallel and perpendicular) orientation was found, and the degree of orientation could be determined. We show that a decrease in ϵ "(t) relative to the initial value indicated a parallel orientation whereas an increase pointed towards an overall perpendicular orientation. Both observations are explained by the final orientation of the end-to-end vector of 1,4-cis-polyisoprene relative to its orientation in the unoriented sample at t=0. Additionally, we have a closer look at the influence of different parameters during LAOS on the final orientation as well as the time evolution of ϵ ". The different time constants (τ) obtained by varying the experimental parameters such as shear frequency, shear strain, or temperature are analyzed and interpreted on a molecular level.

Wednesday 14:40 Arenal / Track 5

EM11

Dichotomous behavior of stress and dielectric relaxations in dense suspensions of swollen thermoreversible hydrogel microparticles

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While large oscillatory stresses are known to mechanically disrupt the microscopic structures in structured complex fluids, changes in the dielectric properties of these macromolecular aggregates due to applications of shear deformations have received far less attention. Using a precision impedance analyzer, we study the dielectric behavior of aqueous suspensions of poly(N-isopropylacrylamide) (PNIPAM) particles under controlled oscillatory strains at different temperatures. The measured dielectric permittivity exhibits distinct relaxation processes at low and high frequency regimes. At temperatures below the lower critical solution temperature (LCST), the dielectric constant and dielectric loss of a jammed aqueous PNIPAM suspension decreases when the applied oscillatory strain amplitude is increased. Moreover, we note a counter-intuitive slowdown of relaxation processes below the LCST in dense suspensions in both low and high frequency relaxation regimes. In contrast, the dielectric response of an aqueous suspension of PNIPAM particles at higher temperatures (near and above the LCST) is comparatively insensitive to changes in the amplitude of the applied oscillatory strain. When compared to the mechanical stress relaxation behavior of shear-thinning PNIPAM suspensions, dielectric relaxation processes are characterized by much faster timescales. We explain our experimental observations by proposing of the formation of jammed fragile PNIPAM clusters that undergo mechanical rupture at high oscillatory strains below the LCST. Our rheo-dielectric study correlates the suspension dynamics over a hierarchy of structural length scales and has important implications in our understanding of the energy storage and dissipation processes in functional materials.

Wednesday 15:00 Arenal / Track 5

EM12

Characterization of flow-induced soft particle glasses with a plane-plane rheometer and small-angle light scattering.

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Yield Stress Fluids (YSFs) forms an extensive and interesting area of soft matter. They are defined as all those materials that at rest exhibit solid-like behavior and when under stress exceeding their own yield stress, they begin to flow. Soft Particle Glasses (SPGs) also belong to this area. SPGs are concentrated suspensions composed of deformable colloidal particles packed at volume fractions exceeding close-packing. These systems have a strong practical interest such as concentrated emulsions, microgel pastes or star polymer solution. Experiments show that the flow curves of many SPGs under steady shear flow exhibit generic features that are well described by the empirical Herschel-Bulkley equation. Since there is growing evidence that flow properties are intimately connected to the dynamics at the microscopic scale, an outstanding challenge is to figure out the underlying physical processes. In this work, we aim to address the challenges related to understanding these processes: the very small-scale motion, the heterogeneity in time and space, and the necessity of decoupling macroscopic deformation and microscopic rearrangements. In order to achieve this, we introduce a novel platform for the simultaneous measurement of the macroscopic rheological properties and the microscopic nonaffine motion in soft materials, including SPGs. This platform is formed by a custom-made plane-plane rheometer coupled to a dynamic small-angle light scattering. We implement a data analysis protocol that allows us to measure particle motion along with different directions with respect to the applied flow field.

Wednesday 16:20 Arenal / Track 5

Shapes of 3D printed filaments of yield stress fluids

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The basic process in additive manufacturing for construction is an extrusion followed by the deposition of a filament of a yield stress fluid onto a surface in translation with respect to the printing head. We study this process with controlled experiments on a model yield stress fluid (clay suspension). By varying the height and printing speed, we observe three main regimes of deposition: a regime where the filament breaks-up at regular intervals (I), a deposition of a continuous line either slightly stretched or squeezed (II), and a deposition as meanders or more complex though stable patterns (III). In order to understand the origin of these phenomena, we focus on the fundamental characteristics of three basic flow types.

- 1. A filament of yield stress fluid extruded from a large height will break-up because of gravity before it reaches the surface. We developed a rheometrical analysis of the extensional properties of a yield stress fluid based on the study of its deformation during such a flow. We show from the evolution of the filament profile with time that we can distinguish the data for which pure elongational stress and strain rate components are effectively dominant so that the elongational flow curve of the material can be deduced [1].
- 2. When the height is reduced, the filament is submitted to a compression at the time it enters in contact with the surface. From a detailed evolution of the filament profile we distinguish two very different flow regimes: either a homogeneous compression of the sample, or a buckling phenomenon during which the sample axis widely curves. We discuss the origin of such a purely plastic buckling, which as far as we know has not been considered in theory.
- 3. We finally show that in regime III the characteristics of the patterns are surprisingly analogous to those of a filament of viscous fluid or an elastic rope falling over a surface.

References:

[1] Geffrault et al., Extensional gravity-rheometry (EGR) for yield stress fluids, J. Rheol, (2021) 65, 887-901.

Wednesday 16:40 Arenal / Track 5

EM14

EM13

Flow onset mechanics of bubbles in yield stress fluids

Masoud Daneshi¹, Marjan Zare¹, and Ian A. Frigaard²

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In this study, we examine the stability of gas bubbles in a yield stress fluid, through an experimental approach. A vacuum system was used to control the concentration and size of bubbles trapped in the fluid. We investigated the stability of bubble clouds as well as single bubbles and multiple bubbles initially positioned at different orientations, in Carbopol gels with different concentrations. Our results indicate that the rheology of the material as well as interaction of bubbles affect the onset of motion significantly. Our results show that in a gel with higher concentration, (i.e. higher yield stress and elastic modulus), a single bubble begins to rise at a larger size and with a longer aspect ratio. In addition our study confirms that bubble clouds become unstable at a smaller bubble sizes in comparison with that of a single bubble. This is likely related to the interaction of the stress field generated by each bubble. In order to explore this point, we have extended the study to looking at a more fundamental scenario, namely two or three bubbles at different orientations and separation distances.

Acknowledgement: This research was made possible by funding from NSERC and COSIA/IOSI (project numbers CRDPJ 537806-18 and IOSI Project #2018-10).

Wednesday 17:00 Arenal / Track 5

EM15

Measuring the stress ratio and the corresponding wall friction coefficient in powders

Margot Coppens¹, Michael Van den Eynde², and Peter Van Puyvelde¹

¹Department of Chemical Engineering, KU Leuven, Leuven, Belgium; ²Janssen Pharmaceutica, Beerse, Belgium

The lateral stress ratio K and the wall friction coefficient μ are critical powder properties to determine the stress present in powder columns and affect powder flow. Nevertheless, in practice, K is often estimated as 0.4, or is based on theoretical models which have been shown to underestimate the experimentally determined value (Kwade et al., 1994). Therefore, this research proposes two experimental methods: (1) to measure the product of K and μ in a setup that is applicable to any rheometer, and (2) to measure μ with an improved protocol for powder rheometry on the Schulze Ring Shear Tester. Method (1) exploits a compressibility protocol during which the stress at the bottom of the powder sample is measured, as previously demonstrated in literature (Di Felice & Scapinello, 2010). For method (2), conventional powder rheometry suggests a kinematic measurement, where the resulting μ is found to be affected by the stress history of the powder. Therefore, a new protocol is proposed: a static measurement of μ , including a compression step aiming at a realistic powder compaction. Both methods have been applied to caster sugar, wheat flour, a TPC-powder for 3D-printing and a pharmaceutical grade MCC . Overall, a lower average wall roughness was found to decrease K μ , whereas the effect of impeller conditioning was limited. The static and stress-considering character of the wall friction measurement resulted in an overall larger wall friction coefficient. The combination of both methods allows to inform stress profiles for industrial application.

This research was funded by VLAIO (Flanders Innovation & Entrepreneurship).

Wednesday 17:20 Arenal / Track 5

EM16

Impact of CaCl₂ concentration and in situ rheometric setup configuration on fast alginate-Ca²⁺ reaction

Ioanna N. Besiri¹, Thomas B. Goudoulas¹, and Natalie Germann²

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Recording the kinetics during the reaction is a challenging task that provides important insights into the physicochemical and mechanical properties of hydrogels. In our recent publication, we presented a custom-made rheometric setup for in situ realtime monitoring of alginate-Ca²⁺ gelation. From the working principle, the method mimicks the operation of a batch reactor where the volume of reactants is constant and there is no input or output during the chemical reaction process. An instant injection of CaCl₂ solution into the alginate through the microholes of the bottom plate initiates the reaction. Considering that the time evolution of viscoelastic parameters is related to the developing gel structure, the reaction kinetics can be analyzed qualitatively. The present study aims to improve the setup by increasing the number of holes to four to achieve a better local distribution of cations in the alginate sample. Furthermore, since we can precisely modulate the volume and concentration of the reactants with the setup, we can study the effects of molarity on gelation. The long-term behavior of the rheological oscillatory shear experiments shows that the response depends on the mass of the cations. Since the elastic modulus increases at high concentration and small volume of CaCl2, we believe that the stoichiometry of the reactants affects the diffusion of the ions. Systematic time sweep experiments show that at low values of the angular frequency ω the driving force of the reaction is mainly related to the diffusion of the ions. At higher values of ω, the increase in elastic modulus may be due to the enhanced mixing of the reactants by the mechanical force of the cone-plate geometry.

References:

I. N. Besiri, Th. B. Goudoulas, and N. Germann. Custom-made setup for in situ real-time rheological characterization of fast alginate-Ca²⁺ gelation, Carbohydrate Polymer, 246:0144-8617, 2020.

Symposium FR

Food Rheology

Organizers: Bettina Wolff, Isabel de Sousa and Ma Jesús Hernández

Giralda 6-7 / Track 6 Wednesday 13:40

FR8

Jamming of non-colloidal plant cell-wall particles: the role of packing, mechanical properties, and surface interactions

Panagiota Mouraka¹, Vincenzo di Bari², and Gleb Yakubov³

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The incorporation of dietary fibres (DFs) in the food systems provides structuring and nutritional benefits. The last decade saw the rise in the use of minimally processed plant cell-wall materials in the food industry to produce healthier products by replacing sugar and starch with nondigestible fibre ingredients (Anderson et al., 2009; Foster, 2011; Yu, Yakubov, Martínez-Sanz, Gilbert, & Stokes, 2018). Since natural DF have different mechanical properties, water holding capacity and surface functionalities, careful consideration of the most appropriate source(s) is necessary to fit the specific food application (Elleuch et al., 2011). The objective of this study is to elucidate the effect of particle properties on the micromechanical behaviour of concentrated DF suspensions. In this work, we use fibre particles of different botanical origin, which enables varying suspension microstructure and packing volume, as well as particle modulus and particle size distribution. The DFs were chosen from wheat, oat, citrus, apple, and pea fibres and were dispersed in sunflower oil to make the suspensions. The icing sugar suspensions were used as control. The Angell's-like plot representation, where suspension's G' is plotted against particle concentration, enabled probing consolidation properties of concentrated suspensions. We show that most cellulose/starch rich fibres show 'fragile' behaviour, whereby G' remains low up until the jamming point, beyond which a rapid increase in G' is observed. By contrast icing sugar suspensions show 'strong' glass behaviour, with G' increasing linearly up until the jamming point. For concentrations above jamming we observe G' to plateau. However, contrary to the expectations, the modulus of suspensions in the jammed state is found to be independent of the particle modulus, as would be predicted by the Evans and Lips model (Evans & Lips, 1990). We propose that the result indicates that the interaction potential between DF particles deviates from the Hertzian hard wall mechanical contact.

Wednesday 14:00 Giralda 6-7 / Track 6

FR9

Extensional stress-relaxation measurements on wheat flour dough – The key to finalizing the Fractional K-BKZ framework?

Yannick Meeus¹, Mathieu Meerts¹, Gareth H. McKinley², Paula Moldenaers¹, and <u>Ruth Cardinaels</u>¹ *Soft Matter, Rheology and Technology, KU Leuven, Heverlee 3001, Belgium;* ² *Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States*

Wheat flour dough is a viscoelastic material with a multi-scale structure. On a microscopic level it consists of a gluten matrix in which starch granules and a variety of minor components are dispersed. The complex interplay of interactions that takes place on this microscopic level results in a macroscopic rheological behavior of dough that is difficult to model accurately. A better understanding of dough rheology is highly desirable in view of the link between dough rheological properties and final bread quality. The linear rheology of dough can be accurately described using the fractional Maxwell model (FMM). By extending the FMM with the K-BKZ equation, the non-linear extensional behavior can be captured as well, at least from a qualitative point of view, although quantitatively an overestimation of the extensional stress growth is predicted. To overcome this limitation, a suitable damping function can be included into the Fractional K-BKZ framework to account for strain-softening at large strains. Conventional shear stress-relaxation measurements, which are typically used to circumvent the difficulties associated with extensional experiments, fail to provide an adequate damping function. Here we show that extensional stress-relaxation measurements performed on a highly-viscous material such as bread dough allow to determine an extensional damping function. Incorporating this damping function into the Fractional K-BKZ framework allows us to account for the disruption in gluten-starch interactions when dough is exposed to extensional deformations. Thereby, the model can accurately predict the extensional viscosity and its strain hardening for a range of extension rates.

Wednesday 14:20 Giralda 6-7 / Track 6

FR10

Improving dough rheology using partially purified algae biomass

Waqas M. Qazi¹, Ines Sousa², Maria Cristiana Nunes², and Anabela Raymundo²

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Gluten proteins are essential to the unique baking attributes of wheat bread. The viscoelastic gluten network enables the dough to retain gas during baking and provide the traditional volume and texture to the wheat bread the consumers are familiar with. People suffering from celiac disease are intolerant to gluten or similar proteins. Celiac disease effects approximately 1-2% of the world population. Celiac intolerants are restricted to gluten free (GF) bread which is difficult to produce resulting in poor texture properties. Microalgae's are enormous resource of valuable nutrients & antioxidants & have been used by researchers to enrich nutritional status of the GF bread. Usually, small addition levels are used that weakens dough strength, deteriorates bread quality and leads to an unpleasant smell & dark coloured bread. In our research, the algae biomasses of three species: Tetraselmis chuii, Chlorella vulgaris and Nannochloropsis gaditana were treated with ethanol to eliminate chlorophylls & lipids, in order to improve sensory profile. A marked improvement in dough rheology with ethanol treated biomass replacement was noticed in the three species examined that had protein content up to 59-62% vs the raw biomass 42 to 48%. Improvement in dough strength was depicted by creep and recovery tests that consequentially lead to bread of high volume and soft texture. The bread made with ethanol treated biomass acquired a positive response in sensory trials nearly like the control with the food grade specie chlorella vulgaris. The nutritional value (proteins, lipids, minerals, carbohydrates) of the GF bread improved with microalgae addition compared to control. Protein content increased in algae enriched bread compared to the control was 14-20% and in the treated vs raw biomass breads up to 8%. The algae proteins seem to play a structure building role. In future studies, 100% purification of algae protein is planned to reduce the use of thickeners and hence contribute to a cleaner label in GF bread formulations.

Wednesday 14:40 Giralda 6-7 / Track 6

FR11

Rheological properties of artificial boluses of cereal foods enriched with legume proteins to quantify food-saliva interactions

Florence Gibouin¹, Ruud G. van der Sman², and Guy Della Valle³

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During oral processing (FOP), food bolus experiences a large range of shear rate and extensional flow. The study of FOP is essential for food design, for instance to enrich foods with legume proteins. The aim of this work is to determine the rheological properties of artificial boluses of cereal foods. In this purpose, the properties of artificial food bolus are studied by dynamic oscillatory and capillary rheometries as function of bolus water content, in the usual range of saliva hydration, for four cereal products: sponge cake, extruded flat bread and their counterpart enriched in legume proteins. The conditions of artificial bolus processing have been set after determining the influence of physiological parameters such as particle size and artificial saliva viscosity. All artificial boluses followed the same rheological behaviour characterised by (1) solid -like in the linear viscoelastic domain and (2) Herschel-Bulkley model for large shear strain. Hence, four characteristic rheological properties are determined: modulus at viscoelastic plateau, characteristic stress at transition to flow, yield stress and consistency in the flow regime (Fig.1). Water content considerably decreased these properties according to an exponential decay, in analogy with time-temperature superposition principle, which allowed determining interactions coefficients. Their values, in the interval [5, 30], are of the same order of magnitude as the plasticization coefficient of starch by water. They were larger than 15 for the extruded pea based and lower than 15 for the sponge cake. The variations for the different rheological properties are discussed in terms of matter state, envisioning bolus as a suspension of swellable particles, and their values

were compared to those encountered for real boluses from same foods. These results open prospects to use rheology to determine a coefficient of interaction of food with saliva.

Wednesday 15:00 Giralda 6-7 / Track 6

FR15

Functional bigels for food uses

Elisabetta Bruno¹, Francesca R. Lupi¹, Noemi Baldino¹, Rosamaria Marino², and <u>Domenico Gabriele</u>¹ *DIMES, University of Calabria, Rende, CS 87036, Italy; ²JRS Silvateam Ingredients srl, Rende, CS 87036, Italy*

Bigels are biphasic systems formed by the combination of two gelled phases based on different solvents. Owing to the simultaneous presence of two structured systems they have peculiar properties, with respect to both traditional unstructured emulsions and monophasic gels, such as the enhanced stability, the improvement in consistency control, the ability of entrap and deliver in a controlled way both lipophilic and hydrophilic agents. Their properties can be very interesting for use in food area, where many systems are heterogenous multiphasic materials, and, therefore, recently, edible bigels were starting to being investigated. In this work water phase was structured using citrus edible fiber whereas olive oil was gelled with policosanol, a mixture of fatty alcohols; both components have excellent gelation properties and are also functional ingredients owing to their healthy properties. Indeed, fiber can reduce risk for developing gastrointestinal and cardiovascular diseases whereas policosanol seems able to decrease lipid levels in the blood. Bigels were prepared by mixing, at room temperature, with a rotor-stator device, policosanol content. Samples were characterized with small amplitude oscillations and contrast phase microscopy to evaluate the material microstructure. It was observed that above 40% of oleogel content, a transition between hydrogel-in-oleogel (H/O) to oleogel-in-hydrogel (O/H) systems occurred. All samples exhibit a prevalent solid-like behavior with G' greater than G" of almost one order of magnitude. Bigel rheological data, in terms of complex modulus at 1 Hz, were related to rheological properties of both phase and dispersing phase content aiming at proposing a rheological model able to describe bigel behavior and suitable to design formulations with expected properties.

Symposium BM

Bio-rheology and Medicine

Organizers: Críspulo Gallegos, Mats Stading and Catarina R. Leal

Wednesday 16:20 Giralda 6-7 / Track 6

BM17

Injectable composite systems of ALG:GG microparticles in pluronic hidrogels for bioactive cargo controlled delivery: Optimization of hydrogel composition based on rheological behavior

Henrique Carrêlo, Paula Soares, João P. Borges, and Maria Teresa Cidade

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Stimuli-responsive hydrogels can be loaded with drugs, cells, and growth factors and control their release by changing the gel structure in response to application of an external stimuli. Thermally responsive hydrogels are very interesting because their gelation and changes in swelling can be triggered by temperature change. The case of injectable thermoresponsive hydrogel is particularly interesting since it is injected in the sol phase and will almost instantaneously gelify when entering the body. Adding loaded nano/microparticles to the hydrogel allows us to obtain a dual active cargo delivery, which may be very interesting to deliver two different types of active cargo, two different drugs, one drug and one growth factor, etc. In a previous study [1], we have added alginate microparticles to a 20 wt% Pluronic F127/water hydrogel and in another paper [2] we have added poly \varepsilon-caprolactone, (PCL) to a (18+2 wt%) Pluronic F127+ F68/water hydrogel. Since the addition of the microparticles decrease the gel transition temperature, Tgel, in both cases the amount of nanoparticles were limited to 10 wt% since Tgel must be a little smaller than body temperature. In the work now presented, for microparticles of alginate/gellan gum (AL:GG 50/50) added to (18 + 2 wt%) Pluronic F127+F68/water hydrogel the maximum amount of microparticles were found to be 2 wt%. Since F68 presents a Tgel much higher than F127, we played with the composition of the hydrogel, in order to increase its Tgel, thus allowing for increasing the amount of microparticles and, consequently, of active cargo, without decreasing to much the Tgel of the composite. The optimization of the hydrogel composition was performed through rheological characterization. The increase of just 3 wt.% F68 (15+5 F127+F68) allowed us to increase the amount of microparticles to 10 wt%. The phase diagram will be presented.

References:

- [1] Cidade et al, Materials, 12, 1083, 2019.
- [2] Delgado et al, Journal of Materials Science, 56, 13416, 2021.

Wednesday 16:40 Giralda 6-7 / Track 6

Shear-induced crystallization of a therapeutic protein

Joana Ferreira, João Carneiro, and João Moreira de Campos

CEFT - Transport Phenomena Research Center, Department of Chemical Engineering, University of Porto, Porto, Portugal

Protein crystalline formulations hold several benefits in the delivery of biopharmaceuticals, including improved stability, controlled release of the active ingredient, etc. [1]. Recent advances in protein drugs revealed a troublesome in handling and delivering protein solutions, typically related to aggregation/agglomeration events and shear viscosity increases [2]. Therefore, a comprehensive understanding of protein solutions' rheology is imperative to manufacture protein-based formulations. This study aims to: (i) characterize the rheology of therapeutic protein (insulin) solutions exposed to uniform and non-uniform shear-fields and (ii) evaluate the formation of insulin crystals and oligomeric aggregates/agglomerates, and their respective distribution over time. Discrete rotational rheometry measurements are required to ensure homogeneous mixtures. The insulin crystalline formulations exhibit a shear-thinning behaviour regardless of the initial protein concentration and shear rate range. Single large insulin crystals are obtained under uniform shear-field for both single and double-shearing experiments. A non-uniform shear-field allows the formation of a high number of very small insulin crystals, which might be formed at distinct shear rate values. Moreover, during the double-shearing experiments, at lower insulin concentrations, three different scenarios are investigated: (I) formation of very small insulin crystals; (II) formation of single rhombohedral insulin crystals with identical rheological behaviour compared to (I); and (III) occurrence of protein aggregation/agglomeration events with a shear viscosity increase by an order of magnitude over time. Lastly, crystal breakage is observed at shear rates above a critical value. This critical shear rate also corresponds to the formation of the largest insulin crystals.

References:

[1] S. K. Basu et al., Expert Opinion on Biological Therapy 4, 301 (2004).

[2] S. Puhl et al., Asian Journal of Pharmaceutical Sciences 11, 469 (2016).

Wednesday 17:00 Giralda 6-7 / Track 6

BM19

BM18

Rheology as a key tool for the characterization of protein-based scaffolds for tissue engineering

Víctor Perez-Puyana, Mercedes Jiménez-Rosado, Antonio Guerrero, and Alberto Romero

Chemical Engineering, Universidad de Sevilla, Sevilla, Spain

Musculoskeletal diseases are complex and little known since they encompass a wide spectrum of pathologies that affect different connective tissues of the skeletal system, including bones, cartilage, muscles, tendons and ligaments. Thus, the regeneration of soft tissues that connect, support or surround other tissues is of great interest. In this sense, protein-based scaffolds have great potential as biomaterials for their regeneration. Among the different raw materials, collagen and gelatin stand out for being highly biocompatible, which, together with their biodegradability and structure, makes them a great alternative for the fabrication of scaffolds. As potential candidates for regenerative medicine, scaffolds must fulfil several requirements (biocompatibility and biodegradability, high porosity with good pore interconnectivity and good mechanical resistance). Therefore, a complete characterization is required, from the mechanical, microstructural and biological perspectives. Specifically, the mechanical analysis of the scaffolds can be assessed using Rheology. Thus, some critical properties can be evaluated such as the critical strain or the stability of the scaffolds over time with the effect of stress, among others. These parameters are highly relevant to establish the conditions for the use of scaffolds in bioreactors or their behaviour in physiological media. This work aimed to evaluate different parameters via rheological analysis for different protein-based scaffolds. In addition, their microstructural conformation has been also studied by scanning electron microscopy. In conclusion, rheological tests have managed to provide information of great interest for the processing of these protein-based scaffolds

Wednesday 17:20 Giralda 6-7 / Track 6

BM20

Designing of polymeric gels mimicking the normal and fibrotic liver tissues: Effect of viscoelasticity on cells adhesion and survival

Claudia Fornasier¹, Rossella Farra¹, Gesmi Milcovich¹, Alice Biasin², Nhung Hai Truong³, Gabriele Grassi¹, Mario Grassi², and Michela Abrami²

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Chronic hepatitis B/C virus, alcohol abuse, and non-alcoholic fatty liver disease are the major causes of liver fibrosis (LF), that leads to the progressive impairment of liver function (cirrhosis), often resulting in hepatocellular carcinoma. Despite the etiology, a key element in LF generation is represented by hepatic stellate cells (HSCs) that, from a quiescent condition, differentiate into proliferative and migratory myofibroblasts (cell activation) which secrete Extra Cellular Matrix (ECM) making the tissue increasingly stiffer. Interestingly, HCS activation is triggered by stiff environments, typical of fibrotic liver tissues (shear modulus G > (5 - 6) kPa for human beings). To study the activation process and novel drugs to down-modulate HSC activation, we developed proper substrates which can effectively mimic the viscoelastic properties of healthy and pathological liver tissue. Therefore, we designed alginates-based gels resembling the healthy and the pathological liver tissues from a viscoelastic point of view. For this purpose, hydrogels characterized by different alginate concentrations were produced to indicatively match healthy and pathological stiffness (crosslinking by CaCl₂). Then, to improve cells adhesion and survival on the gel surface, the water phase was substituted by a proper culture medium. Furthermore, additional studies were carried out in order to add ECM-like substrates to the alginate solution, like collagen or fibronectin or matrigel, to promote cells-gel interactions. Each gels was characterized by stress and frequency sweep tests to get the linear viscoelastic range, the relaxation spectrum (generalized Maxwell model fitting to frequency sweep data) and the shear

 $modulus \ G \ (stiffness). \ Finally, the \ optimal \ gel \ systems \ effectively \ mimicking \ healthy \ or \ pathological \ liver \ tissues \ were \ successfully \ considered \ for \ cell \ seeding \ and \ followed \ their \ adhesion \ and \ survival \ up \ to \ three \ days$

Thursday Morning

Symposium PL

Plenary Lectures

Thursday 9:00 Giralda 1-2 / Plenary Lectures

PL3

Rheological behavior of non-Brownian suspensions: towards a quantitative modeling.

Annie Colin

ESPCI Paris PSL, Paris, France

Dispersions of solid particles in liquids, also called suspensions, are soft matter systems that we encounter on a daily basis. Despite their few constituents, suspensions display very complex flow behaviors: shear thinning, shear thickening, density inhomogeneity, etc.. The understanding of these behaviors -- simple at first glance -- had remained limited until a major advance made by Boyer et al. by borrowing the concepts of dense granular flow. Thanks to dimensional analysis, they show that when the viscous forces at the level of the particles are higher than the inertial forces, the shear stress is proportional to the shear rate. The viscosity of the dispersion increases with the effective solid fraction and diverges close to the jamming point. It varies also with the microscopic friction coefficient between beads. Their analysis suggests that the non-Newtonian behaviors that are observed in suspension flows in homogeneous flow can only arise from a dependence of the friction coefficient or of the effective solid fraction with the shear stress. Currently, the theoretical framework for describing suspensions is well-established, thanks to numerical simulations. Experimental quantitative studies that describe the link between rheological properties and microscopic force measurements are required to check these predictions. By using state-of-the-art technique to measure the microscopic friction coefficient then coupling together with rheology measurements, we show how the details about the pairwise particle interactions govern the rheological properties. Here, we highlight many mechanisms: the swelling of polymeric particles in an organic solvent, the variation of the friction coefficient as a function of the load in the case of particles immersed in silicon oils in shear thinning systems and the role of colloidal repulsive forces and inertia in shear thickening systems.

Symposium IP

Industrial Rheology and Processing

Organizers: María Graça Rasteiro, Francisco Martínez-Boza and Patrick Anderson

Thursday 10:00 Giralda 1-2 / Track 1

IP17

SAOS and LAOS tests response of modified bitumens with SBS supported by morphological characterization Noemi Baldino¹, Simona Aprile¹, Maria Penelope De Santo², Olga Mileti¹, Francesca R. Lupi¹, Domenico Gabriele¹, and Salvatore Coppola³

¹DIMES, University of Calabria, Rende, Italy; ²Fisica, University of Calabria, Rende, Italy; ³Ravenna-Ferrara Research Center, Versalis SpA - Eni, Ravenna 48123, Italy

Modified bitumen plays a fundamental role in road pavements. They are produced by incorporating different types of polymers into the bituminous mixture, improving the properties of the material. One of the most frequently used modifiers is styrene-butadiene-styrene (SBS). Polymers and also any other modifiers can improve road performance in both linear and non-linear conditions, but while the linear viscoelasticity of asphalt binders was well studied, however, the same cannot be said for the non-linear regime. With the aim to better understand the mechanical properties and link them to the structure, rheological and morphological characterization of polymer-modified bitumen (PMB) was performed. Two polymers at 5% w/w were added to a 70/100 pristine bitumen. One polymer with a linear structure and the other with a branched SBS structure were used. The rheological characterization was performed in both linear (SAOS) and non-linear regimes (LAOS). Polymer dispersion was evaluated by fluorescence measurements and morphological characterization was performed by AFM. Rheological measurements were performed at low and high temperatures; values for characteristic temperatures, Tcross, Tonset, and Tß were obtained for all the samples. Fluorescence images showed the cross-linking of the polymer within the mixture. Through LAOS analysis, the nonlinear response for large strain amplitudes at different frequencies was investigated and the dimensionless parameters S and T were derived through Fourier analysis and Chebyschev polynomials. The linear and nonlinear strain results are represented by means of Lissajou-Boldwhich curves (L-B plot).

Thursday 10:20 Giralda 1-2 / Track 1

IP18

How does the rheology of lactose powders influence the pharmaceutical tablets weight consistency?

Aurélien Neveu¹, Pauline Janssen², and Filip Francqui³

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The processability of pharmaceutical powder plays a key role in the design and improvement of production processes for oral delivery systems (e.g. tableting, capsule filling). To control and to optimize processing methods, material properties and behaviour of bulk powder should be characterized. Moreover, good flowing properties of a powder are also required for flow through the tableting system, resulting in uniform flow into the die cavities. Insufficient flow can lead to uneven filling of the dies, resulting in large weight and dosage variations of the final tablets. At high tableting speeds the time to fill dies is reduced, making the flow properties of the blend even more important. The particle properties, mainly size and shape, strongly influence the flowability of the powder and thus the critical filling velocity achievable in die filling. Lactose is one of the most widely used excipients in the pharmaceutical industry. There are many reasons for its popularity, such as the fact that lactose is largely inert, relatively inexpensive, safe, many different grades are available, and it has a long history of usage in successful formulations world-wide. For direct compression processes like tableting, lactose excipients can be used as a filler-binder to provide bulk density, compaction and flow to the formulation. Good flow of a pharmaceutical formulation is critical to produce uniform dosage forms. In this study, the rheological properties of lactose powders have been investigated with a rotating drum method (GranuDrum, Granutools) and confronted with the actual consistency of mass flow achieved in a tableting system. The investigation of powder flowability at different drum rotating speeds gives useful information on the evolution of powder processability at a higher shear rate. Indeed, with the classical angle of repose characterization method, the stress state at which the powder is submitted is far from what the powder experiments in the tableting machine leading to wrong predictions of the processabilit

Thursday 11:10 Giralda 1-2 / Track 1

IP19

Influence of rheology and microscale on graphene-based inks in the gravure printing process

Ahmad Fakhari¹, Célio Fernandes², Laura Campo-Deaño¹, and Francisco J. Galindo-Rosales¹

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Printed electronics refers to the application of printing techniques to fabricate electronic structures, devices and circuits by processing a functional material (ink) from the liquid phase onto a substrate. Graphene-based inks are functional inks consisting of a dispersion of graphene nanoparticles in a carrier liquid, which represent the holy grail for printed flexible electronics. Among the plethora of printing techniques, gravure printing is ideally suited to printed electronics because it allows mass production and offers the possibility of producing high-quality patterns at micron-scale resolution. However, in spite of several research groups having demonstrated gravure-printed features larger than $10\mu m[2]$, few works have gone down to the $1\mu m$ range[3], and, to the best of authors' knowledge, never been for graphene inks.

In this study, we aim at clarifying the role of the shear-thinning behaviour of graphene inks in the transferring process of gravure printing when the length scale of the gravure cell scales down from millimetres to the order of microns. To do so the rheological behaviour of three commercial graphene-based inks was modelled with generalized Newtonian fluid models and 2D axisymmetric numerical simulations were performed by means of OpenFOAM with different gravure cell sizes. Results confirm that surface tension plays a more important role than shear thinning in what concerns the volume fraction transfer when the length scale decreases down to 1 µm range.

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Thursday 11:30 Giralda 1-2 / Track 1

IP20

Phototriggered curing of polyurethane adhesives based on o-nitrobenzyl-protected pentanediol and cadaverine precursors

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Over the recent decades, UV radiation technique has experienced a tremendous expansion in the coatings and adhesives fields owing to their advantages, including high production efficiency, low energy consumption, fast curing, and environment-friendly characteristics (Ge, Wang, Zhang, & Ren, 2018; Kim et al., 2022). In this work, UV-curing polyurethane adhesives (PU) were formulated from methylene diphenyl diisocyanate (MDI), 1.5-pentanediol (PD), 1,5-pentanediamine (cadaverine, CAD), and acetone as the adhesive carrier. In this study UV light-induced curing process of the synthesized PUs was controlled by blocking hydroxyl and amine functional groups with photolabile protecting group 6-nitroveratryloxycarbonyl (NVOC). The photo-triggered adhesive formulation was suitably optimized by assessing the impact of both

carrier content and NCO:OH:NH2 molar ratios on their ultimate rheological and adhesion properties. Thus, upon UV-irradiation (180 mW/cm2), small amplitude oscillatory time sweeps were conducted at room temperature to monitor the evolution of the curing process of the synthesized PU adhesives. The developed lap shear strengths on polyethylene terephthalate glycol (PETG) were also evaluated according to the standard mechanical test ASTM 1002. From this research, not only the proper control of the UV light-triggered curing process but also the strong effect of raw materials proportions on the mechanical response were corroborated. For an optimal ratio of reagents, the shear strength values raised to around 6.5 MPa, in combination with the concomitant substrate failure of the adhesive joint.

Thursday 11:50 Giralda 1-2 / Track 1

IP21

Characterization of the frequency and temperature dependency of the complex Poisson's ratio by combining axial and torsional measurements in a single rheometer

José Alberto Rodríguez Agudo¹, Christopher Giehl¹, Dominik Fauser², Jan Haeberle¹, Gunther Arnold¹, and Holger Steeb²

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Combining a linear and a rotational measuring drive in one rheometer enables the simultaneous determination of the complex Young's modulus (E*) as well as the complex shear modulus (G*) of a single sample in a continuous measurement. These harmonic measurements can be further combined with sweeps in frequency, temperature, or humidity ensuring that the sample is always under the same conditions when the test is conducted. This type of characterization is of interest for isotropic and homogeneous materials in that it is an indirect method to obtain the complex Poisson's ratio and its dependency on frequency and temperature (Tschoegl et al., 2002). We experimentally measured the complex Poisson's ratio of five different polymers using a combined torsional-axial rheometer. Two amorphous polymers, polycarbonate (PC) and polymethyl methacrylate (PMMA), a thermoplastic polyurethane (TPU), a blend of PC and Acrylonitrile butadiene styrene (ABS), and a thermoset (epoxyresin) were considered in this contribution. The tests were performed in a frequency range between 0.1 Hz and 30 Hz and in a temperature range that included the a-relaxation of each of the polymers. The real and imaginary part of the complex Poisson's ratio was inferred in terms of the extensional and shear response through the equations derived by Tschoegl et al. (2002). The results obtained for PMMA, PC, and PC + ABS were found to be in very good agreement with literature data from direct methods. Besides, data extrapolated from the master curve showed good agreement in frequency dependency with recent results for PMMA obtained using strain-gauges rosettes in the kHz regime. For the case of amorphous polymers, a non-monotonic increase of the complex Poisson's ratio with temperature was found. For the rest of the polymers, a monotonic increase in the complex Poisson's ratio with temperature was found. For the rest of the polymers, a monotonic increase in the complex Poisson's ratio with under the a-relaxation with increasing temperature.

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Thursday 12:10 Giralda 1-2 / Track 1

IP22

$Effects\ of\ poly(vinyl\ chloride)\ morphological\ properties\ on\ the\ rheology/aging\ of\ plastisols\ formulated\ using\ nonconventional\ plasticizers$

Sofia Marceneiro¹, Ana Dias¹, Irene Lobo², Isabel Dias², Elisabete Pinho², Hermínio C. Sousa¹, and <u>Maria da Graca Rasteiro</u>¹ *CIEPQPF - Chemical Eng. Department, University of Coimbra, Coimbra, Portugal;* ²*TMG Automotive, Vila Nova Famalicao, Portugal*

The automotive industry employs large quantities of synthetic polymers to manufacture flexible products like artificial leather. Poly(vinyl chloride) (PVC) is one of the most frequently used synthetic resins to produce artificial leather for automotive interiors due to its low cost and tunable capacity. PVC-based artificial leather materials are obtained by plasticization of the resin. The efficiency of poly(vinyl chloride) (PVC) plasticization depends predominantly on the strength of PVC-plasticizer interactions, which depend not only on the intrinsic physicochemical properties of the plasticizer but also on those of the polymer. In this work it was studied the influence of the morphological properties of different PVC grades (two emulsion and one microsuspension PVCs) and of nonconventional greener plasticizers on the rheological/aging properties of PVC-based plastisols. Commercially available castor oil based CITROFOL AHII and GRINDSTED SOFT-N-SAFE were employed as plasticizers, and the phosphonium-based ionic liquid (trihexyl(tetradecyl)- phosphonium bistriflamide ([P6,6,6,14][Tf2N]) as a coplasticizer. Plastisols formulated with the conventional plasticizer di-isodecyl phthalate (DIDP) were also prepared for comparison. Obtained results showed (E70-PVC) and the conventional plasticizer DIDP. The E70-PVC systems formulated using the lower molecular weight emulsion PVC grade (E70-PVC) and the conventional plasticizer DIDP. The E70-PVC systems formulated using DIDP and citrate-based plasticizer presented a pseudoplastic behavior, while all the other systems presented a Newtonian profile. Lower mixing enthalpies were calculated for PVC/DIDP systems, indicating more favorable interactions for PVC/phthalate systems over nonconventional plasticizers. The incorporation of [P6,6,6,14][Tf2N] ionic liquid, as a coplasticizer, significantly decreased the enthalpy of mixing of all the plastisols, favoring PVC/plasticizer interactions.

Symposium SM

Polymer Solutions and Melts

Organizers: Antxon Santamaría, Evelyne Van Ruymbecke and Moshe Gottlieb

Thursday 10:00 Santa Cruz / Track 2

SM17

Interplay of molecular weight distribution, drag reduction and degradation in shear for polyacrylamide

<u>Lukas Brandfellner</u>^{1,2}, Hans Werner Müller¹, Emina Muratspahic¹, and Alexander Bismarck¹

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Polymeric drag reducing agents are applied to reduce pumping costs, enable higher flow-rates and increase outlet pressure. Polymeric drag reduction (DR) is lowering the pressure drop along pipes associated with turbulence (Toms 1948). This is achieved by means of high molecular mass polymer addition. However, the use of these polymers is limited by mechanical degradation, which diminishes the molecular weight and therefore DR capability (Brostow, 1983). For polydisperse agents the highest weight-fraction provides the main contribution to DR but is also the most prone to degrading (Berman, 1977; Buchholz et. al. 2004).

The majority of current numerical models of DR does not account for mechanical degradation. Therefore, they are unable to simulate the long term behaviour of polymeric drag reducing agents in turbulent flow (Xi, 2019). Monitoring DR and molecular weight distribution in degradation experiments in parallel can link macroscopic and microscopic properties and provide valuable input for models. In this work, long term DR experiments with polyacrylamide have been performed in a pilot scale flow facility at high Reynolds numbers ($Re \approx 10^5$). Combining detailed molecular weight analysis and the flow parameters in fully turbulent pipe flow showed the importance of the heigh weight tail for an effective DR. This was especially pronounced after very long flow distances (up to 70 km) when the DR capability almost disappeared while the average molecular weight was still consideribly high.

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Thursday 10:20 Santa Cruz / Track 2

SM18

Linear viscoelasticity of unentangled and entangled linear supramolecular chains with sticky side groups

Alexis André¹, Filip Oosterlinck², Christian Clasen³, and Evelyne van Ruymbeke¹

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Among the wide variety of supramolecular systems, metallo-supramolecular polymers are of particular interest. In these systems, the strength of the bonds can be widely tuned by adjusting the density and the nature of the transition metal ions and/or the ligands. In addition, the metallic complexes can confer valuable magnetic, optical and catalytic properties. In this work, we analyze the viscoelastic properties of both entangled and unentangled linear poly(n-butyl acrylate) chains with terpyridine side groups randomly placed along the backbone. The amount and the nature of metal ions are systematically varied to investigate the tailorable properties of these systems. The network dynamics are assessed using Small Amplitude Oscillatory Shear (SAOS). The viscoelastic responses of our supramolecular polymers are subsequently modelled using the sticky-Rouse model and a tube-based time marching algorithm (TMA) model for the unentangled and the entangled systems respectively. We found that both models satisfactorily fit the data in the terminal regime and in the high frequency portion of the moduli. However, as already seen in the literature¹, a significant discrepancy from the theory still persists in the rubbery plateau regime. We attribute this deviation to the presence of structural defects in the systems. Consequently, we reduce the discrepancies of the models by including primary loops, which act as extra friction point for the Rouse motion of strands larger than the average spacing between two stickers.

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Thursday 11:10 Santa Cruz / Track 2

Keynote

SM19

"Tying the knot", enhanced recycling through ultra-fast entangling across ultra-high molecular weight polyethylene interfaces

Fotis Christakopoulos¹, Enrico Troisi², Nic Friederichs², Jan Vermant¹, and Theo A. Tervoort¹

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Joining of two solid polymer interfaces of identical monomeric composition has important practical applications, as it directly controls the quality of welding and plays a key role in determining properties of mechanical recycled products. It also has interesting theoretical aspects, e.g. related

to adhesion and self-diffusion of macromolecular chains. Ultra-high molecular weight polyethylene (UHMWPE) is a high-end engineering polymer and is the material of choice in numerous applications ranging from high-performance fibers and bulletproof panels to medical stents and bearing material for joint arthroplasty in hip, knee and shoulder replacements. However, the very features that lead to its exceptional properties, i.e. ultra-long macromolecular chains, render joining two surfaces of this material a tedious and slow process, leading to long welding times and impeding mechanical recycling of UHMWPE. A special feature of UHMWPE is that it can be produced through dedicated polymerization protocols in a disentangled state. The possibility of accelerating diffusion using these fully disentangled chains is explored and exploited in the present work. The time evolution of build-up of adhesive fracture energy in the molten state and the reduction in interfacial slip between two molten UHMWPE layers, reveal an order of magnitude increase of the rate of interpenetration compared to the dynamics of a regular UHMWPE-melt interface. This ultra-fast self-diffusion mechanism is insensitive to molecular weight, in contrast to reptation-driven diffusion, and provides a direct indication of the entropy-driven "chain explosion" upon melting of nascent disentangled UHMWPE. The usefulness of fast molecular stitching is demonstrated for enhanced recycling of UHMWPE.

Thursday 11:50 Santa Cruz / Track 2

SM21

Associative properties of poly(vinyl alcohol) solutions

<u>Daniele Parisi</u>¹, Colin D. Ditillo², Aijie Han², Lindberg Seth³, Mark W. Hamersky³, and Ralph H. Colby²

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In this work we performed intrinsic viscosity and flow curve measurements on a set of industrial poly(vinyl alcohol) (PVOH) samples, with varying degree of hydrolysis, molecular weight, concentration and solvent: water and dimethyl sulfoxide (DMSO). It is known that aqueous poly(vinyl alcohol) solutions exhibit clear features of associative polymers, and those significantly depend on the acetate content after hydrolysis. By introducing a "sticky-blob" model, applicable to any associating polymer solution with many stickers inside each correlation blob, we predicted the concentration dependence of the specific viscosity and the chain relaxation time in the entanglement regime. When PVOH polymers are dissolved in DMSO, a strong hydrogen bond acceptor, interchain associations are fully prevented for all relevant degrees of hydrolysis. The specific viscosity and the relaxation time of the chain recover the expected concentration dependence for non-associating flexible polymers. We concluded that the ratio between the terminal relaxation time of solutions in water and DMSO represents the time delay due to associations, and its concentration dependence was also well-captured by the simple sticky blob model introduced in this work.

Thursday 12:10 Santa Cruz / Track 2

SM22

Rheology of associating and non-associating Ethylene-Propylene copolymers in lubricating hydrocarbon oils Salvatore Coppola¹ and Maria Francesca Pirini²

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Ethylene-Propylene copolymers are frequently used as rheology modifiers of lubricating hydrocarbon oils. In this work, we first present an extensive set of rheological data obtained for our "standard" Ethylene-Propylene copolymers (EPR) in hydrocarbon oil. A range of solution concentration spanning from dilute to semidilute unentangled and entangled regime was explored. The results were rationalized based on the existing theoretical framework on polymer solutions. Such rationalization allows designing polymer grades for specific applications. Going beyond the "standard" EPR, we also investigated the rheological behavior of some experimental EPR samples modified by a reactive process developed with the aim of grafting functional polar groups along the chain. We investigated samples having different molar mass and varying levels of functional group addition. Both the polymer melts and the corresponding solutions in hydrocarbon oil showed, as expected, a complex thermorheological behavior. The extent of association or "physical crosslinking", due to van der Waals interaction between polar groups grafted on polymer chains, was characterized by means of rheological methods. A strong change of the rheological response of polymer solutions after exposure to different environmental conditions (humidity and temperature) was observed and analyzed in terms of linear and non-linear rheology. A stronger association effect on rheological properties was observed when functional groups were allowed to undergo hydrolysis reaction. After this reaction, the link between polar groups became even stronger (H-bonding). The reversibility of the association was also investigated. The experimental results of the associating samples in solution were compared with existing theoretical predictions by Rubinstein and Semenov for sticky reptation.

Symposium SP

Suspensions

Organizers: Francisco Rubio, Francisco Galindo-Rosales and Octavio Manero

Thursday 10:00 Nervión / Track 3

SP20

Alteration of the water-soluble organic carbon induced by a simulated rainfall and its effect on natural slurries' rheology

Raffaella Martone¹, Pasquale Marino¹, <u>Claudia Carotenuto</u>¹, <u>Emilia Damiano</u>¹, <u>Elio Coppola</u>², Roberto Greco¹, and Mario Minale¹ Department of Engineering, University of Campania Luigi Vanvitelli, Aversa, Caserta 81031, Italy; ²Department of Environmental Biological and Pharmaceutical Sc, University of Campania Luigi Vanvitelli, Caserta, Caserta 81031, Italy

Debris and silt flowslides are among the most worrisome natural hazards; many studies have been performed to prevent the effects of these disasters. Triggering and evolution of flowslides depend on several factors, and, on the microscale, one of them is the soil organic carbon (SOC) content. In previous studies, we analysed the stabilizing effect of the SOC on the rheology of natural soil-water slurries [e.g., Carotenuto et al., *Colloids and Surfaces A:*466, 57, 2015] showing that the sole removal of water-soluble SOC fraction or Dissolved Organic Carbon (DOC) significantly affects both the flow curve and the yield stress of the slurry. These two parameters may impact on flowslide propagation and triggering, respectively.

We here investigate if and how rainfall infiltration can alter the soil DOC fraction and the rheology of a slurry made of 40%v of this soil. We collected the soil from Cervinara (in an area in southern Italy frequently involved in shallow landslides often evolving in form of flowslides) and repacked it in a cylindrical vessel with a bottom draining area with the moist tamping procedure, so to guarantee the same porosity as of field condition. This system underwent to infiltration of simulated rainfalls with different intensities: 10mm/h, 20mm/h and 50mm/h, lasting until the hydraulic steady regime was reached. After each rainfall, the soil was collected and dried at 40°C, gently pestled and sieved to proceed with rheological tests. They were performed with a strain-controlled rheometer (ARES G2, TA-Instruments) equipped with a 4-blades Vane geometry. To exclude sample drying, the experimental cell was kept under a water-saturated environment. To account for the effect of soil particle sedimentation, a specific fast experimental protocol was performed. Rheological measurements were coupled with granulometry tests and measurements of the DOC content. The major effect of the rainfall infiltration was observed on the yield stress curve.

Thursday 10:20 Nervión / Track 3

SP18

Effects of confinement-induced non-Newtonian lubrication forces on the rheology of a dense suspension

J. Esteban López-Aguilar¹, Alan Rosales-Romero¹, Adolfo Vazquez-Quesada², Sagaya S. Prasanna Kumar³, and Marco Ellero³

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Modelling concentrated suspensions in particle-based methods is typically performed taking into account short-range Newtonian-approximation lubrication contributions [1], with instances of contact frictional forces [2]. From tribology, macroscopically Newtonian liquids under strong confinement exhibit significant deviation from their bulk behavior [3], in the form of strong thickening and shear-thinning when sheared within extremely small gaps. This is connected to the significant zero-shear-rate viscosity increase under extreme confinement reported in [4], rising several orders-of-magnitude over its bulk value, and which has been interpreted as a glass transition [5]. This supports the idea that a lubricant's fluid-like description is still appropriate under strong confinement. In this work, we assume a purely-hydrodynamic (frictionless lubrication) interparticle interaction description and explore the effects of confinement-induced non-Newtonian lubricant rheology on the material properties of concentrated suspensions. We start from and use the effective lubrication algorithm proposed in [1,6] and develop a new gap-size-dependent biviscous lubrication model able to capture qualitatively the main phenomenology of confined lubricants. In contrast to pure Newtonian lubrication interactions, distinct suspension viscosity thinning and thickening regimes are observed and discussed in terms of particle micro-structure and the lubricant rheology. In addition, normal-stress response is negative in both N1 and N2, which is difficult to achieve with contact frictional models.

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Thursday 11:10 Nervión / Track 3

SP19

Rheology of artists' paints: Study of oil-based mock-up paints containing egg yolk proteins

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Artistic painters have been using numerous ingredients as binders for preparing their paints, tuning their properties by varying their composition or the preparation technique. Proteinaceous binders, such as egg yolk, have been extensively used, especially until the end of the 15th century in Italy in a technique called "egg tempera". Studying artistic painting in order to help conservators and scientists in their quest of preservation and conservation of precious artworks in museums has been commonly performed using a top-down approach consisting on analytical techniques to identify the pigment and binder compositions. But very little work has been done in the study of the flow and physico-chemical properties of the prepared paints. Precise knowledge got lost probably when paint production became an industrial process and was not performed anymore by the artists themselves. This study, consisting of a preparation of various mock-up paints, will help to understand how egg yolk additions might have been used to manipulate the flow properties of oil-based paints. Also, several aspects such as the influence of the storage conditions of the pigments but also their particle size distribution and surface properties will be considered. Different types of oil paints containing egg proteins have been prepared and the study of their "impasto" has been monitored through yield stress, complex shear modulus and viscosity measurements. We will also discuss the importance of the paint preparation technique on both the microstructure and the drying kinetics of the obtained paint films.

Thursday 11:30 Nervión / Track 3

SP17

Concentrated suspensions of conductive particles as electronic flowing leads

Dominik S. Schmidt, Minh Q. Bui, and Lola Gonzalez-Garcia

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Today, most electronics and robots are based on solid metals and semiconductors. Here, we propose "Electrofluids", that conduct electrons while flowing, as an alternative to replace solid metal leads in truly soft devices. We formulate highly concentrated suspensions of conductive particles (carbon black and silver) in solvents with different polarity and viscosity. The idea is to create 3D networks of the solid fillers that allow for electron transport, in which the contacts between the particles are transient. The particles can move in the liquid and rearrange under mechanical stress.

We found that the concentration of the solid fillers required to achieve electrical conductivity in the material (percolation threshold) strongly depends on the shape of the particles. While the employed Ag particles are spheroids of 1-3 µm in diameters, C-black is made of fractal aggregates of primary particles with typical sizes of hundreds of nanometres. The concentration required to achieve electrical conductivity using Ag in liquid PDMS lay between 32 vol% and 35 vol%, which is almost an order of magnitude larger than for C-black.

We also observed that the polarity of the liquid matrix employed in the fabrication of electrofluids has a strong impact on the percolation threshold: 4.93 vol% and 0.41 vol% of C-black is required in PDMS and in Glycerol respectively; almost two orders of magnitude difference when comparing this last system with the mixture of Ag particles in PDMS.

We attribute these differences to the particle-particle and particle-solvent interactions that lead to the formation of strong or lose 3D particle networks. To understand the structure formed by the particles in the different matrices, we performed rheoelectrical measurements. A clear correlation between the changes in the electrical properties and the shape of the storage and loss moduli G' and G" was observed. We will exploit this behaviour and discuss the use of these materials as soft strain sensors.

Thursday 11:50 Nervión / Track 3

SP21

The influence of hexagonal boron nitride nanostructures on the xanthan gum rheological behavior

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Thus, this work aims the study of the rheology of hexagonal Boron Nitride (hBN) nanostructures dispersed directly in a polymeric solution. The intention is to analyze how these systems behave with the variation of parameters such as: concentration, temperature, pressure and time in order to obtain more efficient drilling fluids. The polymer matrix chosen was the xanthan gum aqueous solution in different concentrations of h-BN obtained through the liquid exfoliation method. The rheological properties of obtained materials were evaluated for a concentration range of 0 to 60mg/ml in a stress-controlled rotational rheometer Physica MCR501 with cone-plate geometry. The morphology and structure of the h-BN nanosheets were analysed using Zeta Potential, Dynamic Light Scattering (DLS), Scanning Electron Microscope (MEV), X-Ray Diffraction (XRD), Raman Spectroscopy, Fourier Transform Infrared (FTIR), Atomic Force Microscopy (AFM) and Thermogravimetric Analysis (TGA/DTG). The experimental results revealed the increase of h-BN concentration led to higher viscosity, all suspensions showed pseudoplastic behavior and energy storage capacity (G') higher than the capacity of the fluid to dissipate energy in form of heat (G''). The complete study of the mechanical behavior and nature of these fluids helps to investigate the rheological behavior of h-BN suspensions since the polymer matrix has a

rheological response dependent on nanoparticles interactions with the polymer chain. In this way, it is possible to study the behavior of the suspensions produced improving their rheological properties, optimizing processes such as drilling fluids, among others.

Thursday 12:10 Nervión / Track 3

SP22

Slip in soft permeable particles near a rigid wall

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Wall effects are unavoidable when processing dense suspensions of soft permeable particles such as in 3D printing of microgels for artificial cartilage. In this work, we demonstrate the possibility of dynamic stick-slip control via particle properties instead of wall-surface treatments. We present a poro-elastohydrodynamic (pEHD) lubrication theory for dense suspension flowing at different velocities near a rigid wall. The theory couples hydrodynamic pressure, elastic deformation of the particle, and flow through the permeable particle pores. We find that strong flows result in slip. However, for finite particle permeability, there is a critical particle velocity at which a portion of the particle meets the surface resulting in their sticky behavior. This sticking point is determined by the particle permeability and the ratio of viscous to elastic forces. In this case, the pressure in the lubricated film is lower compared to their impermeable counterpart sliding against a smooth surface at the same speed. The particle pores offer an alternative route for the fluid in the film, reducing the lubrication pressure resulting in the particle contacting the surface. A universal function is deduced to predict this slip-stick transition for a range of poro-elastohydodynamic interactions.

Symposium SG

Solids, Glasses and Composites

Organizers: Joamin Gonzalez-Gutierrez, Alexandra Aulova and Nadia El-Kissi

Thursday 10:00 Prado / Track 4

SG1

Relaxation processes in partially arrested soft matter

H. Henning Winter

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Soft solid matter typically contains a substantial fraction of mobile constituents besides the "arrested" components. While the arrested fraction dominates the long-time behavior and is characterized by an equilibrium modulus Ge, the "un-arrested" mobile fraction softens the overall behavior and gives rise to transient viscoelastic phenomena. The longest relaxation time, tau-max, associated with the mobile phase can be quite large, large enough to prevent a direct measurement of Ge. The relaxation of the mobile phase is constrained by the presence of the arrested constituents. An attempt will be made to extract the relaxation time spectrum of the mobile phase from experimental data of soft solids and express its properties separately from Ge. The discussion includes a crosslinked polymer in which the glass transition dynamics competes with the dynamics of the arrested fraction.

Thursday 10:20 Prado / Track 4

SG4

Powder rheological investigations of powder coatings in the fluidized state

Helena M. Weingrill¹, Christina Reichart¹, Timothy Aschl¹, and Denis Schuetz²

¹Department of Rheometry, Anton Paar GmbH, Graz, Styria 8054, Austria; ²R&D Rheometry, Anton Paar GmbH, Graz, Styria 8054, Austria

Powder coatings are dry powders typically consisting of a binder, pigments and flow aids. They are transformed into a film with heat once they are applied on the substrate. As they do not contain any volatiles, their application is part of the current strive towards greener engineering. They are applied when fluidized which means that the interparticle forces are overcome by an introduced volumetric gas flow. In this state, the powder ceases to behave like a bulk solid and acquires a dynamic fluid-like behavior. Thus, its rheological characterization in the fluidized state is crucial for optimizing the coating process. However, the rheological behavior is presumed to be highly dependent on temperature, considering powder coatings are mainly comprised of polymer particles. This leaves a many-sided rheological issue which needs to be examined in detail.

To imitate realistic coating conditions, a polyester-based powder coating in the fluidized state with different amounts of flow aid is characterized rheologically at elevated temperatures. The powder's fluidizability, its air-retention capacity as well as its viscosity in the fluidized state and cohesion strength are determined representing the most crucial properties for the powder coating process. Testing temperatures up to $50~^{\circ}$ C are applied to assess the impact of the polymer's imminent glass transition temperature.

All tested variables prove to be temperature-dependent. However, the fluidizability only depends on temperature when a flow aid is present. Thus, certain interactions between the polymer and flow aid particles are presumed. The viscosity of the fluidized powder additionally depends on the state of fluidization and the shear rate. Both, shear-thickening or shear-thinning behavior are detected depending on the applied volumetric gas flow rate for fluidizing the powder. The study demonstrates the high complexity of the powder coating technology and what solutions powder rheology offers for successful application.

Thursday 11:10 Prado / Track 4

SG3

Probing the mechanical properties of a weakly jammed granular packing through acoustic wave propagation in weightlessness

Adrien Izzet¹, Bruno Andreotti², and Éric Clément¹

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Made of a collection of solid particles, dense granular matter can either flow or be jammed. Granular media are ubiquitous, yet the understanding of their rigidity transition is still an open question. Theoretical and numerical studies (O'Hern et al. 2003) on frictionless particles have revealed anomalies in the evolution of the shear and elastic moduli near the unjamming: the shear modulus decreases faster than the bulk modulus at the approach of the rigidity transition. Both elastic moduli and the confining pressure follow power laws with respect to the distance to the critical volume fraction fc. While the nature of the interaction potential determines this exponent, it is now known that for frictionless particles, the ratio $G/K \sim \Delta f^{-1}/2 = (f-fc)^{-1}/2$ also scales as the distance to the isostatic number of contacts per grain Z-Z_iso. For real grains, the value of Z_iso is still debated (van Hecke 2010) and can be related to several physical characteristics of the particle interactions, especially the nature of the contact near the unjamming (De Gennes 1996, Goddard 1990), and the effect of microscopic friction (Ellenbroek et al. 2007, Magnanimo et al. 2008). In this study, we probe the nature of the contacts through acoustic measurements. We propagate planar waves through a packing of glass beads and by the mean of sound velocity measurements, we measure the evolution of the elastic modulus of the material with respect to the imposed confining pressure. Zero-G parabolic flights enable us to reach vanishing pressures close to the unjamming. We introduce a theoretical model for particle interactions and show that contacts are Hertzian at high pressures while they are dominated by the deformation of a soft superficial layer at vanishing pressures. We argue that this softshell characterizes the asperities at the surface of the grains and we verify its thickness with Atomic Force Microscopy which is consistent with that found by fitting our model to the acoustic measurements.

Thursday 11:30 Prado / Track 4

SG2

The yielding transition of soft glasses

Stefano Aime¹, Domenico Truzzolillo², David Pine³, Laurence Ramos², and Luca Cipelletti²

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Concentrated colloidal suspensions and emulsions are amorphous soft solids, widespread in technological and industrial applications and intensively studied as model systems in physics and material sciences. Soft solids are easily fluidized by applying a mechanical stress. Although the yielding transition has been actively investigated, no consensus on a unified description has emerged so far. Here, we investigate yielding in three classes of soft solids, using analytical and numerical modelling and experiments probing simultaneously the microscopic dynamics and mechanical response under oscillatory shear. We find that at the microscopic level yielding consists in a transition, sharper than for rheological quantities, between two distinct dynamical states. We propose a lattice model with dynamical coupling between neighboring sites that captures the generic features of our experiments, leading to a unified state diagram for yielding. Disorder in the dynamical coupling plays a major role in the emergence of first-order-like vs second-order-like features in yielding, allowing for reconciling previous contrasting observations on the nature of the transition.

Thursday 11:50 Prado / Track 4

SG5

Magnetorheological self-healing elastomers based on thermoreversible Diels-Alder networks

Kenneth Cerdan¹, Joost Brancart², Juan de Vicente³, and Van Puyvelde Peter¹

¹Soft Matter, Rheology and Technology, KU Leuven, Leuven, Belgium; ²Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Brussels, Belgium; ³F2N2Lab, Magnetic Soft Matter Group, University of Granada, Granada, Spain

Self-healing materials have been intensively studied as materials that can mimic the healing properties of biological systems, recently finding a strong interest in the soft robotics field. However, there is a strong gap between the mechanical properties of such actuators and their healing performance. The higher the mechanical properties of the self-healing robot, the stronger the external trigger conditions required to restore the material initial properties and performance, e.g. more elevated temperatures and longer healing times. This trade-off situation imposes a strong limitation for most of the reported self-healing materials previously studied. In this research, we have prepared for the first time magnetorheological self-healing elastomers based on thermoreversible Diels-Alder networks. The development of magnetorheological self-healing elastomers fills the requirements to integrate both high mechanical properties and high healing efficiency in a single system. When the magnetic field is turned off, the proposed systems have a soft behavior by formulating a network with a low crosslink density and high healing efficiency due to the greater polymer mobility under moderate temperatures. Upon the application of an external magnetic field, the embedded particles will orient in the direction of the applied field, thus generating a temporally reinforcing micro-structure within the matrix, enhancing both rheological and mechanical properties. Additionally, the thermoreversible systems mechanical properties can be tailored tuning temperature as an additional variable, thus achieving extra softness by heating the sample so higher magnetorheological effects can be achieved. This is the first time that thermoreversibility of dynamic polymer networks is exploited to achieve highly efficient and self-healing magnetorheological elastomers, being a promising source for the preparation and application of the next generation of stiffness-tunable and self-healing soft robotics.

Thursday 12:10 Prado / Track 4

SG6

Rheological characterization of humidity influences on thermoresponsive Shape Memory Polymers

Dominik Fauser and Holger Steeb

Institute of Applied Mechanics, University of Stuttgart, Stuttgart 70659, Germany

Shape memory polymers (SMPs) have the ability to preserve a reversible temporary shape and recover an initial shape under an external trigger (temperature, lighz, humidity etc.). This class of material offers great opportunities for intelligent solutions in soft robotics, aerospace and biomedical applications. However, differences in relative humidity may occur in the applications described. To account for these influences, we have developed a novel rheological characterization method to measure the temperature-, humidity- and time-dependent influences. For this purpose, the complex shear modulus is measured by iso-thermal and iso-humid frequency-sweeps with a torsional rheometer. For the iso-humid measurements, it must be ensured in advance that the diffusion processes at different humidities are taken into account and that the experiments are carried out in equilibrium. Therefore, diffusion measurements at different humidity influences are carried out in advance. The time-temperature superposition is applied in order to analyse the viscoelastic properties at different relative humidity. In terms of effective material properties, a key result of this study is the shift of material parameters in temperature space due to the presence of humidity. Thus, the humidity-dependent material behavior is fully described by a humidity-dependent glass transition temperature. The rheologically measured experiments provide a complete description of the thermal, humidity and mechanical behavior of SMP.

Symposium EM

Experimental Methods and New Advances in Rheometry

Organizers: Loic Hillou, Paula Moldenaers and Dimitris Vlassopoulos

Thursday 10:00 Arenal / Track 5

EM17

Modeling and optimization of magnetic tweezers design

<u>Alejandro Rodriguez-Barroso</u>, Guillermo Camacho, Oscar Martinez-Cano, Jose R. Morillas, and Juan de Vicente *F2N2Lab, Magnetic Soft Matter Group, University of Granada, Granada, Spain*

Microrheometry encompasses a set of rheometric tools for characterizing the rheological properties of soft materials at a local scale. In particular, magnetic tweezers (MT) have been extensively used in the past to study the mechanics of many soft biological materials and systems, generating large and controllable forces of the order of nanonewtons [1].

The pulling force exerted by a MT is proportional to the magnetic field strength as well as the magnetic field gradient. Such a force is generated by using electromagnetic circuits situated far enough from the sample so that provide a low variation of the magnetic field gradient. This results in roughly constant magnetophoretic forces -along the pathlines described by the magnetic probes- but a high-power supply to reach sufficiently large pulling forces [2].

In this communication we demonstrate that the magnetophoretic force can be substantially increased by simply placing magnetic nanostructured materials between the MT and the sample to locally modify the magnetic permeability and reluctance of the electromagnetic circuit. Interestingly, using this approach, both the magnetic field strength as well as the magnetic field gradient can be locally increased at will. In order to preserve the homogeneity of the pulling force over the region of interest, a detailed geometric and dimensional analysis of these materials is performed. Finite element method calculations are validated with experiments in a newly constructed MT in our laboratory.

References:

- [1] Furst E M and Squires, Oxford University Press. 2017
- [2] Piccolo, J G et al. Journal of Applied Physics. 2021, 130, 134702.

Acknowledgements:

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Thursday 10:20 Arenal / Track 5

EM18

Rheological characterization of microliter sized olefin block copolymers

<u>Daniele Tammaro</u>, Salvatore Costanzo, Gaetano D'Avino, Nino Grizzuti, and Pier Luca Maffettone *University of Naples, Naples, Italy*

We present linear and nonlinear rheological behavior of microliter sized olefin block copolymers (OBC) with different comonomer concentration aiming at the investigation of the effect of polymer structure on phase separation, the melt fracture and processability. The linear rheological behavior has been investigated by means of parallel plates with small diameters to reduce the amount of samples needed for each experiment and by performing continuous frequency modulated oscillations, such as "multi-wave" or "chirp oscillation" rheology to reduce the time needed for each experiment. Classical nonlinear high shear rate measurements are typically performed with capillary rheometers requiring kilograms of sample. To meet the requirements of a high-throughput approach, very recently, some of us developed a microcapillary device, uCR, that is a

simple and cost-effective rheometer for fast and reliable characterization of complex liquids that uses a small amount of fluid (i.e. few-milligram) and is capable of performing experiments in parallel to maximize data production rate. The reduction of experimental time is a relevant feature aiming at High Throughput-Rheological-Experimentation. The uCR allows for an optimal control of the polymer temperature and flow conditions on several decades of shear rates using from 2 up to no more than 50 milligrams of polymer. Furthermore, the flexibility of the new device design also allows for the characterization, in parallel, of other properties, such as surface tension, contact angle, and (possible) melt fracture of OBC. The collected information on OBC, linear and nonlinear rheological behavior, are compared to achieve deeper insights on polymer structure.

Thursday 11:10 Arenal / Track 5

EM19

Measurement and visualization of slip in rubber flow

Patrick Heyer, Christine Wurm, and Harald Ehrentraut

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Commercial flow simulations which are extensively used for process design in commodity plastics often fail when they are applied in rubber injection molding. The presence of slip in rubber rheology seems to be one of the influencing factors for this issue. A better understanding of slip of raw rubber as well as of filled compounds is therefore essential for later improved virtual process design.

The literature describes several methods to determine slip but the application of these methods on typical rubber rheometers is difficult, because of their limited functionality. On the other hand standard rheometers lack of the high torque performance to induce significant deformations into compounds.

The key for a better understanding of slip in rubber is therefore to use a combination of rheometers in slip optimized configurations in conjunction with a visualization. All together is essential to understand the mechanically measured data. The method as well as its application to raw rubber and filled compounds will be presented.

Thursday 11:30 Arenal / Track 5

EM20

Stress-controlled optimally windowed chirp rheometry (σ-OWCh)

Rebecca Hudson¹, Alex Holder¹, Michela Geri², Joshua Rathinaraj², Gareth H. McKinley², and Daniel Curtis¹ Swansea University, Swansea SA1 8EN, United Kingdom; ²Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States

Frequency modulated (chirp) waveforms have previously been applied to the linear viscoelastic characterisation of mutating materials using strain-controlled protocols (e.g. Geri et al., 2018). However, stress-controlled rheometric protocols are often more appropriate for strain sensitive or gelling materials. In the present study, we demonstrate an implementation of a stress-based chirp protocol (σ -OWCh) for the study of such materials. Stress-controlled experiments suffer from an inherent strain offset which, in conventional rheometry, can be removed using a baseline correction. However, in chirp based rheometry, removing the strain offset using a baseline correction of the strain signal is not straightforward. We demonstrate how this problem can be overcome by seeking the complex viscosity, $\eta^*(\omega)$, in place of the complex modulus, $G^*(\omega)$, before using σ -OWCh in the study of gelatin gelation.

Thursday 11:50 Arenal / Track 5

EM21

Measurement of both normal stress differences using two partitions and piezoelectric sensor

Thanasis Athanasiou, Nikolaos Kalafatakis, and Dimitris Vlassopoulos

IESL, FORTH, Heraklion GR-711 10, Greece

Nonlinear rheometry of viscoelastic materials such as polymer melts and solutions is technically demanding due to the intervention of edge fracture instabilities. By means of a partitioned plate fixture, i.e., an inner plate connected to the transducer and an external corona fixed on rheometer's chassis, one can significantly delay or even eliminate edge fracture in the inner measuring geometry. This provides the means to measure the shear stress over a range of shear rates. However, the presence of the partition makes the normal force measurement apparent, and to extract the first and second normal stress differences, two different geometries and/or loadings are needed. To bypass this cumbersome approach, which is also prone to errors, it has been proposed to use two partitions, the so-called CPP3 geometry. Earlier attempts were promising but measurements were too involved and with limited temperature control. In this work we propose a new method to measure the normal forces based on CPP3. While the outer corona mitigates edge fracture artifacts, the inner corona serves as a second fixture to measure the normal forces generated at shear start-up experiment. A piezoelectric sensor is coaxially mounted on the inner partition and the entire tool fit onto the rheometer's temperature control oven. The stiffness of the piezoelectric sensor rules out any force-rebalance complexities while its fast response provides also data in the transient regime. We discuss the design and implementation of this simple, robust tool and present some preliminary results demonstrating the proof of concept by ensuring the two normal stress differences in entangled polymer solutions.

References:

- [1] Costanzo, S. et al., Rheologica Acta. 2018, 57(5), 363-376.
- [2] Schweizer, T., & Schmidheiny, W. Journal of Rheology. 2013, 57, 841.

Thursday 12:10 Arenal / Track 5

EM22

Quantifying simultaneous first normal stress and shear viscosity at high shear rates via capillary rheology for different LDPEs

Masood Khabazian Esfahani¹, Christos Georgantopoulos¹, Ingo Naue¹, Joachim Sunder², and Manfred Wilhelm¹

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²GÖTTFERT Werkstoff-Prüfmaschinen GmbH, Buchen, Germany

First normal stress difference at low shear arte (e.g. $< 10 \text{ s}^{-1}$) is commonly measured in cone-plate geometry. The measurement is limited to low shear rates since the material either generates high torques which is beyond instrument threshold or the material gets out of the gap before the steady state condition. A slit-radial die named Karlsruhe die was recently introduced to measuring first normal stress difference and first normal stress difference coefficient via capillary rheometry at high shear rates, e.g. up to 10^3 s^{-1} . The die consists of two parts, namely the slit part and the radial part. The steady shear viscosity is measured in the slit part and first normal stress difference is measured in the radial part where the slit opens into a circular section. In this study, first normal stress difference coefficient is measured with Karlsruhe die for different LDPEs at high shear rates via capillary rheometry.

Symposium MN

Micro-, Nanofluidics and Microrheology

Organizers: Anke Lidner, Juan Francisco Vega and Amy Shen

Thursday 10:00 Giralda 6-7 / Track 6

Keynote

MN17

Numerical simulations of viscoelastic particle ordering in a microfluidic channel

Gaetano D'Avino and Pier Luca Maffettone

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The formation of equally-spaced structures of particles aligned at the centerline of a microchannel, commonly referred as "ordering", is desired in several microfluidics applications. This is the case, for instance, of the encapsulation of particles in droplets where the frequency of droplet formation must be synchronized with the frequency of particles entering the encapsulation area. Recent experiments have shown that fluid elasticity promotes the particle ordering mechanism. Specifically, particles suspended in a viscoelastic liquid first migrate towards the microchannel centerline. Once aligned, fluid elasticity induces an axial force between the particles leading to the formation of a microstructure characterized by a preferential interparticle distance. Preliminary simulations supported the experimental observations. In this contribution, we carried out extensive numerical simulations to investigate the effect of fluid viscoelasticity on the dynamics of particles aligned at the centerline of a microchannel. The train dynamics is computed by solving the particle motion equations where the particle velocities are taken from direct numerical simulations on a three-particle system. The evolution of the distribution of the interparticle distances is evaluated by varying the particle concentration, fluid rheology, flow rate, and confinement ratio, highlighting the effect of these parameters on the ordering efficiency.

Thursday 11:10 Giralda 6-7 / Track 6

MN19

Microrheology in anisotropic colloidal suspensions by dynamic Monte Carlo simulations

Fabián A. García Daza¹, Antonio M. Puertas², Alejandro Cuetos³, and Alessandro Patti¹

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Complex fluids are characterized with both solid and fluid properties by their elasticity and viscosity, or rheological behaviour. Recently, microrheology has been developed as an accurate technique to obtain rheological properties in soft matter from the microscopic motion of colloidal tracers used as probes, either freely diffusing in the host medium (passive) or subjected to external forces (active). In this work, we investigate passive microrheology in colloidal dispersions of rod-like particles in isotropic, nematic and smectic phases by dynamic Monte Carlo (DMC) simulations. The dynamics of a tracer particle in the host phase is monitored in order to access the linear viscoelastic response of the medium. In particular, a general relationship between the mean squared displacement of the tracer and the bulk rheological properties of the system serves as a measure of the elastic (G') and viscous (G") moduli. The effect of order in the host phase and the size of the tracer on G' and G" are discussed.

Thursday 11:30 Giralda 6-7 / Track 6

MN20

Understanding carbon-nanotube network formation in polymer-based nanocomposites

Alen Oseli, Mohor Mihelcic, and Lidija Slemenik Perše

Laboratory for Experimental Mechanics, University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, None Selected 1000, Slovenia

Anisotropic nature (rod-like geometry) allows carbon nanotubes (CNTs) to establish randomly connected web (network) in polymer matrices, which can be utilized as mechanical reinforcement or conducting pathway in numerous present and future-emerging technologies, from multifunctional structural elements to flexible electronic devices, sensors, etc. (Oseli et al., Macromolecules, 2021). However, functional performance of CNT-polymer nanocomposites mainly depends on the established network and its configuration (dispersed-high reinforcement, aggregated-high conductivity) driven by nanofiller geometry, content, as well as various mechanisms during nanocomposite productions (rupture, erosion, diffusion, etc.). Within this study, we report on the underlying physical principles of such network formation utilizing single-walled carbon nanotubes (SWCNT) in low- and high-density polyethylene matrices. Mechanisms were experimentally observed through plasma etching coupled with electron microscopy as well as rheological flow tests, where Doi-Edwards theory served as theoretical platform explaining particle behavior. Results showed, that established network is constructed from SWCNT bundles, which geometrically entangle at critical volume fraction Fv,crit (number of rods: ß~30). Below Fv,crit, bundles behave as individual units, mainly interacting with host material. However, above Fv,crit, the rotation of bundles is constrained by neighboring units, leading to random network configuration. This "meso-scale superstructure" exhibits long-range particle interactions which result in profound rheological changes (increase 0,rel for ~700×). Moreover, the theory successfully explains SWCNT bundle behavior as Brownian entity and predicts networks formation through diminishing thermo- and hydro-dynamically driven diffusion, which can be manipulated during the production to enhance reinforcing/conductive functional performance of such materials.

Thursday 11:50 Giralda 6-7 / Track 6

MN21

Imaging of the microstructure of Carbopol dispersions and correlation with their macroelasticity: a microand macrorheological study

<u>Claude Oelschlaeger</u>, Jonas Marten, and Norbert Willenbacher

Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany

We developed a new data analysis strategy, the so-called Micro-Rheo-Mapping technique, based on multi particle tracking (MPT) experiments to obtain an accurate and direct visualization of the microstructure of commercial acrylate thickeners of Carbopol-type with high (Ultrez 10), intermediate (ETD 2020) and low (ETD 2050) degree of crosslinking. At low polymer concentration, individual Carbopol microgels are formed comprising a highly crosslinked core of diameter 43, 56 and 10 µm for Ultrez 10, ETD 2020 and ETD 2050, respectively, surrounded by a shell of dangling polymer chains. For ETD 2050, the least crosslinked thickener, this shell is thicker than for ETD 2020 and Ultrez 10. At technically relevant polymer concentrations, our results indicate, for all three thickeners, that the microstructure is highly heterogeneous with regions of different crosslink densities. One region inaccessible for tracer particles corresponding to the highly crosslinked core and a second, diluted enough to be accessible and which exhibits both elastic and viscous characteristics. The study of the impact of pH, polymer concentration and crosslink density on these local structural and viscoelastic heterogeneities as well as macrorheological properties allowed us to establish a correlation between microstructure and macroelasticity. In particular, we found that the fraction of inaccessible area follows the same trend as the bulk shear modulus, making this microscopic parameter the most suitable for describing the macroelasticity of Carbopols.

Thursday 12:10 Giralda 6-7 / Track 6

MN22

Investigating the micro-rheology of an aging colloidal clay suspension using an optical tweezer

Rajkumar Biswas, Vaibhav Parmar, Anson Thambi, and Ranjini Bandyopadhyay

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Optical tweezers (OT) have been employed to measure pico-Newton forces acting on a colloidal particle trapped in a medium and can be used to successfully probe complex systems having fragile structures. In this work, we use an optical tweezer setup to study aging aqueous suspensions of Laponite clay particles of different concentrations. Laponite particles in aqueous suspension form fragile networks whose rigidities grow with time due to the gradual evolution of inter-particle electrostatic interactions. We study the displacements of a trapped micron-sized colloidal bead in a Laponite suspension medium during the evolution of the underlying structures. Analyzing the power spectrum, we demonstrate that the viscosity of the aging Laponite suspension increases with time. Furthermore, we perform active micro-rheology experiments wherein we apply a sinusoidal oscillation to the sample cell while keeping the particle trapped in the Laponite suspension. Simultaneously, the force response of the trapped particle is recorded during the controlled applied oscillation. The phase lag between the applied oscillatory signal and the force experienced by the trapped particle due to the oscillatory deformation is calculated. A range of frequencies is applied to estimate the elastic (G') and viscous (G'') moduli of the Laponite suspension over a broad range of time scales and at different suspension ages. It is found that G' is lower than G'' at the lower frequencies and eventually crosses G'' at a frequency that depends on the Laponite concentration. We next investigate the concentration- and aging-dependences of the fragile structures in Laponite suspensions of different concentrations using cryogenic electron microscopy. The average pore areas of these structures are seen to decrease with increasing Laponite concentrations. We show that the crossover frequency of G' and G'', obtained from micro-rheological measurements, is proportional to the average diameter of the pores in the Laponite gel measured using electron microscopy

Thursday Afternoon

Symposium GS

Gels and Self Assembling Structures

Organizers: Joao Maia, Domenico Gabriele and Juan de Vicente

Thursday 13:50 Giralda 1-2 / Track 1

GS33

Ageing study of Bentonite, Attapulgite clays and their mixture

Camille Boulet¹, Carl Formstone², and Dirk Aarts¹

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The ageing of clay-based gels is a burden for many industries: rheological properties change over time, syneresis (release of water at the top of the gel) may occur, as well as the collapse of the clay gels. Here, we study the ageing of bentonite, attapulgite, and their mixtures by means of rheology, since syneresis is observed for attapulgite clay, but not for bentonite clay. We mixed the two clays in equivalent proportion, and performed the ageing study over two months, during which samples were stored undisturbed at 50° C. The rheological measurements were performed using a vane rotor and comprised an oscillatory stress sweep followed by a creep recovery test. The storage modulus and the critical stress of bentonite and bentonite-attapulgite gels were fitted with the Leong model. However, this model could not properly fit the data obtained for attapulgite showing a much slower increase of G' at the beginning of ageing and a constant critical stress over two months. We found that G' for the mixture of the clays followed the same trend with time as bentonite, but at much higher values: interactions between the clays lead to a strengthening of the gel. The results from the creep test were fitted with a Burgers model and the evolution of the parameters G_0 , G_1 , η_0 , η_1 with time was followed (here, 0 refers to the Maxwell element, 1 to the Kelvin-Voigt element). Again, only the values of G_0 and G_1 for bentonite and bentonite-attapulgite could be fitted with the Leong model. A similar trend as for G' was found for G_0 , but the values obtained for G_1 for bentonite and bentonite-attapulgite showed no synergistic effect between the two clays. It was also found that the viscosity of the free dashpot increased much more with time than the viscosity of the dashpot of the Kelvin-Voigt element. These results will help in understanding and designing rheological properties of clays for use in industry.

Thursday 14:10 Giralda 1-2 / Track 1

GS34

Ascertaining universal scaling behavior in a thermoresponsive polymeric system

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The universality of critical scaling laws for sol-gel transition has been previously reported in the literature. In this work, we extend this approach to understand the gelation transition of a thermoreversible polymeric system under isothermal as well as non-isothermal conditions. We use an aqueous solution of poly(Vinyl Alcohol) (PVOH) which undergoes sol-gel transition while freezing and gel-sol transition on thawing. The hydrogen-bonded polymer segments lead to the formation of a space spanning percolated network as the temperature is gradually decreased and these segments participating in the network dissolve to bring about the gel-sol transition upon thawing. Interestingly, we observe sol-gel and gel-sol transition in PVOH solution to occur spontaneously under isothermal conditions. We validate the scaling relations for sol-gel and gel-sol transitions under isothermal and non-isothermal conditions, thus highlighting the universality of the scaling laws. We also investigate the kinetics of gel transition and examine the applicability of the modified Bailey criterion which has been widely used to study the kinetics of chemical crosslinking reactions and aqueous colloidal suspensions.

Thursday 14:30 Giralda 1-2 / Track 1

GS35

Self-diffusion, rheology and network topology of star-shaped associative polymer gels studied by Molecular Dynamics simulations

Jorge Ramirez and Javier Oller

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Recently a model has been proposed to understand the complex self-diffusive behaviour in unentangled associating polymers. The observed anomalous behaviour has been attributed to the existence of several diffusive mechanisms that act on different length and time scales. However, some of the predictions may be affected by the choice of a mean-field approach to represent intermolecular association. Here, we explore the same problem but using Molecular Dynamics simulations, using the Kremer-Grest model with explicit solvent, which fully takes into account fluctuations of the network, and a Monte Carlo algorithm to account for sticker association. We relate the topology of the network to the measured

values of relaxation modulus and self-diffusion, exploring concentrations from below the overlap to very concentrated solutions and analyzing the different types of defects that can be observed in the network.

Thursday 14:50 Giralda 1-2 / Track 1

GS36

Carbon-black assemblies in highly concentrated suspensions: Influence of the solvent polarity and solvent mixtures on the structure

Dominik S. Schmidt and Lola Gonzalez-Garcia

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Most common leads in soft electronics consist out of solid conductive materials. In our work, we use solid conductive fillers (C-black) dispersed in a liquid matrix, which remains in viscoelastic fluid state while still providing suitable electrical properties. The conductivity is ensured due to the transient percolation of the fillers at sufficient volume fraction. The structure of the filler network determines then both the electrical and the rheological properties of the material. Cheng et al. reported how the viscosity plays a role in the structure formation of C-black assemblies in liquid PDMS. (Rwei et al., 2002) Here, we introduce additional solvent parameters, like polarity, into the discussion. We found that using different types of liquid matrices influences the structure of the filler's network leading to a change of the percolation threshold. The usage of polar solvents, like glycerol, causes the non-polar carbon fillers to form large, room filling clusters, reducing the percolation threshold by an order of magnitude in comparison to their nonpolar counterparts like PDMS, which is in good agreement with the simulation results. (Coupette et al., 2021) We investigate the electrical properties of these mixtures in situ during rheological measurements by means a rheometer coupled with an impedance spectrometer and found a dramatic increase in the resistance at the loss modulus peak. Based on these results, more complex materials using two solvents were designed, inspired on the well-known double percolation systems from polymer blends. Mixtures combining a non-polar (preferential phase) and a polar solvent (non-preferential phase) render a constant electrical conductivity while the viscosity as well as moduli increase in comparison to the pure solvent systems. We will discuss the possibilities that this kind of materials bring to the field of soft electronics.

Thursday 15:10 Giralda 1-2 / Track 1

GS37

Viscous fingering in a non-Newtonian liquid radial displacement by oppositely-charged surfactant-polymer interaction

<u>Yorgos Stergiou</u>^{1,2}, Alexandros Perrakis^{1,2}, Behnam Keshavarzi^{1,2}, Aliyar Javadi^{1,2}, Kerstin Eckert^{1,2}, and Karin Schwarzenberger^{1,2}

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We investigated a miscible displacement of a less viscous liquid by a more viscous shear-thinning liquid in a Hele-Shaw cell. Due to a coacervation reaction between both liquids, a hydrodynamic instability appears in the form of inward viscous fingering. The liquids consisted of a solution of the anionic biopolymer xanthan gum, as the injection liquid, which displaced a cationic surfactant (C₁₄TAB) aqueous solution (Keshavarzi et al., 2019). In the contact zone between the two solutions, the oppositely charged species form polymer-surfactant complexes due to electrostatic interactions. The electrostatic and hydrophobic interactions between these complexes lead to a self-assembly process, forming a membrane structure separated from the main solution. During the continuing radial displacement, a large variety of patterns can emerge which is attributed to the rheological properties of the system involving viscosity gradients, the non-Newtonian nature of the displacing solution and the complex rheology of the coacervate phase. Variation of the flow rate and gap width of the Hele-Shaw cell revealed distinct instability regimes and allowed to identify main contributing mechanisms. These insights open the door for further investigation of fluid mechanics problems (i.e. Saffman-Taylor instability) (Saffman & Taylor, 1958) in multiphase systems of complex rheology and its applications in engineering and technology.

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Symposium NF

Non-Newtonian Fluid Mechanics and Computational Rheology

Organizers: Miguel Nóbrega, Baltasar Mena and Corneliu Balan

Thursday 16:00 Giralda 1-2 / Track 1

NF28

Drag reduction assisted emulsification in cross-slot microchannel

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An experimental study of the turbulent dynamics of emulsification in a cross-slot microfluidic device is presented. The continuous phase contains a minute amount of an inelastic polymer (xanthan). The Reynolds numbers are sufficiently large so the drag reduction phenomenon is observed during the emulsification process. The statistics of droplet sizes in the resulting emulsions are measured ex-situ by means of digital microscopy in a wide range of Reynolds numbers and polymer concentrations in the continuous phase. Integral measurements of the statistics of the pressure drops in the micro-channel allow one to systematically map the drag reduction states. Corresponding to each state, the space-time dynamics of the emulsification process are assessed by means of in-situ high speed imaging of the interface between the two fluids which further allows one to extract the characteristic time and space scales associated to the dynamics of the interface. Various dynamic regimes of the microscopic emulsification process are mapped in terms of the Reynolds number and shear thinning rheology of the continuous phase.

Thursday 16:20 Giralda 1-2 / Track 1

NF34

Filament-stretching dynamics of elastoviscoplastic materials

<u>Pantelis Moschopoulos</u>, Eleni Kouni, Yiannis Dimakopoulos, and John Tsamopoulos Department of Chemical Engineering, University of Patras, Patras, Achaia, Greece

The way a filamentous bridge of a yield stress material breaks when it is stretched is of paramount importance, for example in 3D printing, or inkjet printing. Although plasticity and elasticity were thought to be mutually exclusive, recent works [1, 2] demonstrate undeniably that both must be considered when the flow is predominantly extensional. Therefore, we undertake a computational study of the extension of an elastoviscoplastic material that is confined by two coaxial disks initially forming a cylindrical filament, when the disks are pulled apart. The rheological behavior of the material follows the Saramito-Herschel-Bulkley [3] model and yields according to the von Mises criterion. Assuming axial symmetry, the governing momentum and mass balance equations along with the stress constitutive model are solved numerically using PEGAFEM-V [4]. We monitor the evolution of the bridge shape, particularly its minimum radius, velocity, and stress fields. Our results indicate that elasticity prevails especially at the last stages prior to pinching. When the filament starts shrinking at an accelerating pace, the material elasticity starts to oppose the evacuation of the neck, thus an extended neck is formed like in filament-stretching of viscoelastic materials. This structure is also observed in experiments using yield stress materials, but it cannot be explained by ideal viscoplasticity because the latter excludes elasticity. Also, we perform a detailed parametric study by varying several parameters, such as the yield stress, the shear modulus, or the upper plate velocity. Finally, we investigate whether the decrease of the minimum radius exhibits a universal behavior during the pinch-off of elastoviscoplastic materials.

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- [4] Varchanis, Syrakos, Dimakopoulos, Tsamopoulos, JNNFM, 2020, 284.

Thursday 16:40 Giralda 1-2 / Track 1

NF35

Density unstable displacement of a Newtonian fluid by a viscoplastic fluid: Effect of buoyancy

Abdallah Ghazal and Ida Karimfazli

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Inactive oil and gas wells are often plugged using multiple mechanical or non-mechanical barriers. Non-mechanical barriers are often cement plugs placed at different positions along the well. The early stages of the plug placement involve pumping cement slurry through an injector in wells that are otherwise filled with lower density wellbore fluids. A buoyancy-driven displacement flow is, thus, likely to develop below the injector. While density unstable displacement flows in vertical pipes are well understood, they are relatively unexplored when the displacing fluid is injected from a tube inside the pipe. We develop a hydrodynamic model of the early stages of injecting cement slurry in a wellbore. Our objective is to characterize the displacement flow dynamics around the injector. We consider a two-dimensional domain where an injector is centralized in a channel. We model the wellbore fluid as a Newtonian fluid and the cement slurry as a viscoplastic fluid. We explore a wide range of Atwood numbers to investigate the role of buoyancy on flow dynamics. We identify diffusive and advective flow regimes. In the advective regime, a distinct finger of the viscoplastic fluid often develops below the injector. We characterize the interface shape and front dynamics. We also illustrate that the flow is reminiscent of a free fall when the Atwood number is close to unity.

Thursday 17:00 Giralda 1-2 / Track 1

NF36

Numerical study of particle suspensions in elastoviscoplastic (EVP) duct flows

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Elastoviscoplastic (EVP) fluids are ubiquitous in nature and industries, from biological fluids, food products such as chocolate and mayonnaise, slurries and drilling fluids, building materials, to pharmaceuticals and 3D printing. EVP fluids are often mixed with particles, which either move with the flow or be trapped in fouling regions; the interaction between EVP fluids and particles has not been well characterized. Here, we perform interface-resolved 3D direct numerical simulations (DNS) to study particle suspensions in a pressure-driven EVP duct flow. In particular, we investigate the effects of plasticity (Bingham number), elasticity (Weissenberg number), inertia (Reynolds number), and shear-thinning (flow index). The Saramito constitutive equation is applied to account for elastoviscoplastic stresses. EVP fluids behave like soft solids where the imposed stress on them is small (unyielded regions, below yield stress), and flow like viscoelastic fluids in regions where the imposed stress is large (above yield stress). We observe that different types of unyielded regions appear in the single-phase flow: a moving "plug" at the center and four static fouling regions at the corners of the duct. Unsteady structures, including secondary flows and re-circulation regions, are present, and their intensity increases with inertia and elasticity of the fluid. Furthermore, we observe particle migration depending on the particle inertia: particles with low inertia concentrate at the corners, while a uniform distribution of particles around the plug region is observed when increasing the particle inertia. Particles trapped in the unyielded regions do not migrate, and instead move with the same velocity as the plug region, as observed in our previous study of a single particle (Chaparian et al., 2020). A certain combination of elasticity and plasticity parameters is observed to facilitate particle deposition into the core plug region.

References

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Symposium SM

Polymer Solutions and Melts

Organizers: Antxon Santamaría, Evelyne Van Ruymbecke and Moshe Gottlieb

Thursday 13:50 Santa Cruz / Track 2

SM23

On the synthesis and dynamics of polymer networks formed by dynamic covalent bonds and moving in a sticky polymer matrix

Rowanne Lyons¹, Alexis André¹, Larissa Hammer², Renaud Nicoläy², Charles-André Fustin¹, and Evelyne van Ruymbeke¹ IMCN, BSMA, UCLouvain, Louvain-la-Neuve, Belgium; ²Chimie Moléculaire, Macromoléculaire, Matériaux, ESPCI Paris, Paris, France

Polymer networks are created by crosslinked polymer chains. These links can be either covalent (permanent) or non-covalent (reversible) with consequent effects on the material properties. Both types of networks have advantages and disadvantages: covalent networks resist flow and creep but are difficult to process and recycle, while non-covalent networks are reversible but susceptible to structural changes in the long term. In a class of their own, dynamic covalent bonds are a special type of covalent bond which undergo reversible exchange reactions under specific conditions such as temperature or pH, imparting them with the advantages of both covalent and supramolecular bonds.²

Our material, studied in the melt state, is based on two interpenetrating poly(n-butylacrylate) (PnBA) networks built from two types of reversible crosslinks with largely different dynamics. The first network, based on rapidly exchanging metal-terpyridine complexes, is densely crosslinked, and acts as the sacrificial network. The second, based on slowly exchanging dynamic covalent imine-aldehyde bonds, is sparsely crosslinked and maintains the structure of the double network under strain. Both types of crosslinks become more active at high temperature.

Due to the large difference in molecular weight and bond lifetime between the two base polymers and association types, the behaviour of our double networks can be separated into a high frequency regime dominated by the first network and a low frequency regime dominated by the second network. In this work, we show how to control the properties of the double networks by varying the crosslinking density of both the first and second networks. Analysis of the double networks through creep-recovery tests reveals a lower residual creep compared to the individual networks, and a greater recovery at high stress upon heating.

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SM24

Thursday 14:10 Santa Cruz / Track 2

What determines the drop size in sprays of polymer solutions?

Antoine Gaillard, Rick Sijs, and Daniel Bonn

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The fragmentation of a liquid sheet or jet into droplets is a complex process known as spraying which involves different hydrodynamic instabilities. Understanding how the droplet size distribution depends on external control parameters is particularly important in agricultural crop spraying where droplets typically smaller than 100 micrometers don't reach the target plants as they are blown away by the wind, causing environmental pollution. It has been shown that polymer additives could be used to reduce the amount of these aerosol droplets while also increasing the efficiency of droplet deposition on hydrophobic plants by reducing the amount of bouncing and splashing during droplet impact. In this experimental study, we investigate the effect of viscoelasticity on sprays generated from agricultural flat fan nozzles, which produce expanding liquid sheets, using dilute aqueous solutions of polyethylene oxide (PEO). Measurements of the droplet size distribution reveal that polymer addition to water results in the formation of overall bigger droplets with a broader size distribution. The median droplet size is found to increase linearly with the extensional relaxation time of the liquid and to be well captured by a simple empirical expression in terms of non-dimensional Weber and Deborah numbers. We show that this increase in droplet size can be partly attributed to an increase of the wavelength of the flapping motion responsible for the sheet breakup, resulting in the formation of larger ligaments from which droplets are formed. We also show that droplet size distributions are well described by a compound gamma distribution where the parameters encoding for the ligament corrugation and the width of the ligament size distribution saturate at sufficiently high polymer concentrations.

Thursday 14:30 Santa Cruz / Track 2

SM25

A study on the thixotropic response of a filled polymer melt system

Raviteja Miriyala¹, Abhijit P. Deshpande², and Parag Ravindran¹

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A general thixotropic elasto-viscoplastic (TEVP) material shows characteristics such as yield stress, shear thinning, structural breakdown and rebuilding under shear and structural re-building at rest. In order to study the phenomenological response and the associated microscopic mechanisms, a model material system which possesses the above features, is of value. Additional requirements on the system are that it exhibit negligible particle settling, solvent evaporation and chemical aging. A dispersion of fumed silica and polyisobutylene in paraffin oil is the most common model material system for TEVP materials in literature. In this work a new material system for study of TEVP materials is presented: a fumed silica filled polyethylene melt system that possesses yielding type behaviour at low shear rates followed by shear thinning behaviour at higher shear rates. In step shear rate tests, this material system exhibits a well-defined viscoelastic relaxation followed by structural breakdown/rebuilding. When compared to similar results for the paraffin oil system from literature, the signatures of viscoelastic and thixotropy are equally prominent. Using extant thixotropic models, viscoelastic and thixotropic timescales are examined in both the polymer melt and paraffin oil systems.

Thursday 14:50 Santa Cruz / Track 2

SM26

Rheological study and phase change behavior of adipic acid as a PCM for thermal energy storage at 150 °C Hazhir Fatahi¹, Sébastien Poncet¹, and Jérôme Claverie²

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The use of phase change material (PCM) in thermal energy storage applications can fill the gap between energy supply and demand in a sustainable approach. PCMs can store and release a high amount of thermal energy mostly through a transition from solid to liquid and vice versa. Due to the dependence of stored and released thermal energy on the PCM thermal properties, thermal characterization of PCMs is crucial. Most researches have studied their properties from a calorimetric perspective. However, considering the importance of natural convection and its dependence on viscosity, specially during PCM melting, a rheological study is deemed necessary for further numerical analysis. This provides the designer with realistic data to design a thermal storage system based on PCM (Delgado, Gschwander, Lázaro, Peñalosa, & Zalba, 2012). The present paper aims at studying the rheological behavior of adipic acid as an organic PCM with a melting point at around 150 °C for medium temperature range applications such as industrial waste heat recovery. One carries out a series of rotational and oscillatory tests under thermal insulation using a controlled stress rheometer (TA DHR-2) and a heat break plate geometry. The linear viscoelastic region of the PCM in both melted and transition states is determined and consecutive measurements are carried out in this region. Finally, comparing the rheological results obtained by oscillation temperature ramps with calorimetric heat flow results demonstrate the phase change profile of the material (Tipvarakarnkoon, Blochwitz, & Senge, 2008). Therefore, regarding the importance of determining an accurate phase transition range in PCM application, one compared the heat flow graph obtained by Differential Scanning Calorimetry (DSC) analysis to the rheological oscillatory test results. It is shown that the end of phase transition in rheology has a negligible dependency on the heating rate unlike in the DSC.

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Thursday 15:10 Santa Cruz / Track 2

SM27

Dynamics and structure of metallo-supramolecular polymers based on telechelic precursors

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We study the viscoelastic properties and the structure of polymer building blocks end-capped by terpyridine ligands. Adding metal ions in the samples leads to the formation of metallo-supramolecular junctions between the blocks and the formation of the transient polymer network [1,2]. Depending on the nature of the building blocks and on the amount of ions added to the system, phase-separation of the complexes can take place. In particular, we show that the difference in polarity between short telechelic hydrogenated polybutadiene (HPB) building blocks and the metalligand complexes leads to the phase-separation of the complexes into well-organized structures. By playing with the nature and amount of metal ions added to the system, with the temperature, as well as with the sample thermal history, we show that it is possible to modulate these associations and obtain a very rich range of properties. While increasing the density of metal ions leads to the sample reinforcement, it also causes decrease of its melting temperature. This result is linked to the structure of the sample, which is characterized, in specific conditions, by the co-existence of two lamellar structures, that we attribute to the co-existence of bis- and mono-complexes. The stability of these two lamellar structures is discussed, based on the structural evolution during several heating and cooling ramps. We also show that the usually observed lamellar structure can be changed into a hexagonal structure if a large excess of metal ions is added to the sample.

References:

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Thursday 16:00 Santa Cruz / Track 2

SM28

ABA triblock copolymers as precursors for transient double networks with multiscale viscoelastic response Clement Coutouly, Charles-André Fustin, and Evelyne van Ruymbeke

IMCN, BSMA, UCLouvain, Louvain-la-Neuve, Belgium

ABA block copolymers can form microphase-separated structures (lamellae, spheres...) in bulk or self-assembled into various structures (micelles, vesicles...) in a selective solvent of the A or B block. ABA block copolymers can form similar structures than their simpler AB diblock counterpart except that the ABA triblocks can form loops where the two A blocks are in the same domain, or form a bridge between two A domains, and this has a strong impact on the properties of the formed structures. This bridging can be used as reversible crosslink to form a network and yields thermoplastic elastomers (TPEs). Our objective is to study polystyrene-n butyl acrylate based triblocks (SAS) to determine a proper composition to obtain a thermoplastic elastomer with multiscale dynamics. Here, we report on the effects of the variation of the block length and temperature on the phase separation of the triblocks, and the impact on the viscoelastic properties. Precisely, we investigate SAS symmetric triblock copolymers and discuss the influence of different parameters such as the PS content, block length, and temperature on the material properties. We investigate the relationships between the structural properties obtained by SAXS and the linear viscoelastic properties obtained by rotational shear rheometry. From the peculiar micro-phase separation behavior of PS-PnBA-PS triblock, which increases with temperature, and the relationship between micro-structure and the linear rheological response, we design a PS-PnBA-PS thermoplastic elastomer which can form physical bonds at high temperature to create a stable network able to resist flow at elevated temperatures.

Thursday 16:20 Santa Cruz / Track 2

SM29

Polymer degradation and ageing of the poly(ethylene oxide) drag reduction reference system in long-distance turbulent pipe flow

Hans Werner Müller¹, Lukas Brandfellner^{1,2}, and Alexander Bismarck¹

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Since decades polymeric additives are used for drag reduction in many turbulent flow systems like pipelines, sewage systems, for fire fighting and for fracking. The shear forces in the turbulent flow break up the flexible, long-chain polymers which are required for drag reduction in turbulent flows (Horn & Merill, 1984). This mechanical degradation of the polymers diminishes their drag reduction capability in long term applications. The break-up mechanism is understood rudimentary only (Soares, 2020) as the whole polymer-fluid interaction in drag reduction. Related to the degradation are two major questions: how rapid does the polymer break-up occur? Will the degradation come to a stop before the drag reduction is fully lost? Brostow's model suggests such a behaviour (Brostow, 1983). We utilised poly(ethylene oxide) as drag reducing agent in water. The polymer degradation was followed up over more than 30km in a pilot-scale flow device at a Reynolds number of Re~10⁵. Beyond mechanical degradation in the flow, a second break-up mechanism was observed: polymer ageing which is a polymer degradation in time. Both processes cause a continuous decrease in drag reduction until a complete loss. We will present an empirical scaling for the polymer ageing and compare the experimental observations on the mechanical drag reduction loss to the Brostow model.

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Thursday 16:40 Santa Cruz / Track 2

SM30

Dynamics and rheology of polymer melts via hierarchical atomistic and coarse-grained simulations

Alireza Foroozani Behbahani¹, Anastassia Rissanou¹, Anthony Chazirakis¹, Petra Bacova¹, Manolis Doxastakis², Patrycja Polinska³, Craig Burkhart⁴, and Vagelis Harmandaris⁵

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The Computational prediction of the dynamical and rheologiacal properties of polymers is challenging because of the broad ranges of time scales and length scales involved in their motions. Here we present the results of atomistic and coarse-grained (CG) simulations for the dynamical and linear viscoelastic properties of cis-1,4-polybutadiene (cPB) melts. The CG model is parameterized based on the results of a finer level united atom model. At the CG level, few chemically bonded atoms are mapped into one CG bead. Therefore, the model is a moderately CG presentation which preserves the chemical identity of the underlying atomistic model. Furthermore, the nonbonded interactions of the CG model are hard enough to prevent chain crossings and hence the model preserves entanglement effects. The CG interaction potentials are derived by matching local structural distributions of the CG model to those of the atomistic model through iterative Boltzmann inversion. For matching CG and atomistic dynamics, the CG time is scaled by a time scaling factor, which compensates the lower monomeric friction coefficient of the CG model than that of the atomistic one. Time scaling factor is chain-length and temperature dependent, however, in phase with the chain length dependence of bulk density, it converges to a constant value for large chains. cPB chains of various lengths, covering the range from the unentangled to the moderately entangled regime are studied and the transition between these two regimes are analyzed. The simulation results are compared with the experimental data from the literature.

Symposium SP

Suspensions

Organizers: Francisco Rubio, Francisco Galindo-Rosales and Octavio Manero

Thursday 13:50 Nervión / Track 3

Keynote

SP23

Suspensions of plate-like particles with slip can display negative intrinsic viscosity

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One of the accepted features of suspension rheology is that the effective viscosity of a suspension of rigid particles increases with solid loading. Challenging this assumption by designing solute particles that reduce the viscosity of the solvent, i.e. negative intrinsic viscosity suspensions, would enable to add useful properties to a fluid without the penalty of increased friction and viscous loss. Through a combination of MD simulations and micro-hydrodynamic theory, we have demonstrated a new class of viscosity-reducing suspensions, obtained by a mere change of particle shape and a judicious selection of surface hydrodynamic slip properties and aspect ratio of the particles. Key features are a plate-like particle shape and a hydrodynamic slip length larger than the thickness of the particles. The effective viscosity reduction, consequence of the change in rotational dynamics of the particles (Kamal et al., *Nat. Comm.*, 11(1), 2020; Kamal et al., *J. Fluid Mech.* 919, 2021; Gravelle et al, *Phys. Rev. Fluids* 6(3), 2021), has been analysed in our group via i) numerical calculation of the (dilute limit) particle-stress for plate-like particles with Navier-slip at their surface, ii) molecular dynamics simulations of few-layer graphene nanoparticles in water and other solvents, and iii) dynamic multiparticle Boundary Integral simulations at increasing volume fractions. The results indicate that there is a practically realisable geometric and concentration range in which a suspension of plate-like particles can have a viscosity significantly smaller than that of the suspending fluid, and that this range may be realisable with suspensions of 2D nanomaterials such as graphene.

This work is supported by the European Research Council through grant n. 715475 (project FLEXNANOFLOW)

Thursday 14:30 Nervión / Track 3

SP25

Instability analysis of suspensions with a polymer solution matrix

Moritz Neukötter, Steffen Jesinghausen, and Hans-Joachim Schmid

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Selective laser sintering (SLS) is an additive manufacturing technique of which further development and spread is currently hindered mainly by the insufficient supply of new materials and improvements of material variability. To tackle problems like solvent resistance, flame retardance and rigidity, additives, fibers or additional particles can be used. The latter are often referred to as "Filled Material" and regarding SLS come with the challenge that particles have to be incorporated during the already difficult production of polymer powder. Two different approaches are mixing in the cold state and merging in the actual laser sintering process or admixing during production in novel manufacturing methods, such as

the filament extension atomization process. In filament extension atomization, individual polymer filaments are continuously stretched at large strain rates until instabilities form and decay into droplets even for strain hardening fluids. The process of instability formation can be described in some terms by Plateau-Rayleigh instability, but is often random and results in a broad droplet size distribution. At this point, solid particles can be used as some kind of precursor to generate specific instabilities and defined particle sizes, as well as coated particles for new applications. For the experiments, various polymers were dissolved in water and used as matrix fluid for suspension. In these solutions, monodisperse particles, among others hollow glass spheres of similar densities to the solutions, with different particle sizes were added at different concentrations. The timing of instabilities as well as concentration-dependent droplet sizes formed (both polymer and particle concentration-dependent) were investigated to address the question of whether the number and size of the droplets can be selectively adjusted.

Thursday 14:50 Nervión / Track 3

SP26

Rheology of a particle-laden soap film

Jonathan Lalieu, Georges Gauthier, and Antoine Seguin

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Particle-stabilized foams have proven to be promising candidates in the construction industry for their mechanicals properties, with gas marbles being able to undergo large over- and under-pressure, but their rheology has still to be understood. We investigate experimentally the behaviour of a 2D model suspension constituted of slightly polydisperse polystyrene spheres in suspension in a single film made of a tetradecyl trimethyl ammonium bromide (TTAB) and glycerol aqueous mixture of the same density as the particles. The particles being of a diameter greater than the typical film thickness (\emptyset 40 μ m), they cross both interfaces and the surface tension gives rise to cohesive interactions. An original double-ring geometry is used to perform stress-imposed rheometry with a narrow-gap and low-curvature configuration. These results are compared with local shear rate measured through image correlation. We show that, at dense particle fraction, the granular film exhibits a complex visco-plastic behaviour that differs from the one observed in usual bulk granular suspensions. In addition, the rheology of granular films is largely influenced by interfacial parameters such as surface tension and surface viscosity of the carrying fluid.

Thursday 16:00 Nervión / Track 3

SP28

Settling dynamics of Brownian colloidal chains

<u>Lucas Hildebrand Pires da Cunha</u>, Jingjing Zhao, Fred MacKintosh, and Sibani Biswal Chemical and Biomolecular Engineering, Rice University, Houston, TX 77030, United States

Understanding the settling dynamics of elastic filaments under the influence of thermal fluctuations is a problem of great interest in a vast range of fields, from transport mechanisms in microbiological systems to the rheological behavior of complex materials. The coupling between elastic, hydrodynamic, and Brownian effects induces rich dynamics of deformation, reorientation, and diffusion, directly impacting the micro and macro aspects of transport phenomena. In this sense, we investigate the sedimentation of elastic filaments under the effect of thermal forces using experimental, computational, and theoretical approaches. The filaments under consideration are composed of colloidal particles linked by filaments of DNA leading to bead-spring-like chains. Under the action of gravitational forces, the non-local hydrodynamic interactions cause the filaments to bend and rotate to get their end-to-end direction perpendicular to gravity. Different reorientation mechanisms are verified for different regimes of flexibility, characterized by the elasto-gravitational number. The thermal forces promote shape and orientation fluctuations around the steady configurations of the reciprocal non-Brownian chains. The competition between the reorientation mechanisms and the Brownian effects results in normal distributions of the orientation of the chains. These fluctuations may cause the chains to fall faster than their reciprocal non-Brownian cases. Moreover, flexibility also plays a key role in the lateral diffusion of the chains while sedimenting.

Thursday 16:20 Nervión / Track 3

SP29

Rheology of Amino-Functionalized Graphene Oxide Suspensions on Yield Stress Fluid

Lorena R. Moraes¹, Mônica F. Naccache¹, Ricardo J. Andrade², and Helio Ribeiro³

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The use of graphene and its derivatives for development of nanofluids shows promising results. A great potential for applications is in non-Newtonian fluids, due to its use in many diverse areas. Rheological characterization provides essential information for the processing and final application of suspensions [1]. Then, an attention must be given to the study of the rheology of graphene derivatives suspended in complex fluids. In this work, amino-functionalized graphene oxide (AFGO) was used [2]. This material contains oxygenated and nitrogenated groups in its surfaces and edges, which enable its high dispersibility and reactivity, and it can present negative and/or positive charges depending on the pH of the medium where it is dispersed. The base fluid used was the yield stress Carbopol aqueous dispersion. The effects of AFGO concentration and of system pH on the suspensions rheological properties are evaluated. The suspensions were characterized by zeta potential experiments, and steady-state and oscillatory rheological tests. The AFGO suspensions on Carbopol hydrogel with pH 7 showed decrease in viscosity, yield stress and storage modulus with increasing nanosheets concentration. AFGO facilitates the mobility between particles involved in the system, weakening the fluid's microstructure. Zeta potential results indicated that at neutral pH the surface charge of AFGO is negative, however the electronegative magnitude of charge of Carbopol macromolecules is of a higher order. Evaluations of AFGO suspensions in aqueous Carbopol systems under different pH values are conducted to investigate how the surface charge of AFGO nanosheets and of Carbopol macromolecules influence the rheology.

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- [2] Lima, M.C.F.S et al. Carbon, 109 (2016) 290-299.

Thursday 16:40 Nervión / Track 3

SP30

Effects of a non ionic surfactant on the rheology of colloidal suspensions

Antoine Aubel, Julie Goyon, and Xavier Chateau

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Dispersing agents are widely used in paste processing to preserve good rheological properties while increasing the solid content in blends. These chemicals are better known as superplasticizers in the cement industry. They are used to maintain the workability of fresh cement pastes having high particle volume fractions. This improvement enables to formulate concretes with lower carbon impacts by incorporating mineral additions such as industrial by-products (fly ashes, slag, silica fumes...), but also with higher mechanical strength and durability.

Despite dispersing agents are commonly used, the way they modify colloidal interactions and their impact on rheological properties are not yet fully understood. Such understanding requires to work with model systems which have properties that can be finely controlled. In this work, we experimentally study the influence of a non-ionic surfactant, which mimic superplasticizers, on both the yield stress and the shear elastic modulus of concentrated suspensions of silica beads and crushed quartz grains dispersed in an ionic solution of calcium salt. By combining rheometry, Total Organic Carbon, zeta potential, confocal microscopy and laser tweezers experiments, we show that variations of rheological properties scale very well with the surfactant adsorption on particles. Two regimes are then observed: one where the surfactant coverage is low and both the yield stress and the shear elastic modulus increase due to hydrophobic interactions; and another one where the surfactant coverage is high enough to induce steric repulsion which leads to a drop in rheological properties. Both regimes are currently assessed with laser tweezers to investigate how the surfactant modifies contact properties between particles.

Thursday 17:00 Nervión / Track 3

SP31

Stress relaxations upon flow cessation in dense soft sphere packings

Manon C. Marchand¹, Vinutha H. Anantharamai², Marco Caggioni³, Vishwas Vasisht⁴, Emanuela Del Gado², and Véronique Trappe¹

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We explore the state of dense packings of athermal soft spheres subjected to constant shear rates. Upon flow cessation, we observe that the stress relaxes to a finite residual stress.

Our investigations cover both experiments and simulations, where we vary the viscosity of the continuous phase. This enables to expose a striking difference between the transient relaxation and the final stress. While the stress relaxation process is *exclusively* determined by the shear rate applied before, the residual stress depends on the *viscous stress* defined as the product of the shear rate and of the continuous phase viscosity.

This discrepancy suggests distinct physical origins for relaxation processes and residual stresses, an observation providing clues for a better understanding of the microscopic processes occurring during the flow of soft particle dispersions.

Symposium SG

Solids, Glasses and Composites

Organizers: Joamin Gonzalez-Gutierrez, Alexandra Aulova and Nadia El-Kissi

Thursday 13:50 Prado / Track 4

SG7

Influence of biopolymeric fractions on rheological, mechanical and functional properties of rice bran-based bioplastics

María Alonso-González, Manuel Felix, and Alberto Romero

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Great efforts have been made to develop biodegradable plastics from renewable natural resources with the aim of producing biodegradable materials that resemble the behaviour of fossil-based polymers. Rice bran is an underutilized by-product of rice production, containing three main fractions: proteins, lipids and carbohydrates (mainly starches). They are generally able to form intramolecular and intermolecular interactions and cross-linking, forming a semi-rigid three-dimensional network. The whole rice bran fraction has already been used to manufacture bioplastics. However, the high oil content (18-22 %) may have a detrimental effect on bioplastic properties, where it is becoming increasingly attractive due to its variety of applications in the food, pharmacy and cosmetic industries. Moreover, as filler, fibre may also affect the rheological, mechanical, and functional properties of bioplastics. This work analyzes the effect of the different components of rice bran on the rheological properties of the final bioplastics, correlating it with their microstructure and functional properties (i.e., water uptake capacity, WUC). Rice bran refining was carried out by extracting the oil and fibre fractions. In this way, it was possible to establish a correlation between the rheological properties and

further mechanical and functional properties of the active matter employed and, thus, on the molecular interactions and the microstructure developed. The results revealed the beneficial effect of removing the lipid fraction on the rheological properties, exhibiting higher viscoelastic moduli that also led to better tensile properties, while decreasing the WUC and the soluble matter loss of the samples. However, no significant improvements were observed for systems produced from fibre-free rice bran, indicating that fibres can reduce the mobility of macromolecules, obtaining materials with lower frequency dependence (i.e., higher solid character).

Thursday 14:10 Prado / Track 4

SG8

Processing and mechanical behavior of extruded starch-protein composites

Imen Jebalia¹, Magdalena Kristiawan¹, Maria Charalambides², Samuel Humphry-Baker³, Sofiane Guessasma¹, and <u>Guy Della</u> Valle¹

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Extrusion is an efficient and versatile process for pulse-based food processing that leads to starch melting and protein aggregation. The texture of these extruded foods depends not only on their density and cellular structure, but primarily on the mechanical properties of the cell wall material, considered as a dense starch/protein composite material. This work aims to study the morphology and to determine the constitutive laws of this material. Dense pea-based composites of various composition (pea flour and blends of Starch/Protein: 2/1, 1/1, 1/2) are processed by twin-screw extrusion under various thermomechanical conditions, spanning an order of magnitude in specific mechanical energy (SME=102-103kJ/kg). Their viscous behavior, determined on a capillary rheometer with pre-shearing, depends first on S/P ratio, and resulting power law model can be used to simulate the extrusion, thanks to Ludovic® software. Various composite morphologies, dispersed and co-continuous, are evidenced by CSLM, and their images are quantified by (%) protein area and interface index. The mechanical properties of the composite depended not only on particle (protein+fibers) volume fraction and morphological features, but also on local mechanical properties of the phases and interphase, which were determined by nano-indentation. The experimental results are integrated in a finite element mechanical model based on composites microstructure. The model revealed a significant stress localization at the starch-protein interphase.

Thursday 14:30 Prado / Track 4

SG9

Extrusion instabilities in highly-filled wood fiber biocomposites

Sajjad Pashazadeh¹, Tobias Moberg², Anders Brolin³, and Roland Kádár¹

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Biocomposites are key industrial ingredients in the context of overarching societal efforts to promote and increase the use of renewable materials. Specifically, the use of wood fiber-based biocomposites as sustainable materials can lead to a significant reduction in the consumption of plastic materials and subsequently, much less carbon footprint. The processing of wood fiber biocomposites, and in particular, extrusion process is accompanied by multiple challenges among which agglomeration, entanglement, slippage, or surface instabilities are the most common ones. In the current work, we focus on the dynamics of surface instabilities during the (single-screw) extrusion of wood fiber biocomposites. The biocomposites are polypropylene based with up to 40% wood fiber content of commercial-grade (DuraSense®, StoraEnso) samples. To quantify the dynamics of surface instabilities, inline image analysis was applied using an optical visualization system positioned at the die exit. Therefrom, space-time diagrams were constructed, and thereafter via 2D-Fourier transform analysis the temporal and spatial periodicities of the surface instabilities were determined as function of the die shear rate (Weissenberg number, *Wi*) and moisture content of the biocomposites. The rheological properties of the biocomposites were assessed using rotational and capillary rheometry. In order to address the influence of slippage, the Mooney method was used in capillary rheometry. The results showed that while the neat polypropylene showed no surface distortions in the investigated *Wi* range, the biocomposites exhibited a form of surface-tearing instability present starting with the lowest *Wi* investigated that decayed asymptotically to the surface roughness with increasing *Wi*.

Thursday 14:50 Prado / Track 4

SG10

Topology and dynamics: The two faces of the mechanical reinforcement in crystallizable polymersMatthias Nebouy¹, Julien Morthomas¹, Claudio Fusco¹, Laurent Chazeau¹, Sara Jabbari-Farouji², and <u>Guilhem P. Baeza¹ INSA-Lyon, MATEIS, Polymer group, Villeurbanne, -, France; ²Institute of Physics, Johannes Gutenberg-University, Amsterdam, The Netherlands</u>

Quantifying the impact of crystallization on the mechanical properties of polymers remains a challenging problem. To address this question, we carry out coarse-grained molecular dynamics simulations of multiblock copolymers consisting of a linear succession of hard-(crystallizable) and soft-(amorphous) segments. This molecular architecture offers the opportunity to increase progressively the volume fraction in crystallites with the aim to study its impact on the elastic modulus that we compute via the Green-Kubo method (G(t)). By unifying these simulations with a recent mechanistic model and experimental data, we first evidence that the mechanical reinforcement at low crystallites content (< 8 vol.%) essentially originates from the network's topology. Above this threshold, we unambiguously show that the modulus is dominated by the amorphous phase dynamical slowdown. This works quantifies the role of the two pillars governing the mechanical properties of polymers that are topology and dynamics, and may be used as a basis in future studies addressing the description of more complex semi-crystalline homopolymers.

Thursday 15:10 Prado / Track 4

SG11

Dynamics and rheology in the vicinity of rough silica surfaces: Insight from the atomistic simulations

Petra Bacova¹, Alireza F. Behbahani¹, Craig Burkhart², Patrycja Polinska², Manolis Doxastakis³, and Vagelis Harmandaris⁴

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The understanding of the dynamics of polymer chains in the polymer/solid intephase region is the first step for the description and the prediction of properties of a wide family of commercially-used polymeric nanocomposites.

We employ atomistic molecular dynamics simulations to obtain an insight on the behavior of polybutadiene films confined within realistic amorphous silica surfaces. We show the coupling between polymer conformations and relaxation times, and we analyze both properties as a function of mutual polymer-surface positions and the chain length. The width of the polymer/silica interphase is estimated from static as well as dynamical properties. In contrast to the polymer behavior on ideal, perfectly planar surfaces, the perpendicular and lateral motions of the polymer chains in the vicinity of the rough surfaces are altered [1].

We also present a methodology for extracting the local stress relaxation moduli in the interphase, which is essential for the development of coarse-grained models operating at longer time and length scales.

References:

[1] Bacova, P., et al. Nanomaterials. 2021, 11, 2075

Thursday 16:00 Prado / Track 4

SG12

A cusp catastrophe model with disorder for the yielding transition of soft glasses

Domenico Truzzolillo¹ and Stefano Aime²

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Motivated by recent experimental findings in our group [1] on the microscopic features of the yielding transition in soft glassy materials under oscillatory strain, we introduce a simple on-lattice model in which the dynamics of mesoscopic portions of a glass result from both spontaneous and shear-induced relaxation processes, and from the coupling between the dynamics of neighboring sites. A mean field solution of the model yields a law of correspondent states equivalent to trajectories on a "cusp catastrophe" [2] manifold, a well-known class of problems, including first order phase transitions of real gases and involving an abrupt jump of the system state properties upon a continuous change of a control parameter, the strain amplitude here. We show that disorder in the coupling between neighboring sites is a key ingredient to obtain states in which fluid and glass portions of the system can coexist, determining the sharpness of the yielding transition. The fundamental aspects relating disorder and a reduced effective temperature, that serves as a measure of glassiness, will be finally discussed.

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Thursday 16:20 Prado / Track 4

SG13

From stiff to soft: glass characterization with dynamic mechanical analysis (DMA) up to 950 °C Matthias Walluch, José Alberto Rodríguez Agudo, Daniela Ehgartner, <u>Gunther Arnold</u>, and Christopher Giehl *Anton Paar GmbH*, *Graz*, *Austria*

Dynamic mechanical analysis (DMA) is a powerful method to characterize viscoelastic properties and phase transitions for a wide range of materials. It is often used to characterize polymers and their temperature-dependent behavior, including thermal transitions like the glass transition temperature Tg, via determination of storage and loss moduli in tension (Young's modulus, E) and torsion (shear modulus, G). While production and application temperatures for polymers are often limited to several hundred degrees, material properties of glasses usually require characterization at temperatures exceeding 600°C. The use of DMA by three-point bending and torsional measurements enables the characterization of glass with increasing temperature, from the solid, mainly elastic state up to the continuous transition into the viscoelastic state and associated softening. Viscoelastic materials show frequency-dependent mechanical behavior, which additionally allows the determination of relaxation times of primary (Tg) and secondary transitions. Three-point bending and torsional measurements on different glasses are presented, with E and G moduli as a function of frequency and temperature. In addition, multiwave measurements performed by superimposing simultaneous frequencies in a single temperature sweep are considered. This type of test results in a considerable reduction of the experiment time and allows to evaluate structural changes of the material and their frequency dependence at a given time of temperature. This contribution outlines the possibilities of DMA in tension and torsion for an extended temperature range. It allows the precise mechanical characterization of material behavior from room temperature up to the glass transition and the softening temperature interval. Compared to other thermo-analytical methods, like Dynamic Scanning Calorimetry (DSC), the frequency-dependence links measurement results (e.g. relaxation times) to real applications where mechanical stress is neglected.

Thursday 16:40 Prado / Track 4

SG14

Modelling creep behavior of PEEK at different temperatures using artificial neural networks

Alexandra Aulova^{1,2} and Marko Bek²

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Using neural networks (NN) for real-time structural health monitoring of polymer-based structures has advantages compared to existing methods. While existing structural health monitoring systems deal mostly with geometrical changes (cracks, delamination) NN can be trained to detect changes in material properties due to environmental conditions and time.

With this contribution we demonstrate the capabilities of Multilayer Perceptron (MLP) neural network for response prediction of time- and temperature-dependent high performance polyether ether ketone (PEEK) at different temperatures. We investigated two different shear stress loading conditions at different temperatures: constant shear stress rate [1] and harmonical shear stress excitation. Training data was obtained experimentally by means of rotational rheometer. This contribution covers experimental procedure for training data generation and neural network design steps, including training procedure, choice of data for better generalization and topology optimization. We have shown that proper choice of temperatures corresponding to training data is of crucial importance for behavior prediction quality.

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Thursday 17:00 Prado / Track 4

SG15

Linear viscoelasticity of PP/PS/MWCNTs composites: investigating of co-continuous morphology evolution and filler network stability during steady shear

Daria Strugova, Eric David, and Nicole R. Demarquette

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In this work, blends of two immiscible polymers, polypropylene/polystyrene containing different amount of multiwall carbon nanotubes (PP/PS/MWCNTs) presenting co-continuous morphology were prepared by melt mixing and characterized rheologically, morphologically, and electrically. Morphology probing small amplitude oscillatory shear (SAOS) tests and scanning electron microscopy (SEM) have been done before and after steady shear for the understanding of the dynamics of morphology evolution. The SAOS response was fitted to a model based on the estimation that the complex modulus of the co-continuous blends is a sum of components contribution and interface contribution (YZZ model) [1] to evaluate the change of morphology undergone by the different samples when subjected to steady shear. Electrical properties during steady shear were also evaluated using a rheometer coupled with an impedance-meter. The results obtained from both SAOS and SEM observations before any deformation indicated that, upon the addition of MWCNTs, the characteristic domain size of co-continuous PP/PS/MWCNTs decreases drastically, indicating that MWCNTs refined the morphology. Using the YZZ model, it was shown that MWCNTs could stabilize the morphology of a co-continuous blend once added at a certain concentration, the same behavior was observed for electrical conductivity.

References

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Symposium El

Emulsions, Foams and Interfacial Rheology

Organizers: Jan Vermant, Teresa Sanz and Mario Minale

Thursday 13:50 Arenal / Track 5

EI17

Response of a surfactant- and particle-laden bubble surface to asymmetric shear flow

Milad Eftekhari^{1,2}, <u>Karin Schwarzenberger</u>^{1,2}, Sascha Heitkam^{1,2}, Aliyar Javadi^{1,2} and Kerstin Eckert^{1,2}

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The shear stress of an axisymmetric flow field triggers a nonuniform distribution of adsorbed surfactants at the surface of a rising bubble. This creates a surface tension gradient that counteracts the viscous shear stress of the flow and thus reduces the mobility of the interface. However, in technological processes the flow field often is asymmetric, e.g. due to vorticity. Under such conditions, the interface experiences an unbalanced shear stress that is not free of curl, i.e. it cannot be compensated by the redistribution of the surfactants at the interface (Vlahovska et al., 2009).

Here, we conduct model experiments with a bubble at the tip of a capillary placed in a defined asymmetric flow field, in the presence of surfactants and nanoparticles. Unlike classical surfactants, nanoparticles adsorb irreversibly at the bubble surface. Thus, a different interaction between the bulk flow and the interface is expected.

In this study, we show a direct experimental observation of the circulating flow at the interface under asymmetric shear stress (Eftekhari et al., 2021a,b). The results indicate that the interface remains mobile regardless of the surfactant concentration. Additionally, we show that the nanoparticle-laden interface adopts a solid-like state and resists the interfacial flow upon surface compression. Our results imply that the immobilization of the interface can be described by the ratio of the interfacial elasticity to the bulk viscous forces.

References:

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Thursday 14:10 Arenal / Track 5

EI18

The effect of polymer chain flexibility on the interfacial viscoelasticity at the Air/Water Interface

<u>Daniel Ashkenazi</u>¹, Stelios Alexandris², Jan Vermant³, Dimitris Vlassopoulos², and Moshe Gottlieb¹

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Polymer laden fluid interfaces play a crucial role in many biological and industrial process. Exploration of the still poorly understood interplay between polymer molecular characteristics, polymer organization at the interface, and their effect on the mechanical properties of the interface is a prerequisite for a proper design for multitude of interface dominated processes. In previous observations we found that large variations of polymer chain flexibility results in significant differences both in interfacial rheology and microstructure. Flexible polyacrylates such as poly(n butyl acrylate) were found to have microstructure composed of discrete islets of polymer, with no discernible rheology of the interface. Whereas interfacial rheology measurements for relatively rigid polymethyl acrylates such a poly(tert-butyl methacrylate) show a transition from a liquid-like to elastic solid-like interface and uniform sheet morphology. In this contribution we focus on the rheological properties of the elastic films formed by several high Tg polymethyl methacrylates with Tg ranging from 35 to 150°C. We will illustrate how gradual decrease in flexibility affects the evolution of the liquid-to-elastic transition and on the resulting elasticity of the films at the air/water interface. A combination of classical rectangular Langmuir-Pockels trough, Brewster's angle microscope, and interfacial shear rheometers have been employed.

Thursday 14:30 Arenal / Track 5

EI19

Nonlinear interfacial strain profiles and constant strain operation modes in the magnetic needle ISR Pablo Sánchez-Puga¹, Juan M. Pastor², Miguel A. Rubio¹, and Javier Tajuelo³

Table Saichez-ruga, Juan W. Paster, Wilguer A. Kubio, and Javier Tajuero

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A common issue to all the shear rheometry techniques, no matter whether we talk about bulk or interfacial systems, is trying to have well controlled shear profiles across the sample. In bulk rheometry the long history of this problem goes back at least to the discussion on the gap/surface-loading conditions in bulk shear rheometers [1]. Since then, it is well known that both fluid and instrument's probe inertia play an important role in this concern.

In interfacial rheometry the problem is even more complex due to the probe inertia [2] and the coupling of the interfacial and bulk subphase flows [3-5], so that nonuniform interfacial strain fields may be the rule rather than the exception [5-7].

Since strain is used as the parameter to characterize the deformation of the interface, the question arises immediately: what strain value characterizes the interface state if the interfacial strain field in the sample is not uniform?

Using the magnetic needle ISR [8] as experimental platform and fatty alcohol Langmuir monolayers as model systems, here we discuss and compare the nominal strain (the probe amplitude to the shear channel width ratio) with the local strain at the probe's rim. We discuss how the local strain can be used as the control parameter in experiments. Moreover, we show that the constant local strain operation mode yields a much smaller span of the local strain field, therefore assuring smaller strain gradients and a better rheological condition of the sample.

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Thursday 14:50 Arenal / Track 5

EI20

Interfacial rheology of crowded phospholipid monolayers shows a fluid behaviour

Damian Renggli and Jan Vermant

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The membrane fluidity of phospholipid bilayers plays a central role in many biological processes, e.g. for cell homeostasis. These membranes not only compartmentalize the cytoplasm and various organelles in eukaryotic cells, but they are also relevant for cell signalling where fine-tuning of the membrane fluidity is a necessity. Furthermore, the formation of metastatic cancer cells relies on an increase in membrane fluidity, which represents just one of many diseases related with membrane fluidity dysfunction. Phospholipid monolayers-one leaflet of the lipid bilayer-not only serve as model materials for bilayers but have a relevance of their own as they coat the alveoli in the lung. Therefore, phospholipids are used in pulmonary lung surfactant replacements to prevent lung collapse in premature infants (neonatal respiratory distress syndrome) as well as in adults. We investigate monolayers of various phospholipids at buffer-oil interface, controlling temperature and surface pressure relevant for cell membranes. The linear viscoelastic regime is probed with oscillatory interfacial shear rheology by the interfacial needle stress rheometer (ISR), which is a macroscopic technique.[1] The lipid mixtures under investigation consist of phosphatidylcholines with saturated (palmitoyl) and unsaturated (oleoyl) fatty acids leading to different melting temperatures of the hydrophobic tails. At sufficiently high surface pressures, the saturated lipids pack efficiently and form liquid condensed phases in a continuous liquid expanded matrix. The area fraction of the liquid condensed phase is measured simultaneously to the rheology by a custom fluorescent microscope mounted on the ISR. We conclude that the interfacial viscosity does not diverge with increasing area fraction of condensed phase compared to a Brownian hard disk system and the interface maintains its fluidity even at very large area fractions of the liquid condensed phase.

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Thursday 15:10 Arenal / Track 5

EI4

Rheological characterization and processing optimization of lemon oil nanoemulgels for the encapsulation of vitamin ${\bf E}$

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A nanoemulgel-based delivery system formulated with lemon oil was developed for the encapsulation of vitamin E. Firstly, in order to evaluate the interfacial and emulsifying properties of Tween 80, interfacial rheology at lemon oil/water interface was investigated. From surface pressure isotherm and interfacial rheology measurements of Tween 80, a maximum surface concentration and a limiting elasticity have been obtained. In the second step, the development of nanoemulsions by microfluidization, the influence of primary homogenization rate, microfluidization pressure and number of cycles on mean droplet sizes and polydispersity have been studied and analysed by response surface methodology. Minimum mean droplet diameter was obtained for an optimized emulsification process using 6000 rpm at the primary homogenization and 21000 psi and 5 cycles at the Microfluidizer 110P. Lastly, a fumed silica (Aerosil 200) was used as a thickener to modify the rheological properties of the nanoemulsions and hence, to improve their physical stability. In this sense, nanoemulgels were developed by adding different concentrations of the fumed silica to the optimized nanoemulsion. The rheological characterization demonstrated that all nanoemulgels formulated with more than 3 wt.% of fumed silica presented a very shear-thinning behavior. In addition, viscoelastic properties increased with Aerosil 200 concentration. G' (elastic modulus) was higher than G" (viscous modulus) in all the frequency range studied for all nanoemulgels presented. These systems showed very little frequency dependence and they do not exhibit G' and G" crossover point. The resulting vitamin E-loaded nanoemulgels successfully protected the encapsulated bioactive ingredient during the storage period. The characterization of these systems involved droplet size distributions, Cryo-SEM and optical microscopy, flow and oscillatory shear tests, as well as multiple light scattering.

The financial support received (Project US-1380760, I+D+i FEDER Andalucía 2014-2020) from the Junta de Andalucía (Consejería de Economía, Conocimiento, Empresas y Universidad) and the European Commission (FEDER Programme) is kindly acknowledged.

Thursday 16:00 Arenal / Track 5

EI22

Fingers formation and oscillatory Kelvin-Helmholtz instability in miscible fluids

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Hydrodynamic instabilities in stratified immiscible/miscible fluids are common in natural phenomena and in industrial and technological applications [1], as spin coating processes [2]. The interface between two phases has well-defined physical features which influence the instability onset. In spin coating processes, there is an air/liquid interface and centrifugal force is applied to accelerate viscous thin films spreading. If the flow is not axisymmetric, edges became unstable and the fluid flows preferentially through radial fingers [3]. Miscible stratified systems with low diffusion, in which there is a well-defined interface between the two phases, have received scarce attention so far. In these systems, stabilizing effects due to surface tension are missing. We here report the observations of a novel radial fingering instability, which is different from what we found in the literature. We studied a stratified system made of Polydimethylsiloxane (PDMS) and acetone under alternating rotation around the

central container axis. We observe a Kelvin-Helmholtz instability [4] due to shear stresses acting on PDMS interface. Under certain conditions, the formation of radial, finger-like protrusions is observed. In the oscillatory experiments, the Kelvin-Helmholtz instability creates the typical superficial waves, from where the fingers start and propagate due to the centrifugal force. We found a clear relationship between Kelvin-Helmholtz instability and the number and dimension of fingers. The destabilization scenario is also supported by theoretical predictions.

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Thursday 16:20 Arenal / Track 5

EI23

Emergent patterns and stable interfaces during radial displacement of a viscoelastic fluid

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The displacement of a more viscous fluid by a less viscous fluid renders the fluid-fluid interface unstable and leads to intricate patterns called viscous fingers. Since the fluids experience shear during displacement, it should be possible to influence the emergence of patterns and instability dynamics through control of rheological parameters, such as elasticity or relaxation time in case of a viscoelastic fluid. In this article, we record and analyze the interfacial fingering patterns that emerge when a Newtonian fluid (glycerol-water mixtures of different viscosities) displaces a shear-thinning viscoelastic fluid (aqueous cornstarch suspensions of varying concentrations) in a radial Hele-Shaw cell geometry. While Newtonian-non-Newtonian fluid pair displacements have drawn attention of researchers in the past, the current work showcases the various regimes of emergent patterns over a wide range of viscosity ratios of the two fluids, and the effect of fluid elasticity on the rate of its displacement. As the ratio of viscosities of the inner and outer fluids is increased, radial branched patterns are replaced by more stable interfaces that display finger coalescence. Increasing the viscosity of the displacing fluid and the concentration-dependent elasticity of the outer viscoelastic fluid both lead to significant suppression of interfacial instabilities. A linear stability analysis of the interface, using viscosity ratio as the only control parameter, is employed to predict the dominant wavelength of interfacial perturbation. The perturbation wavelength computed numerically is found to match closely with the spacing between fingers measured experimentally at the onset of interfacial instability. It is suggested that control of instabilities during miscible displacement of a viscoelastic fluid (mud slurries, for example) by a Newtonian fluid has implications in material processing, such as in ensuring minimal mixing of phases while maximizing sweep efficiency during material recovery.

Thursday 16:40 Arenal / Track 5

EI24

Probing the elongational behaviour at interfaces of immiscible polymer systems using the dilational tensiometry: Effect of viscosity and temperature on the interfacial rheological properties

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The study of 2D rheology of polymer systems represents tremendous importance in many plastic processing fields such as coextrusion, foaming, melt blown extrusion and additive manufacturing. For all these processes, probing in a direct manner the rheological responses of such stretched surfaces/interfaces represents a high scientific and technological challenge. In the present work, interfacial dilational rheology testing based on the rising oscillating drop method was used to probe surface (and interfacial) properties of model polymer melts based on polyisobutylene (PIB) and polydimethylsiloxane (PDMS). Firstly, dilational rheology measurements of air-polymer and polymer-polymer systems in both oscillatory and static drop regimes were carefully corrected, considering the inertia and the contribution of the subphases viscosities during the processing of the numerical data. The effect of molecular weight and temperature on the resulting interfacial properties was also examined. It was found that from a specific viscosity the formation of an interphase was demonstrated, confirming short chains diffusion at the interface between coexisting components. Secondly, a new method was developed to extract dilatational relaxation times of the studied polymer systems based on a straightforward square pulse relaxation test. The activation energy was assessed based on the Arrhenius law. A comparison with the Capillary Breakup Extensional Rheometry revealed similar overall values than those obtained with the pulse method. Finally, using interfacial shear rheology, an attention was paid to highlight the Trouton correlation between shear and dilational surface rheology. A link between shear surface viscosities and elongational relaxation times was evidenced for the first time and over the entire viscosity range studied.

Thursday 17:00 Arenal / Track 5

EI25

Heterogeneous viscoelastic fluids in porous media

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In pharmaceutical, polymer or petrol industries, correct mixing of heterogeneous non-Newtonian fluids plays a key role on the features exhibited on their final products. The complex rheology of viscoelastic fluids, i.e. long relaxation times, shear-thinning or shear-thickening behaviours lead to complications for an efficient mixing.

Therefore, we study the effect of passive homogenization by injecting a diphasic viscoelastic fluid through a channel with a porous section which will disperse and/or break the inclusions. We use shear-thinning polyacrylamide solutions composed of two phases at different concentrations so

as to study a wide range of viscoelasticity contrasts (relaxation time of the matrix higher, lower or the same than the inclusion's relaxation time). Then, we explore the mixing performance of the porous medium at different shear rates for all these cases by characterising the aspect of the inclusion after it went through it.

Two main outcomes are found: (1) the inclusion breaks into smaller pieces or (2) the inclusion stays as a whole without any apparent effect after the porous media. At a given inclusion size, the limit between these two behaviours is perfectly delimited by a constant Weissenberg number which suggests that it is the elasticity of the inclusion which controls the process. When reaching the obstacle, the inclusion either (1) divides or (2) elongates and then reforms after passing the obstacle. This behaviour implies, rather counterintuitively, that lower shear rates lead to a more efficient mixing of the diphasic viscoelastic fluid by more efficient fragmentation of the inclusion.

Symposium MN

Micro-, Nanofluidics and Microrheology

Organizers: Anke Lidner, Juan Francisco Vega and Amy Shen

Thursday 13:50 Giralda 6-7 / Track 6

MN23

Identification of the thermal response of confined fluids to mechanical shear deformation

Laurence Noirez, Eni Kume, and Patrick Baroni

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Anisotropic nature (rod-like geometry) allows carbon nanotubes (CNTs) to establish randomly connected web (network) in polymer matrices, which can be utilized as mechanical reinforcement or conducting pathway in numerous present and future-emerging technologies, from multifunctional structural elements to flexible electronic devices, sensors, etc. (Oseli et al., Macromolecules, 2021). However, functional performance of CNT-polymer nanocomposites mainly depends on the established network and its configuration (dispersed-high reinforcement, aggregated-high conductivity) driven by nanofiller geometry, content, as well as various mechanisms during nanocomposite productions (rupture, erosion, diffusion, etc.). Within this study, we report on the underlying physical principles of such network formation utilizing single-walled carbon nanotubes (SWCNT) in low- and high-density polyethylene matrices. Mechanisms were experimentally observed through plasma etching coupled with electron microscopy as well as rheological flow tests, where Doi-Edwards theory served as theoretical platform explaining particle behavior. Results showed, that established network is constructed from SWCNT bundles, which geometrically entangle at critical volume fraction $\Phi_{v,crit}$ (number of rods: $\beta \approx 30$). Below $\Phi_{v,crit}$, bundles behave as individual units, mainly interacting with host material. However, above $\Phi_{v,crit}$, the rotation of bundles is constrained by neighboring units, leading to random network configuration. This "meso-scale superstructure" exhibits long-range particle interactions which result in profound rheological changes (increase $\eta_{0,rel}$ for $\sim 700\times$). Moreover, the theory successfully explains SWCNT bundle behavior as Brownian entity and predicts networks formation through diminishing thermo- and hydro-dynamically driven diffusion, which can be manipulated during the production to enhance reinforcing/conductive functional performance of such materials.

Thursday 14:10 Giralda 6-7 / Track 6

MN24

Electrorheological characterization of vegetable oil and nanoparticles based ecolubricants

<u>Samuel David Fernández-Silva</u>, Claudia Roman, Moisés García-Morales, and Miguel Ángel Delgado Departamento de Ingeniería Química, Pro2TecS, Universidad de Huelva, Huelva 21071, Spain

Newest lubricants based on more sustainable constituents are known to be taking part in current developments, while facing stricter environmental policies. In this context, the present research aims to explore nanoparticles-based ecolubricants with tunnable properties under the action of an electric field. These electro-sensitive ecolubricants are based on nanocellulose or nanoclay dispersions in castor oil, at concentrations ranging from 0 to 6 wt.%. A preliminary dielectric characterization demonstrated that cellulose nanofibrils and montmorillonite nanoparticles exhibited interfacial polarization, mechanism which sustains the electrorheological (ER) effect. With this in mind, the influence of both nanoparticle concentration (from 0 to 6 wt.%) and electric field strength (up to 4 kV/mm) on the lubricant's ER behavior was studied and modelized. Thus, their ER potential was assessed by determining the magnitude of the yield stress induced by the electric field, from steady flow curves at 25 °C. It was found that the nanocelluloses and the montmorillonite suspensions showed an enhancement of up to three orders of magnitude in their yield stress values at 4 kV/mm. Preliminary electro-tribological tests were also carried out by using a ball-on-three plates setup and voltages of up to 50 V. Noticeable variations of the friction coefficient were observed under the influence of an electric field. This outcome leaves the door open for the development of environmentally friendly electro-active lubricating fluids, based on cellulose nanofibrils and montmorillonite nanoparticles, which might assist in reducing the friction and wear through the application of controlled electric fields.

Symposium FR

Food Rheology

Organizers: Bettina Wolff, Isabel de Sousa and Ma Jesús Hernández

Thursday 14:30 Giralda 6-7 / Track 6

FR13

Model gluten as near-critical gels

Ameur Louhichi¹, Salvatore Costanzo², Marie-Hélène Morel³, <u>Laurence Ramos</u>¹, and Amélie Banc¹ *Laboratoire Charles Coulomb, Université de Montpellier, MONTPELLIER 34095, France; ²University of Naples, Naples, Italy;
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The origin of the unique rheological properties of gluten, the water-insoluble protein fraction of wheat grain, is crucial in bread-making processes and questions scientists since many decades. To better understand the supramolecular structure of gluten and its link to the material properties, we develop and characterize model gluten using a combination of rheology, biochemistry and scattering techniques. In this framework, we investigate the linear and non-linear viscoelastic properties of samples produced by the dispersion of gluten proteins in a solvent. We vary the quality of the solvent, the protein concentration, and the protein composition, which we finely control thanks to a novel protocol based on a liquid-liquid phase separation (Morel et al., 2020). We show that the complex viscoelasticity of the gels exhibits concentration / aging time (Dahesh et al., 2020) / solvent composition (Costanzo et al., 2020) superposition principles, demonstrating the self-similarity of the gels produced in different conditions. All gels can be regarded as near critical gels with characteristic rheological parameters, elastic plateau, and characteristic relaxation time, which are related to one another, as a consequence of self-similarity, and span several orders of magnitude when changing the parameters. Structural features probed by X-ray, neutron and light scattering experiments provide a quantitatively consistent physical picture of near-criticality and provide crucial molecular clues of the role of intramolecular H-bonds in the gelation process. In addition, using start-up shear experiments we characterize the non-linear behaviour of gluten samples that depends on the gelation state and we try to rationalize in the critical gel framework. This work provides new insights for understanding gluten viscoelasticity.

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Thursday 14:50 Giralda 6-7 / Track 6

FR14

Creation of plant particles weak gels through High Pressure Homogeneization (HPH) to limit sedimentation in juices

Paula Khati, Delphine Huc-Mathis, and <u>Cassandre Leverrier</u> SayFood, Massy, France

Weak gels of biopolymers are frequently used for food or cosmetic applications, particularly to limit the sedimentation of products containing particles added in suspension. However, the trend of clean labelling tends to limit the use of added polymers in food. In this work, we point up the ability of a mechanical treatment to structure the dispersion and to modulate the rheological properties of the products so as to promote interactions between the particles in order to limit or even stop the sedimentation without addition of texturizer. We also question the influence of the shape of the particles on their packing fraction. Fruit beverages containing fruit pulp, sugar and water were thus formulated and processed using high pressure homogenisation. The physicochemical, structural, and rheological properties as well as the physical stability of the juices were studied. In addition to a significant reduction in particle size, HPH induced particle shape alterations and greatly modified the rheological properties of the samples. The existence of a weak interconnected particle network that withstands sedimentation over time in treated juices was confirmed through microstructure observations and enhanced dynamic rheological parameters (yield stress and elastic modulus), passing them from liquid behaviour to weak gel behaviour. Above the yield stress, processed beverages have the ability to flow and to instantly restructure after flow. From a macroscopic point of view, the process used in this study allowed to stop sedimentation and to stabilise the fruit beverages without the addition of additives.

Thursday 15:10 Giralda 6-7 / Track

FR12

Inverse quenching on gelatin solutions

<u>Pietro R. Avallone</u>¹, Rossana Pasquino¹, Salvatore Costanzo¹, Andrea Sarrica², Marco Delmonte², Francesco Greco¹, and Nino Grizzuti¹

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Gelatin is a biopolymer composed of proteins, mineral, salts and water and it is employed in food, pharmaceutical, photographic and biomedical fields due to its gelling properties. Furthermore, it can be used as stabilizer, thickener and texturizer. Gelatin gels are known to be non-equilibrium systems, due to the continuous growth and shuffling of the junction zones, over a long-time scale. This makes hard to perform rheological experiments on a distinct microstructure characterized by a definite number of junctions. To understand modeling, and predicting the transformation processes of gelatin solutions, it would be crucial to find a relation between the relative degree of crosslinking and macroscopic

elasticity. In isothermal conditions, indeed, the density of physical crosslinks evolves indefinitely, and network formation cannot be arrested. Inspired by the inverse quenching technique applied in the past to semi-crystalline polymers, we here apply an unusual thermal history to an aqueous solution of gelatin in the semi-concentrated regime 6.67% wt pig-skin gelatin, to freeze the system in a metastable condition for a time sufficiently long to perform a rheological characterization. The solution, initially kept in the sol-state at 60°C, is rapidly cooled below gelation temperature, and isothermal gelation is started at 10°C. After soaking at this low temperature for a given time, the sample is rapidly heated (inverse quenching) up to a value in the range 24-29°C, where kinetics is monitored. By fixing the soaking time and the inverse quenching temperature, rheological experiments can be reliably carried out. In fact, with this thermal history, the sample elasticity will be stationary for a large time window.

Thursday 16:00 Giralda 6-7 / Track 6

FR16

Clean Label emulsions based on vegetable proteins

Marta Cabrita¹, Estefanía Álvarez-Castillo², Diogo Castelo-Branco³, Ana Tasso³, Diogo Figueira³, <u>Sara Simões</u>¹, Antonio Guerrero², and Anabela Raymundo¹

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The consumer's perception that food is one of the main determining factors for health, increases the demand for foods in line with this trend. The food industry is researching new ingredients, formulations and technologies aiming to respond to this demand. Namely, product formulations are increasingly less complex, with less additives, and manufactured with commonly known ingredients, leading to the concept of clean label products. This work is part of a project (POCI/ANI/46080/2019 CleanLabel+: Innovative natural, nutritious and consumer oriented clean label foods) involving several research entities and companies, namely Mendes Gonçalves (MG), a market leader in the production of mayonnaise and salad dressings. This work aimed to develop a vegan and clean label mayonnaise, replacing egg yolk by vegetable protein, creating a product aligned with both trends. Vegetable protein sources that fulfil the required technical properties, without compromising the sensory perception and potentially improving on traditional recipes were selected. Emulsions with 1.5% (w/w) powdered aquafaba, pea, lupin and faba bean proteins were prepared and compared to the standard MG mayonnaise. Color, texture (TPA) and rheology (SAOS) measurements showed that emulsions with lupin and faba bean protein had significant differences (p<0.05) from the standard. Thus, these two proteins were assessed in a mixed system using different proportions - total protein content of 1.5% (w/w). Additionally, lupin protein showed a significant impact on mayonnaise structure and consistency. Backscattering and droplet size distribution measurements indicated that, except for faba bean, the emulsions of these two studies are stable and have a high potential for scale-up. Therefore, it is possible to develop a vegan mayonnaise with a rheology and texture behavior similar to the commercial mayonnaise, even further developments are needed in order to improve the emulsions taste and creaminess.

Thursday 16:20 Giralda 6-7 / Track 6

FR17

Heat treatment of concentrated milk protein system affects viscosity and enzymatic coagulation properties <u>François Martin</u>¹, Romain Jeantet¹, Luisa Azevedo-Scudeller², Arnaud Paul³, Florence Rousseau¹, Marie-Hélène Famelart¹, Emeline Goussé¹, Gaëlle Tanguy¹, and Cécile Le Floch-Fouéré¹

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Dairy ingredients with highly concentrated protein contents are high added value products with expanding market. They are known to have specific properties adapted for a multitude of applications (cheese, bakery, infant formulae, nutritional products for the elderly and sportspeople...). Fabrication of such dairy protein ingredients is conducted by a succession of unit operations where heat treatment is a key step that induces major changes in protein structures and thus ingredients functionalities. However, due to an incomplete understanding of phenomena taking place at these high protein concentrations, shedding light on these mechanisms is simultaneously a scientific challenge and an industrial need. For this purpose, we used an original approach to investigate the influence of heat treatment and mineral environment of concentrated milk protein system on viscosity and enzymatic coagulation properties. Experiments were conducted with fresh whey protein isolates (WPI) and native phosphocaseinates (NPC) according to the ratio 20:80 (WPI:NPC) using 4 different technological routes: without heat treatment (Control); with one heat treatment at 10% w/w protein; with one heat treatment at 20% w/w protein and with two heat treatments at 10% and 20% w/w protein. Interestingly, the protein concentration of the heat-treated solution greatly modulates the denaturation and aggregation process of whey proteins, which modifies the association mechanisms between WPI and NPC. Indeed, the increase of protein content leads to a higher particles collision probability and a shorter inter-protein distance modifying protein-protein interactions. Furthermore, the nature of complexes formed during the heat treatment and the amount of aggregates present in solution are two parameters that can modulate the rheological properties (here viscosity and enzymatic coagulation ie, gel time and gel strength) of the system. Influence of lactose and mineral environment is discussed in a second time.

Thursday 16:40 Giralda 6-7 / Track 6

FR18

Effect of acid precipitation on the gelation properties of quinoa protein isolate

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The heat-induced gelation properties of quinoa protein isolate (QPI) have been increasingly studied due to its high nutritional quality and potential to substitute animal proteins in food systems. Preliminary studies showed that our extracted QPI formed weaker heat-induced gels than those reported by Ruiz et al. (2016), using the same extraction conditions. To assess this discrepancy, we investigated the acid used for the isoelectric precipitation step during the extraction process as a factor to control gel strength (Cai et al., 2020). In addition to the commonly used HCl (H), we

applied citric acid (C) and acetic acid (A), which present higher kosmotropic effects than H (Hofmeister, 1888). QPI was extracted from quinoa flour at pH 9, precipitated at pH 4.5 with the different acids, neutralised and freeze-dried before resuspension in distilled water (10, 15 and 20%, w/w) to assess heat-induced gelation properties using a small amplitude oscillatory shear test. Samples were heated to and held at 90°C, then cooled to 20°C. Both elastic (G') and viscous (G") moduli increased during all stages of the gelation protocol. At 10% QPI, the final G' of the cooling stage for QPI-A was significantly higher (p < 0.05) than for QPI-H and QPI-C. However, at 15 and 20% QPI, the final G' values for QPI-A and QPI-C were significantly higher (p < 0.05) than for QPI-H. Although the QPI gels were still not as strong as previously reported, we concluded that the extraction with kosmotropic acids exerted protective effects on the protein structure, improving its heat-induced gel strength. Other sources of variation of the gelation properties of QPI, and possibly of other plant protein isolates if no standardised products are available commercially, are the botanical variety of quinoa and the composition of our isolate, as only around 60% are protein. Our research contributes to eventually paving the way for successful formulation of products designed with dairy protein alternatives.

Thursday 17:00 Giralda 6-7 / Track 6

FR19

Rheology, texture, and chemical characterization of Halloumi cheese enriched with algae biomass

<u>Héctor Hernández</u>¹, Rémi Romancer², Maria Cristiana Nunes¹, Catarina Prista¹, and Anabela Raymundo¹ *LEAF-Linking Landscape, Environment, Agriculture and Food, Universidade de Lisboa, Lisbon, Portugal;* ²Department of Food Sciences, Institut Agro, Agrocampus Ouest, Rennes 35042, France

The use of algae as healthy ingredients has been studied in several food products. Algae are potential sources of bioactive compounds, but they can influence the mechanical behavior and the sensory profile. Their incorporation in dairy products has been of increasing interest to obtain more sustainable and nutritive fermented products. Halloumi is a traditional semi-hard cheese originated from Cyprus, currently produced all over the world, which can be made from a mixture of goat and sheep milk, or just with cow milk. This cheese, with unique sensory characteristics, has a high melting point, so it can be easily fried or grilled and used as a meat substitute. In this sense, the rheology behavior, namely its melting characteristics, is crucial for sensory acceptance. In the present work, we intended to evaluate how the incorporation of algae (Chlorella vulgaris and Algaessence - a mixture of C. vulgaris microalgae, and Fucus vesiculosus and Ulva rigida macroalgae), interfere with the cheese rheological properties. Frequency sweep tests (SAOS) were performed at 20° and 90° C, the impact of adding algae was not noticed for the studied levels (1% to 5%). Even after heating to 90° C, the cheeses presented G' > G' / G' despite a higher frequency dependence. Texture analysis of the cheeses performed by using cutting and puncture tests revealed the impact of algae when added at higher levels. Nutritional composition (protein, lipids and ash) was significantly (p<0.05) influenced by the addition of different algae levels, revealing a boost in the mineral profile and bioactive pigments. Despite de color changes with algae addition, instrumentally evaluated by a colorimeter, sensory analysis of Halloumi cheeses resulted in highest scores for overall acceptability and purchase intention for the control (0% algae) and 1% algae cheeses, indicating a high probability of consumption of these innovative and hybrid cheeses, made from animal and vegetable sources.

Poster Session

Symposium PO

Section: Bio-rheology and Medicine (BM)

Virtual Asynchronous Online / Poster Session

PO1-BM

Protein-based electrospun scaffolds with potential application in tissue engineering

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The field of electrospinning has constantly been growing and evolving for the past 20 years. This technique allows the formation of nanofibrous membranes. These membranes present a high surface area making them excellent candidates for several applications, including Tissue Engineering. In particular, the formation of skeletal muscle tissue in vitro is one of the topics of greatest interest in recent years in the field of biomedical research and, although great advancements have been made, nowadays, finding the optimal conditions that must be applied in the cellular environment is still a challenge. In this sense, nanofibrous scaffolds are highly recommended due to their microstructure and the possibility to modulate their mechanical properties. In general, synthetic polymer-based scaffolds tend to be used as they allow greater control of the properties of the fibers obtained, as well as better processability. However, these synthetic polymers are usually combined with natural polymers to improve the hydrophilic character of the membranes or to make the mechanical properties similar to those that are optimal for subsequent biological treatment. In this sense, rheological analyses are useful to determine, in either dry or wet conditions, the behavior of the nanofibrous scaffolds in physiological conditions. Therefore, this study evaluates the influence of biopolymer incorporation on the properties of nanofiber scaffolds obtained from synthetic polymers. In conclusion, the results demonstrate that is possible to adapt the properties of electrospun scaffolds in order to be used for specific regenerative applications.

Virtual Asynchronous Online / Poster Session

PO2-BM

3D printed collagen scaffolds for sustained bioactive delivery

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The knowledge and control of rheological properties are of great relevance to analyze and design the 3D-printing process. Hence, stress sweep, frequency sweep, and flow tests were performed to analyze rheological properties before 3D printing. First, stress sweep tests were performed to determine the linear viscoelastic range (LVR) of tetrahydrocurcumin (THC)-collagen doughs and then, frequency sweet tests were carried out within the LVR. A predominant elastic behavior was observed in all samples since the storage modulus (G') was greater than the loss modulus (G'') in the studied interval. Additionally, small dependence on frequency was observed in the loss modulus, while the storage modulus remained nearly constant, demonstrating the system stability. Furthermore, the hydrogel behavior did not show noteworthy differences with the addition of THC. The viscosity suitable for 3D printing must be low enough to permit easy extrusion through the nozzle and high enough to be cohesive with the previously deposited layer while maintaining the shape. Therefore, the flow behavior of THC-collagen samples was analyzed. All samples displayed similar steady-state viscosity pattern of non-Newtonian fluids with a shear-thinning behavior and a tendency to reach a Newtonian region at a low shear rate (Newtonian plateau zone). The shear-thinning performance indicated that collagen chains were affected by the shear stress between the layers when the flow rate increased, thereby reducing the force between them. This behavior was reported beneficial in the 3D-printing process for gels to be extruded through a nozzle. After rheological characterization, collagen gels were 3D printed and the obtained scaffolds showed swelling capacity and a controlled release of THC, highlighting the potential of these collagen scaffolds as sustained THC delivery systems.

Virtual Asynchronous Online / Poster Session

PO3-BM

Single-cell analysis platform to probe in-vitro capillary blood flow

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Blood is mainly comprised of red blood cells (RBCs) that determine the unique flow properties of blood in the circulatory system. In this study, we present a microfluidic-based approach to analyze the flow behavior of RBCs under confined flow conditions as they are in the microcirculation.

In narrow vessels, RBCs exhibit characteristic shapes that depend on their confinement, velocity, and intrinsic cell properties. Here, we use a high-precision pressure device to pump highly diluted RBC suspensions through microfluidic capillaries with a cross-section similar to the RBC size covering a broad pressure drop range. The single-file flow is recorded with a highspeed camera, and individual RBCs are analyzed with a customized neural network to determine the cell morphology. Based on the cell morphology in the flow, we derive the shape phase diagram (fraction of cell shapes versus the cell velocity) for both healthy and diseased RBCs. Additionally, the cell size and distribution across the channel width are determined as a function of the cell velocity. We discuss how the analysis of shape transitions and dynamics of RBCs in capillary flow can be used as a biomarker for diseases or treatment tests, to study the effect of drugs in-vitro, and for quality assessment of stored blood bags.

Virtual Asynchronous Online / Poster Session

PO5-BM

Extensional magnetorheology of a high elastic blood analogue: Influence of the intensity magnetic field João M. Nunes¹, Francisco J. Galindo-Rosales¹, and <u>Laura Campo-Deaño</u>²

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A complete understanding of the rheological properties of whole human blood is of paramount importance as it could constitute the basis for a more precise diagnostic and more effective treatment in most cases of cardiovascular diseases. Moreover, the response of the blood flow under the application of an external magnetic field can provide more insight into the hemodynamics, opening new doors in the area of medicine. Previous work of the same authors (Nunes et al., 2021), showed that in the case of a weakly viscoelastic blood analogue fluid (XG100), the presence of magnetic particles and the application of an external magnetic field induced the formation of the beads-on-a-string structure. The same behavior was observed for larger concentrations of XG. Nevertheless, still significant work remains unexplored, as can be the study of the influence of larger magnetic fields, different particle sizes and concentrations in the magnetorheological properties of human blood. In this work, we present the results of applying different magnetic field intensities to a high elastic blood analogue with different concentrations of magnetic particles (10 and 15 % w/w). The rheological characterization under extensional flow was performed in the Capillary Breakup Extensional Rheometer (HAAKE CaBER-1, Thermo Fisher Scientific), and the evolution of the minimum diameter was recorded by means of a highspeed camera (Photron FASTCAM Mini UX100). The application of a variable magnetic field parallel to the extensional flow was carried out by means of an apparatus developed by Sadek et al. (2020.

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Virtual Asynchronous Online / Poster Session

PO6-BM

Blood clot deformation (LAOStress) of patients under anti-platelet therapy

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Anti-platelet therapy with acetylsalicylic acid (ASA) or/and clopidogrel reduces the occurrence of thromboembolic events, but little is known if this is due to a better mechanical performance of blood clots. We recently described a protocol to determine the behavior of clots under increasing sinusoidal shear stress amplitudes (Windberger & Läuger, 2020), which we now applied to thrombi from whole blood and plasma of forty individuals (18 patients receiving ASA, 4 patients ASA+clopidogrel, 18 age matched controls). Platelet counts and fibrinogen concentrations were similar in these groups. In the ASA group (ASA classification 2.2) coagulation started earlier (p<0.05) considering hypercoagulability, but mean G' was slightly lower compared to controls (ASA class 1.3). So, clots did not become stiffer at same time. In the subsequent LAOStress tests the general behavior of clots from ASA and control groups was similar, only the mean J-moduli were higher in the ASA group, pointing to a slightly better compliance. This supports present knowledge of ASA influencing fibrin(ogen) network formation towards thicker protofibrils with bigger gaps, which might facilitate clot lysis or remodelling. Plasma clots from both groups deformed elastic until \approx 10 Pa shear stress (LVE) and showed similar shear stiffening thereafter. This is in contrast to ASA+clopidogrel clots, where a pre-stress had to be worked out before stiffening could occur (G'-shoulder with \approx 10 Pa maximum). We further calculated the number of clots that broke apart at a distinct shear stress. More clots "survived" higher cyclic shear stresses in the control group, but the shear strain at rupture was similar in patients. Our patient cohort showed similar thrombus deformation, but a lower ability to withstand large oscillatory shear stresses, which is of interest regarding the planned interventional approach.

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Virtual Asynchronous Online / Poster Session

PO9-BM

Rheological characterization of PEGylated fibrinogen hydrogels for 3D in vitro neuronal networks

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Neuronal cultures are a very powerful tool to develop models of brain connectivity in vitro. In response to the simplicity of 2D neuronal cultures, which poorly represent the real connectivity of the brain, 3D models are emerging to build better in vitro models (Cembran et al., 2020). In this context, material selection is a key element since neuronal development and function are extremely sensitive to the mechanical properties of their surroundings (Koser et al., 2016). To replicate as closely as possible the brain extracellular matrix and its mechanical environment, we chose a semisynthetic hydrogel to develop primary neuronal cultures in vitro. In this communication we present rheological measurements of PEGylated Fibrinogen gels adapting the protocol described by Zuidema et al. (2014). We tracked the ageing of the storage modulus (G') over time. G' did not exhibit changes between day 0 and 14 after preparation, neither in the frequency sweep test nor in the strain one. We also performed measurements on PEGylated Fibrinogen gels seeded with neurons at different developmental stages. Results show a lower value of G' that also remains constant for higher values of oscillation strain. This analysis evinces that the development of the neuronal network within the hydrogel alters the mechanical properties of the scaffold.

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Virtual Asynchronous Online / Poster Session

PO12-BM

Oscillatory and steady-shear flow properties of commercial urological lubricants

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There is an increasing interest in Urology Units of hospitals to gain a deeper insight into the rheological properties of urological lubricants. The target of this research was to assess the shear flow properties of four commercial urological lubricants which are widely used at present in hospitals. All of them exhibit soft gel consistency under quiescent state but their rheology essentially depends on the type of polymers used as thickening agents. Three out of the four lubricants studied contain a semisynthetic polymer (hydroxyethyl cellulose, HEC). The fourth lubricant studied is formulated with biopolymers; namely, maize-starch and tragacanth gum exudate. Steady shear stepwise flow curves and oscillatory shear tests were carried out with a CS-rheometer using a coaxial cylinder measuring system at 20°C and 37 °C. In addition, temperature ramps at constant shear rate, 100 (1/s), between 20°C and 37°C were run with a cone & plate geometry, such that the first difference of normal stresses (N1) could be recorded in parallel to shear stress. Urological lubricants containing HEC showed a wide linear viscoelastic range and mechanical spectra typical of entangled macromolecular semi-dilute solutions, while that formulated with starch and tragacanth gum exhibited a frequency dependence of dynamic viscoelastic moduli typical of extremely weak gels. The terminal relaxation times (tr) of lubricants containing HEC were markedly lower than that of the lubricant formulated with biopolymers. Steady-shear flow curves allowed the zero-shear viscosity to be calculated by fitting data to the Cross equation and exhibited marked shear thinning properties as expected for lubricants. Interestingly, temperature ramp results showed that N1 values were much higher than shear stress, which highlights the importance of elastic properties of urological lubricants even at steady shear.

Virtual Asynchronous Online / Poster Session

PO14-BM

Combination of bulk and interface measurements for the study of the stability of synthetic biomarkers Simona Itri¹, Danila del Giudice¹, Saray Pérez Robles², Claudia Carotenuto², Simonetta Grilli¹, and Mario Minale²

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Alzheimer's Disease (AD) is the most common dementia with nearly 10 million new cases every year. AD is made up of a set of complex conditions. The symptoms including loss of memory and executive functioning. A major neuropathological feature of AD is a disorder of the physiological metabolism in the brain of different peptides, included the Amyloid β (A β) peptides. This leads to inflammation and oxidative stress, that contribute to neurodegeneration. A β 1-42 aggregates are one of major toxic species of A β . Considering the severity of the disease, intense research efforts are focusing on early diagnosis using synthetic A β 1-42 peptides to mimic the real pathological conditions and investigate novel research strategies. A practical issue is that tests which involve the use of synthetic biomarkers are often constrained by a short lifetime of the biomarkers themselves. For instance, in the case of A β 1-42, its stability is certified for two weeks after opening. However, as far as we know this aspect has not been properly investigated yet. As a result, we propose to characterize this instability by studying the interfacial rheology of A β 1-42 as well as the immunofluorescence reaction to determine the fluorescence signal (FS). A pendant drop tensiometer was used to carry out transient interfacial tension measurements and small amplitude oscillations. The measurements were repeated at different times, during the protein storage after opening. Additionally, different protein concentrations (800 μ g/mL, 400 μ g /mL, 40 μ g mL) were investigated. We focused on the kinetics of protein adsorption at the air-water interface. The main features of the adsorption of proteins, include (i) the diffusion of the protein

from the bulk to the interface, (ii) adsorption, and (iii) aggregation within the interfacial layer. The kinetic constants which characterized (i), (ii) and (iii) and the FS values collected, allowed to better understand the protein changes in time.

Symposium PO

Section: Emulsions, Foams and Interfacial Rheology (EI)

Virtual Asynchronous Online / Poster Session

PO15-EI

Mechanical properties of cellulose ether oleogels as healthy fat alternative for food applications

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Growing public concern about the adverse health effects of trans fatty acids and saturated has contributed to the rising research interest in the field of using vegetable fats and oils to construct edible structured oils as fat-based alternatives. This paper used hydroxypropyl methylcellulose and methylcellulose to prepare oleogels by the emulsion template and the foam template approaches. The physicochemical properties of the oleogels were measured by microscopy (SEM), texture, rheology, and oil retention capacity. The results showed that the initial emulsion structure of the emulsion-based oleogels was affected during the drying process. However, the cellulose still effectively inhibited the aggregation of droplets. The dry emulsion still showed an independent droplet form with 100% oil retention capacity. The foam-type oleogels absorb liquid oil through a network of dry cellulose foam. In this case the oil retention rate of the oleogels was negatively correlated with the initial oil content. The oleogels prepared by both methods have excellent mechanical properties and gel strength. The viscoelastic properties showed a predominancy of the elastic moduli versus the viscous moduli along the frequency sweep evaluated and no temperature dependence on the viscoelastic functions was found. Hydroxypropyl methylcellulose and methylcellulose had different degrees of influence on the structure and mechanical properties of the two oleogels. The effects of preparation method, cellulose type and oil content on the properties of oleogels are discussed in order to provide guidance for the development and application of cellulose-based oleogels as a new healthy fat with zero-trans and low saturated fatty acids.

Virtual Asynchronous Online / Poster Session

PO16-EI

Characterization of natural cosmetic film-formers as alternatives to microplastics: Rheology and texture analysis

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While the restrictions proposed by ECHA on microplastics are under discussion in Europe, due to the growing concern about their impact on the aquatic ecosystem, cosmetic industries are working in advance to identify natural alternatives to synthetic texturizers. The aim of this study was to characterize the applicative properties of natural film-forming agents and texture modulators, comparing their performances to those of nylon and polymethyl methacrylate (PMMA), the most popular synthetic texturizers used in cosmetics. We selected five organic and four inorganic polymer-based raw materials that have been incorporated at different amounts in an oil in water emulsion, and we evaluated their physic-mechanical properties by means of rheological and texture analyses. The rheological tests were conducted in continuous and oscillatory flow conditions using a rotational rheometer to study the spreading properties and the viscoelastic characteristics of the systems. The emulsions' firmness, adhesiveness, and stringiness were measured through an immersion/de-immersion test conducted with a Texture Analyzer. We developed a method to evaluate the adhesive properties of the residual film formed by the products after application on a silicone surface that simulates the skin. The results obtained showed that the inorganic polymers such as silica, kaolin, and mica, formed fluid and viscous emulsions, with high spreadability and stringiness, but low adhesiveness. Among the organic polymers, the starch-based ones formed weak-gel systems with higher elastic G' modulus and higher adhesiveness. The statistical processing of rheology and texture data highlighted the correlation between these techniques and permitted to select the starch-based polymers as viable alternatives to synthetic texturizers. Rheology and texture analyses can be used in parallel to study the physic-mechanical properties of complex systems and easily identify green alternatives to synthetic cosmetic ingredients.

Virtual Asynchronous Online / Poster Session

PO17-EI

Interfacial rheology of non-spherical organo-silica particles with matching convex and concave asperities Lukas A. Woolley, Florence J. Müller, Damian Renggli, Laura Stricker, and Jan Vermant Materials, ETH, Zurich 8093, Switzerland

Surface roughness of colloids highly influences their self-assembly behaviour, therefore dictating the mechanical properties in such systems. Here, we report the macroscopic interfacial rheology of microparticle networks in different ratios of topologically matching convex and concave surface asperities measured with a double wall ring (DWR) interfacial rheometer. In this set-up, a Langmuir through with an adapted DWR attached to a stress-controlled rheometer was used to probe the mechanical properties. The surface coverage and local events are investigated using a light

microscope during the experiments. The organo-silica particles with concave features, also known as golf ball-like particles (GBPs) were synthesized following an approach from Liang et al. (2020) The particles with a convex featured were synthesized following a novel one-pot synthesis, based on a co-condensation reaction of two organo-silane precursors. These particles consist of smaller corona particles condensed to a larger core particle and can be referred to as raspberry-like particles (RBPs). These particles were spread at a water-air interface in different ratios and compressed to different surface coverage to measure their interfacial mechanical properties. Preliminary results show a highly elastic and strong interface in the high frequency regime due to interlocking be tween particles.

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Virtual Asynchronous Online / Poster Session

PO18-EI

Rheological and surface properties in oceans, lakes and sewage sludge: Tuning rheometric methods to the relevant scales

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Oceans, lakes and sewage treatment plants all contain water suspending a biota dominated by bacteria and the organic matter (OM) they secrete following expression of their genes. This OM regulates electrical layers at cell and molecule surfaces as well as rheological properties in the intercellular medium. OM also affects processes such as adsorption and diffusion of gases and other small molecules. We will treat these processes in foams, at solid and at atmospheric surfaces, in cyanobacterial scums and in organic aggregates. We explore the tuning of rheometric methods to the spatiotemporal scales and geometries in deformation and diffusion within such mixtures. We further explore planetary and socio-economic applications of such rheological measurement and control.

Virtual Asynchronous Online / Poster Session

PO19-EI

Investigation on the surfactant impact on the thermal energy storage functionality of PEG4000/Silicone Oil Phase Change Material Emulsions

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Owing to their exceptional trade-off between effective heat storage, appropriate fluidity and simple fabrication procedure, phase-change-material emulsions (PCME) are currently gathering momentum in the energy storage and transportation fields. Besides the rather limited research on anhydrous PCME, the selection of the appropriate emulsifying agent may entail the avoidance of likely emulsion instabilities and promote the energy transfer performance. Thus, in this research, polyethylene glycol 4000 (PEG4000) as PCM was dispersed into a selected industrial silicone oil at the weight ratio of 1:9. The impact of the surfactant nature on the ultimate heat storage functionality, thermomechanical stability, and rheological behaviour of the so-prepared PCMEs has been assessed by using two different commercial silicone surfactants with a comb-like structure, at 2 wt.% concentration. Therefore, PCME were characterised through frequency sweep tests along with heating-cooling oscillatory temperature ramp cycles within the temperature range from -20 up to 80 °C. Furthermore, modulated differential scanning calorimetry (MDSC) and optical microscopy techniques were also conducted aimed at analysing their heat storage capacity and morphological properties. According to the results, both surfactants seem to modify not only the viscoelastic behaviour, but also the PCM liquid-solid transition, noticing a downward shift in the crystallization peak.

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Virtual Asynchronous Online / Poster Session

PO20 EI

Competition of rapeseed proteins and oleosomes for the air-water interface - explained by large amplitude oscillatory dilatational rheology and AFM microstructure imaging

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Foams are multiphase systems with air bubbles in a water phase, and it is key to understand the interfacial properties of stabilizers. In food systems, proteins are common stabilizers. Nowadays, there is a great interest in replacing animal-based fat/oil droplets with plant-based alternatives. One option is oleosomes (a.k.a. oil bodies or lipid droplets), which are natural oil droplets from plants. However, the impact of oleosomes on the proteins in an air-water interface and foam is not yet understood. Here, we present a study on rapeseed protein and oleosome mixtures by studying the mechanical properties of the interface by using large amplitude oscillatory dilatational (LAOD) surface rheology and Lissajous plots. In addition, the interfacial microstructure was studied by performing AFM on Langmuir-Blodgett films. Oleosomes can rupture at the interface, leading to weak interfacial layers. In a mixture with proteins, ruptured oleosomes can destabilise the protein-stabilized interface and foam. On the other hand, we demonstrated a less detrimental effect on foam stability by oleosomes, when varying the protein content and protein-to-oleosome ratio. By microstructure imaging and rheology, we discovered how a pre-formed protein layer could reduce the detrimental effect of oleosomes. With these findings, the effect of oleosomes in protein-stabilized foams can be controlled: either no/limited destabilization or a complete antifoaming effect.

Virtual Asynchronous Online / Poster Session

PO21-EI

Surface tension and interfacial rheological behavior of the mixtures buffalo whey protein concentrate - vitamin ${\bf E}$

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Buffalo whey proteins were recently reported as a promising carrier agent of vitamins by complexation. However, the impact of involved molecular interactions on surface properties of proteins were not yet assessed. By this reason, the objective of this work was to explore the impact of vitamin E on surface activity and interfacial dilatational rheology of a whey protein concentrate (BWPC). With this purpose, BWPC was dispersed at 1.6 - 1.3 x10-5 % w/v in phosphate buffer pH 7 and opportunely mixed with 4.7 x10-3 % dl-a-tocopheryl acetate (a-TOC). BWPC dispersions without and with a-TOC were equilibrated at 4 °C for 24 h and the equilibrium superficial pressure (p) was registered through Wilhelmy plate method. Additionally, the rheological dilatational behavior (10 % deformation amplitude and 0,1 Hz of angular frequency) of BWPC solutions with 2.6 x10-2 % of proteins were assessed over 3 h. Plate tensiometry showed that p of BWPC solutions increased from 1.18 to 28.52 mN/m at higher BWPC concentrations, showing a sigmoidal behavior typically described for protein adsorption at air/water interface. The rheological measurement indicated a gradual increase in dilatational modulus (E) over time, indicating an improvement in solid character of the films. In the presence of a-TOC, higher p values were observed which could be attributed to better arrange of complexes at surface than proteins. Rheological measurements showed lower E values with decreasing trend over time, indicating that complexation lead to weak molecular interactions among surface active proteins. In conclusion, the surface activity of BWPC is clearly affected by complexation with a-TOC. Despite vitamin improved the increasing surface pressure, it reduced the solid character of surface films, which may impact on functionality of studied proteins.

Virtual Asynchronous Online / Poster Session

PO22-EI

Elastic characteristic of polymer solutions triggering interfacial instability

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The spreading of multicomponent droplets on a soap film is a phenomenon rich in physics. During such spreading a sophisticated interplay takes place between elastic, viscous, and capillary forces. We observed when the concentration of polymer exceeds a critical threshold, a counterintuitive instability occurs at the spreading front. Using thorough rheological characterization methods we discovered that the increased elastic response of the solution above the entanglement concentration of the polymer precipitates the instability on the leading edge. Below this critical concentration, however, the spreading front is smooth and the spreading dynamics are governed by surface tension gradients and extensional viscous forces.

Virtual Asynchronous Online / Poster Session

PO23-EI

Effect of crystallisation on the thermo-rheological properties of polyethylene glycol-in-silicone oil phase change emulsions

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Anhydrous emulsions have been scarcely examined up so far, hence there is a lack of information about scientific background data and the technological developments on the subject. However, the relatively low number of publications, compared to the water-based emulsions in which

there is extensive scientific literature, contrasts with the growing demand for anhydrous emulsions for a variety of applications. In the present work stable polyethylene glycol-in-silicone oil phase change emulsions were successfully prepared with a selected silicone surfactant. Both phases used to prepare the emulsion have highly remarkable properties, not only for cosmetic/pharmaceutical compositions, but also for energy recovery applications. Thus, the use of polyethylene glycol (PEG4000) with a melting peak temperature of 58-61°C allow exploring the possibility of using such systems as novel phase change material (PCM) emulsion with potentials for the use as heat transfer fluid. Optical morphology, thermophysical properties and rheological behaviour of the emulsions as well as the binary blends of their compounds were measured and analysed. All those properties were greatly dependent on parameters such as surfactant concentration, volume fraction of the disperse phase and processing conditions. Particularly interesting is the effect that some of these parameters had on the crystallinity fraction and crystallization mechanism of the disperse phase. Interestingly, those changes in the disperse phase crystallinity remarkably modified final thermal and rheological properties of the emulsion.

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Virtual Asynchronous Online / Poster Session

PO24-EI

Rheology and microstructure of oil-in-water emulsions stabilized by lignin

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Lignin is a common renewable polymer which has a high number of chemical sites present in its structure which could lead to its use in potential value-added applications. However, due to its heterogeneous structures and poor properties ends up burned to obtain energy. This work evaluates the emulsifying ability of three lignin-rich products recovered from black liquor wastewater of bioethanol production or kraft pulping. Firstly, silicone oil emulsions were prepared to study the influence of lignin source, disperse phase concentration and emulsification pH. After having acknowledge the impact of the given variables a waste vegetable cooking oil (RVO), a recycled lubricating oil (RLUB) and a 160/220 penetration range soft bitumen were introduced as disperse phases. Model silicone oil emulsions undergone significant variations on droplet size, Z-potential and viscosity with emulsification pH and surfactant source. Viscosity tests showed a non-Newtonian viscous behaviour that has been fitted to the Sisko or Carreau model, depending on formulation, and a wide span bimodal droplet size distribution. Emulsion stability was directly affected by droplet-droplet flocculation, due to entanglements among emulsifier biomolecules, which appear to be responsible of the rheological response of these systems. Bioethanol-derived lignins showed greater aggregates at low pH values whereas Kraft lignin exhibits a better prevention to particle aggregation, producing stable RVO and RLUB emulsions from pH 9 to pH 13 and bitumen emulsions at pH 9 and 11. However, the bioethanol-derived lignins produced the most stable emulsions with a lower droplet size and more developed non-Newtonian character.

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Virtual Asynchronous Online / Poster Session

PO26-EI

The influence of methylcellulose on rheological properties, structure and lipid digestibility of emulsions of pork fat stabilized by soy protein

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Soy proteins are commonly used as food emulsifying agents; however, mixed protein-polysaccharide systems improve the functionality of oil-in-water (O/W) food emulsions stabilized only by proteins. Oil-water interfacial adsorption of protein-polysaccharide complexes depends on whether complexation occurs before or after emulsification, as this generates different structures at the interface, which may influence lipid digestibility. Among polysaccharides, methylcellulose (MC) tends to accumulate at the O/W interface due to its high surface activity, providing many technological applications. This study was aimed at determining the effect of MC, added by simultaneous and sequential emulsification methods, on the structure, rheological properties and lipid digestibility of pork lard O/W emulsions stabilized by soy protein concentrate (SPC). Three emulsions (SPC, SPC/MC-sim, SPC/MC-seq) were prepared and compared using confocal laser microscopy, dynamic viscoelastic properties, and in vitro digestion (INFOGEST 3.0 method). MC presence and stage of incorporation affected the emulsion microstructure, as reflected by more spherical, homogeneous and smaller oil droplets. Lipid droplets were entrapped by a protein layer in the SPC emulsion, which was thicker when MC was present, providing greater resistance against environmental stresses during gastrointestinal digestion. MC addition in the SPC-coated oil droplets resulted in a larger linear viscoelastic region without affecting the network rigidity, exerting a delaying effect on the crossover temperature, which was more evident in SPC/MC-seq. The stage of MC incorporation affected the rate and extent of lipolysis, with SPC/MC-seq presenting a lower concentration of free fatty acids, probably because MC, due to its affinity for the O/W interface, hinders the access of lipase to the oil droplet. Decreased extent of lipolysis observed in SPC/MC-seq may be beneficial in the production of animal fat products with reduced fatty acid uptake

Virtual Asynchronous Online / Poster Session

PO28-EI

A two fluid data analysis scheme for the Magnetic needle interfacial shear rheometer (MNISR): The effect of the air drag

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Interfacial shear rheometry data obtained on interfacial systems confined between two bulk fluid phases contain information on the hydrodynamic resistance of both adjacent bulk phases. Thus, the two bulk phases contributions must be carefully separated from the total drag to obtain an accurate value of the interfacial rheological variables. Different approximations have been used in the analysis of the experimental data of the MNISR, from a simple model with a linear velocity profile at the interface and additive contributions, to more sophisticated data analysis schemes that rely on an iterative solution of the hydrodynamics equations.

However, the data analysis schemes that consider just the subphase and the interface are limited in two fundamental aspects: on the one hand, they cannot deal appropriately with experimental data on interfacial systems confined between two liquid bulk phases, and, on the other hand, they cannot account for the drag of the air layer inherent to the most often studied case of air/water interfaces. In fact, the air layer drag must impose a lower threshold in the resolution of the conventional, single bulk phase, data analysis schemes for modern high resolution interfacial rheometers (DWR, MNISR, micro-button).

Here we report on the development of a flow field-based data analysis scheme for the MNISR geometry considering the upper bulk fluid layer. We will illustrate the performance of the data analysis scheme on two bulk fluids interfacial systems, with particular emphasis on the case of air/water interfaces in order to clarify in what conditions the contribution of the upper air phase is relevant. We will discuss the different flow configurations obtained as a function of the characteristic length scales and we will illustrate, through numerical simulations, how the operating windows of the MNISR are affected by the air layer drag at low values of the interfacial viscosity.

Virtual Asynchronous Online / Poster Session

PO29-EI

Use of the foam-templated approach for obtaining healthier reduced saturated fat chocolates

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Chocolate is primarily composed of cocoa butter (CB). The CB continuous phase provides a network structure determining its microstructure, texture, crystallization, and rheological properties, and conferring chocolate its characteristic flavor (Li & Liu, 2019). In turn, a specific range of triglycerides (TAGs) contributes to the unique CB physical properties (Bahari & Akoh, 2018), and its appealing sensory characteristics. Reformulation of chocolates seeks to find alternatives to CB that adhere to nutritional recommendations to replace saturated fats with unsaturated ones. In this research, chocolates were elaborated by substituting CB with an oleogel (OG) formulated with hydroxypropyl methylcellulose (HPMC) by using the foam-templated approach (Patel, Schatteman, Lesaffer, & Dewettinck, 2013). Four CB/OG blends were prepared as CB substitutes (0% control), at replacement levels of 30, 50, 70 and 100%, and CB/OG-based chocolates (CB/OG-Ch) were formulated with each blend (100/0-Ch, 70/30-Ch, 50/50-Ch, 30/70-Ch and 0/100-Ch). Chocolates were characterized by dynamic (frequency sweep tests at 20 °C) and stationary (flow behavior and thixotropy at 5 s-1 at 40 °C) rheology and texture (penetration tests); in addition, a sensory analysis was performed and the lipid profile of chocolates was analyzed. Viscoelastic moduli evidenced that 100/0-Ch, 70/30-Ch and 50/50-Ch samples had similar internal structures with storage modulus close to 107 Pa. Both 30/70-Ch and 0/100-Ch, with higher percentage of CB replacement with the OG, had significantly lower viscoelastic moduli and displayed the highest Casson yield stresses. Sensory analysis showed that it would be possible to replace up to 70% of CB with the OG without negatively affecting the overall acceptability of the chocolates. As compared with lower risk of chronic degenerative diseases.

Symposium PO

Section: Experimental Methods and New Advances in Rheometry (EM)

Virtual Asynchronous Online / Poster Session

PO31-EM

Advances in high temperature material characterization: from salt melts to glass melts to metals

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This contribution presents advances of high temperature rheometry methods above 600°C: viscosity measurements on low viscous salt melts, oscillatory measurement on viscoelastic glass melts and dynamic mechanical analysis (DMA) on damascene steel. Salt melts are used as heat transfer or energy storage medium in solar power plants and molten salt reactors in the solar and nuclear energy sector, where they act inter alia

as a storage medium or as a heat transfer fluid. Rheological investigations on molten salts help to study and select new, enhanced salt recipes. The combination of high operation temperatures, low viscosities and high corrosiveness is a challenge met with an advanced rheometer setup. Different salt melts, like carbonate mixtures, were investigated as a function of shear rate and temperature. Oscillatory rheometry serves as a powerful toolbox for glass melt characterization beyond viscosity measurements. Heating and cooling rates and the time-dependent visco-elastic behavior influence the temperature where materials undergo the glass transition. This study presents first quantitative thermo-mechanical visco-elasticity measurements on reference glass DGG 1. The material properties of steel depend, among others, on composition and heat treatment. In case of damascene steel, DMA enables to track the tempering curves of both the individual steel components and the complex layered laminate. In this example, two components of a lamellar damascene steel were investigated over a wide temperature range using a three-point-bending geometry.

Virtual Asynchronous Online / Poster Session

PO32-EM

Viscoelastic characterization of gels with an oscillatory squeeze rheometer

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We have studied a soft xanthan gel with an oscillatory squeeze rheometer at varying the aspect ratio between plate radius and gap width. The linear viscoelastic range and the detected storage and loss moduli depend strongly on the aspect ratio. The loss tangent remains about constant at large aspect ratios and increases for small ones. Theoretical considerations derived for viscoelastic liquids in an oscillatory squeeze rheometer show that the experimental findings at large aspect ratios can be traced back to the strong impact of shear in this parameter range (Bell et al., 2006; Wingstrand et al., 2016). At small aspect ratios, however, strong deviations point to a crucial role of surface tension and inertia in this regime.

References:

Bell, D., Binding, D. M., & Walters, K., *Rheologica acta*. 2006, 46(1), 111-121. Wingstrand, S. L. et al., *Journal of Rheology*. 2016, 60, 407-418

Virtual Asynchronous Online / Poster Session

PO34-EM

Microelectrorheometer for characterizing electrorheological fluids

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Electrorheological fluids (ERFs) are suspensions of fine and electrically active particles in an electrically insulating fluid. Under the presence of an external electric field, their rheological properties change reversibly. At the macroscale, rotational rheometers are conveniently equipped with an electrorheological cell so that the external electrical field is perpendicular to the direction of the shear flow imposed to the fluid sample[1]. For extensional flows, the CaBER-1 device can be equipped with an electrorheological cell so that ERFs can be characterized under the uniaxial extensional flow conditions and an external electric field aligned with the direction of the flow[2]. Thus, only two out of the four possible flow-field configurations are currently covered at the macroscale. In recent years, microfluidics has been recognized as an excellent platform for rheometric purposes, with several microrheometers already available in the market[3]. All these microfluidic rheometers impose either shear or extensional flow to the fluid sample, but none of them can impose an external electric field, neither parallel nor perpendicularly to the flow direction. Therefore, to the current state of the knowledge, it is not possible to perform shear/extensional electrorheometry-on-a-chip. In this work, we present four microelectrorheometers designs allowing the electrorheological characterization of ERFs in the four possible flow-field configurations[4].

- [1] Applied Science 2019, 9(24), 5273
- [2] Journal of Rheology 64, 43 (2020)
- [3] Complex fluid-flows in microfluidics, Springer (2018)
- [4] PCT/IB2021/059053

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Virtual Asynchronous Online / Poster Session

PO35-EM

Characterizing rheological behavior of paints using Orthogonal Superposition

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Viscoelastic properties of dispersions and weak structured fluids can be investigated using Superposition techniques. In Orthogonal Superposition (OSP), the material undergoes a small amplitude oscillation in the axial direction, orthogonal to a rotational steady shear. OSP can also be used to perform 2D oscillation, in the axial and radial direction. OSP techniques provide valuable information about the change in material structure under shear such as the relaxation time, structure orientation, and thixotropy of the samples without conducting extra tests. Paints, for instance, exhibit complex rheology behavior under shear to achieve demanding performance requirements - brushing, spreading, avoiding drips, surface leveling, etc. Being interested in performance during painting process, paint industries can use OSP to measure storage and loss modulus under the same

shear rates used during painting. Therefore, the OSP data can be used to establish a new relationship between the formulation, the change in the microstructure, and the performance of dispersions. In this study, multiple structured fluids were investigated to highlight the potential applications of the OSP technique. The orthogonal measurements are presented in conjunction with both steady shear and oscillatory viscosity measurements in a modified Double Walled Couette geometry.

Virtual Asynchronous Online / Poster Session

PO39-EM

Innovative fused deposition modelling of medical composites based on poly(lactic-acid) and bioglass: Healing and rheological properties relationships

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Osteosynthesis systems could combine an inorganic bioactive filler with a biopolymeric resorbable matrix. The combination of BG and a resorbable polymer (Poly(d-lactic-acid)) enable tailor-made medical devices by considering the mechanical and physiological demands of the host tissue. Firstly, a set of composites PDLA/BG (45S5, S53P4, and 72S) were prepared by a direct in-situ extrusion/injection process to limit thermomechanical and hydrolytic degradation phenomena and to gain a fundamental understanding of the relationships between shear rheological and morphological properties depending on the BG nature, mechanical properties and shape factor. Hereto, we demonstrate that linear rheology is a suitable tool to probe and model the effects of BG bioactivity, shape factor and content on the viscoelastic properties of the developed suspension model systems. Secondly, for innovative Direct Pellet Printing (DPP) multi-extrusion process, the influence of the 3D print experimental conditions in the interfacial properties were investigated in the melt by a shear rheological approach in both linear and non-linear regimes. Both SAOS (Small Amplitude Oscillatory shear experiments) and step strain experiments up to different pre-shearing conditions were investigated to probe and model the relaxation modulus and induced orientations during a transient step of filament deposition. Hence, we propose a physical model that considers non-isothermal polymer relaxation considering the macromolecular chain orientations based on the studies of Yang & Pitchmani [1], McIlroy [2] and our previous work [3]. Moreover, a focus is dealing with the modelling of healing and welding between the neighbouring symmetrical layers.

References:

Yang, F., & Pitchumani, R. Macromolecules, 2002, 35(8), 3213-3224.

McIlroy, C., & Olmsted, P. D. Journal of Rheology. 2017, 61(2), 379-397.

Zhang, H., Lamnawar, K., & Maazouz, A., Polymer Engineering & Science. 2015, 55(4), 771-791.

Virtual Asynchronous Online / Poster Session

PO40-EM

A rolling ball viscometer for low viscosity polymer solutions in volatile solvent

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Performing viscosity measurements on dilute and semidilute polymer solutions in volatile solvents is often a difficult task. The precision and accuracy needed is often difficult to obtain even using state-of-the-art rotational rheometers. In fact, it is well-known that with low viscosity fluids, various spurious effects can affect measurements reliability in rotational rheometers equipped with different devices. Other options like glass capillary viscometers and Rolling Ball Viscometers are of limited usefulness when the solvents are volatile and/or the contact with air at high temperature might induce polymer degradation. Examples of such kind of materials are polybutadiene solutions in n-hexane and cyclohexane and HPAM solutions in sea water. In this work, we present a Rolling Ball Viscometer based on a steel tube, a hermetic (airtight) system of valves, and a manometer. This allows to fill the tube with the liquid to measure and to pressurize it with an appropriate gas (in our case, pure nitrogen gas) up to 30 bar gauge. The whole system is located in a convection oven if higher than room temperature is needed. The specific setup for volatile liquids consisted of a 4 mm (i.d.) steel tube and a set of non-stainless-steel balls of varying diameter, spanning the range between 2 and 3.15 mm. With this setup, using magnetic sensors, we were able to measure the rolling ball descent times at various inclination angles for a set of different reference liquids such as lubricating oil, water, cyclohexane, n-hexane. Using a set of different tubes and ball/tube diameter ratio. We then tested polybutadiene solutions in cyclohexane, measured at different temperatures, from 20°C up to 100°C. The nitrogen pressurization successfully allowed the prevention of any contact with air during the measurement at high temperature as well as any significant solvent evaporation.

Virtual Asynchronous Online / Poster Session

PO41-EM

Investigating heat-induced gelation of whey protein using simultaneous rheology and FTIR spectroscopy Nathan C. Crawford and Fabian Meyer

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Whey protein is a liquid byproduct of the cheese manufacturing process and it is believed to have excellent nutritional benefits and exceptional physicochemical properties. As a result, whey protein products are used in a wide range of food applications as foaming agents, stabilizers, emulsifiers, and gelling agents (to name a few). When a concentrated aqueous whey protein solution is heated, it induces denaturation and aggregation of the protein molecules, and a gel-like network can be formed. The protein gel structure directly influences the sensory response and structure of food products, and thus, gelation is considered one of the most important functional properties of proteins.

In this study, rheology coupled with *in situ* Fourier transform infrared (FTIR) spectroscopy was used to examine the thermal denaturation and gelation of aqueous whey protein solutions (50% w/w). This multimodal analytical technique allowed the bulk mechanical properties of the whey protein specimen (namely the elastic and viscous moduli; G' and G", respectively) to be directly correlated in real-time with conformational changes at the molecular level (increases in intensity and wavenumber shifts of the Amide I band). Using simultaneous rheology with *in situ* FTIR spectroscopy allowed for deconvolution of the multi-step whey protein gelation process, including protein molecule unfolding, aggregation, and aggregate growth and rearrangement. The hyphenated technique provides corroborating evidences, from both macroscopic and molecular perspectives, to unravel a complex, multi-step process that cannot be fully revealed by either individual analytical technique.

Symposium PO

Section: Food Rheology (FR)

Virtual Asynchronous Online / Poster Session

PO25-FR

Effect of different structuring agents on the rheological properties of xanthan gum based oleogels

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Xanthan gum solutions have gained increasing interest for their use as environmentally friendly chemicals in the oil industry. Xanthan is compatible with most concentrate brines used for controlling formation damage and fluid loss. Particularly, formate brines reinforce the ordered structure of the biopolymer in solution, gel strength, and the density of the resulting fluid. In this work, the effect of thermal aging on the rheological behaviour of xanthan solutions as a function of the concentration in potassium formate has been studied. In linear viscoelasticity, xanthan in solution behaves as a weak gel, with values of the storage modulus being higher than those of the loss modulus at the same frequency. The gel strength increases with the concentration of formate in solution. Aged solutions show an important loss of strength in their mechanical properties due to thermal degradation of the structure. Highly concentrated formate brines are necessary to maintain the strength of the rheological properties after exposure to high-temperature environments.

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Virtual Asynchronous Online / Poster Session

PO30-FR

Nonlinear viscoelastic properties (LAOS) of low digestibility cellulose-based emulsions used as fat source in foodstuffs

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A recent strategy for controlling excessive fat intake consists on decreasing fat bioaccessibility through the employment of specifically designed emulsions. It has been proved that digestibility of fats is reduced due to a physical barrier effect exerted by cellulose ethers when they are included in an emulsion. In this work oil in water emulsions formulated with two types of methylcellulose ethers having different substitution degree and molecular weight were analysed in order to evaluate emulsions response to large deformations implied in real food processing. Flow curves and mechanical spectra in LVR showed different shear thinning character and revealed differences in internal structure of both type of emulsions. In order to complement this characterization we evaluated non-linear viscoelastic response by using Fourier Transform Rheology and orthogonal stress decomposition on raw waveform data at 1, 100, and 1000% strain. All rheological measurements were performed at room temperature in a AR-G2 rheometer (TA Instruments), using TRIOS software for measurements and calculations. Strain sweeps tests were carried out from 0.1 to 1000% at 3 different frequencies (0.1, 1 and 5 Hz). Differences in LVR extent, yield and and flow point were analysed. Lissajous-Bowditch curves at 1% (SAOS), 100% (MAOS) and 1000% (LAOS) strain, together with stiffening and thickening ratios for the whole strain interval were studied, comparing results at the 3 frequencies considered. Results showed shear thinning and strain stiffening behaviour in both types of emulsions, showing significant differences between them, especially for the highest deformations tested. Therefore, nonlinear viscoelastic analysis allows improving the textural characterization of emulsions so it would be helpful to consider these results when establishing the most suitable formulation of the final food product.

Virtual Asynchronous Online / Poster Session

PO42-FR

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In this work, new beverages from different pulses (i.e. pea, chickpea and lupin) were developed using technologies that enable the incorporation of a high level of seed components, with low or no discharge of by-products. Different processing steps were sequentially tested and discussed for the optimization of the sensorial features and stability of the beverage, considering the current commercial non-dairy beverages trends. The rheological flow behavior of the developed pulse-based beverages were compared with eight commercial non-dairy beverages, selected from a

previous study [1], in order to serve as a guide for the preferred consumers mouthfeel and texture. The morphological examination of pulse beverages was conducted by bright field optical microscopy at $20\times$ magnification. The particle size was evaluated by photon correlation spectroscopy using a Zetasizer Nano ZS. The shear viscosity of the pulse-based beverages was measured using a controlled-stress rheometer (Haake MARS III, Germany), at 20 ± 1 °C, with a CCB/CC25 DIN Ti concentric cylinder geometry to avoid phase separation. The steady shear measurements were performed with shear rates from 1.0×10^{-5} to 1.0×10^{3} s-1. The flow curves were fitted to the Carreau model. The optimization of the milling step enhanced the stability of beverages. Although the chickpea beverage had the smallest particles, its sedimentation was remarkably faster compared to the other beverages, which may be significantly affected by the lower viscosity of the solution and higher bulk density of its particles. Sensory results showed that chickpea beverage with cooking water had the best taste. All pulses-based beverages are typical non Newtonian fluids, similarly to current non-dairy alternative beverages. In this respect, the sprouted chickpea beverage, without the cooking water, presented the most pronounced shear-thinning behavior of all formulations.

References:

[1] Lopes M., et al., Foods. 2020, 9, 1458.

Virtual Asynchronous Online / Poster Session

PO44-FR

Moringa beverages and yoghurts, the importance of rheology measurements on product development Adèle Gautier¹, Carla M. Duarte², and <u>Isabel Sousa</u>³

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Moringa oleifera (MO) leaves are used, in powder or pills, as nutraceutical. Therefore, the seeds are left, in large quantities, after the leaves collection and are an amazing source of nutrients: PUFA rich edible oil (39%); protein (36%); vitamins, minerals, antimicrobials and polyphenols and glycosylates, with major impact on prevention/reduction of diseases like diabetes, high cholesterol and cancer. Despite MO-based foods present a very good and nutritionally well-balanced composition, they face some issues related to processing and sensory properties. Soaking and heat treatment (toasting, cooking, pasteurization) are able to remove some of the bitterness that the MO seeds present, which is the most challenging barrier to consumer acceptance. Different processing methods were tried, following a previous work (Lopes et al., 2020), and MO beverages and yoghurts, using a commercial soy yoghurt as a fermentation starter, were produced. It was not possible to obtain a debittered beverage, but MO-based yoghurt, when incubated during 4h30m, achieved a nice flavor. The MO seeds-based yoghurts and beverage displayed a flow curve with a well-defined Newtonian plateau at low shear rates followed by a shear-thinning region and the MO beverage presented the less extended shear-thinning behavior compared to other plant-based beverages like chickpea and lupin ones. This suggests that its supramolecular structure was more easily destroyed by the applied shear and that the micro-scale structures within the fluid rearrange/align to facilitate shearing, reaching sooner the second Newtonian plateau. The MO beverage's viscosity behavior would be the closest to the chickpea beverage ($\eta_0 = 176.4 \text{ Pa·s}$). In conclusion, the processing strategies adopted, and the optimizations performed with the help of the rheology measurements, led to the development of MO-based yoghurts, with several appealing features, highly competitive in the current commercial non-dairy markets.

References:

Lopes M., et al., Foods. 2020, 9, 1458.

Virtual Asynchronous Online / Poster Session

PO45-FR

High-moisture extrusion: A small-scale approach to analyze the technological properties of plant proteins for the production of meat substitutes

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Meat substitutes cover one of the top trends in the food market in the wake of sustainable nutrition and the associated reduction of the carbon footprint. In order to achieve a high level of customer acceptance for the "meat-like" structures made from plant proteins, the challenge is to imitate the taste, aroma and structure as authentically as possible. High moisture extrusion is considered as key technology for continuous production of meat substitutes. A twin-screw extrusion process (Thermo Scientific Process 11 Hygienic Extruder) combined with a special die head that can cool the extruded protein in a long flow channel to create a fibrous, meat-like structure proved to be a suitable solution. Common practice in the food industry is that product and process development is a labor-intensive development process that requires large volumes of test material of > 10 kg/h. Thermo Fisher Scientific's laboratory extruder enables small-scale production to significantly reduce development effort and test novel protein sources (e.g., rape seed, peanut protein, or algae).at a scale of 0.02 kg/hr. The extruder is also ideally suited for scale-up to industrial sizes of up to 50 kg/h. In order to objectively evaluate the quality of the meat substitutes in terms of customer acceptance, product characteristics were investigated by different techniques. An important product feature is the fibrous, anisotropic structure, which resembles the product texture of muscle meat. This was evaluated using an electron microscope and image analysis. For the assessment of mouthfeel, rheological measurements and texture analysis tests were performed using a Thermo Scientific HAAKE Rheometer. Results show how these measured data can be related to product structure and used as quantitative measure to compare meat analogs' product properties.

Virtual Asynchronous Online / Poster Session

PO46-FR

Rheological and textural characterization of a dessert designed for people with dysphagia: Effect of storage conditions

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Texture modified foods using different hydrocolloids are mainly used in dysphagia management. This work investigates the effect of storage conditions on the viscoelastic and textural properties of a fiber and protein-enriched strawberry dessert. Three formulations of a strawberry dessert containing casein (15%) and inulin (8.5%) were prepared and stored under refrigeration (4°C) and freezing (-18°C): one with xanthan gum (0.2%), one with modified starch (4%), and the control (without hydrocolloids). Textural (back extrusion) and rheological parameters were measured at 10°C after 1 day of refrigeration and 5 days of frozen storage. Results indicated that frozen storage significantly increased every parameter of the back extrusion test for the control and, especially, for the samples with modified starch, whereas the samples containing xanthan gum showed no significant differences between refrigerated and frozen samples. Regarding the rheological parameters, complex modulus (G*), elastic modulus (G'), viscous modulus (G"), and loss tangent (tan d= G"/ G') were determined. G' was higher than G" over the entire range of frequency for all of the samples. Significant increases were observed for G*, G', and G" after freezing for control and samples containing xanthan gum. In samples with modified starch, a slight decrease was observed for G*, G' and G" after frozen storage. Tan d values ranged from 0.289 and 0.303, in both storage conditions, for all of the samples, indicating a weak gel structure. It has been suggested that a weak gel structure of the food bolus, and, therefore tan d values between 0.1 and 1, can be used as a rheological criterion for safe-swallow foods for people with dysphagia. In conclusion, all formulations may be suitable for people with dysphagia. Textural properties seem to be more susceptible to frozen storage than viscoelastic ones in this type of sample. Xanthan gum reduced structural changes in textural parameters caused by frozen storage.

Virtual Asynchronous Online / Poster Session

PO48-FR

Characterization of the bread dough behavior during kneading by modeling the power curve Maude Dufour¹, Florence Hugon¹, Hubert Chiron², <u>Guy Della Valle</u>², Kamal Kansou², and Luc Saulnier²

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The food industry has multiplied the number of flour references used, which have different behaviors during kneading. The physical changes of the flour biopolymers that occur during this stage depend on the mechanical energy delivered to the dough by the kneader, developing the gluten network. Tracking the power curve P(t) provides an indicator of the kneading time to reach the optimum network structure, for processing and bread quality. However, the curves are difficult to handle because the usual method involves reading a dozen parameters at specific points, such as the maximum power of value. The objective is therefore to adjust the curve P(t) by a mathematical model to extract the characteristic parameters. The power curves obtained by mixing dough at 67% hydration on a spiral mixe,r for 36 wheat flours, are fitted by a Gaussian law (R²mean=0.97). Four parameters are then extracted: the power at the end of frasing, the standard deviation of the curve SD, the time to reach the maximum power and the power of the dough during its texturation. They are correlated to those from the initial method but they better explain the variability of the kneading curves of the flours (Adjustment: 91.2%; Initial method: 82.7%). Furthermore, the extensibility capacities of the dough (L and G from the Chopin alveograph) are correlated with SD, which provides information on the tolerance of the flour to kneading. These results underline the importance of the contribution of dough extension during kneading. They open prospect to enlighten the rheological behavior and its relation with the hydration of the flour components.

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Virtual Asynchronous Online / Poster Session

PO49-FR

Rheological and mechanical characterization of starch based film and film-forming solution for food packaging Olga Mileti, Noemi Baldino, Francesca R. Lupi, Domenico Gabriele, and Vincenza Calabrò DIMES, University of Calabria, Rende, Italy

Food packaging has a primary role in extending the shelf life of foods. To be adequate, it must be thin and resistant, compatible with the contents and able to retard all the degradation phenomena that naturally occur in foods contained within. The packaging industry is increasingly focusing on the research of biocompatible and bio compostable materials for their greater sustainability. A suitable alternative to petroleum-based plastics is the use of polysaccharides and additives. In particular, the use of starch for packaging film has many advantages, such as low cost and transparency as well as lack of smell and high barrier properties. Starch is a biodegradable polymer, mainly consisting of amylose and amylopectin in different percentages and obtainable by different sources. In this work starch from potato was chosen and glycerol was used as plasticizer, in different percentages and ratios to obtain food films by casting. Film-forming solutions were characterized by controlled stress rheometer equipped with parallel plates, performing Step Rate Temperature Ramp Tests (SRTRT) in a temperature range between 25 and 90°C and frequency sweep tests, in linearity. The frequency sweep results were fitted by the weak-gel model. Creep-recovery tests were also performed and the results were analyzed by Burger model. The film-forming solutions were used to obtain biopolymeric films by casting and they were characterized by colorimetry for color acquisition, contact angle tests to have information about wettability and tensile tests to analyze the mechanical properties. Finally, a scanning electron microscopy (SEM) investigation on the different films was performed to observe their regularity and uniformity. The obtained biofilms showed good mechanical properties and seem to be suitable to be a good base for potential use in packaging.

Virtual Asynchronous Online / Poster Session

PO50-FR

Study of steady shear and viscoelastic rheological properties of some commercial dysphagia-oriented products mixed with unstimulated human saliva

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In order to develop safer food products for dysphagia patients, it is necessary to evaluate the steady, viscoelastic and extensional rheological properties of dysphagia-oriented products in the swallowing process. Saliva increased the bolus cohesiveness and elasticity and it also produced a significant decrease in bolus viscosity, which can increase the risk of aspiration for this type of patients. There are few works about the viscoelastic behaviour of dysphagia products mixed with human saliva. The objective of the present work was to characterize steady and viscoelastic rheological properties of four commercial dysphagia products before and after mixing with unstimulated saliva of five healthy individuals to study the bolus behaviour for dysphagia management. Three Resource instant purées(Vegetables and beef (VB), Vegetables and codfish (VC) and Chicken with rice and carrots (CR)) and one Meritene instant cereal cream (IC) were mixed with fresh saliva from 5 healthy human volunteers (S1-S5) and/or tap water (W) in proportion (1:20). Steady and viscoelastic properties were measured at 37 °C, and composition of saliva samples was also determined. Before the addition of saliva, all the commercial products behaved as structured-liquid systems showing shear-thinning behaviour. IC and CR showed the higher consistency and viscosities values. The addition of saliva produced a remarkable decrease of viscosity and a loss of conformational structure (lower smax and G* values and higher tan d) in all the products, but especially in CR and IC. A high compositional variability was observed between the five saliva samples giving rise to different viscoelastic behaviour when they were added to the same product. Therefore, it is very important to consider the differences in personal salivary patterns when designing dysphagia-oriented products.

Virtual Asynchronous Online / Poster Session

PO51-FR

Assessment and rheological characterization of food grade emulgels formulated with a mixture of avocado oil and lemon oil and stabilized by microalgae extract

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In this work, a mixture of avocado an lemon oil was used for the development of food-grade emulsions and emulgels stabilized by phycocyanin and pectin complex. For this purpose, laser diffraction, rheological and multiple light scattering measurements were carried out. This led to the optimum emulsifier concentration by using droplet mean diameter and turbiscan stability index as objective functions to minimize. The results of the study of the influence of the concentration of phycocyanin (0.5-2.5% w/w) on the droplet size of the emulsion showed polydisperse systems with the main peaks in the range of 10-15 µm. In the physical stability analysis, a fast destabilization process by creaming was observed. By adding pectin in the formulation of the most stable emulsion (1.5% w/w of phycocyanin), an increase in the viscosity and the viscoelastic properties of the emulsion due to the gelling effect of the biopolymer in the emulsion system was taken place. This increase in viscosity and viscoelastic properties results in a better stability. The emulgels obtained with the highest pectin concentrations used were still weak systems with a large fluid character. However, it was observed a tendency to increase the viscosity and viscoelastic properties when the concentration of pectin is increased. In order to obtain high-structured emulgels it would be necessary to use higher pectin concentrations in the formulation. This application with these valuable resources that can be used in sustainable processes, could contribute to the both new strategies such as bioeconomy and circular economy and therefore supporting to the ecological transition.

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Virtual Asynchronous Online / Poster Session

PO52-FR

Relationship between rheological properties, encapsulation efficiency and microstructure in food emulgels with high content in omega-3 fatty acids

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The objective of this study was to formulate a novel emulgel with nanoscale droplet size, longest physical stability and enhanced rheological properties. The active bioingredient (β-carotene) was encapsulated through microfluidization in linseed oil emulgels containing an eco-friendly surfactant derived from wheat biomass (Appyclean 6552) and formulated with two different food grade biopolymers (xanthan gum or guar gum). Linseed oil has attracted a lot of attention of food industry since it is rich in essential fatty acids such as α-linolenic acid. It presents health benefits related to the prevention of cardiovascular diseases and breast and prostate cancers (Goyal et al., 2014). Firstly, mean droplet sizes were used to optimize the processing variables (homogenization pressure and number of cycles). The results showed that the smallest diameter was obtained using 15000 psi and 2 cycles. The addition of xanthan gum or guar gum solutions in different concentrations to the linseed oil emulsions provoked

the formation of emulgels with enhanced viscoelastic and viscous properties. Interestingly, emulgels formed with xanthan gum showed very poor stability, probably due to a depletion flocculation mechanism. \$\beta\$-Carotene was highly efficiently encapsulated in the linseed oil droplets of the emulgels containing guar gum. In addition, these emulsions protected \$\beta\$-carotene against oxidation, which was proved by spectrophotometry. Hence, results pointed out that there is a relation between viscoelastic properties of the guar gum emulgels and the encapsulation efficiency of \$\beta\$-carotene. The results provided may be quite useful to the design of stable delivery systems for the encapsulation of bioactive substances.

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Virtual Asynchronous Online / Poster Session

PO53-FR

Stability assessment of a commercially viable 'dairy-mayonnaise'

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The sauce market has not stopped growing in recent years, being mayonnaise by far one of the most worldwide accepted dressings. Although an authentic mayonnaise cannot be produced without egg, an increasing tendency toward vegan diets and a greater concern for a healthier diet among consumers has aroused manufacturers to produce egg-less, vegan, low-fat and organic mayonnaise variants. However, these eggless mayonnaise dressings behave as semi stable systems. Alternatively, the use of cow's milk to replace egg is common in homemade mayonnaise, although it is difficult to find commercial foodstuffs of these variants. The main aim of this research is to get a viable formulation for a stable salad dressing emulsion able to be industrially processed and commercialized by using milk as a natural emulsifier. In the present work, the formation and stabilization of mayonnaise-type sauces have been studied using powdered cow's milk, whole and skimmed, with xanthan gum as a stabilizing agent. The results obtained, both through backscattering and drop size distribution techniques, as well as through the analysis of the rheological characteristics, allow to establish that these formulations have a good consistency and high stability even three weeks after preparation, which makes them an interesting alternative for industrial processing. The substitution of the egg for milk proteins provides a sauce with natural ingredients, analogous to those of artisan elaboration, and with a similar texture and mouthfeel to those of the original product while extending its shelf life. This product is suitable both for a more demanding traditional consumer and for flexitarians, who base their diet on plant products but also include foods of animal origin.

Virtual Asynchronous Online / Poster Session

PO54-FR

Study of the pasting behavior of starch kernel from different varieties of mango (Mangifera Indica)

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Starch is a polysaccharide of plant origin widely used in the food, biomedical, pharmaceutical, chemical, and paper industries. Due to its low cost, biodegradability, biocompatibility, and non-toxic properties. The processing of mango produces considerable amounts of waste, such as peels and seeds, being the mango seed is a good source for obtaining starch. The objective of this research is to study the pasting behavior of starches obtained from different varieties of Mango (Hilaza, sugar, and Tommy). Pasting properties were determined on a Hakee Mars 60 Advanced Modular Rheometer. The pasting curves were analyzed using the mathematical model proposed by Palabiyik et al., which describes the behavior of the curve using sigmoidal gelatinization, exponential, and Arrhenius temperature models. Peak viscosity, pasting temperature, through viscosity, breakdown viscosity, setback viscosity, and final viscosity were determined from the pasting curve. The results obtained show that there are significant differences (p<0.05) in the pasting properties (peak, trough, and breakdown viscosity) between the sugar-Tommy and sugar-Hilaza varieties. The values of the peak, though, and breakdown viscosity are between 1.7175 and 2.195 Pa·s, 0.5671 and 0.75125 Pa·s, 1.1504 and 1.4490 Pa·s, respectively. The adjustment of the model proposed by Palabiyik et al shows values of correlation coefficients R²=0.91, indicating a good correlation between the model and the experimental data. The parameters obtained to allow the kinetics of gelatinization, retrogradation, swelling, water retention capacity, and resistance to stress and heat of starch. The results obtained are of great interest because they provide us with information on the behavior of starches, which is necessary for the development of new food products based on starches.

Virtual Asynchronous Online / Poster Session

PO55-FR

Viscoelastic properties of collagen matter assessed by slit rheometer and pressure hole method

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Collagen is the most abundant protein in the human body and has got a large usage not only in medicine or tissue engineering but also in the food industry. The rheological parameters of the collagen water solution with a high mass content of the collagen (up to 9 % w/w) were evaluated. The tested material resembles with its structure a bread dough and is solid-like when no stress is applied. Its unique structure caused by high dry matter content brings up challenges in the determination of rheological properties. The own-constructed slit rheometer which is suitable to operate at high shear rates was used for experiments. Construction of rheometers allows achieving large shear rates range 100-10000 1/s, which is gained by the variable speed of the hydraulically driven piston which is pushing the measured material through capillary. The capillary cross-section has 20 mm width and 2 mm height, the aspect ratio is 0.1 for "pressure-hole measurement. The capillary is divided into upper and lower part. Upper part is equipped by one pressure transducer located in the base of the hole according to the theory of "pressure hole". The lower part is equipped with five flush-mounted pressure transducers located at a regular distance along the capillary for exit pressure interpolation. From pressure differences of the upper and lower part of capillary, first normal stress differences were evaluated. The rheology of collagen matter was identified from five

different shear rates measurement (repeated three times). Shear viscosity dependency on shear rate was evaluated from measured pressure drop along the capillary and flow rate of collagen matter in the capillary. Extensional viscosity dependency on shear rate was evaluated by two approaches, from measured pressure difference by "pressure hole" method and flow rate of collagen matter in the capillary, and from evaluation of exit pressure and flow rate

Virtual Asynchronous Online / Poster Session

PO56-FR

PECs-based hydrogels: Physicochemical, microbiological and rheological characterization

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Biopolymers, such as polysaccharides and proteins, present ideal properties to be used in wound dressing solutions, due to their biocompatibility and biodegradability. Many biopolymers behave as polyelectrolytes, and thanks to this, by combining oppositely charged biopolymers, it is possible to form a polyelectrolyte complex (PEC) hydrogel, without the need for an additional crosslinker. The application of PECs in the pharmaceutical and biomedical fields has been the topic of many studies. However, one of the main challenges with biopolymeric materials is their sterilization, essential for application in these fields. Conventional methods (e.g., steam heat, ethylene oxide) compromise the physicochemical properties of many polymeric materials, especially biopolymers. ScCO2 sterilization appears as an alternative method, that has already been tested in some biomedical devices, hydrogels and aerogels and proven efficient as a sterilization method. In this work, several hydrogel PEC formulations, chitosan/pectin, deacetylated chitosan/carrageenan, gelatine/xanthan gum and alginate/gelatine were tested. Rheological studies of the PEC hydrogels were performed, for a better understanding of the interactions between biopolymers and of their stability once dried and sterilized. Frequency sweeps confirmed that all formulations were in their gel state, proving the formation of a hydrogel. Flow curves revealed that all formulas had shear-thinning behaviour, a characteristic that is suited for wound dressing applications. The hydrogels were then freeze-dried (obtaining cryogels) and sterilized by scCO2. The efficiency of the sterilization process was evaluated by classical and molecular microbiological analyses, and its impact on the material's structure was assessed, by SEM, DSC and FTIR analysis.

Virtual Asynchronous Online / Poster Session

PO57-FR

Rheology as a tool to evaluate printability of microalgae healthy snacks

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Food printing is a promising area, which contributes to the acceptance of new food ingredients, such as microalgae, in foods with appealing texture and appearance. Study of rheology properties of food pastes has been widely performed to evaluate printability, allowing maximization of printing performance when optimum extrudability conditions are met. To assess printability and define whether a food paste is suitable for printing, rheology properties are studied, and useful information is provided regarding the food's viscoelastic behavior and its viscosity. Successful printing conditions are met when a food material is smoothly extruded, after a certain mechanical force is exerted, and when a food material can retain its shape during printing layer's deposition and during post-processing treatment (e.g. baking), if needed. Low printability, caused by irregular deposition of layers and manifested by poor shape retention, or by non-extrudable dough through the nozzle (i.e. reaching unprintability), achieving the printers' maximum load pressure. This reveals that food materials require a suitable rheology behavior to achieve optimal printing performance. In this study, an enriched snack with Chlorella vulgaris (CV) was formulated to study the impact of increasing microalga incorporations on the snack's printability. Previous studies have shown that microalgae incorporation in bakery products produce a large impact on these products' texture and rheology properties (Nunes et al., 2020). Increasing CV incorporations from 2 to 30% led to doughs which could not be extruded. CV snacks that were successfully printed presented, therefore, a range of limiting rheology values (in terms of viscosity and viscoelastic functions) for smooth extrudability. This study enabled the presentation of optimal rheology behavior of the CV pastes for printing, providing printability maps, to be used as guiding values when printing algae-based food pastes.

Virtual Asynchronous Online / Poster Session

PO58-FR

Simple rheological tests to assess the swallowing capacity of foods

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Many empirical rheological tests are commonly performed in the industry, in order to predict the processability of materials. Although an exhaustive review appears foolhardish, these tests may be classified into three main categories, according to the type of stress or strain imposed. Furthermore, for practical reasons, they have to be easily handled, require short measurement time, and, ideally, their relevance should be ascertained by a comparison with scientific rheological measurements. Regarding food, these constraints are not only requested for processability, but also to predict sensory properties and more especially the capacity of the food to be swallowed safely. For instance, this last property is essential for individuals suffering from dysphagia. In this regard, the International Dysphagia Diet Standardisation Initiative (IDDSI) has compiled

an useful approach to characterize the flow properties of foods at the point of consumption, using only a syringe, a fork and a spoon. This presentation aims at reviewing the main features of simple tests in order to delineate their main limitations and possible improvements by: a) comparing with accurate shear and extensional rheometry to highlight their usability for different classes of food textures; b) simulating their flow/deformation behavior in the current and in the improved testing devices; c) suggest prospects to develop new approaches that do not rely only on human intervention and on subjective qualitative judgement.

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Virtual Asynchronous Online / Poster Session

PO59-FR

Linking intermolecular interactions and rheological behaviour in capillary suspensions

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Capillary suspensions feature networks of liquid bridges between particles suspended in two immiscible liquids. The capillary force exerted by the added liquid on the particles can be cleverly used to tailor the texture normally obtained using regular fat, ultimately allowing the production of stable and healthier particulate-based food products. However, this is conditioned by a good understanding of the intermolecular interactions controlling both the formation of the liquid bridges and the rheological behaviour of the capillary suspensions. Through a combination of experimental and numerical methods, we present a novel approach, based on Hansen Solubility Parameters (HSP) computed from Molecular Dynamics (MD) simulations, to link the rheological behaviour of capillary suspension to the intermolecular interactions of its elementary constituents. The HSP theory allows to identify the range of bulk liquids (or solvents) and secondary immiscible liquids that are likely to form capillary suspension-based gels. The approach's predictions are confirmed experimentally by rheological measurements and microscopy (CLSM) analysis. We show that hydrogen-bonding and polar interactions control the formation of capillary suspensions. Furthermore, we find that the affinity between the bridging liquids and the dispersed particles, in terms of their intermolecular interactions, dominates the formation of the capillary network, and correlates well with the strength of the obtained gel. This simple approach can guide the selection of adequate solvents and secondary immiscible liquids for particles with specific physico-chemical properties, providing opportunities for obtaining new particulate-based food gels.

Virtual Asynchronous Online / Poster Session

PO61-FR

Effect of thermal and mechanical rejuvenation on rheological behavior of chocolate

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Chocolate is known to undergo solid-liquid transition upon an increase in temperature as well as under application of deformation field. Upon sudden reduction in temperature from a molten state (thermal quench), rheological properties of chocolate undergo evolution as a function of time under isothermal conditions, a behavior reminiscent of physical aging in polymeric glasses. Then again, subsequent to cessation of shear flow (mechanical quench), chocolate shows temporal evolution of the rheological properties, a behavior similar to physical aging in soft glassy materials. In this work, we evaluate three rheological properties, namely, dynamic moduli, relaxation time spectrum and characteristic relaxation time of chocolate, and compare their evolution after thermal as well as mechanical rejuvenation. We observe that the evolution of the rheological properties subsequent to mechanical rejuvenation is distinctly different from that of thermal rejuvenation, wherein the evolution is more gradual in the former case. On the one hand, this work provides unique insights into how shear affects the rheological behavior of chocolate. On the other hand, this work clearly suggests that chocolate explores different sections of the energy landscape after mechanical rejuvenation compared to that of thermal rejuvenation.

Virtual Asynchronous Online / Poster Session

PO62-FR

Solution To honey adulteration and imitation in Nigeria: A rheological method

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Adulteration and imitation of honey constitute the most important quality assurance concerns in the utilisation of this natural product. Pure honey was serially diluted with sugar melts, glucose, fructose or water and analysed for their rheological profiles at 27 °C. Pure honey at ambient temperatures exhibits a peculiar non-Newtonian rheological behaviour while the behaviour of sucrose, glucose, and fructose tends towards Newtonian. The adulteration of honey with these materials or with water (a Newtonian fluid) drags its viscosity towards Newtonian flow behaviour. The results show that the Carreau-Yasuda model correlates the rheology of pure honey samples while the Power-law model correlates sucrose melt. The parameters of both empirical models were observed to reflect the quality of the samples and thus aided their classification. Modified with the insertion of the Mark-Houwink's relation the Carreau-Yasuda model yielded average molecular weight data on the samples. The Structural Kinetic Model was utilized to give rheological structural information and a second independent assessment of average molecular weight from the rheograms. The average molecular weight ranges of 245-252 g/mol were obtained using the Structural Kinetic model while 250-260 g/mol were obtained using the amended Carreau-Yasuda model. The rheological curve fitting showed that the new model fitted the experimental data well. Using the Structural Kinetic Model, the best fits to data were obtained at 3rd order deformation kinetics suggesting the presence of three major components or groups of components in honey.

Virtual Asynchronous Online / Poster Session

PO63-FR

Jamming of non-colloidal plant cell-wall particles: The role of packing, mechanical properties, and surface interactions

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The incorporation of dietary fibres (DFs) in the food systems provides structuring and nutritional benefits. The last decade saw the rise in the use of minimally processed plant cell-wall materials in the food industry to produce healthier products by replacing sugar and starch with non-digestible fibre ingredients. The objective of this study is to elucidate the effect of particle properties on the micromechanical behaviour of concentrated DF suspensions. In this work, we use fibre particles of different botanical origin, which enables varying suspension microstructure and packing volume, as well as particle modulus and particle size distribution. The DFs were chosen from wheat, oat, citrus, apple, and pea fibres and were dispersed in sunflower oil to make the suspensions. The icing sugar suspensions were used as control. The Angell's-like plot representation, where suspension's G' is plotted against particle concentration, enabled probing consolidation properties of concentrated suspensions. We show that most cellulose/starch rich fibres show 'fragile' behaviour, whereby G' remains low up until the jamming point, beyond which a rapid increase in G' is observed. By contrast icing sugar suspensions show 'strong' glass behaviour, with G' increasing linearly up until the jamming point. For concentrations above jamming we observe G' to plateau. However, contrary to the expectations, the modulus of suspensions in the jammed state is found to be independent of the particle modulus, as would be predicted by the Evans and Lips model. We propose that the result indicates that the interaction potential between DF particles deviates from the Hertzian hard wall mechanical contact. Instead, the G' is governed by the inter-particle adhesion energy. These insights allow an improved control of suspension rheological and micromechanical behaviour when plant fibre is used in food formulations.

Symposium PO

Section: Gels and Self Assembling structures (GS)

Virtual Asynchronous Online / Poster Session

PO64-GS

Rheological behavior of gels formulated with hydrocolloids extracted from mango peels (Mangifera indica) variety Tommy Atkins

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The food industry generates large amounts of waste that can be used to develop new products. Mango ($Mangifera\ indica$) is a tropical fruit that is demanded worldwide; however, peel waste has not been properly used. This research aims to study the rheological behavior of gels formulated with hydrocolloids from the peel of mango (Mangifera indica) variety Tommy; that were extracted at different solubilization pH (3 - 10), having yields among $4.21 \pm 0.22\%$ and $7.82 \pm 0.72\%$. Hydrocolloid gels were evaluated rheologically in terms of viscosity and viscoelasticity, performing steady-state flow tests, stress and frequency sweeps, and viscoelastic temperature ramp; the properties were studied adjusting the values through the "Carreau-Yasuda" model, obtaining a minimum correlation coefficient of $R^2 = 0.996$, with pseudoplastic characteristic; the mechanical spectrum shows a gel solution typical behavior with a macromolecule entangled network in all hydrocolloids, where the value of the storage modulus (G') is greater than the loss modulus (G''); however, this condition varies with increasing angular velocity and temperature. Moreover, they have an intrinsic relationship with microstructural characteristics, where the hydrocolloid polymeric chains extracted at acidic pH are shorter, enhancing the ability to form intermolecular hydrogen bonds. These results are of great interest to develop novel products using green technologies based on agricultural by-products. It is potentially helpful for future studies in the food industry to extract microcomponents with technological functionality and process design. Keywords: Mango ($Mangifera\ indica$), by-products, hydrocolloid, rheological properties.

Virtual Asynchronous Online / Poster Session

PO66-GS

Adding humic acids to gelatin hydrogels: a way to tune gelation

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Exploring the chance to convert bio-wastes into a valuable resource, this study tests the potential role of humic acids (HA), a class of multifunctional compounds obtained by oxidative decomposition of biomass, as physical agents to improve gelatin mechanical and thermal properties. To this purpose, gelatin-HA aqueous solutions were prepared at increasing HA content. HA/gelatin concentrations changed in the range 2.67 (wt/wt)% - 26.67 (wt/wt)%. Rheological characterization proved that HA increased gel strength and thermal stability up to a concentration of 13.33 (wt/wt)% and led to a weaker gel at higher concentrations. The physicochemical properties of gelatin-HA systems were assessed through different techniques. FT-IR and DSC results proved that HA can establish non-covalent interactions through H-bonding with gelatin. At higher concentrations, HA established preferential bonds with water molecules, preventing them from coordinating with gelatin chains. Such features were accompanied by a change in the secondary structure of gelatin, which lost triple helix structure exhibiting an increase in the random coil

conformation. Current findings may be useful to enable a better control of gelatin structures, modified with composted bio-wastes, extending their exploitation for a large set of technological applications.

Virtual Asynchronous Online / Poster Session

PO67-GS

Effect of electron beam irradiation of collagen solution on its rheological and electrical properties

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This contribution deals with the measurement of rheological properties by squeezing flow of collagen solution (aqueous solution of bovine skin collagen) irradiated with different doses of electron beam radiation affecting changes in the structure of collagen. The electrical properties were measured together with the squeezing flow. The general goal of our research was to study the effect of electron beam radiation dose on the rheological and electrical parameters of collagen samples. The squeezing is the quasi-static compression flow of the test material between two approaching plates. The rheological properties can be evaluated from the relationship between the thickness of the gap between the two plates, the speed of the moving plate and the normal force acting on the moving plate. The tested samples were prepared from a natural aqueous solution of bovine skin collagen (solids content 8% w/w) and were irradiated with an electron beam with different doses of radiation. A texture analyzer was used for compression flow experiments. The initial distance between the plates was 20 mm, the speed of the movable top plate was 1 mm/s. The normal force acting on the top plate, the distance of the top plate from the bottom plate and the time were recorded continuously. The power approximation parameters of the first normal stresses were obtained from the measured data. The stainless steel top and bottom plates also served as electrodes connected to a Keysight LCR meter to measure electrical properties such as conductivity, impedance and dielectric properties in the frequency range up to 500 kHz. The electrical properties were measured only in the initial and final position of the movable plates. The results show an increase in consistency with increasing radiation dose, probably due to a higher proportion of cross-links in the collagen structure. Measurements of electrical parameters confirmed changes in the structure of collagen (cross-link formation caused by irradiation).

Virtual Asynchronous Online / Poster Session

PO69-GS

Effect of thermal degradation on the rheology of xanthan gum in formate brine

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Xanthan gum solutions have gained increasing interest for their use as environmentally friendly chemicals in the oil industry. Xanthan is compatible with most concentrate brines used for controlling formation damage and fluid loss. Particularly, formate brines reinforce the ordered structure of the biopolymer in solution, gel strength, and the density of the resulting fluid. In this work, the effect of thermal aging on the rheological behaviour of xanthan solutions as a function of the concentration in potassium formate has been studied. In linear viscoelasticity, xanthan in solution behaves as a weak gel, with values of the storage modulus being higher than those of the loss modulus at the same frequency. The gel strength increases with the concentration of formate in solution. Aged solutions show an important loss of strength in their mechanical properties due to thermal degradation of the structure. Highly concentrated formate brines are necessary to maintain the strength of the rheological properties after exposure to high-temperature environments.

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Virtual Asynchronous Online / Poster Session

PO70-GS

Viscoelastic relaxation mechanisms in Fe(III)-poly(acrylic acid) hydrogels

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Hydrogels based on the interaction of a metal species and a coordinating polymer exhibit unique dynamical mechanical properties. Self-healing is an attractive feature of such materials, as the metal species is highly mobile within the polymer matrix and can easily form new bonds after rupture. Here, we investigate viscoelastic relaxation in hydrogels composed of poly(acrylic acid) coordinated to Fe(III), which undergo a sol-gel transition upon increasing the concentration of the crosslinking species. The observed evolution of viscoelastic properties suggests different regimes of relaxation, which we explain with microdynamical models of chain and crosslink dynamics. While the viscoelastic behavior depicts Rouse-like characteristics at short timescales for all samples, terminal relaxation at long timescales is significantly altered by the addition of ferric ions. Applying the time-temperature superposition principle for each relaxation mechanism allows us to determine two separate activation energies. In order to fit the obtained mastercurves, we use a combined model, consisting of a generalized Maxwell model and a fractional model to account for crosslinker and chain relaxation, respectively. As a result, we gain insight into the gelation of the investigated system.

PO71-GS

Self-healing organogelators of vegetable oil and w/o emulsions

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The powerful applicability of oil gelators is envisaged in food, cosmetics, pharmaceutical industry, paints and coatings, and agrochemicals. Concerning regulations requiring the elimination of saturated fats, rising concerns among consumers health and ecological damage caused by palm oil production motivated us to design small organic molecules capable to efficiently transform liquid oil to solid state. In order to replace saturated fats (solid fat) with unsaturated fats (liquid oil) without disturbing structural and sensory characteristics of the food product, the properties of the liquid oil have to be structured to the state of solid fats. Patent protected Low molecular weight organic gelators show remarkable gelation efficiency in vegetable oils and emulsions, a thermal and mechanical stability, self-healing properties, a long period of stability and simultaneous delivery of hydro and liposoluble bioactives. The gelators of the present invention showed thermoreversible and thixotropic properties in vegetable oil and emulsions with a minimum gelation concentration of 0.025 wt%. Oil gels subjected to rheological measurements showed moderate to strong gelation ability examined at low concentrations from 0.5 to 0.05 wt%. Storage modulus (G') values of the gels from 0.1 to 0.5 wt% were in the range from 1 to 100 kPa, and yield point values from 10 Pa to 100 Pa, respectively. Frequency sweep studies of the gels indicated that the storage modulus (G') and the loss modulus (G'') values are independent of the applied frequency. The properties of the gels and w/o gelled emulsions were analysed by TEM, SEM, POM microscopy, X-ray scattering, DSC calorimetry and oscillatory rheology.

Virtual Asynchronous Online / Poster Session

PO72-GS

Influence of cellulose pulp acetylation process on the rheological properties of gel-like dispersions in vegetal oil Manuel Trejo-Cáceres, J.E Martín-Alfonso, M.Carmen Sánchez, Concepción Valencia, and José M. Franco *Pro2TecS, Universidad de Huelva, Huelva, 21007, Spain*

The use of cellulosic materials as oil thickeners for different applications has experienced a remarkable growth in recent years (Sánchez et al., 2009). The main aim of this study was to investigate the influence of cellulose pulp acetylation process on the rheological properties and microstructure of gel-like dispersions in castor oil. Cellulose pulp was treated with acetic anhydride and sulphuric acid as a catalyst by modifying three different variables (Hu et al., 2011), i.e. reaction temperature (20, 40, 60, 80, 100°C), cellulose pulp/acetic anhydride weight ratio (1:7, 1:15, 1:30) and the reaction time (1, 2, 3, 5, 8, 12, 24 h). Acetylated cellulose pulp samples were characterized by means of acetylation degree determination by heterogeneous saponification and back titration with HCl, thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The results confirm that the optimal values of temperature and the ratio of reagents were 80° C and 1:15 respectively. It was found that linear viscoelastic functions, determined in small-amplitude oscillatory shear (SAOS), and viscosity values of acetylated cellulose pulp-based gel-like dispersions in castor oil increase with the acetylation degree up to 0.8 and decrease for values above this. This work demonstrates that the optimization of the acetylation process is a key issue to achieve the final desired properties of the acetylated cellulose pulp based gel-like dispersions in castor oil for a potential use as lubricants. Keywords: cellulose pulp, acetylation, castor oil, oleogel, rheology.

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Virtual Asynchronous Online / Poster Session

PO73-GS

Rheological properties of eucalyptus kraft lignin/cellulose acetate nanostructures-based oleogels

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The present work focuses on the development of eucalyptus kraft lignin (EKL)/cellulose acetate (CA) electrospun nanostructures by electrospinning and its ability to structure castor oil. The physicochemical properties of the EKL/CA solutions in N,N-dimethylformamide/acetone were characterized by rheological, surface tension and electrical conductivity tests, and the morphology properties of the electrospun nanostructures were obtained by scanning electron microscopy. The morphology of electrospun nanostructures mainly depends on the rheological properties of the solution. Rheological and tribological characterization of the electrospun membranes in castor oil was carried out. The rheological properties of the oleogels may be tailored by modifying the EKL/CA ratio and nanostructures content. In general, electrospinning of EKL/CA solutions can be proposed as a simple and effective method to produce nanostructures for the structuring of castor oil, leading to eleogels with potential applications in the lubricant industry.

Virtual Asynchronous Online / Poster Session

PO74-GS

Rheological characterization of chitosan-pectin gels for 3D printing

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Rheological properties of chitosan (CHI)-pectin (PEC) systems were characterized to determine the most suitable gel composition for 3D printing. First, frequency sweep tests were performed. On the one hand, the single system containing chitosan (CHI2PEC0) showed a predominantly viscous response with the loss modulus (G") greater than storage modulus (G') in the low frequency regime and a crossover point at high frequency, while

CHIOPEC3 systems presented a predominantly viscous behavior (G'' > G') in the whole frequency range, indicating a liquid-like behavior. On the other hand, binary systems showed a weak gel-like behavior, with G' values higher than G'', regardless of the frequency analyzed. It is worth noting that a gel-like behavior typically results in proper stability to maintain dimensional firmness during deposition on the printing bed. Additionally, stress sweep tests were carried out, and the critical train (γ_c) was determined. Results revealed significant differences (p < 0.05) between single and binary systems, since a decrease of critical strain was observed for the latter, suggesting that the gel network had lower deformation capacity due to the interactions between chitosan and pectin that result in electrostatically stabilized complexes. Among chitosan-pectin gels, no significant difference (p > 0.05) was observed. Therefore, considering that gels exhibited small critical strain values ($\gamma_c < 0.05$) and moderately low loss tangent values ($\gamma_c < 0.05$), chitosan-pectin hydrogels can be considered weak gels with the capacity to flow without fracture, recover their structure, and achieve the properties required for 3D printing. Since high concentrations of pectin with low concentrations of chitosan showed aggregation and, thus, heterogeneity, CHI2PEC2 gels were selected for 3D printing.

Virtual Asynchronous Online / Poster Session

PO75-GS

Emergent dynamics and biomimetic 3D structures in magnetic soft matter

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Many complex dynamics and anisotropic structures in living organisms and biological tissues can be mimicked by using magnetic colloids confined to air-liquid or liquid-liquid interfaces (Snezhko & Aranson, 2011), droplets of a magnetic liquid in an immiscible fluid (Solis & Martin, 2014) and iron microparticles in polymeric matrices containing human mesenchymal stem cells (Nardecchia et al., 2021). Ten years ago our research group started a set of research projects towards the fabrication of an unprecedented magneto-rheoconfocal device that has just shed light, It is capable to generate highly-controlled non-stationary magnetic fields in the time and space domains -up to frequencies of ~ kHz in millimetric three-dimensional volumes-, at the same time the collective dynamics are visualized using high-resolution and high-speed confocal microscopy. This device is capable to generate synchronized fields by a delicate balancing between magnitude and homogeneity. In particular, it can generate high-quality pulses in the field by means of an overfeeding of the circuit at their rising and falling edges. In this communication we first show some remarkable examples of emergent dynamics and biomimetic 3D structures. Then we demonstrate that the superposition of orthogonal magnetic pulses speeds up the self-assembly process in orders of magnitude generating novel exotic structures such as the formation of circles and square sheets in the field plane. A phase diagram is built describing the dependence on field frequency and strength in both directions, and a master curve for the characteristic length scale of the system is constructed.

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Symposium PO

Section: Industrial Rheology and Processing (IP)

Virtual Asynchronous Online / Poster Session

PO76-IP

On the preparation and thermo-rheological behavior of sustainable nanofibrillated cellulose-based lubricating greases

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Fully sustainable lubricating fluids based of nanofibrillated cellulose were produced by methanol-based solvent exchange and their thermorheological behavior characterized. With this purpose, a TEMPO-mediated oxidized nanofiber and two nanofibers obtained by mechanical treatments (either bleached or non-bleached) were used and evaluated, at concentrations up to 2.8 wt.%. The nanofibrils were initially present in a hydrogel, at concentrations of around 2 wt.%. The preparation strategy consisted in their transfer to castor oil, as mediated by methanol. Oleogels were successfully produced based on water molecules being displaced away from the cellulose nanofibrils by subsequent methanol washes. Methanol-wetted fibers were properly dispersed in castor oil, such that an oleogel formed when methanol was vacuum-assisted removed. The nanocelluloses showed an extraordinary thickening capacity in castor oil. Attration forces (H-bonding) between the hydroxyl groups on the glucose units of cellulose and those on the ricinoleic fatty acid of castor oil contributed to the formation of a gel-like structure. In a similar way to traditional lubricating greases, the steady state viscous flow curves of the sustainable lubricating greases produced were characterized by a yielding behavior, typical of plastic fluids. It is noteworthy that the higher the nanofibrillated cellulose concentration was, the stronger the yielding behavior. Furthermore, a minimum in the shear stress vs. shear rate curves, which became more noticeable as temperature was raised from 25 to 180 °C, was observed. High temperatures had a direct effect on lowering the intermolecular attraction forces between cellulose and triglyceride molecules.

Such a circumstance seems to provoke changes on the oleogel internal structure which yielded non-homogeneous flow within a moderate shear rate range.

Virtual Asynchronous Online / Poster Session

PO77-IP

Effect of concentration on the rheological properties and miscibility in Bitumen/Paraffin wax blends

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Paraffin waxes, the most commonly used organic phase change materials for heat storage, are thermoregulation purposes, with potential uses in bitumen modification for road and building applications. In these uses, the solid to liquid phase change gives rise to a huge modification of the macroscopic physical properties that may limit the potential performance. Both, phase change temperatures and rheological properties, are strongly dependent of the miscibility of paraffins with other components in mixtures. Here, binary paraffin/bitumen mixtures have been analysed in a wide concentration range by means of linear viscoelastic measurements, polarised microscopy and Differential Scanning Calorimetry. From the results it can be clearly deduced that the developed microstructure of paraffin rich phases with concentration exerts a major role in the rheological behaviour and thermal properties. In addition, a minor partial compatibility of bitumen molecules with the paraffin crystals is also reported, leading to a small reduction of the normalised phase change enthalpies and therefore a good potential for thermal energy storage. Keywords: phase change material, bitumen, thermal energy storage, paraffin, linear viscoelasticity.

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Virtual Asynchronous Online / Poster Session

PO78-IP

Influence of the rheological properties on release kinetic of biobased polyurethane comprising active compounds

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In recent years, different formulations of polyurethanes based on renewable resources have been studied for many industrial applications like adhesives, coating and lubricants, in order to replace the petroleum-based commercially available that suppose some environmental concerns. In this sense, multiple applications related with cleaning purposes frequently involve the compatibility of hydrophobic/hydrophilic compounds with the polymer matrix, including active substances that need to be properly released. Therefore, the dispersion of these ingredients through the microstructural newtork requires a deep research, where the fundamental properties of such products seem to play an important role as the release profile of the active ingredients will provide insight into their best application. In this work, different polyurethane-based prototypes containing active substances were synthetized in order to study the influence of their rheological properties on the hydrophobic compound release kinetics. The amount of crosslinking agent was varied during the synthesis process, evaluating both viscoelastic moduli, as well as the 60-days release profile of prototypes containing a contant amount of the active ingredient. SAOS functions inside the linear viscoelastic region, at room temperature, were measured after finishing the synthesis process, also evaluating the rheological properties with aging time to assess microstructural changes promoted by the release process.

Virtual Asynchronous Online / Poster Session

PO79-IP

Rheological response of novel thickening lignin-based formulations via chemical crosslinking with epoxy groups

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During the last century, the global society has become increasingly interested in substituting petroleum-based products by others bio-sourced and/or biodegradable materials. In this respect, lubricant formulations are turning to the replacement of mineral oils by vegetable oils as promising alternative, which provides excellent tribological performance and biodegradable characteristics. Nevertheless, their use as lubricants is restricted as a result of their fundamental properties, and different chemical modifications are needed to improve these characteristics. Besides, the viscosity also impairs the functionality of this type of material, being necessary to obtain a large range of viscosities, from low viscous liquids to semi-solid or gel-like products, to cover different applications. Epoxidation seems to be a promising option to improve these properties, which allows to increase the viscosity with the extent of modification, as well as their reactivity with others compounds. In this work, epoxidation degree of castor oil was properly modified, studying its effect on the rheological properties, as well as its chemical interaction with a lignocelulosic material. The chemical crosslinking, expected to ocurr througout the epoxy ring opening by nucleophilic attacks of lignin hydroxyl groups, was explored to further modify the rheological properties, obtaining a variety of rheological responses from Newtonian liquids of increasing viscosities (from 1 to 500 Pa·s) to non-Newtonian viscoelastic liquids.

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PO80-IP

Effect of phase change on the thermorheological behaviour of bitumen/paraffin wax blends

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The development of bituminous phase-change materials is of great interest in building applications for thermal energy storage or thermoregulation, in order to improve the energy efficiency. This work focuses on the development and characterization of novel bituminous membranes containing a paraffin wax for outdoor applications as an improved alternative to the existing waterproofing membranes. In this study, a reference membrane containing 40 wt.% PCM was prepared and characterized with particular focus on the solid-to-liquid phase change on the thermorheological performance. Thus, steady-state viscous flow curves and oscillation frequency sweep tests were performed in a wide temperature range along with polarised optical microscopy and differential scanning calorimetry (DSC) measurements. The obtained results clearly indicate that binary mixture presents an intermediate and more complex rheological behaviour than the pure compounds, as consequence of the development of a multiphasic system in which both phases contribute to different extents to the bulk thermomechanical properties depending on the testing temperature. In addition, the appearance of a mesophase region prior to the melting transition is attributed to solid-solid transitions of paraffin crystals, having a significant impact on the thermomechanical properties of the mixture. Keywords: phase change material, bitumen, thermal energy storage, paraffin, linear viscoelasticity.

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Virtual Asynchronous Online / Poster Session

PO81-IP

RAP ad laboratory aged bitumen: differences from a rheological and microstructural point of view

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In recent years the principal aim of the research on asphalt and bitumen is focused on the sustainability and life extension of the road surface to obtain the so-called perpetual road pavements and reduce and eventually recycle the RAP (reclaimed asphalt pavement). In particular, this type of research is associated with numerous environmental and economic advantages: waste reduction, the contrast of high preliminary costs and conservation of natural resources. The traditional extraction of RAP, however, is not a convenient option for a quick field study and it also requires the use of a huge amount of solvent. Then, the major part of the studies on this topic is carried out with bitumen aged in the laboratory, following well-consolidated procedures. Unfortunately, there are differences between bitumen aged in the laboratory and in service. The existing laboratory aging methods cannot fully represent the real conditions due to the complexity of the natural aging, caused by various factors, such as the seasonal and local characteristics of the concerned areas, the UV exposition, the thermal shocks, ect. Moreover, it can be assumed that the chemical reactions at high temperatures are not necessarily the same as those that occur during aging tests in the laboratory. In this work, the differences between naturally aged bitumen and laboratory aged are investigated both rheologically, through the use of DSR (high temperatures) and DMA (low temperatures), and microscopically with the use of FTIR spectrometer.

Virtual Asynchronous Online / Poster Session

PO82-IP

Rheology and microstructure of ethylcellulose/polyphosphoric acid bituminous binders

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Nowadays, pavement scientists and practitioners are searching for more affordable/sustainable technologies able to reduce processing/application temperatures (i.e., energy savings and reduced CO2 emissions) and based on modifiers from renewable resources. This works studies the rheological properties and microstructure of novel bituminous binders prepared from ethylcellulose (EC) and polyphosphoric acid (PPA) for paving applications. Two different rheological tests were performed: (a) viscous flow measurements at 60 and 135 °C; and (b) temperature sweep tests in oscillatory shear, at 10 rad s-1 and within the linear viscoelastic interval, from 30 to 100 °C, at a heating ramp of 1 °C min-1. Rheological tests revealed that the addition of 0.5 wt% PPA to a binder containing 5 wt% EC, along with a thermal curing for 24 h at 180 °C, leads to binders with improved rutting resistance at high in-service temperatures, compared to binders prepared solely with EC or PPA. TLC-FID chromatography, FTIR spectroscopy and modulated DSC were conducted on binders to provide more information about the modification route. From them, it is possible to state that the rheological enhancement is related to a change in SARAs fractions (i.e., binder colloidal index), derived from the asphaltenes disaggregation and formation of new phosphorylated adducts. These outcomes may encourage paving industry to use lignocellulosic material, like ethylcellulose, as promising raw materials to obtain bituminous bindersaerc with enhanced rheological properties at high in-service temperatures for paving applications.

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PO83-IP

Tribological characterisation of stearic acid-in-oil phase-change-material emulsions

Esperanza Cortés-Triviño, Clara Delgado-Sánchez, <u>Adrián Tenorio-Alfonso</u>, and Francisco Javier Navarro *University of Huelva, Pro2TecS-Chemical Product and Process Technology Centre, Huelva 21071, Spain*

Phase-change-material emulsions (PCME) have recently drawn the attention of researchers due to their highly efficient energy storage and transport performance since they exhibit a noteworthy thermal energy storage density while preserving their flow characteristics. Furthermore, there is very little research reporting the manufacture of non-aqueous emulsions to be properly applied as phase change materials with potential energy recovery and storage functionalities. In this study, novel oil-in-oil PCME were prepared by dispersing different proportions of stearic acid (1-10%) in silicone oil. Bearing in mind the likely energy absorption ascribed to the as-prepared PCMEs, particularly during machinery operation, their potential application in lubrication tribological contacts has been analysed by conducting stationary and temperature ramp friction tests. Moreover, the impact of the phase change process on the PCMEs' rheological response has been evaluated through flow tests, frequency sweeps, and rotational temperature ramps within the temperature range from 30'80 °C. Additionally, their thermal energy storage and morphological properties were also assessed by means of modulated differential scanning calorimetry and optical microscopy. From the results the appropriate enhancement of the surface behavior of the ensuing PCMEs has been evinced, judging by the remarkable reduction in the friction factor (40-65%) within the whole temperature range studied, when compared to the tribological response attributed to pure silicone oil.

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Virtual Asynchronous Online / Poster Session

PO84-IP

Reliability of steric acid-in-silicone oil emulsions for energy storage applications

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Non-aqueous phase change material emulsions (PCMEs) are multifunctional fluids consisting of phase change materials (PCMs) and carrier fluids, both being oily phases. The PCMEs themselves are potential candidates as thermal energy storage systems due to the possibility of using the same medium for transport and storage and the ease of pumping transportation and circulation. Those systems are widely used worldwide for efficient utilization and conservation of energy, cleverly exploiting clean energy resources and decreasing energy consumption. Moreover, and more specifically, the non-aqueous PCMEs have the advantage of being able to be used in systems where the pressure and temperature conditions are more extreme. The present work was aimed to study the reliability of a novel non-aqueous emulsion of a phase change material, stearic acid, with a melting peak temperature of 68-71°C and silicone oil to explore using such systems as thermal energy storage systems. For industrial applications, the emulsion must be able to present suitable thermal stability after a long-term utility period and resist cyclically (melting and crystallisation cycles), as well as, recover their rheological properties after those heating-cooling cycles. Thus, a comprehensive investigation of the thermophysical properties of the emulsion, the viscous behaviour, as well as microstructure of the emulsion, was carried out. The present PCME was able to resist heating-cooling cycles and remain stable at ambient temperature for at least one month, keeping its heat storage capacity intact. Moreover, it achieves a total recovery of the rheological properties after heating-cooling temperature sweep tests in steady shear. Therefore, the resultant emulsion is a very promising material for its potential use in heat storage technologies and transport applications.

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Virtual Asynchronous Online / Poster Session

PO85-IP

Interfacial shear and elongational rheology of multi-micro/nanolayered polymers based on polyethylenes with varying architectures: New Insights into nanostructure effects and the modeling of interfacial properties

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The aim of this study is to understand the confinement effects on the rheology and molecular dynamics in multilayer polymeric systems. Various nano-structured multilayer structures composed of LDPE/LLDPE, LDPE/PS and LDPE/PC with multiple layer structures were fabricated forced assembly layer coextrusion. Interestingly, we found that confinements arising from the high Tg layers and the layer multiplication strongly affect the microstructure, morphology and molecular orientations of the confined polyethylene's. Moreover, both shear and extensional rheological investigations indicated that partly miscible pair of LDPE/LLDPE resulted in a good entanglements density and robust interphase between neighboring polymer layers. Hereto, strain hardening behaviors was observed by increasing the number of layers in the studied systems. For immiscible pairs of LDPE/PS, different shear rheological phenomena presented depending of the compositions owing the confinement by rigid PS chains allowed disparate degrees of interfacial entanglements at the trigged interphases. Obviously, negative deviation of the shear and extensional viscosities was observed only in the case of PC/PE systems whatever the composition and the degree of confinement. Layer confinement effects was more significantly demonstrated by the hindering of strain hardening in LDPE/PC from micro to nanolayered films. Whereas, the geometric confinement imposed by the PS layers allows interaction between single chains with SCB, LCB and its abounding, which promotes strain hardening especially in nanolayered systems which the contribution of the interphases is more dominating the rheological behaviors. Furthermore, the interfacial tension for both immiscible LDPE/PS and LDPE /PC system was predicted by modelling the elongational experiments. Reasonable interfacial tension values got in most of the situations and especially in nanolayered systems. They gave substantial supports and corroborate the obtained results from emulsion models.

PO86-IP

Extrusion as a potential alternative to develop eco-friendly bioplastics from soy-based agro-wastes

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Agro-wastes are attractive and potential raw materials for the fabrication of bioplastics due to their high content in biopolymers (i.e. proteins and polysaccharides) that they content. In addition, their origin and biodegradability give bioplastics an eco-friendly character that is in accordance with the circular economy that is sought today. However, the industrial scaling of these bioplastics has not yet been achieved due to their difficult processing. Therefore, the main objective of this work was to evaluate extrusion (a process widely used in the manufacture of conventional plastics) as a processing method to develop bioplastics from a soy-based agro-waste that is rich in protein (91 wt%). The bioplastics were rheologically characterized in order to evaluate their themomechanical properties. Thus, the rheological characterization of soy-based extruded bioplastics was carried out by applying small amplitude oscillatory uniaxial tensile measurements. This include strain, frequency and temperature sweep tests. In addition, their water uptake capacity was evaluated as functional property. The results show that this agro-waste and processing method may be regarded as sustainable to develop bioplastics, where extrusion parameters determine their final properties. In conclusion, the results demonstrate that is possible to adapt the production of these bioplastics on a large scale and that they can offer excellent potentials in different applications, such as packaging and hygiene products.

Virtual Asynchronous Online / Poster Session

PO88-IP

Rheological phase diagram of SLES - water system

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Surfactants are amphiphilic molecules characterized by a hydrophobic tail and a hydrophilic head, that are fundamental for an extremely wide range of applications, including home- and beauty- care, everyday use goods of interest for food and pharma industries, such as drug delivery systems, as liposomes. Due to their complex molecular structure, surfactant-water systems show different morphologies as function of concentration, establishing a complex phase diagram, where surfactant pastes show relevant and non-monotonic changes in their rheological properties as function of concentration and temperature due to the formation of complex phase structures. In particular, the presence of cubic phases in confined region of the phase diagram, not easy to identify, lead to dramatic growth of fluid viscosity, that can heavily affect process efficiency. A detailed investigation of the rheological behaviour of surfactant water system is of strategic importance for a variety of industrial application. Despite this interest a rheological phase diagram of these system is missing. The main goal of this work is to fill this gap in the knowledge, providing a systematic rheological characterization, not available in the literature, of one of the most used anionic surfactants, Sodium Lauryl Ether Sulphate (SLES), to quantify the influence of two key parameters, concentration and temperature. In detail, the rheology of SLES-water mixtures was investigated in the range 35-72 % wt of SLES and in a range of temperature 30-60°C. Three phases were identified and characterized: hexagonal, cubic and lamellar. All phases show a shear-thinning non-Newtonian behaviour, in agreement with previous results from literature.

Virtual Asynchronous Online / Poster Session

PO89-IP

Examining thixotropic models for vogurt

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Thixotropy is a characteristic behavior of many yield stress materials wherein, the material exhibits a time dependent shear-thinning behavior due to structural breakdown when sheared and may regain its original structure over time at rest. In this study, the thixotropic behavior of three commercially available stirred yogurts is examined. The goal of the study is to examine the capability of various models to predict the thixotropic behavior of yogurts between different thixotropy tests. Thus, experimental data from hysteresis loop tests, i.e., applying shear rate sweep up and down while recording shear stress response, is fitted with various thixotropic models having an equation of state and a rate equation. Yogurt shows a hysteresis loop due to differences in the rate of structural breakdown and buildup. The fitted model parameters are then used to predict the behavior of the test samples in thixotropy recovery tests, i.e., having multiple applied low and high shear stresses below and above the yield stress. Several experimental protocols for both hysteresis loop and thixotropy recovery test are considered to evaluate model fitting and predictions.

Virtual Asynchronous Online / Poster Session

PO90-IP

Rheological behaviour of fresh concrete mixtures

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Knowledge of the rheological behaviour of UHPC (ultra-high-performance concrete) is required when studying processes that run in the mixture during its preparation, transport, and application. The mixture consists of water, powdered compounds, plasticizer, and metal or organic fibres. The presence of additives makes it impossible to measure the flow properties using classical rheometers with common geometries, e.g. coaxial cylinders. We used a measuring system consisting of a cylindrical flat-bottomed vessel and an eccentrically placed screw agitator to measure the flow properties of UHPC. The shaft torque and the rotations of the agitator were measured to determine the apparent viscosity of the mixtures. A

power characteristic of the agitator (dependence of power necessary for reaching a steady state rotation on Reynolds number) has to be known for the used agitator. Moreover, the dependence of the Reynolds number on the shear rate of the liquid flowing around the agitator surface must be known. A Metzner-Otto concept was used for this purpose. Newtonian (silicon oil) and non-Newtonian power-law liquid (CMC) were used to actualize constants of the power characteristic as well as the Metzner-Otto constant of the used agitator. The flow properties of the model fluids were determined using the modular compact rheometer MCR 102 with standard coaxial cylinders (CC27) in the range of shear rates corresponding to the values that can be expected in the observed processes (order of tenths to units of reciprocal seconds). The rheological properties of fresh concretes and also their change during the solidification process were determined. The results showed that the mixtures can be divided into two groups that differ in the value of the yield stress. A Herschel-Bulkley model was used for practical description of the flow behaviour. The contribution presents the results of the methodology used to measure the flow properties of fresh concretes or similar inhomogeneous mixtures in which a solidification process can occur.

Virtual Asynchronous Online / Poster Session

PO166-IP

Rheology as a tool to study the stability of non-drying plasticines

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Plasticine is a modeling material with pseudo-elastic behavior that is widely used in early childhood education. Different types of plasticines can be found in the market, being one of the most popular the non-drying plasticine. This type of plasticine keeps the molding ability for long time, maintaining unchanged its physical properties, such as hardness and consistency, over time. Besides this important property, to attain good acceptability these materials should not stick to the hand or clothes. The present work has the objective of use rheology to evaluate the properties and the stability over time of new formulations, gluten free and highly biodegradable plasticines. To do so, oscillatory stress sweep and frequency sweep tests were performed to evaluate the viscoelastic properties (complex viscosity, storage modulus (G') and loss modulus (G'')) of the developed materials for different ageing times. Additionally, the effect of temperature on the rheological properties of the new materials was evaluated. It was found that the new formulations were stable, without relevant changes on the rheological properties during more than 30 days, exposed to air, at room temperature.

Symposium PO

Section: Micro-, Nanofluidics and Microrheology (MN)

Virtual Asynchronous Online / Poster Session

PO93-MN

Rheometry of microgels using Capillary Micromechanics

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Capillary Micromechanics is a method that was developed for measuring the elastic modulus of soft spherical particles like microgel beads or biological cells at microscopic length scales. The method employs tapered glass capillaries, with a diameter at the tip that is smaller than the diameter of the particles to be probed. As a result, as a suspension of particles is flown through such a capillary, a single particle will become trapped in the tapered section and block further flow of fluid. The deformation of this particle can then be monitored as a function of the applied pressure difference, yielding information on the mechanical properties of the soft particle. Until now, the entire process of regulating the applied pressures and quantifying particle deformations was performed manually, which is a cumbersome process that is prone to poor repeatability. Moreover, no efforts have been made to use the method to gain additional information on the viscoelastic properties of the particles, beyond extracting elastic moduli. In this poster we present a semi-automated implementation of Capillary Micromechanics (Wyss et al., 2010). In our setup, once a particle is trapped in the tapered capillary, the entire process of pressure regulation and image acquisition is automated. This has significantly increased the ease of operation and the repeatability in measurements of the elastic moduli of the particles. In addition, we have extended the Capillary Micromechanics method by using it in time-dependent measurements such as oscillatory tests and creep tests. These measurements enable us to extract additional information on the viscoelastic properties and the size-dependent swelling/deswelling dynamics of the soft particles, including properties like their characteristic relaxation times, or the frequency-dependent viscoelastic moduli of the particles.

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Virtual Asynchronous Online / Poster Session

PO94-MN

Transport dynamics of rigid fibers in three-dimensional microfluidic vortex flows

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The motion of particles in flows is of fundamental importance in several industrial and natural processes. In many of these processes, the transported particles are not simple spheres but anisotropic particles, such as fibers. Examples include paper making, plastic debris aggregating in

oceans, clogging of arteries with biofilm streamers or ice crystals in turbulent clouds. Recent studies have focused on the interactions of these elongated particles, rigid or flexible, in laminar or fully turbulent flows and their morphology and transport dynamics have been investigated. Depending on their size, initial orientation or inertia, fibers exhibit complex behaviors involving rotation or preferential distribution in specific flow regions. However, the transport of such particles, at intermediate unstable flow regimes, is yet to be explored. Here, we investigate experimentally the interactions between fibers and a single stationary and three-dimensional vortex. Experiments are conducted within a microfluidic cross-lot geometry, to generate a well-controlled vortical flow at moderate Reynolds number (Re=?Uw/??50 where U is the flow velocity, w is the channel width, ? and ? are the fluid's density and viscosity respectively). Preliminary observations of fibers suspended in a Newtonian fluid show complex orientation dynamics for fibers with high aspect ratio, whereas fibers with low aspect ratio seem to follow the orientation of the streamlines. In addition, we show that fibers can either diverge from the vortical flow streamlines or follow them and act like tracer particles. This study will set the foundation to further investigate deformable fibers. The results of this study will advance numerous applications, such as cleaning and water treatment techniques in oceanic flows or improved particle sorting and transport techniques in industrial flows.

Virtual Asynchronous Online / Poster Session

PO96-MN

Single DNA molecule dynamics in extensional flows

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Extensional flows of dilute polymer solutions are found in a wide variety of applications, from inkjet printing to oil-recovery processes. It is therefore of great interest and practical importance to investigate the dynamics of single polymer chains under such flow types. Polymer chains that are coiled in their equilibrium configuration at rest, undergo the so-called coil-stretch transition and unravel when subjected to an extensional flow above a certain strength (given by the dimensionless parameter Wi, the Weissenberg number). Notably, even if all molecules start from similar initial conditions and are immersed in the same flow, they all unravel in a different way before reaching their steady state (fully stretched in a straight line) due to the thermal fluctuations of the chains. We investigate the molecular individualism of the coil-stretch transition of single polymer chains trough experiments and simulations using DNA as the model polymer. Our experimental set-up consists of a hyperbolic microfluidic channel optimized to produce a constant strain rate. The molecules start from a coiled state and are followed as they are transported and deformed by the extensional flow. The numerical simulations reproduce these conditions. We compare the behavior, such as the maximum extension of a molecule or its configuration at a given time, for numerical and experimental molecules that have a similar random initial configuration, for instance comparable initial extension or comparable orientation with respect to the flow direction. The goal is to elucidate whether there is a unique and deterministic relation between the molecule's dynamics as it unravels and its random initial configuration and, if that is the case, under what conditions. The effect of the flow strength on the dynamics is also investigated by exploring different values of Wi.

Virtual Asynchronous Online / Poster Session

PO97-MN

Rheology of attractive soft microcapsules

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Microcapsules of around 100 micrometers composed of a membrane obtained by complexing polyelectrolytes at the water-oil interface. Suspensions are these capsules are generated using membrane emulsification. In addition, the elastic properties of the particles are characterized by an automated measurement of their deformation in a microfluidic elongational flow chamber (Maleki et al., 2021). The rheological properties of the suspensions are characterized by rotary rheometry in oscillation, in steady state and in shear inversion experiments for volume fractions varying from 20 to 55%. Surprisingly, the suspensions obtained exhibit a Bingham type behavior with a yield point for volume fractions as low as 20%. The yield stress increases with the volume fraction. Just after shear, the elastic modulus of the suspension increases over time, which is a signature of an aggregation mechanism. The viscoelastic behavior of the suspension after pre-shearing, in order to break up the capsule clusters, is characteristic of the behavior of attractive colloidal suspensions (Trappe & Weitz, 2000). This behavior was rather unexpected given the large size of the microcapsules, and suggest long range interactions at the scale of tens of micrometers. Its physical origin remains unclear, but should probably involve induced dipole interactions, as we found that it depends on the permittvity of the external liquid phase, and as the microcapsules form chains under an electric field. We also performed shear inversion experiments. These experiments highlight that the yield point is associated with the formation of a microstructure under flow, contrary to colloidal gels which remains isotropic. Above the yield stress, the behavior of the suspens microcapsules is very similar to that of suspensions of rigid spheres with lubricated contacts. In conclusion, the microcapsule system formed by the complexation of polyelectrolytes has the behavior of attractive supsensions.

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Memory effect of red blood cells in a 3D microfluidic chip

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The significance of healthy blood vessels and blood flow for proper brain functioning is becoming more recognized as the involvement of brain vasculature in the development of human neurodegenerative disorders, notably Alzheimer's disease. Therefore, it is necessary to develop a platform to investigate blood flow and blood cells behavior through brain vasculature. The field got a boost with the introduction of microfluidics, which allowed to study the effects of these parameters systematically, mostly using 2D channels with rectangular cross section, very different from the physiological vessels. The main drawback of this approach is that the micro-channels are inherently different from the physiological vessels, not only because the channels are rectangular, but also because they are confined to 2D (Mehri et al., 2018). A model 3-D microfluidic channels is used to study the RBCs flow through different vessels geometry and their flow dynamics. The breakup of red blood cell aggregates as well as red blood cell dynamics will be studied by systematically varying the interaction strength between the red blood cells and the complexity of flow geometries. To this end, we will make use of a novel technique, Selective Laser-induced Etching (SLE), to produce 3D structures in glass that allows the design of bifurcations into different planes with any desirable shape (Hermans et al., 2014). To study the shape memory of the vessels the second generation of the bifurcation has been implemented with a parallel and perpendicular orientation relative to the first bifurcation. This 3D design will be exploited to investigate shape memory effects and traffic of the red blood cells, using ultra-fast confocal microscopy.

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Symposium PO

Section: Non-Newtonian Fluid Mechanics and Computational Rheology (NF)

Virtual Asynchronous Online / Poster Session

PO102-NF

PO98-MN

Curvature ratio dependence of elastic instability onset of giant micelles solutions in Taylor-Couette flow Xiaoxiao Yang^{1,2}, Darius Marin¹, Charlotte Py¹, Anke Lindner², and Sandra Lerouge¹

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A complex fluid is characterized by a microstructure, with typical timescales, that may couple with an external flow, leading to complex interactions and even instabilities. Giant micellar solutions based on surfactant molecules are benchmark complex fluids for the study of the flow-structure coupling. They have generated abundant literature regarding various types of instabilities, for example, the shear-banding instability, elastic instabilities, and turbulence. We focus on the effect of the curvature ratio of a Taylor-Couette(TC) geometry on the onset of elastic turbulence. In our experimental situation, the solution of giant micelles is placed in the gap between two concentric cylinders in a TC geometry, the inner cylinder being fixed to the shaft of a Physica MCR 301 rheometer working in strain-controlled mode using a feedback loop. Semi-dilute solutions of CTAB/NaNO3 and CPCl/NaSal are chosen as fluid samples. We investigate the flow dynamics for different curvature ratios as a function of Wi. Utilizing flow visualizations, we elucidate the temporal evolution of the flow patterns along the flow curve. Specifically, we demonstrate that the transition between the shear-banding plateau and the elastic turbulence regime is characterized by a typical hysteresis loop in the flow curve for the lowest curvature ratios. With increasing curvature ratio, the hysteresis loop gradually disappears, and a so-called 'turbulent burst' regime can be captured. We have proven that this regime is an intermittent and permanent state with a dominant switch frequency. In addition, we find that, in a 'turbulent burst' cycle, complex turbulent structures located in the high shear band, two stable shear bands, as well as an unstable interface characterized by Taylor-like vortices, can transiently coexist. In shear startup experiments, we observe normal stress effects, coupling with the stretched and entangled-to-unentangled microstructures that are regarded as possible mechanisms driving the turbulent burst periodic phenomenon.

Virtual Asynchronous Online / Poster Session

PO103-NF

Mixing of heterogeneous fluids: Buoyancy effects

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The mixing of stratified fluids is an important subject in various industrial fields. In characterizing mixing flows, it is common practice to neglect the inhomogeneity of the fluid properties and use the spread of a passive scalar to characterize mixing. We consider a model problem to explore the effect of inhomogeneity on mixing flows. We study the stirring of a heterogeneous fluid using a rotating disk in an axisymmetric container. Initially, the bottom and top halves of the container are filled with heavy viscoplastic and light Newtonian fluids, respectively. We investigate the effect of buoyancy due to the density difference between two fluids by comparing the flow dynamics at different Richardson numbers. The finite volume numerical simulations are carried out using the OpenFOAM toolbox. We use twoLiquidMixingFoam solver for modeling the miscible

mixing of two incompressible fluids. We examine different mixing characteristics to illustrate how inhomogeneity can affect mixing by introducing an analogous homogeneous model. We develop an analytical solution for mixing in the systems to identify different stages of mixing.

Virtual Asynchronous Online / Poster Session

PO104-NF

Particle redistribution in a horizontal Couette

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Transport of large quantities of solid particle suspensions using a liquid continues to be of great industrial importance; for example, clearing cuttings whilst drilling oil, gas or geothermal wells, i.e. hole cleaning. During such processes, identifying transition criteria, i.e. critical flowrates and/or applied pressure gradients required to induce significant solid bed mobilisation, is of great importance. In this work, we investigate the flow conditions encountered during hole cleaning processes. We study solids transport within suspensions in a horizontal Couette geometry consisting of two concentric horizontal cylinders using a series of detailed numerical and experimental techniques. In the numerical part of this study we have adapted a constitutive model, originally formulated for simple-shear flow conditions that describes the stress tensor for a mixture of particles in a liquid, into a two-phase finite-volume solver. Here, the mathematical platform describing the interaction of two-phases is obtained using the conservation of mass and momentum in each phase, from a Eulerian-Eulerian perspective. The governing equations are coded in a solver developed in-house using OpenFOAM. To extend our investigation and to benchmark the numerical results, a series of detailed experiments have been carried out. Using numerical simulations with supporting experimental data we show that as the rotation speed of the inner wall reaches a critical value, a flow field with secondary flow vortices replaces the simple undirectional flow. These secondary motions of the fluid flow, also known as Taylor-vortices, are shown to be the key element for the solid-bed redistribution and resuspension during a hole cleaning process. The results obtained from the experiments show excellent agreement with numerical simulations carried out with our numerical solver. The strong agreement suggests the mathematical platform can be successfully used to simulate the interaction of suspension with a fluid flow even in complex flow conditions.

Virtual Asynchronous Online / Poster Session

PO105-NF

Dynamics of immiscible liquids in rotational motion

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This work is dedicated to the experimental investigations of the interface's stability between two immiscible liquids. In a confined cylindrical vessel, one pure viscous liquid and viscoelastic polymer solutions are put in motion by the rotation of an upper disk or a concentric cylinder connected with the MCR 301 Anton Paar rheometer. The dynamics of the interface is simultaneously visualized with two digital cameras at 60 fps and 4000 fps, respectively. The rotational speed (n) and the torque (T) are measured, one of the two being the INPUT or the OUTPUT. The viscoelastic samples are PEO - water solutions at different concentrations of the polymer and the viscous fluids are silicone oils. The controlled parameters are the viscosity ratio between the immiscible fluids and the Weber, Reynolds and Elasticity numbers, respectively. The aims of the study are: (i) to identify for each tested pair-fluid samples the flow regime corresponding to the Kelvin-Helmholtz (KH) instability (if it exists), (ii) to correlate the interface topology with the measured T(n) diagram and with the fluids properties, in particular with the PEO concentration in the polymer solution, (iii) to detect the existence of the critical/bifurcation points, and eventually the onset of the chaotic regime, using the experimental phase diagrams: T(n) and T(dT/dt) or n(dn/dt), at controlled speed/torque experiments.

Virtual Asynchronous Online / Poster Session

PO107-NF

Rheology of immiscible two-phase flow including compressible and incompressible fluids in a capillary tube varying radius

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We perform steady-state simulations with two-phase flow of a compressible and an incompressible fluid in a capillary tube varying radius, corresponding to various pressure conditions. From these simulations, time-averaged and time-dependent quantities are computed. The time-averaged quantities are average volume flow rate and saturation. The time-dependent quantities are the growth of bubbles and volume flow rate. Our results are based on the analytical derivation and numerical simulations. Our conclusion is that the relationship between applied pressure drop and average volume flow rate is linear. Furthermore, we conclude that the interplay between the effects of compressibility and capillary force results in both saturation and growth of bubbles.

Virtual Asynchronous Online / Poster Session

PO109-NF

Breakup of viscoelastic filaments in air and in immersed Newtonian oils

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The paper is concerned with the experimental investigations of viscoelastic filaments breakup in air and in immersed Newtonian viscous oils. The viscoelastic samples are polymer solutions at different concentrations of PEO (Polyethylene Oxide with Mw = 1 million) in water. The filament's profile in the vicinity of its minimum diameter is determined by image processing using an original code developed in Matlab environment. The

visualizations are performed with a fast camera in the interval 2000 fps to 50000 fps. The parameters followed in our investigations are the time evolution of the filament neck and the corresponding thinning velocity before the droplet/jet breakup. Three flow regimes are observed as the relative time approach to zero (when breakup occurs): (i) an exponential increasing of the neck thinning velocity, followed by (ii) a non-monotonous variation of the thinning velocity and, (iii) the final pinch-off region, where thinning velocity is decreasing to a constant value or oscillates until the rupture of the filament. The values of the thinning velocity are correlated with the polymer concentration and the sample's elasticity measured in oscillatory shear. The influence of the ratio between the viscosity of the tested samples and the viscosity of the Newtonian oils is also investigated. The results of this experimental study have potential in developing novel techniques and more precise procedures in determining the interfacial rheology of complex fluid in dominated elongational flows.

Virtual Asynchronous Online / Poster Session

PO110-NF

Sedimentation of a spherical particle in an elasto-viscoplastic fluid near a wall

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Sedimentation of particles in non-Newtonian fluids in unconfined and confined systems has received significant interest due to a large number of industrial applications involving this kind of flow. The dynamics of particles in viscoelastic and viscoplastic fluids has been extensively investigated to understand the effect of particle shape, rheological properties of the suspending liquid, and confinement. In contrast, studies on the settling dynamics of particles in elasto-viscoplastic fluids are few and limited to unconfined geometries. In the present study, the sedimentation of a single particle in an elasto-viscoplastic fluid near an infinite flat wall is investigated by direct numerical simulations. The particle is assumed to be rigid and spherical, and inertia is neglected. The fluid is modelled by the Saramito constitutive equation accounting for both elasticity and yield-stress. An Arbitrary Lagrangian-Eulerian finite element method is employed to handle the motion of the particle near the wall. The effect of fluid elasticity (Weissenberg number) and plasticity (Bingham number) of the fluid, and the particle-wall distance on the settling dynamics is investigated.

Virtual Asynchronous Online / Poster Session

PO111-NF

Experimental determination of radial wicking velocities for complex fluids

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The study of fluid transport in porous media can offer valuable information for the improvement of various technologies, such as printing, filtering or paper-based sensing platforms. Wicking in paper has been studied before, but in most cases only simple fluids have been used. Here, we offer an analysis of the wicking process for viscoelastic fluids, in order to identify the influence of their material properties over the spreading mechanism. For this purpose, solutions of PEO (polyethylene oxide), with ranging concentrations, and silicone oils, with different molecular masses, were created and their rheological properties were investigated. While until present most studies focused on the process taking place inside the substrate, here we bring a different perspective, by studying the process from a lateral view. This in turn, brings into focus the behaviour of the drop remaining at the top of the substrate, as it is consumed and absorbed in the paper. The evolution in time of the drop shape was analysed and the spreading velocities were calculated.

Virtual Asynchronous Online / Poster Session

PO112-NF

Learning physically-informed differential viscoelastic constitutive equations from data

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Although a substantial body of work has been dedicated to deriving viscoelastic constitutive equations for particular classes of materials directly from physical considerations, these models often cannot sufficiently describe the diverse response space of viscoelastic materials in common experimentally and industrially relevant conditions. Recently, the advent of widely available machine learning (ML) tools has given rise to a new approach: learning constitutive models directly from data. While current ML approaches have shown some success in very particular circumstances, they are not easily portable to different flow conditions, accommodate training data taken only by specific experimental protocols, and do not enforce key physical constraints such as invariance to rotating frames of reference. Here, we present a framework for learning physically-informed differential viscoelastic constitutive equations that combines the salient features of ML and physically-informed approaches. These models, which we call "rheological universal differential equations" (RUDEs), are composed of the upper-convected Maxwell (UCM) model with an added tensor-valued neural network, which takes the rate-of-deformation and stress tensors as inputs. The UCM model provides an underlying viscoelastic skeleton for the model, and the neural network provides a tool for learning material-specific features while preserving physical constraints such as frame invariance. Moreover, because RUDEs are differential and tensorial in form, they may be trained on -- and ultimately used to predict -- any observable related to the stress or strain obtained in an arbitrary flow protocol. We demonstrate these predictive capabilities using RUDEs trained on synthetic data from well-known constitutive models. With increased availability of a wide breadth of experimental data for viscoelastic materials, RUDEs open new avenues for efficient and accurate data-driven rheological modeling.

PO113-NF

Virtual Asynchronous Online / Poster Session

Dynamic yield surfaces and apparent elastic limits

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One of the main goals of rheology is to derive simple constitutive equations that cover a wide range of complex material behaviour. We study creep and yield phenomena with a nonlinear Maxwell model. This model is based on the separation of the Maxwell relaxation time into two components; one component to describe deformation-driven structural relaxation and one component to describe internal relaxation mechanisms. In the glassy limit the latter is assumed to vanish leaving only the deformation dependent relaxation time. We will present two implications of this assumption: First the prediction of an apparent elastic yield strain and second the prediction of a dynamic yield surface which in first order resembles an empirical criterion for yielding postulated by von Mises. The relation of predictions based on the nonlinear Maxwell model to standard criteria for yielding found in engineering literature will be discussed.

Virtual Asynchronous Online / Poster Session

PO114-NF

The effect of cohesion on the discharge of a granular material through theorifice of a silo

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Cohesive granular materials are encountered in many geo-physical and industrial applications, examples being fine sand, cement, or flours. Whereas many advances have been made in the description of cohesionless granular flows, the behavior of cohesive powders remains elusive. Since the concept of cohesion overlaps a great complexity, there is a need of a simple definition and a good control of the cohesion to perform quantitative experiments. We recently developed a cohesion-controlled granular material (CCGM) (Gans et al., 2020) where cohesion arise from a polymere coating around particles. This CCGM has proven to be very useful to develop experimental studies where a bulk cohesion needs to be implemented.

Using this recently developed method, we experimentally consider the mass flow rate of cohesive grains through the orifice of a silo. This configuration has been extensively studied in the case of cohesionless granular material. Several studies already showed that the mass flow rate is mostly controlled by the diameter of the orifice D (Beverloo et al., 1961). In our study, we characterize the effect of the cohesion on the initiation of a flow, as well as the effect on the mass flow rate of a cohesive granular material at the outlet of an axisymmetric, and a quasi-2D silo. Our experimental results for the quasi-2D configuration are compared to numerical simulations based on a Navier-Stokes solver (Zou et al., 2020) with the help of A. Abramian and P.-Y. Lagrée at d'Alembert Institute, Paris, in the framework of the COPRINT project (ANR-17-CE08-0017).

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Asynchronous Online / Poster Session Virtual

PO117-NF

Passive transport of SARS-CoV-2

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Since 2019, the virus SARS-CoV-2 has been a critical topic worldwide because of its health impact on millions of people. Currently, different studies about virus genetics, biochemistry, infectivity, physics, and dynamics, have been addressed. Here, we investigate the diffusion of SARS-CoV-2 virions using computational simulations. Due to the morphological features, virions can be seen as decorated nanoparticles and are characterized according to their translational and rotational diffusivity. We used the Rigid Multi-Blob (RMB) (Balboa Usabiaga et al., 2017) methodology and Smoothed Dissipative Particle Dynamics (SDPD) (Espanol & Revenga, 2003) to simulate the effect of the spike proteins in the virions transport. Using RMB we construct virion models by discretizing the structures as a set of rigidly connected spherical beads, later we compute their mobility tensor to determine the diffusion. The results revealed the effect of spike arrangement, number, and morphology on virion transport, and shed light on its possible effects on viral infectivity. In general, randomness in the distribution of the spike decreases the hydrodynamic drag of the particles facilitating their transport. Using the same blob discretization of RMB, we conduct SDPD simulations, without the rigid-body restriction between envelope and spikes. This approach allowed us to characterize the effects of spike motion and localization on the rotational diffusivity of the virion. We identify that passive microrheology can provide relevant information about viruses, and offer potential novel biomarkers.

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Symposium PO

Section: Solids, Glasses and Composites (SG)

Virtual Asynchronous Online / Poster Session

PO118-SG

Rheologically assisted design of conductive adhesives based on carbon nanotubes and graphite nanoplatelets for surface mounting technology

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Electrically conductive adhesives (ECAs) based on epoxy, carbon nanotubes (CNT), and exfoliated graphite (EG) were designed for soldering electronic components to Printed Circuit Boards (PCB) in surface mounting technology (SMT). Because the rheology of the adhesives is paramount for the success of the deposition process, which is based on stencil printing, a rheological analysis of the process was first performed. The analysis goes beyond stencil printing as the placement of electronic components on PCB and their conveying to the soldering oven are considered. An experimental protocol was then defined to assess the relevant viscoelastic characteristics of the adhesives under flow and stress conditions at play during SMT. Different composite formulations of epoxy/CNT/EG were produced, optimizing the results or an earlier study Lopes et al., 2020). Their rheological characteristics were established following the designed protocol and benchmarked with a commercial solder paste. The thermal and electrical properties of the composite formulations were also characterized. As a result, a new, electrically conductive adhesive was delivered with potential to be an eco-friendly alternative to the solder paste currently used in stencil printing of PCB.

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Virtual Asynchronous Online / Poster Session

PO119-SG

Rheological characterization of bioplastics from an invasive brown macroalgae

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In this work, the use of the algae Rugulopteryx okamurae is proposed for the development of bioplastics as a possible solution to the contamination produced by plastic industries. This algae species original from the Pacific Ocean, classified as invasive in the Mediterranean Sea, seriously affects the native biodiversity. An analysis of its chemical composition revealed a low protein content (9.9%), together with lipids (11.6%), ashes (18.5%) and moisture (13.5%). Physical-chemical properties have also been characterized by means of different methods such as granulometry, thermogravimetry (TGA) or differential scanning calorimetry (DSC) of the grinded biomass used for the manufacture of bioplastics. Doughs with different algae/glycerol ratios (50/50, 60/40, 70/30) were fed into an injection molding device, keeping the mold temperature at 120°C. The rheological and mechanical properties of these bioplastics were determined, as well as their water uptake capacity. When bioplastics were heated, the rheological response detected was similar to that of thermoplastics, displaying a decrease in both the elastic (E') and the viscous (E'') moduli. Frequency sweep tests were also performed before and after every heat treatment, observing a strengthening of the samples through an increase in E' and E'' after the treatment. E' was always greater than E'' for all samples, which implied a predominantly elastic behaviour, being the 70/30 sample the one presenting higher values for both viscoelastic and tensile properties. Water uptake capacity decreased with the increase of algae in the mixture, being 262% in dry weight for the 50/50 ratio, 220% for 60/40 and 181% for 70/30. This is in agreement with the low solubility in water detected for the starting material. Therefore, even if further research is required to assess its real potential, these results point out that this algae could be employed as raw material in environmentally friendly materials.

Virtual Asynchronous Online / Poster Session

PO120-SG

Urban wastes as fillers in biocomposites based on porcine plasma protein

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Whey protein is a liquid byproduct of the cheese manufacturing process and it is believed to have excellent nutritional benefits and exceptional physicochemical properties. As a result, whey protein products are used in a wide range of food applications as foaming agents, stabilizers, emulsifiers, and gelling agents (to name a few). When a concentrated aqueous whey protein solution is heated, it induces denaturation and aggregation of the protein molecules, and a gel-like network can be formed. The protein gel structure directly influences the sensory response and structure of food products, and thus, gelation is considered one of the most important functional properties of proteins. In this study, rheology coupled with in situ Fourier transform infrared (FTIR) spectroscopy was used to examine the thermal denaturation and gelation of aqueous whey

protein solutions (50% w/w). This multimodal analytical technique allowed the bulk mechanical properties of the whey protein specimen (namely the elastic and viscous moduli; G' and G", respectively) to be directly correlated in real-time with conformational changes at the molecular level (increases in intensity and wavenumber shifts of the Amide I band). Using simultaneous rheology with in situ FTIR spectroscopy allowed for deconvolution of the multi-step whey protein gelation process, including protein molecule unfolding, aggregation, and aggregate growth and rearrangement. The hyphenated technique provides corroborating evidences, from both macroscopic and molecular perspectives, to unravel a complex, multi-step process that cannot be fully revealed by either individual analytical technique.

Virtual Asynchronous Online / Poster Session

PO121-SG

Functional and processing-related properties of polymer-based magnetic composite filaments for additive manufacturing

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In fused deposition modeling (FDM), the most extended additive manufacturing (AM) method, a polymeric filament is extruded above its melting point and deposited into thin layers. There is a high interest in the use of composite filaments, formed by a polymeric matrix with functional fillers, for the AM of functional parts. Apart from uniform filament diameter for the dimensional quality, an even distribution of fillers is required when using composite filaments for a uniform functionality of printed parts. Homogeneous soft magnetic PLA composite filaments for FDM have been recently reported, in which a customized feedstock of PLA capsules filled with the functional fillers is employed (Díaz-García et al. 2020). A demagnetizing factor of ~ 1/3 (spheres) is found for all the samples regardless of the concentrations of fillers (30, 39, and 52 wt.%). The addition of the fillers causes a remarkable shift in the thermal degradation temperature of the PLA. Increasing filler content in composites produces an abrupt drop in the complex moduli above the glass transition, which shifts to lower temperatures according to tan(d) and DSC measurements. A decrease in the melt viscosity is also observed, which changes the extrusion and printing conditions of the filaments for filler contents above 30 wt. %. The reduction of the viscosity of the composites requires the lowering of the temperatures for their extrusion and printing with respect to the typical ones for PLA.

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Virtual Asynchronous Online / Poster Session

PO122-SG

Influence of MWCNT amount in rheological behavior of poly(lactic acid) conductive filament

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Fusion deposition modelling (FDM) 3D printing based on a thermoplastic material has become a powerful tool to rapidly fabricate 3D objects with unique shapes from low-cost raw materials. This technology has great potential in the electronic and energy storage devices industry since it allows the integration of sensors, conductors, devices with different electronic functions. However, there is a low availability of suitable materials with specific properties, for instance electrical conductivity, to be used in FDM printing. To design new filaments suitable for 3D printing, we have studied a polymer composite based on poly(lactic acid) (PLA) and multi-walled carbon nanotubes (MWCNT), a conductive nanofiller. PLA is one of the most popular thermoplastics used in FDM due to its good processability, low glass transition temperature, cheapness, and biodegradability. Furthermore, with the proper dispersion of the MWCNT in the PLA matrix, the polymer composite gains electrical conductivity as well as thermal stability. Several rheological studies have been performed for the sake of obtaining a precise estimation of the rheological percolation threshold. In this context, the optimized amount of nanofiller has been calculated. Additionally, electrical conductivity measurements and thermograms obtained by thermogravimetric analysis (TGA) were used to support the results. Keywords: FDM, electrically conducting polymer composite, poly(lactic acid), MWCNT

Virtual Asynchronous Online / Poster Session

PO123-SG

The anatomical wax models of the "La Specola" Museum: Understanding the degradation through calorimetry and rheology measurements

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"La Specola" Museum in Florence houses the world's most well-known collection of anatomical waxes. The over 1400 models include all body parts, from small bones to whole figures, thus representing a complete three-dimensional treatise of anatomy. One of the first creations is "La Venere" (Venus), the only model made of dismountable wax parts, where various layers or sections can be removed to reveal underlying body

parts including a small fetus. The anatomical models are mainly constituted by beeswax, a durable material that has been used over centuries for numerous purposes, from the production of candles or seals to the manufacture of ex voto or of models for the artists' workshops. Though extremely durable, beeswax undergoes several degradation processes, ranging from cracking to materials losses. Periodically, a white crystalline layer, called "wax bloom", appears on the models' surface, obviously impairing their aesthetical characteristics. Many mechanisms of formation have been hypothesized, including the partial hydrolysis of esters, the chemical degradation of additives, the polymorphic transformation of fats and wax favoured by temperature changes, and the reaction among components. Our thermal and X-ray measurements indicate that a poor solid miscibility between the wax bloom compounds and other beeswax components leads to phase separation and, in turns, to the migration of immiscible materials towards the surface. Besides the aesthetical issue, another question must be addressed: Can the loss of material change the mechanical properties of the objects affecting their durability? Rheology measurements, performed both on fresh and ancient samples, reveal that, upon ageing, models undergo a significant embrittlement given the higher storage moduli and critical strain ascribed to the linear viscoelastic region. Hence, this research provides a unique correlation between rheological, chemical and microstructural properties when assessing the wax degradation.

Virtual Asynchronous Online / Poster Session

PO124-SG

Effect of morphology and friction on the unusual shear resistance of crumpled materials

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Crumpling of a thin sheet is an everyday observation, but it also offers a novel way of creating random meta-structures with peculiar properties. Due to their significant stiffness despite their low density, crumpled materials are excellent candidates for manufacturing robust low weight composite materials, such as sandwich panels. However, so far crumpled materials have been studied only under uniaxial or isotropic compression, and the shear resistance has been mostly ignored. Here we study the response of crumpled structures to shear and compaction deformations via short/large amplitude oscillatory shear (SAOS/LAOS) experiments, and the influence of morphology and friction on their shear resistance and nonlinear rheology. The internal morphology, in the form of stacked layers parallel to the shear direction, resulted in lower shear storage modulus, and increased energy dissipation through layers sliding, compared to layers normal to the shear direction. The reduction of surface friction allowed for easier internal rearrangements during shear. Our results pave the way to better understand the full mechanical response of crumpled systems and tune their desired properties for practical applications.

Virtual Asynchronous Online / Poster Session

PO142-SM

High performance polystyrene/polyisoprene thermoplastic elastomers using PS/PI block copolymers and the POM-POM topology

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Thermoplastic elastomers (TPE) of Polystyrene-b-Polyisoprene-b-Polystyrene block copolymers (SIS) are used in many applications such as adhesives, coatings, fibres, and films. High bridging of the polymer chains between different polystyrene (PS) phases is the key to high strength and toughness of these materials. The influence of the POM-POM architecture on the tensile properties of PS/PI TPEs was investigated. The PS/PI TPEs with a POM-POM topology - PS backbone, PS-b-PI sidechains at both ends of the backbone - were synthesized via anionic polymerization and grafting-onto, resulting in well-defined molecular properties. The four synthesized POM-POM samples are based on the same PS backbone (MW, BB = 100 kg mol-1). The PI content of the samples is varied between 30 vol% and 90 vol% through the PS/PI composition of the side chains (MW, SC ~ 80 kg mol-1, nSC ~ 2x15). The molecular parameters of the synthesized PS/PI POM-POMs were characterized using size exclusion chromatography, 400 MHz 1H NMR, small-angle X-ray scattering, and differential scanning calorimetry. Tensile specimens were characterised in monotonic uniaxial and cyclic testing. The samples up to 70 vol% PI showed ductile behaviour, including yielding, whereas the samples with 90 vol% PI showed rubber-like behaviour. Overall, the POM-POM topology significantly increases toughness and ultimate tensile stress. In comparison to linear SIS triblock copolymers and other model systems from the literature with similar PI content, the ultimate tensile stress is increased by about 20 to 50 % beyond known limits to 30 MPa, whereas the strain at break of up to 1400 % is within the range in literature, while the (high) E-Moduli are not affected by the topology.

Symposium PO

Section: Polymer Solutions and Melts (SM)

Virtual Asynchronous Online / Poster Session

PO91-SM

In-line slit capillary rheometer for highly charged polymer melts

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The PGSS process is an innovative method for particle generation from liquefiable solids. Simplified, the material to be micronized is melted and a supercritical fluid (e.g. CO₂) is dissolved into the melt. Subsequently, the mixture is sprayed through a nozzle into ambient pressure. Due to the sudden drop in pressure, the CO₂ changes its state of aggregation and the solubility of the CO2 in the melt decreases drastically. The escaping gas breaks the matrix fluid down into fine droplets that solidify in a spray tower. For an uniform pulverisation a homogenous mixing of supercritical CO₂ is crucial. Additionally, the thus lowered viscosity allows for a decent spraying process in the first place. In the present application, a polymer is compounded using a twin-screw extruder while supercritical CO₂ is injected at the same time. Further homogenization of the polymer/supercritical fluid mixture takes place in a following dynamic mixer. The control over the mixing quality is the key part for a sufficient micronization. To asses this parameter, the viscosity of the polymer/gas mixture is to be measured during the process. Therefore, three slit capillaries are constructed to enable in-line rheological measurements during operation. Besides the observation process this set up can be used to investigate the viscosity of gas laden polymers in general. The poster explains the set-up of the PGSS system, which provides the polymer/gas mixtures to be measured and describes the rheological measurements where 3 different shear rates can be investigated at the same time using three consecutive slit dies. The validation of the measuring system is discussed in a comparison with a high-pressure capillary rheometer and finally, first measurement results of different polymers at different gas loadings are shown.

Virtual Asynchronous Online / Poster Session

PO87-SM

Study of rheological, morphological properties, dynamics and miscibility in poly(lactid acid) - poly(hydroxybutyrate-co-hydroxy valerate) blends

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The purpose of the present work is to gain a fundamental understanding of the composition dependence among rheology, morphology, miscibility and thermal stability of Poly(lactide-acid) (PLA) Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) biopolymer blends by melt mixing at whole ranges of compositions. Firstly, restricted processing conditions were chosen due to inherent heavy thermal degradation of PHBV proved by Small-amplitude oscillatory shear rheology (SAOS) and Steric Exclusion Chromatography (SEC). Based on this, the composition dependence of blends was characterized by SAOS and supported by SEM analysis. Then, the observed changes of Tgs from DMA and DSC are supported by coupling SAOS to Dielectric Relaxation Spectroscopy (DRS). Hitherto, the composition dependence of thermos-rheological complexity of PLA/PHBV blends in the melt was revealed. The origin of this dependence was due to the disparate properties between PLA and PHBV on the basis of their interfacial properties at different scales. Irregular structure morphologies caused by high viscoelastic mismatched properties illustrated the degree of partial miscibility. Moreover, thermo-rheological complexity appeared in the asymmetric PLA-rich phases, could also be explained by the crystal-amorphous interfacial MWS polarization because of their different crystallization morphologies. This miscibility suffers also from the lower thermal stability of PHBV. Hence, their melt-induced degradation process seems to be a responsible of some in-situ self-compatibilization or plasticization mechanisms. Therefore, the miscibility and thermo-rheological simplicity were improved in the intermediate compositions and PHBV-rich phases at lower temperature, their properties are more governed by the heavy degradation of PHBV. Finally, the present studies will further understand the morphological changes of PLA/PHBV blends towards controlling their micro/nanostructure by co-extrusion in multi micro-/nanolayered films for ultra-high barrier applications.

Virtual Asynchronous Online / Poster Session

PO129-SM

Polyethylene/PHBV/carbon nanotube composites for EMI shielding applications

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The environmental problem caused by plastic waste is leading the development of new composites with a lower environmental impact. Blending poly (3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), a well-known bio-based and biodegradable polymer, with conventional polymers and adding a conducting filler, like multiwalled carbon nanotubes (MWCNTs), could be a good strategy for making greener conducting polymer polymers. The main goal in this work is the development of new conducting polymer composites based on 50/50 high density polyethylene (HDPE)/PHBV matrix with carbon nanotubes as conducting nanofiller. In addition, a grafted polyethylene was included with the aim of improving the dispersion of nanotubes within the polymer matrix. The composites were appropriately designed, with a segregated morphology, which maximises the electrical properties with lower filler amounts by blend melting. The study was focused on thermal, mechanical, and morphological behaviour of new composites, but mainly in the relationships between their rheological and electrical properties. The results obtained display the

composites performance for EMI shielding and its processing on an industrial scale. At the end new composites with low amount of nanotubes and an adequate conductivity and electromagnetic shielding values were obtained. This contributes a breakthrough for industrial applications were more polymers environmental friendly with identical applications to conventional polymer are required.

Virtual Asynchronous Online / Poster Session

PO130-SM

Linear and nonlinear shear rheology of marginally entangled H-polymer melts and solutions

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We investigate the linear and nonlinear shear rheology of H-polymer melts and solutions at the transition from the unentangled to the entangled regime. In particular, we study the rheological behaviour of a H-polymer melt that has less than two entanglements per arm and backbone. It is the polymer synthesized by Roovers & Toporowski (1981), coded as H4A1A. Furthermore, we examine two polymer solutions prepared diluting well-entangled H-polymers (coded as H3A1A and H5A1 in Roovers & Toporowski, 1981) in linear polystyrene oligomer with molecular weight of 2 kDa. The dilution is carried out at volume fractions such as to match the same number of entanglements of H4A1A. Despite the lack of entanglements, the linear viscoelastic spectrum of H4A1A features a narrow elastic plateau in the intermediate frequency range. The linear and nonlinear viscoelastic behaviour of H4A1A is compared with that of a marginally entangled linear polymer having approximately same span molecular weight. In nonlinear regime, it is observed that the H-polymer has a broader overshoot and a larger strain corresponding to the viscosity peak compared to the linear counterpart. Concerning the solutions, despite having same Z and similar topology, they do not have the same scaled linear viscoelasticity of the melt H4A1A due to dynamic dilution effects (Lentzakiset al., 2019). These effects are larger for the solution with the smaller volume fraction of H-polymer, which displays a linear rheological behaviour typical of unentangled polymeric systems. In nonlinear regime the two solutions are stretched close to the finite extensibility limit. Consequently, shear hardening occurs.

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Virtual Asynchronous Online / Poster Session

PO131-SM

Reactive extrusion of PLA: Rheological indicators for long chain branching (LCB) detection

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Biodegradable polymers are attracting much attention in the plastics industry because of their use reduces environmental impact in a scenario where petroleum resources are limited. One of the environmentally friendly polymers with a large volume of commercial production is poly(lactic acid) (PLA). However, as with many biodegradable polymers, its processing has a distinct disadvantage due to its low melt strength value. This is evident in industrial processes involving stretching and drawing, which require stiffer and stronger polymers to prevent or delay breakage and thinning during stretching. The ability to develop an optimal response is given by the strain hardening phenomenon, which refers to a rapid increase in uniaxial extensional viscosity beyond a critical strain. One of the most effective approaches to improve the melt strength of polymers is to generate long chain branches (LCB) without reducing the parent polymer molecular weight. In this work, to achieve a good control of these properties through branching, reactive extrusion is used to prepare LCB-PLA. A commercial styrene-glycidyl acrylate oligomer, Joncryl®, was melt blended with linear PLA. According to the rheological characterisation, both linear and nonlinear viscoelasticity and elongation behaviour were significantly affected: i) The extensional transient viscosity revealed a strain hardening behaviour. ii) The study of the viscoelastic behaviour analysed by SAOS/LAOS shows structural modifications from a linear to a typical rheology dominated by long branching. In particular, LCB-PLA was characterised by a slower relaxation process indicating the formation of longer molecules and long chain branches during reactive extrusion. The intrinsic nonlinearity value Q0, determined in the MAOS regime, as well as the viscous and elastic nonlinearities in terms of thinning-thickening and softening/stiffening behaviour analysed in the LAOS regime, showed important changes that could serve as sensitive indicators of the presence of LCB.

Virtual Asynchronous Online / Poster Session

PO135-SM

Relating polymer structure to monomeric friction under flow conditions: Effect of chain overlapping Nuofei Jiang and Evelyne v. Ruymbeke

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These recent years, the concept of monomeric friction reduction in polymeric liquid under flow conditions has drawn extensive attention. However, a deeper understanding of the origin of friction reduction is still needed. In this work we suggest that monomeric friction should rely on interchain packing which determines the frequency of collision of the molecular segments. Based on that, it is predicted the monomeric friction in one specific direction can be related to the projection area in the plane normal to this direction, when the polymer coil is coarse-grained as an ellipsoid with uniform segment density distribution. This idea is supported by molecular dynamics simulation on standard melt system with unentangled bead-spring chains. In the simulation, we directly measured monomeric friction under steady shear flow and with stretching force, using the methods suggested in literature. It is found that monomeric friction varies with deformation in an anisotropic way and depends on molecular

parameters like chain length and rigidity. But all the friction components and the corresponding projection areas fall into a master curve. Such a universal relationship will enable us to correctly incorporate the nonlinearity of monomeric friction into the dynamic equation and give a more appropriate prediction for rheological functions.

Virtual Asynchronous Online / Poster Session

PO137-SM

Mechanical vs thermal determination of the glass transition temperature of polymers

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The glass transition temperature of polymers can be determined using thermal measurements, by measuring the change in the heat capacity of the sample as it undergoes the glass transition or by mechanical measurements, by measuring the change in the dilation coefficient or the elastic modulus of the sample as a function of temperature. The first method uses differential scanning calorimeter (DSC) whereas the latter uses either a dilatometer (DIL) or a termomechanical analizer (TMA). These three techniques are available at the Servicio de Caracterización Funcional of the Universidad de Sevilla. We have measured the glass transition temperature of a material with the three techniques. The differences in the results and the causes of the differences are discussed.

Virtual Asynchronous Online / Poster Session

PO138-SM

Rheology-electrospinning relationships of nanofibers based on ethylcellulose and the role of solvents and molecular weight

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Nowadays, there is a great interest in the development of electrospun nanofibers from biodegradable polymers, in order to obtain materials with innovative applications within areas such as biomedicine, healthcare, agriculture, sensor devices and food technology, and so on. The selection of an appropriate solvent is essential to determine the rheological properties and electrospinnability of the solution, the productivity, and the morphology of nanofibers. In this work, ethylcellulose (EC) solutions were prepared in four binary-solvent systems and one solvent to investigate the effect of different solution properties on nanofiber morphology and diameter. Conductivity, surface tension and viscosity of each solution were measured. The morphology of electrospun nanofibers was observed by scanning electron microscopy (SEM). Of all the solvent systems used tetrahydrofuran (THF): dimethylacetamide (DMAc) gave the highest fiber productivity and best defect-free nanofibers. Hence, this binary-solvent system was used for varying the molecular weight of EC. Also, the polymer concentration in this solvent system was varied to investigate the effect on nanofiber morphology and solution properties. Morphological investigations were done in correlation with rheological measurements: beaded nanofibers structures were collected from solutions with low concentrations ($\approx 3\%$ wt.%), while defect-free nanofibers were produced around the critical entanglement concentration ($\approx 6\%$ wt.%). Further investigation of the effect of the EC molecular weight (Mw) on the critical entanglement concentration showed that at each Mw, there is a minimum concentration needed to produce uniform fibers (entanglement concentrations decrease with increasing polymer MW). The results showed that the solvent properties and molecular weight of biopolymer have a significant effect on morphology and diameter distribution of the EC nanofibers.

Virtual Asynchronous Online / Poster Session

PO139-SM

On the relationship between stress and conformation tensors in state-of-the-art constitutive models for polymer melts and the possible additional role of chain tumbling

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Polymer Solutions and Melts Large-scale numerical calculations of viscoelastic flows require a constitutive equation encoding the relationship between flow kinematics and stress tensor in the momentum transport equation. Typically, such a constitutive relationship includes: 1) an evolution equation for one or more mesoscopic observables (the structural variables) carrying information about the conformation and/or stretching of polymer chains, and 2) a relation connecting the (extra) stress tensor with these mesoscopic structural variables. Typical choices of structural variables employed in such models include the conformation tensor, the chain stretch ratio, the tube survival probability function, etc. In the modern literature, one can come across several state-of-the-art differential models capable of describing the first relationship quite accurately (Stephanou et al., 2009). In contrast, the second relationship, between stress and structural variables, is often overlooked. In the present work, we use nonequilibrium molecular dynamics simulations of unentangled, linear polyethylene melts to check the relationship between stress tensor and chain end-to-end conformation tensor. In our analysis, we make use of the Cayley-Hamilton theorem (Beris & Edwards, 1994) to check consistency with the most general form of the derivative of the Helmholtz free energy with respect to the conformation tensor allowing the presence of a term quadratic in the conformation tensor. We also check whether the tumbling motion of polymer chains contributes or couples to the stress tensor. Our work provides a framework for checking the validity of constitutive models routinely used in polymer liquids numerical calculations and suggests ways of improving these models by utilizing information from lower-scale simulations.

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Virtual Asynchronous Online / Poster Session

PO140-SM

Rheological monitoring of the curing kinetics of bio-based epoxy formulations

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Nowadays, as a result of the environmental awareness, different industrial sectors aim to replace petroleum-derived components in end-use formulations by others from natural resources without impairing their functional properties. In this work, a new approach has been expored to develop castor oil-based gel-like dispersions for coating applications using lignin as a thickening agent. The proposed 3-step procedure comprises the mixing of the reagents, including a diamine and a diepoxy compound as crosslinkers, at different times and at room temperature, which allows to obtain gel-like dispersions with remarkable properties in a simple way. The influence of the diamine concentration on the rheological properties of final gel-like formulation has been studied by means of Small-Amplitude Oscillatory Shear (SAOS) tests. The viscolastic moduli increase with the diamine concentration. Moreover, the curing kinetics and the formation of a three-dimensional crosslinked network was monitored by evaluating both the rheological response and infrared spectroscopy curves over time, for 2 weeks. On the other hand, a rheoreactor equipped with an anchor impeller coupled to a rheometer was used to monitor the viscosity of samples during the preparation procedure. Overall, promising gel-like formulations for coating applications were obtained.

Virtual Asynchronous Online / Poster Session

PO141-SM

Modeling the nonlinear shear response of linear polymer melts with tube models

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TThis poster presents the development of a new approach to describe the overshoot observed in the transient response of the stress growth coefficient, and focuses on monodisperse linear polymer melts. A first assumption is to consider that at very early times, the polymer chains are fully entangled while at longer times (at steady-state regime) the chains are partially entangled. The overshoot can be seen as the transition of the chain from fully entangled to partially entangled state, taking place in addition to chain stretch. As a first approach, we propose a simple expression to determine the proportion of entanglements that remain from the initial state of the chain. The TMA model developed by the UCLouvain group (van Ruymbeke et al., 2005) and further implemented with this new approach leads to a good agreement with experimental data, despite the model approximations. In order to further explore this disentanglement process, we then focus on the model developed by Xie and Schweizer (2018), and implement their idea in the TMA model. To this end, we compare the initial timescale at which disentanglement of the chains occurs in the TMA model with the delay in the retraction of the chain due to a force imbalance between the interchain grip forces and the intrachain retraction force involved in the Xie and Schweizer model.

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Virtual Asynchronous Online / Poster Session

PO143-SM

Magnetic field orientation of graphene nanosheets in polymers

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The isolation of graphene in 2004 by Novoselov and co-workers with the scotch tape method opened the doors to a new class of materials: 2D materials. Graphene gained interest rapidly due to its large-exposed surface area, high electrical and thermal conductivity, and excellent mechanical strength. Owing to these extraordinary properties, graphene has the potential to address some of the most critical global crises, including energy storage and a shortage of fresh water. However, the most critical part of these applications is how the graphene nanosheets are oriented (vertically/horizontally) in the polymer nanocomposite. This work will focus on the orientation of graphene nanosheets in a polymer using an induced magnetic field. The behavior of the graphene nanosheets in the polymer solution under magnetic field depends on its geometry, the strength of the magnetic field, the interaction of graphene surface with the polymer solution/melt, and essentially, on rheological properties of the latter. Therefore, in this work, the optimization of polymer solution composition for graphene orientation is done based on the rheological properties of the polymer solutions with added graphene nanosheets. Therefore, the effect of graphene concentration, polymer solution composition, and molecular properties on steady shear and dynamic shear properties is studied for the designed system. Acknowledgment: The authors acknowledge the financial support of 2D Tech Vinnova Competence Centre.

PO144-SM

Predicting flow induced crystallisation of a binary polymer blend in complex flow William P. Grant

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The crystalline structure within a polymer determines almost every useful solid-state property such as strength, transparency and flexibility. Under flow conditions crystallisation rates can increase dramatically, owing to the polymer chains becoming more aligned during flow and thus the entropic penalty for forming crystals is reduced. Fully understanding how polymer crystallisation occurs during flow would enable optimisation of the crystalline structure by tailoring the processing conditions to suit. Predicting the enhancement of the rate of crystallisation requires coupling a calculation of the polymer chain configuration to a calculation of the energy barrier to crystal nucleation. Here we demonstrate how this can be done for a binary polymer blend in which the enhancement arises from the extension of the long chain component. We use the Rolie Double Poly (RDP) model (Boudara et al, 2019) to calculate the flow and chain configuration combined with the polySTRAND model (Read et al, 2020) to predict the crystallisation rate within the flow using parameters obtained from the RDP model. These have been implemented in the OpenFOAM using the RheoTool (Pimenta & Alves, 2017) library. With all this in place we hope to show preliminary results for flow induced polymer crystallisation in a range of complex flow geometries.

Virtual Asynchronous Online / Poster Session

PO146-SM

Extrusion flow instabilities of rubber compounds: Influence of filler dispersion

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Extrusion flow instabilities[1,2] is one of the most crucial challenges that polymer processing industry is facing at the end of extrusion dies. Particularly, for rubber compounds the process complexity is increased because often more than three different components (polymer, filler, lubricants, coupling agent, etc.) are mixed together. Within this study the wall slippage and the extrusion behavior of a low silica filled (f = 0.155) rubber formulations is investigated as a function of silane coupling agent amount between 0.00 phr, 0.70 phr, 1.44 phr, and 2.88 phr. Consequently the influence of filler dispersion is investigated. Using capillary rheology, equipped with slit die (L = 30 mm, H = 0.5 mm, W = 10 mm) the slip velocities[2,3] are quantified. In addition the spatial characteristic wavelength? of the surface extrusion instabilities is quantified by optical microscopy. The spatial characteristic wavelength? is fitted by a qualitative model[3] and the ratio of the extensional (Ys) and shear (sx) stress at the die exit region is obtained. The stress ratio is latter correlated with the molecular properties of the compounds such as the relaxation time and the amount of silane coupling agent.

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Symposium PO

Section: Suspensions (SP)

Virtual Asynchronous Online / Poster Session

PO125-SP

Early age cohesion of building materials via SAOS

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The worldwide use of concrete is linked to its excellent solid properties, developed during the hardening process and triggered by the precipitation of calcium silicate hydrate C-S-H. The cohesion developed during the early hydration defines the fresh properties of the cement paste and is extremely important for the final solid ones. Despite the many studies on cement cohesion, direct measurements during early age hydration are scarce (Lesko et al. 2001), and C-S-H precipitation and morphology are studied at longer timescales (Van Damme et al. 2013). Small oscillatory rheology (SAOS) has proved a promising method to measure the nature of interactions between particles of inorganic materials (Liberto et al. 2019). In order to further understand the early cohesion development in cementitious pastes, the fresh and cohesive properties of a model paste of tricalcium silicate (C3S) and a pure C-S-H gel are measured by SAOS. These measurements show that the C-S-H gel and the C3S paste, despite the common viscoelastic behavior, have an intrinsic different nature in terms of elasticity (i.e., $G'(\gamma)$) and reactivity (i.e., G'(t)). In particular, the temporal evolution of the elastic modulus (G') shows the reactive nature of the C3S paste (due to C-S-H nanoparticle formation in a strong ionic environment), in contrast with the non-reactive one of the C-S-H gel. We strongly believe that these results are related to the different ionic composition of the interstitial solution in the two samples, leading to a different material structure. In this context, the X-ray total scattering data presented here provides structural information at the atomic- and nanoscale to further this analysis.

PO147-SP

Coffee-ring effect associated with dynamical clustering and band formation of particles in a droplet

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Evaporation of a droplet containing microparticles results in the deposition of particles in various patterns, including the so-called "coffee-ring" pattern. Addition of a biocompatible, surfactant-like polymer (Polyethylene glycol, PEG) into particle suspensions. Addition of a biocompatible, surfactant-like polymer (Polyethylene glycol, PEG) into particle suspensions altered the internal flow dynamics, such as Marangoni vortex, of a droplet. Due to the altered flow dynamics, there were also changes in particle migration and self-assembly on a substrate. The present study observed the formation of bands of particles in a rotating Marangoni vortex. The mechanism underlying the formation of banded MV was found to be capillary meniscus forces between two particles near the air-liquid interface. In particular, the banded Marangoni vortex can be manipulated by tuning the surfactant concentration and particle concentration. Our findings would provide a new direction in understanding the particle deposition pattern of a colloidal droplet in many applications such as inkjet printing, coating, and many other droplet-based industrial processes.

Virtual Asynchronous Online / Poster Session

PO150-SP

High-pressure characterization of fluids with a capillary viscometer

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Drilling and completion of deeper wells require high performance fluids to overcome the challenges associated to the extreme high-temperature and high-pressure environments. The successful of these operations in challenging wells depends in a great extent on the thermo-rheological properties of the fluid, its stability and thermal resistance over time. The viscous behaviour of the fluids as a function of pressure and temperature is a critical issue in developing products with technically and economically suitable characteristics. In this work we present isothermal viscosity-pressure data for both Newtonian fluids and non-Newtonian suspensions obtained with a high-pressure capillary viscometer developed in our laboratory. The calibration of the device was performed using liquids of well-known viscosity-pressure-temperature characteristics. The effects of wall slip, non-isothermal flow due to viscous heating, high-pressure, and time have been analyses using capillary dies of different L/D ratio. Acknowledgements: This research was funded by the EU-FEDER Program grant code P18-RT-4684.

Virtual Asynchronous Online / Poster Session

PO151-SP

Wettability of carbon nanofilms with different fluids: Preliminary results

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In recent decades, research has tried to create highly hydrophobic surfaces with potential applications in very different markets, from the textiles to the solar panels and, more in general, to produce self-cleaning, anti-icing or anti-bacteric coatings. It has been shown that soot deriving from flame is suitable for the preparation of superhydrophobic surfaces by means of a rapid, modular and economical production process. The carbon nanofilm (CNF) can be produced by repeatedly inserting the desired substrate into a flame for a few milliseconds. The residence time in the flame is so short as to prevent heating of the substrate, but long enough to allow the deposition of soot particles by thermophoretic forces (from the hot flame to the cold substrate). The chemical-physical properties of the nanofilm and its thickness can be finely modulated by acting on various process parameters (type of fuel, fuel/comburent ratio, position - duration - number of insertions of the substrate in the flame, etc.). The wettability of the samples produced with the discussed technique is measured using the "sessil drop" method, with a tensiometer. From the wettability study with distilled water it emerged that all samples that have an adequate coverage of soot are superhydrophobic: water, having a high interfacial tension, is unable to enter into the roughness of the nano-rough surface, the drop of water cannot spread on it, and assumes a spherical shape, typical of drops on a surface with low wettability. Therefore, water droplets are not sensible to the alteration of CNF morphology and chemical-physical properties. This leads to the need of finding a fast and rapid method to discriminate among various types of samples produced in different flame conditions. In particular, it was decided to carry out measurements with different liquids having surface tensions lower than that of water, to determine a correlation between the flame condition, CNF deposition methods and the nanostructure of the film.

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Virtual Asynchronous Online / Poster Session

PO152-SP

Thermophysical properties of the phase change of silica particles in coconut oil-cutting fluid mixture

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Latent heat thermal energy storage (LHTES) through the use of phase change materials (PCMs) to store and release thermal energy is one of the most efficient and reliable ways to reduce energy consumption. PCMs have a high heat storage capacity and nearly isothermal phase change

behaviour (Umair et al., 2010). This work is concerned with the rheological behavior of hydrophilic silica suspensions in coconut oil. Special attention to the phase change flow was paid. The viscosity-temperature curves of coconut oil at different heat flow of 0.25 K/min, 0.5 K/min, 1 K/min and 1.5 K/min were carried out. The shear rate influence was also studied. The values of 1 s⁻¹, 5 s⁻¹, 10 s⁻¹ and 15 s⁻¹ were tested. The conditions of 0.5 k/min, 1.5 K/min and 5 s⁻¹ were used to carry out the viscosity-temperature curves at 0.01, 0.02, 0.03, 0.04 and 0.05 silica particle concentrations. To find out the better thermophysical conditions the isobaric specific heat capacity was also obtained. Considering thermal and flow properties the more suitable composition for industrial purposes (Saleel, 2021) was 0.03 volume fraction of silica particles. A cooling experiment on a power supply laptop was performed. The temperature-time curve was obtained with a thermographic camera. A very noticeable reduction of temperature was detected. Keywords: Hydropillic silica, coconut oil, phase change materials, rheology, viscosity-temperature curves.

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Virtual Asynchronous Online / Poster Session

PO153-SP

Rheology of manufacturing fluids with eco-friendly additives

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Recently, cooling lubricants have included nanoparticles (NPs). The use of nano-additives in the form of NPs is highly efficient due to their high chemical and biological activity. These so-called nano-lubricants has attained much attention in the machining field of manufacturing processes (Peña-Parás et al., 2020). This work deals with the rheological behavior of a mixture of taladrine cutting fluid and coconut oil in 1:9 proportion. The base fluid obtained, coconut oil with 10 % of taladrine (CO-0.1T), was filled with hydrophilic silica particles, A200 in 0.01, 0.03 and 0.05 volume fractions. The viscosity curves were recorded in a wide range of temperatures from 19 °C to 30 °C. The more concentrated suspensions, i.e., 0.03 and 0.05 of silica presented a gel-like microstructure. For these suspensions, the viscosity curves were also recorded at 40 °C and 50 °C. Even at these temperatures the viscosity of the suspensions was still very high, and the phase change was nearly indiscernible in terms of viscosity. They were able to maintain the gel microstructure at high temperatures even though part of the CO was melted. All the viscosity curves filled with 0.03 and 0.05 of silica were adjusted to a power law model. The 0.01 silica suspensions and the base fluid (CO-0.1T) showed a Newtonian behavior at temperatures over 22 °C and shear rates over 1 s-1. However, the better thermal properties were obtained for 0.01 silica suspensions. Nevertheless, for manufacturing processes like drilling high consistency is desirable to remove metal swarf. An example of a drilling process with CO-0.1T and 0.03 silica was presented. Keywords: Hydropillic silica, coconut oil, taladrine, phase change materials, rheology.

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Virtual Asynchronous Online / Poster Session

PO156-SP

Rheo-imaging of cement pastes in a parallel plate geometry: Shear rate heterogeneities and shear banding under rotational shear

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Cement pastes are usually made in solid volume fractions between 0.35 and 0.52. Upon adding water, nano-particles of hydration products are formed on the surface of cement grains and in the interstitial space, leading to the formation of a paste (with a measurable yield stress, Y.S). The paste, composed of nanometer-sized hydrate particles, micron-sized cement particles and interstitial fluid (water with high ion concentration) displays a very complex rheological behavior.

The proper measurement of Y.S the is critical in the characterization of cement pastes, and can be a selective parameter for specific industrial uses. In this work, we record the Y.S values of cement pastes using different rheometer geometries, and compare the results with mini-cone slump test. Surprisingly, we observe significant differences in Y.S values. The Y.S obtained from vane and helical geometries were similar to the ones from mini-cone slump tests, whereas Y.S from parallel plate and Couette geometries were significantly lower. In order to investigate more, the sample placed in the parallel plate geometry was optically imaged on its outer radius with a high-speed camera. Image analysis shows the formation of shear bands: A moving band existed near the top plate of the geometry, and a stationary band near the bottom plate under rotational shear. Using particle tracking velocimetry, velocity profiles were generated.

The spatio-temporal behavior of the bands was obtained for different applied top plate velocities, water/cement ratios and cement particle sizes. Our goal is to provide an insight on the physics governing the flow of cement paste, and thereby explain the apparently contradicting measurements of Y.S using different geometries.

PO157-SP

QL-LAOS studies on a hydrophilic fumed silica suspension

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While some authors suggest that stress-dependent models are inappropriate to predict the behavior that results from structural changes of suspensions [1], others consider that shear stresses are directly responsible for changes in the microscopic state [2]. This controversy has less relevance when studies are limited to the linear viscoelastic response recorded with SAOS tests, in which the choice of stress or strain/shear strain as input magnitude is indifferent. Nevertheless, things are dramatically different when the non-linear viscoelastic behavior of fluids (recorded with LAOS tests) is considered. The study of non-linear viscoelastic behavior is an extremely difficult task, not only due to experimental limitations but also, and much more important, by the difficulty to give physical meaning to results. Fortunately, if the time frame of the experiment is shorter than the characteristic time of the fluid, the microstructure does not show significant change. Consequently, the material will show apparent linear behavior because the response will be sinusoidal, although dependent on the amplitude of the input signal, i.e., it will not be strictly linear. This specific analysis was proposed and developed by Souza Mendes group [3] and is named quasi-linear LAOS (QL-LAOS). The aim of this work is to test the utility of QL-LAOS approach previously confirmed with viscoplastic fluids [3], on a shear-thickening suspension. Striking differences between both materials are: viscoplastic materials studied by Souza Mendes and co-workers were shear-thinning with stress threshold, while the suspension here considered exhibits shear-thinning and shear-thickening behavior regions.

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Virtual Asynchronous Online / Poster Session

PO159-SP

Shear induced particle migration in cement mortars

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We show in this study that pumping mortars over long distances can lead to microstructural heterogeneities. This work follows numerous studies on particle migration of Newtonian-fluid-based suspensions under flow, where particles migrate from areas of higher shear rates (in a pipe, near the wall) to areas of lower shear rates (center of the pipe). Our fluid is here a mortar, made of a white cement slurry filled with 30 vol% red glass beads of approximate average size 500 um. After estimating that the distance needed to reach steady-state in mortars would be on the orders of hundred meters (Nott & Brady, 1994), we built a setup where the flow imposed on the suspension is a large-amplitude oscillatory flow (Butler et al. 1999, Snook et al. 2015). We performed experiments with three different mixtures, where the suspension yield stress and cover distance vary. As we could not measure particle concentration in-situ during flow, we let the mortar set and measured solid volume fractions in various cuts and polished sections of the pipe. Each image was treated with ImageJ to measure the local particle concentration as a function of the radial position. Quantification of the wall steric hindrance, as well as the stability (lack of settling of particles) of all three mixtures were controlled in reference samples (tube of same diameter of pumping pipe, but where no pumping was imposed). In almost all cases, particle migration is clearly evidenced, with a dependence on the cement yield stress.

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Virtual Asynchronous Online / Poster Session

PO161-SP

Modelling and simulation of macroscopic flows of dense suspensions

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The rheology of highly concentrated suspensions of solid particles dispersed in a viscous fluid features a number of surprising phenomena. By varying the rate of deformation we can observe shear thinning, continuous or discontinuous shear thickening and, at very high concentrations, even the phenomenon of shear jamming. For real world applications, it is important to develop continuum models and reliable simulation strategies. Building on a recently proposed tensorial model for shear-jamming suspensions [1], we investigate how to improve the simulation performance by choosing suitable numerical schemes for the time evolution. Moreover, we extend the scope of the model by introducing further tensorial evolution equations that allow the representation of rate-dependent phenomena. Results of finite element simulations based on these models will be illustrated and analysed.

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PO162-SP

Rheological investigations of thermoresponsive core-shell nanoparticles in suspension above the colloidal glass transition

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Understanding the mechanical behavior of high concentrated colloidal suspensions of hard spheres, i.e. colloidal suspensions in the glassy state, under applied mechanical fields is a long-standing problem in colloid physics. While the flow properties of colloidal suspensions in homogeneous shear flows are well understood, approaches to inhomogeneous, boundary-driven, non-shear or mixed flows remain largely phenomenological up to now. To gain more insights into the mechanical properties under those flows, comprehensive rheological investigations on a well characterized colloidal model system are crucial. For this purpose a polystyrene-poly(N-isopropylacrylamide) (PS-PNIPAm) core-shell system was synthesized in a two-step synthesis procedure. After the synthesis, the core-shell particles were purified using ultrafiltration. The size of the core-shell particles was investigated by disc centrifuge sedimentation (DCS) and dynamic light scattering (DLS). The synthesized system is thermoresponsive, i.e. the hydrodynamic radius RH and therefore the volume fraction F of the colloids is adjustable in situ by changing the temperature, as investigated by DLS. With this batch of a well characterized colloidal suspension a comprehensive rheological study of the glassy state (F>Fg) of colloidal suspensions is feasible. We already showed, that the intrinsic nonlinearity parameter Q0, which is a measure for the deviation from the linear behavior, of a colloidal suspension diverges at the glass transition. We now plan to further investigate the mechanical behavior close to the glass transition. For this purpose we are using large amplitude oscillatory shear (LAOS) to further investigate the nonlinear behavior of the colloids, capillary rheology and elongational rheology to investigate flow instabilities and extensional flows and parallel and orthogonal superposition of shear to investigate mixed flows and the yielding behavior.

Virtual Asynchronous Online / Poster Session

PO163-SP

Temperature and particle concentration influence on the complex viscous behavior of a hydrophilic fumed silica suspension

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While some authors suggest that stress-dependent models are inappropriate to predict the behavior that results from structural changes of suspensions (Yziquel et al., 1999), others consider that shear stresses are directly responsible for changes in the microscopic state [de Souza Mendes & Thompson, 2019). This controversy has less relevance when studies are limited to the linear viscoelastic response recorded with SAOS tests, in which the choice of stress or strain/shear strain as input magnitude is indifferent. Nevertheless, things are dramatically different when the non-linear viscoelastic behavior of fluids (recorded with LAOS tests) is considered. The study of non-linear viscoelastic behavior is an extremely difficult task, not only due to experimental limitations but also, and much more important, by the difficulty to give physical meaning to results. Fortunately, if the time frame of the experiment is shorter than the characteristic time of the fluid, the microstructure does not show significant change. Consequently, the material will show apparent linear behavior because the response will be sinusoidal, although dependent on the amplitude of the input signal, i.e., it will not be strictly linear. This specific analysis was proposed and developed by Souza Mendes group (de Souza Mendes et al., 2014) and is named quasi-linear LAOS (QL-LAOS). The aim of this work is to test the utility of QL-LAOS approach previously confirmed with viscoplastic fluids (de Souza Mendes et al., 2014), on a shear-thickening suspension. Striking differences between both materials are: viscoplastic materials studied by Souza Mendes and co-workers were shear-thinning with stress threshold, while the suspension here considered exhibits shear-thinning and shear-thickening behavior regions.

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Virtual Asynchronous Online / Poster Session

PO164-SP

Thermal and rheological properties of hydrophobic nanosilica suspensions at high pressures

María José Martín-Alfonso, Javier Pozo, Clara Delgado-Sánchez, and Francisco J. Martinez-Boza

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The industry is continuously looking for solutions with the aim of solving issues presented by heat transfer and storage. In this way, the continuous improvement in developing sustainable and environmentally friendly fluids with high efficiency at extreme conditions is the main trend to achieve the new sustainability challenges. Vegetable oils and derivatives structured with nanoparticles could be an alternative to mineral or synthetic oils for sustainable fluid formulations. Hydrophobic nanoparticles have the capability to change the rheological behavior of oil in suspensions, providing a large variety of non-Newtonian behaviors over a wide range of temperatures depending on the concentration and hydrophobicity. This permits the design of fluids with selected characteristic for a large variety of applications. In this work, different fluids have been formulated using vegetable and synthetic oils and nanoparticles such as organoclays. Rheological and physicochemical properties have been measured as a function

of pressure and temperature. Both, surface tension and viscosity, show a pronounced dependence on pressure and temperature, the presence of nanoparticles enhances both mechanical and physicochemical properties depending on concentration and processing conditions.

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Virtual Asynchronous Online / Poster Session

PO165-SP

Thermal and rheological proprieties of fluids structured with organoclays at high temperature and pressure María José Martín-Alfonso, Javier Pozo, Antonio A. Cuadri, and Francisco J. Martinez-Boza

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Author Index

Aarts, D., GS33:87 Abadie, T., NF10:16 Abad-López, M. J., PO122:139, PO129:141 Abbasi Yazdi, A., PO110:136 Abedi, B., IP13:63 Abrami, M., BM7:25, BM20:70 Abrougui, M., GS22:42 Adrover, A., BM7:25 Afonso, A. M., NF22:39 Agassant, J.-F., IP9:62, IP10:62 Agrawal, A., SP23:93 Agrawal, R., NF12:16 Aguilar, J. M., PO53:121 Aguirresarobe, R., GS27:57, IP8:61 Ahirwal, D., IP6:46 Ahlinder, A., FR1:49 Ahmed, J., PO59:123 Aime, S., EM12:65, NF30:55, SG2:81, SG12:97 Akbari, E., PO35:115 Alarico, S., PO56:122 Alexandris, S., EI18:99 Alfaro-Rodriguez, M.-C., EI4:100, PO12:109 Almdal, K., SM4:43 Almeida, P. L., BM14:27 Alonso-González, M., SG7:95 Álvarez, M. D., PO26:113, PO29:114, PO50:120 Álvarez de Cienfuegos, L., GS17:40, GS22:42 Alvarez-Barajas, R., PO24:113, PO69:125 Álvarez-Castillo, E., FR3:50, FR16:104, PO74:126, PO120:138 Alves, L., GS14:20, PO166:132, SM15:61 Alves, M. A., PO96:133 Amarsid, L., SP16:7 Ambrosi, M., PO123:139 Amin Ahmed Abdullah, J., PO86:131 Amini, K., EM7:49, NF36:90 Amoroso, D., NF16:17 Anantharamai, V. H.,

Anderson, P. D., EI13:30, IP2:45, NF26:54 Andonegi, M., PO2:107 Andrade, R. J., SP21:79, SP29:94 André, A., SM18:76, SM23:90 Andreotti, B., SG3:81 Andrew, C., PO104:135 Ane, P., MN2:12 Angellier-Coussy, H., PO120:138 Anidiobu, V. O., PO62:123 Ansorena, D., PO46:119 Antunes, F., GS14:20 Aprile, S., IP17:73 Arantxa, A., MN2:12 Ares-Pernas, A. I., PO122:139, PO129:141 Arias-Ferreiro, G., PO122:139, PO129:141 Arjona Escudero, J. L., Arlov, D., PO89:131 Arnold, G., IP21:75, PO31:114, SG13:97 Arratia, P. E., SP1:5 Arroyo, M., Aschi, A., GS10:19 Aschl, T., SG4:80 Ashkenazi, D., EI18:99 Astiasarán, I., PO46:119 Athanasiou, T., EM21:83 Aubel, A., SP30:95 Aubrun, O., NF23:40 Aulnette, M., MN9:32, PO94:132 Aulova, A., PO143:144, SG14:98 Aussillous, P., PO114:137 Avallone, P. R., FR6:51. FR12:103, PO66:124 Azevedo-Scudeller, L., FR17:104

Bachnak, R., EII:10 Bacova, P., SG11:97, SM6:44, SM30:93 Baeza, G. P., SG10:96 Bakal, K. J., PO93:132 Balan, C., NF3:2, PO105:135, PO109:135, PO111:136 Balboa-Usabiaga, F., PO117:137, SP9:23 Baldino, N., EI7:28, , IP17:73, PO49:119, PO81:129 Banaei, A. A., MN9:32 Banc, A., FR13:103 Bandyopadhyay, R., EI23:101, EM11:65, MN22:85 Baratto, G., PO16:110 Barcelos, E., SP13:24 Barent, R. D., Barnes, C. M., EM2:47 Baroni, P., MN23:102 Barquero, M., PO52:120 Bashir, K. M., BM10:26. Basu, S. K., BM10:26, Batista, A. P., PO120:138 Baué, J.-T., MN13:34 Behbahani, A. F., SG11:97 Bek, M., SG14:98 Bellettre, J., MN12:33, NF28:89 Bellotto, M., PO125:145 Ben Yahia, A., GS10:19 Benarroche, C., SP3:6 Benedí, J., PO26:113 Bengoechea, C., FR3:50, PO74:126, PO119:138, PO120:138 Bento, C., PO56:122 Berdalet, E., PO18:111 Berghe, L. S., IP13:63 Bermúdez, M., IP8:61 Berton-Carabin, C. C., PO20:112 Besiri, I. N., EM16:67 Bessaies-Bey, H., EM13:66 Bhattacharyya, T., GS34:87, PO61:123 Bi. D., BM11:26 Biasin, A., BM7:25, BM20:70 Bindgen, S., NF20:38 Bismarck, A., SM17:76, SM29:92 Biswal, S., SP28:94 Biswas, R., MN22:85 Blanc, F., SP3:6 Blandón Cumbreras, F. G., IP20:74 Bodiguel, H., EI25:101, GS18:40, PO97:133

Boitte, J.-B., NF23:40

Bonaduce, I., SP19:79 Bonn, D., SM24:91

Bonacci, F., MN7:32, SP6:7

Bonnecaze, R. T., SP22:80 Borger, A. L., SM4:43 Borges, J. P., BM17:69 Boromand, A., SP13:24 Borrego Algarra, M., PO138:143 Borrero-López, A. M., GS16:21 Bossis, G., SP10:23 Botta, D., PO111:136 Botto, L., SP23:93 Boulet, C., GS33:87 Boyer, S. E., IP9:62, IP10:62 Braga, M., PO56:122 Brancart, J., SG5:81 Brandfellner, L., SM17:76, SM29:92 Brandt, L., MN9:32, NF36:90 Brasiello, A., SM5:44 Bratu, A. M., PO109:135 Braunreuther, M., BM8:26 Brenn, G., BM5:9 Brice, S.-M., GS4:4 Broboana, D., PO105:135 Brolin, A., SG9:96 Bui, M., SP17:79 Burghelea, T., MN12:33, NF28:89 Burkhart, C., SG11:97, SM30:93 Burshtein, N., MN9:32, PO94:132 Busata, L., PO16:110 Bussonnière, A., EI12:30 Bustos, L. F., PO21:112 Cabrita, M., FR16:104

Caggioni, M., SP31:95 Calabrese, V., MN3:12 Calabrò, V., PO49:119 Calafel, I., IP8:61, MN2:12 Calero, N., PO51:120, PO52:120 Camacho, G., EM17:82, PO75:127 Camacho Villar, G., GS8:18 Campo-Deaño, L., IP19:74, PO5:108 Campos Assumpçao de Amarante, M., FR18:104 Cantat, I., EI12:30, MN13:34 Capobianchi, P., EI5:11

SP31:95

Cardinaels, R., FR9:68. GS13:20, GS30:58 Carneiro, J., BM18:70, SP4:21 Carotenuto, C., GS23:42, PO14:109, PO151:146, SP15:24, SP20:78 Carranza, T., PO2:107 Carrelo, H., PO56:122 Carrêlo, H., BM17:69 Carrera, C., PO21:112 Carrillo, F., EI4:100 Carrozza, M. A., EI13:30 Cartagena, M., PO46:119 Carvalho, M. d. G., SM15:61 Casanellas, L., MN5:13 Casas-Ferrer, L., MN5:13 Caserta, S., BM9:26, PO88:131 Castelo-Branco, D., FR16:104 Catherine, K., SP23:93 Caudri, A. A., PO24:113 Causa, A., IP5:46, PO146:145 Cavaco, G., BM14:27 Cerdan, K., SG5:81 Chakrabarti, B., MN7:32 Champenois, J. B., GS7:18 Chan, S. T., IP4:46, NF26:54 Chaparian, E., NF27:54, NF31:55, NF32:56, NF36:90 Charalambides, M., SG8:96 Charles, C.-A., SM11:60 Chateau, X., SP6:7, SP30:95 Chatzigiannakis, E., EI1:10, Chazeau, L., SG10:96 Chazirakis, A., SM30:93 Chenal, J.-M., PO39:116 Cheon, H. L., PO107:135 Chin, W.-C., PO18:111 Chiron, H., PO48:119 Cho, M.-G., BM10:26, Choquart, F., IP9:62 Christakopoulos, F., SM19:76 Ciccone, G., GS20:41 Cidade, M. T., BM17:69 Cidade, T., EI4:100, PO56:122 Cipelletti, L., SG2:81 Cirillo, A. I., MN14:34 Clara, D.-S., PO19:111, PO23:112 Clasen, C., SM8:59, SM18:76 Claverie, J., SM26:91 Clément, É., SG3:81

Cloitre, M., EM12:65. NF30:55 Cochran, J. O., NF29:55 Cofrades, S., PO26:113, PO29:114 Colby, R. H., SM21:77 Coletti, M., PO35:115, Colin, A., NF23:40, PL3:73 Collins, T., SM14:60 Colly, A., NF6:3 Conese, M., BM7:25 Confalonieri, M., BM7:25 Coombs, S. J., SM9:59 Coppens, M., EM15:66 Coppola, E., SP20:78 Coppola, S., IP17:73, PO40:116, SM22:77 Cordobés, F., PO53:121 Cortés-Triviño, E., IP16:64, PO78:128, PO79:128, PO83:130, PO140:144 Costa, C., EI9:29 Costa, P., PO129:141 Costantini, A., PO16:110 Costanzo, S., EM18:82, FR12:103, FR13:103. GS28:57, PO130:142, SM1:43, SM10:59 Cotts, S., PO35:115, Courtial, E.-J., NF6:3 Coussot, P., EM13:66 Coutouly, C., SM28:92 Cramer, C., PO70:125 Crawford, N. C., PO41:116 Criado, C., PO50:120 Cuadri, A. A., PO69:125, PO77:128, PO80:129, PO82:129, PO165:150 Cubero-Cardoso, J., IP16:64 Cuetos, A., MN19:84 Curtis, D., EM8:64, EM20:83,

da Nóbrega, H. J., PO34:115 Dal Sasso, G., PO125:145 Dalloz, B., PO114:137 Dalmazzone, C., EI2:10 Dalne, M., PO141:144 Damiano, E., SP20:78 Daneshi, M., EM14:66, IP3:45, MN16:35, NF27:54 Daneshvar Garmroodi, M. R., PO103:134 Dapas, B., BM7:25 Darras, A., MN1:11 David, E., SG15:98 Davies, R., EM8:64, D'Avino, G., EM18:82, IP1:45, MN11:33,

MN17:84, NF4:2. PO110:136, SP12:23 Davoodi, M., NF13:16, PO104:135 De Corato, M., EI14:31, EI22:100. De Falco, G., PO151:146 de la Caba, K., PO2:107, PO74:126 De la Fuente, J., PO53:121 de la Sen, A., PO96:133 De Loubens, C., GS18:40, PO97:133 De Maeseneer, T., GS13:20 De Micco, M., NF4:2 de Oliveira Silva, R., GS13:20 De Rosa, S., IP1:45 De Santo, M. P., IP17:73 de Sousa, H. C., PO56:122 de Souza Mendes, P. R., IP13:63 de Vicente, J., EM17:82, GS8:18, , PO75:127, SG5:81, SP7:22 Del Gado, E., SP31:95 del Giudice, D., PO14:109 Del Giudice, F., EM2:47, MN8:32, MN10:33 Delgado, I., PO118:138 Delgado, M. Á., MN24:102, PO76:127 Delgado-Sánchez, C., EI6:11, PO82:129, PO83:130, PO84:130, PO164:149 Della Valle, G., FR11:68, PO48:119, PO58:122, SG8:96 Delmonte, M., FR12:103 Demarquette, N. R., SG15:98 den Doelder, J., SM14:60 Denis, M., PO18:111 , SM25:91 Dhar, S., PO156:147 di Bari, V., FR8:67, PO63:124 Di Dio, B. F., NF30:55 Di Lorenzo, M. L., PO131:142 Di Maio, E., EI16:31, FR6:51 Di Martino, M., IP6:46 Di Natale, F., PO151:146 Di Spirito, N. A., EI16:31 Dias, A., IP22:75 Dias, I., IP22:75 Díaz-García, Á., PO121:139 Dietemann, P., SP19:79 Dijksman, J. A., EI3:10

Dimakopoulos, Y., BM6:9, NF34:89 Ding, H., PO18:111 Ditillo, C. D., SM21:77 Divoux, T., GS7:18, GS31:58 Dobre, O., GS20:41 Domann, S., PO113:137, Domínguez Franco, M. D. D., PO137:143 Dopico García, M. S., PO122:139 Dostál, M., PO90:131 Doxastakis, M., SG11:97, SM30:93 Drabek, J., SM3:43 du Roure, O., MN4:12, MN7:32, PO96:133 Duan, J., PO18:111 Duarte, C. M., FR7:51, PO44:118 Duce, C., SP19:79 Duchet-Rumeau, J., EI24:101 Duez, B., IP12:63 Dufour, M., PO48:119 Duran, J. G., GS17:40, GS22:42 Dutcher, C., EI1:10 Dutertre, F., GS11:19 Eckert, K., EI17:98, GS37:88

Edera, P., NF30:55 Edlund, H., EI9:29 Eftekhari, M., EI17:98 Ehgartner, D., PO31:114, SG13:97 Ehrentraut, H., EM19:83 El Haddad, K., SM9:59 El Omari, Y., EI24:101 Elfring, G. J., MN16:35 Elias, F., PO18:111 Elke, S., PO59:123 Ellero, M., NF1:1, NF2:2, NF17:37, PO117:137, SP7:22, SP9:23, SP18:78 Empadinhas, N., PO56:122 Emri, I., PO18:111 Esfahani, M. K., IP5:46, PO146:145 Español, P., NF1:1 Espert, M., PO15:110, PO25:117, PO29:114, PO30:117 Esposito, G., MN11:33 Esteban, L., EI25:101 Etxabide, A., PO2:107

Faccio, D., MN15:34 Faizi, H. A., NF26:54 Fakhari, A., IP19:74

Fall. A., SP16:7 Famelart, M.-H., FR17:104, Farra, R., BM7:25, BM20:70 Fatahi, H., SM26:91 Fauser, D., IP21:75, SG6:82 Feijoo Vázquez, I., IP7:47 Felix, M., PO119:138, PO121:139, SG7:95 Fengler, C., EM6:49 Fernandes, C., IP19:74 Fernandez, M., GS27:57, MN2:12, PO131:142 Fernández, D., PO129:141 Fernández Díaz, E. D., PO157:148, PO163:149 Fernandez-Prieto, S., PO78:128 Fernández-Silva, S. D., MN24:102, PO76:127 Ferraro, R., BM9:26, PO88:131 Ferreira, J., BM18:70, SP4:21 Fielding, S., BM11:26, NF29:55 Figueira, D., FR16:104 Figueiredo, H., PO118:138 Filipe, A., GS14:20 Fischer, L. S., PO162:149 Fischer, P., BM3:8, GS21:41, GS25:56 Fonseca, B. S., IP13:63 Formstone, C., GS33:87 Fornasier, C., BM7:25, BM20:70 Foroozani Behbahani, A., SM30:93 Founta, D., BM3:8 Franca, H. L., NF19:38 Frances, J.-M., NF6:3 Francescato, S., PO16:110 Franco, J. M., GS16:21, IP16:64, IP20:74, PO72:126, PO73:126, PO78:128, PO79:128, PO140:144, PO138:143 Franco, V., PO121:139 François, G., IP9:62 Francqui, F., IP18:74 Friederichs, N., SM19:76 Frigaard, I. A., EM14:66, IP3:45, MN16:35, NF31:55, NF32:56 Frith, M. G., GS7:18 Fuchs, M., PO162:149 Fueyo, N., EI14:31 Fuller, G. G., BM8:26, EI22:100 Furst, E. M., SP6:7 Fusco, C., SG10:96

Fustin, C.-A., SM23:90. SM27:92, SM28:92 Fyhn, H., PO107:135 Gabriele, D., EI7:28,, IP17:73, PO49:119, PO81:129 Gadige, P., EM11:65 Gaillard, A., SM24:91 Gala, L. D., EI22:100 Galindo-Rosales, F. J., IP19:74, PO5:108, PO34:115 Galloway, K. L., SP1:5 Gálvez, C., FR2:50 Gamelas, J., SM15:61 Gans, A., PO114:137 Garcia, M. d. C., FR2:50 García Daza, F. A., MN19:84 Garcia de Beristain, I.. NF17:37 Garcia Zapateiro, L. A., PO54:121, PO64:124 García-Morales, M., MN24:102, PO76:127 García-Sánchez, C., PO12:109 Garcimartín, A., PO26:113 Gauthier, A., NF23:40 Gauthier, G., SP26:94 Gautier, A., PO44:118 Geffrault, A., EM13:66 Geisel, S., BM15:28 Georgantopoulos, C., EM22:84, IP5:46, PO146:145 George, P., GS4:4 Geri, M., EM20:83, GS7:18 Gerin, F., BM7:25 Germann, N., EM16:67 Gerstner, D., IP12:63 Ghai, V., PO143:144 Ghanbari, R., NF9:15 Ghazal, A., NF35:89 Ghiassineiad, S., SM27:92 Gholivand, A., PO98:134 Giacomin, A. J., SM9:59 Giacomin, C. E., BM3:8 Giannokostas, K., BM6:9 Gibaud, T., GS5:5, IP11:63 Gibouin, F., FR11:68 Gibson, G. M., GS20:41, MN15:34 Giehl, C., IP21:75, PO31:114, SG13:97 Gila-Vilchez, C., GS17:40, GS22:42 Gilbert, D., SP14:24 Gilbert, E., EI8:29 Gimenez-Ribes, G.,

PO124:140

Giura, L., PO46:119 Giuseppe, M., GS28:57 Giusteri, G. G., NF5:3, PO161:148 Gkolfi, E., SM6:44 Gojard, P., FR7:51 Gomes Rrodigues, D., GS7:18 Gómez Barreiro, S., IP7:47 Gómez-Merino, A. I.,, PO152:146, PO153:147, Gontard, N., PO120:138 Gonzalez-Garcia, C., GS20:41 Gonzalez-Garcia, L., GS36:88, SP17:79 González-Rodríguez, M. V., PO129:141 Gottlieb, M., EI18:99, GS26:57 Goudoulas, T. B., EM16:67 Goussé, E., FR17:104 Gowda. V, K., EM7:49 Goyon, J., SP6:7, SP30:95 Gracia Fernández, C. A., IP7:47 Graham, M. D., NF7:15 Grant, W. P., PO144:145 Gras, S., FR18:104 Grasselli, Y., SP10:23 Grassi, G., BM7:25, BM20:70 Grassi, M., BM7:25, BM20:70 Gravelle, S., SP23:93 Greco, F., FR12:103 Greco, R., SP20:78 Griffo, R., PO151:146 Grilli, S., PO14:109 Grizzuti, N., EI16:31. EM18:82, FR6:51, FR12:103, GS15:20, GS28:57, PO66:124, SM1:43, SM10:59 Guerrero, A., BM19:70, FR3:50, FR16:104, GS12:19, PO1:107, PO74:126, PO86:131, PO119:138, PO120:138, PO121:139 Guerrero, P., PO2:107, PO74:126 Guessasma, S., SG8:96 Guido, S., MN14:34, Guidolin, C., EI10:29 Guilbert, E., GS18:40 Gupta, R. R., MN16:35 Gutiérrez-Blandón, C., PO77:128, PO80:129 Guzmán, D. B., IP20:74

Guido, S., MN14.34,
Guidolin, C., E110:29
Guilbert, E., GS18:40
Gupta, R. R., MN16:35
Gutiérrez-Blandón, C.,
PO77:128, PO80:129
Guzmán, D. B., IP20:74
Haas, J., PO6:108
Huttet, Mr., E115.30
Huysecom, A.-S., GS30:58
Iaccarino, P., FR6:51
Ianniello, V., PO130:142,
SM1:43, SM10:59
Ianniruberto, G., GS28:57,
SM1:43, SM5:44,
SM10:59

Ilavsky, J., GS7:18 Inn, Y., SM13:60 Innings, F., PO89:131 Isa, L., GS6:5, NF25:53 Itri, S., PO14:109 Itziar, M.-S., MN2:12 Izzet, A., SG3:81

Jabbari-Farouji, S., SG10:96 Jamali, S., GS1:4 Jan, S., PO55:121 Jannin, L., PO94:132 Janssen, P., IP18:74 Jaouadi, N., IP15:64 Jaromír, Š., PO55:121 Javadi, A., EI17:98, GS37:88 Jaziri, M., IP15:64 Jean-Sébastien, T., IP12:63 Jeantet, R., FR17:104 Jebalia, I., SG8:96 Jenkinson, I. R., PO18:111 Jeric, I., PO71:126 Jesinghausen, S., EM3:48, PO91:141, SP25:93 Jeyasountharan, A., MN8:32 Ji, Y., MN12:33 Jiang, N., PO135:142 Jiménez-Galea, J. J., PO152:146, PO153:147, Jiménez-Rosado, M., BM19:70, GS12:19, PO1:107, PO86:131 Jirout, T., PO90:131 Jiroutová, D., PO90:131 Jixiang, L., PO85:130 Joanny, J.-F., NF23:40 John, T., BM4:8, MN1:11 Jordi, S., PO9:109 José, G., GS14:20 José Javier, Q. C. Q., PO137:143 Joshi, Y. M., GS34:87, PO61:123 Jullien, M.-C., MN13:34 Jung, D.-h., BM10:26,

Kabashi, V., PO159:148
Kádár, R., GS19:41, IP5:46,
NF9:15, PO89:131,
PO143:144, PO146:145,
SG9:96
Kaestner, L., BM12:27,
MN1:11, PO3:107
Kalafatakis, N., EM21:83
Kalpathy, S. K., EI23:101
Kanso, M. A., SM9:59
Kansou, K., PO48:119
Karimfazli, I., NF35:89,
PO103:134
Karjala, T. P., SM14:60

Karn, S. K., PO18:111 Katzenschlager, R., PO6:108 Keaveny, E. E., NF15:17 Keshavarz, B., GS7:18 Keshavarzi, B., GS37:88 Khabazian Esfahani, M., EM22:84 Khani, S., SP13:24 Khati, P., FR14:103 Kirkensgaard, J. J., SM4:43 Kogan, D., GS26:57 Kool, L., EI3:10 Kool, L., SP1:5 Koos, E., NF20:38 Kouni, E., NF34:89 Kraiem, W., GS10:19 Krapez, M., NF23:40 Kristiawan, M., SG8:96 Kuechenmeister-Lehrheuer, C., PO45:118 Kume, E., MN23:102 Kurecic, I., PO71:126 Kusina, C., NF23:40

Lacambra Andreu, X., PO39:116 Lacayo-Pineda, J., EM6:49 Laeuger, J., EM5:48 Lage-Rivera, S., PO122:139 Lalieu, J., SP26:94 Lamnawar, K., IP15:64, PO39:116, PO85:130, PO87:141, SP5:7 Landfeld, A., PO67:125 Lappa, M., EI5:11 Lasagabáster-Latorre, A., PO122:139 Laschke, M., MN1:11 Latshaw, A., PO35:115, Laukkanen, O.-V., EI21:31 Laure, P., IP9:62, IP10:62 Lavergne, F. A., EI11:30 Law, J. Y., PO121:139 Lawrence, G., IP3:45 Lavachi, M., MN5:13 Le Floch-Fouéré, C., FR17:104 Leal, C. R., BM14:27 Leão, S., PO166:132 Lecanu, R., PO58:122 Lee, S., BM10:26, Legrand, G., GS31:58 Lehéricey, P., GS6:5, NF25:53 Lemaire, E., SP3:6, SP14:24 Lemaitre, A., SP6:7 Lenavetier, T., EI12:30 Lennon, K. R., EM4:48, PO112:136 Lenoch, A., PO70:125 Leon-Cecilla, A., GS17:40

Lerouge, S., PO102:134 Lettinga, M. P., PO98:134 Leverrier, C., FR14:103, PO58:122 Li, Y., SM27:92 Li, Z., MN4:12 Li, Z., PO18:111 Liberto, T., PO125:145, PO156:147, PO159:148 Liebi, M., NF9:15 Ligoure, C., SM11:60 Lin, C.-A., NF12:16 Lindman, B., EI9:29, GS14:20 Lindner, A., MN4:12, MN7:32, MN9:32, PO94:132, PO96:133, PO102:134, SP1:5 Liu, H., SM5:44 Lobo, I., IP22:75 Lobry, L., SP3:6, SP8:22 Lopes, P. E., PO118:138 Lopez, M., BM12:27, PO3:107 López-Aguilar, J. E., NF17:37, SP18:78 López-Castejón, M. L., PO119:138 López-González, Y., PO53:121 López-León, C. F., PO9:109 Lopez-Lopez, M., GS17:40, GS22:42 Louhichi, A., FR13:103, SM11:60 Lu, K., SM14:60 Lucchetti, S., PO16:110 Luciani, G., PO66:124 Lukácová-Medviďová, M., NF5:3 Lundell, F., EM7:49 Lupi, F. R., EI7:28, IP17:73, PO49:119, PO81:129 Lutz-Bueno, V., GS25:56 Lyons, R., SM23:90

Maazouz, A., EI24:101, IP15:64, PO39:116, PO85:130, PO87:141, SP5:7

Mac Intyre, J., EI10:29

MacKintosh, F., SP28:94

Maffettone, P. L., EI14:31, EI22:100, EM18:82, IP6:46, MN17:84, SP12:23

Magalhães, S., PO166:132, SM15:61

Maia, J., SP13:24

Maier, M., PO162:149

Majesté, J.-C., SP2:6

Majhi, A., EI3:10 Malej, A., PO18:111 Maleki, M., PO97:133 Manero, O., NF11:16 Manneville, S., GS31:58 Marceneiro, S., IP22:75 Marchand, M. C., SP31:95 Marchesano, Y., EI7:28, PO81:129 Mari, R., SP3:6 Mari, X., PO18:111 Maria, R., GS14:20 Marin, D., PO102:134 Marino, P., SP20:78 Marques, P. S., PO34:115 Marquette, C., NF6:3 Marraffa, C., EM12:65 Marrucci, G., SM1:43, SM5:44 Marsiglia Fuentes, R. M., PO64:124 Marten, J., MN21:85 Martens, J. H., PO91:141 Martin, F., FR17:104 Martín Alfonso, J. E., PO138:143 Martín-Alfonso, J. E., PO72:126, PO73:126 Martín-Alfonso, M. J., EI6:11, PO69:125, PO82:129, PO84:130, PO150:146, PO164:149, PO165:150 Martinetti, L., SM14:60 Martinez, M., NF27:54 Martínez, I., PO78:128, PO123:139 Martínez Cano, Ó., GS8:18 Martinez-Boza, F. J., PO24:113, PO69:125. PO150:146, PO164:149, PO165:150 Martinez-Cano, O., EM17:82, PO75:127 Martone, R., SP15:24, SP20:78 Maschio, M., BM7:25 Masghouni, E., SP5:7 Massiera, G., MN5:13 Massoli, P., MN12:33 Matar, O. K., NF10:16 Matsumoto, A., NF26:54 Maurer, F., BM4:8 Mavrantzas, V. G., PO139:143 McDougall, M., EI5:11 McKinley, G. H., EM4:48, EM20:83, FR9:68, GS7:18, NF10:16, PL2:37, PO112:136 Medina-López, R.,

PO12:109

Pyckhout-Hintzen, W.,

Medronho, B., EI9:29. GS14:20, SM15:61 Meerts, M., FR9:68 Meeus, Y., FR9:68 Menger, M., MN1:11 Meyer, F., PO41:116 Mezzenga, R., GS25:56 Miguel Antonio, B. B. B., PO137:143 Mihelcic, M., MN20:85 Milcovich, G., BM7:25, BM20:70 Mileti, O., EI7:28, IP17:73, PO49:119 Minale, M., GS23:42. PO14:109, PO151:146, SP15:24, SP20:78 Miranda, J., SP4:21 Miriyala, R., SM25:91 Mirzaagha, S., EI16:31 Mishra, A. A., PO89:131 Misra, C., EM11:65 Missi, E., MN12:33, NF28:89 Moberg, T., SG9:96 Moldenaers, P., FR9:68, GS13:20, GS30:58 Molitierno, S., SP15:24 Montillet, A., MN12:33, NF28:89 Moraes, L. R., SP29:94 Moratille, Y., SP14:24 Moravec, J., PO90:131 Moreira de Campos, J., BM18:70, SP4:21 Morel, M.-H., FR13:103 Moreno, D., PO117:137 Moreno, N., NF2:2, PO117:137 Morillas, J. R., EM17:82. PO75:127 Morillas Medina, J. R., GS8:18 Morris, J. F., PL1:1 Mortensen, K., SM4:43, SM27:92 Morthomas, J., SG10:96 Moschopoulos, P., NF34:89 Motaghian, M., PO22:112 Mouraka, P., FR8:67, PO63:124 Müller, A. J., PO131:142 Müller, F. J., GS3:4, PO17:110 Müller, H. W., SM17:76, SM29:92 Muñoz, J., FR2:50, PO12:109, PO51:120, PO52:120 Muñoz-Calahorro, C., PO12:109 Muratspahic, E., SM17:76

Mutschler, L., NF9:15 Nabizadeh, M., GS1:4 Naccache, M. F., SP21:79, SP29:94 Naccahe, M., SP13:24 Nardecchia, S., PO75:127 Natacha, C., GS14:20 Naue, I., EM22:84, IP5:46, PO146:145 Navarro, F. J., EI6:11, PO19:111, PO23:112, PO24:113, PO77:128, PO80:129, PO82:129, PO83:130, PO84:130, PO150:146 Nebouy, M., SG10:96 Neukötter, M., SP25:93 Neuner, M., PO32:115 Neveu, A., IP18:74 Niazi Ardekani, M., NF36:90 Nicolas, M., PO114:137 Nicoläy, R., SM23:90 Nie, S., EM6:49 Nieto Simavilla, D., NF1:1 Niggel, V., NF25:53 Nikiforidis, C. V., PO20:112 Nikiforidis, V.-M., PO139:143 Noirez, L., BM5:9, MN23:102 Norgren, M., EI9:29 Nunes, J. M., PO5:108 Nunes, M. C., FR10:68, FR19:105 Nygård, K., NF9:15

O'Brien, J. P., SM14:60 Oelschlaeger, C., MN21:85 Ogunkeye, A., EM8:64, Oishi, C. M., NF19:38 Oliveira, F., SP13:24 Oliveira, M., EI5:11, PO96:133 Oliveira, R. M., IP13:63 Oliveira, S., FR3:50 Oliveira, S., PO57:122 Oliver, W., PO18:111 Oller, J., GS35:87 Oosterlinck, F., SM18:76 Orsi, M., SP8:22 Oseli, A., MN20:85 Owczarz, P., BM16:28 Owolabi, B., NF12:16

Padding, J. T., NF18:38 Paiva, M. C., PO118:138 Palak, P., EI23:101 Paolini, M., EI7:28 Parisi, A., PO151:146 Parisi, D., SM21:77

Parmar, V., MN22:85 Partal, P., EI6:11, PO24:113, PO77:128, PO80:129, PO82:129, PO84:130, PO150:146 Pashazadeh, S., , SG9:96 Pasquino, R., EI16:31, FR6:51, FR12:103, GS28:57, PO66:124, SM1:43, SM10:59 Pastor, J. M., EI19:99, PO28:114 Patti, A., MN19:84 Paul, A., FR17:104 Pedro, P., PO19:111, PO23:112 Pepe, V., BM9:26 Pereira, A., NF21:39, Perez, O. E., PO21:112 Perez Robles, S., GS23:42 Pérez Robles, S., PO14:109 Pérez-Mateos, M., PO26:113 Perez-Puyana, V., BM19:70, GS12:19, PO1:107, PO86:131 Perrakis, A., GS37:88 Peter, V. P., SG5:81 Peters, F., SP3:6, SP8:22 Peters, G., IP2:45 Peuvrel-Disdier, E., IP10:62 Pietsch, V. L., PO45:118 Pimenta, F., PO96:133 Pine, D., SG2:81 Pinho, E., IP22:75 Pinho, F. T., EI5:11 Pirini, M. F., SM22:77 Pischel, U., IP20:74 Pizones, V. M., PO21:112 Planet, R., PO9:109 Polinska, P., SG11:97, SM30:93 Poncet, S., SM26:91 Poole, R. J., NF12:16, NF13:16, NF22:39 Portela, R., BM14:27 Poryles, R., EI12:30 Poulard, C., EI8:29 Poulesquen, A., GS7:18 Pourzahedi, A., NF31:55 Pozo, J., PO150:146, PO164:149, PO165:150 Pozo-Bayón, M. Á., PO50:120 Prasanna Kumar, S. S., SP7:22, SP18:78 Prista, C., FR19:105 Psevdos, C., BM6:9 Puertas, A. M., MN19:84

IP12:63 Pyromali, C., SM16:61 Qazi, W. M., FR10:68 Qiao, H., PO87:141 Ouint, S., BM12:27, PO3:107 Quintana Martinez, S. E., PO54:121 Radford, J., MN15:34 Radulescu, A., IP12:63 Raimbault, C., IP9:62 Ramaioli, M., PO58:122 Ramirez, J., GS35:87 Ramirez Brewer, D., PO54:121 Ramos, L., FR13:103, SG2:81, SM11:60 Ranquet, O., SP19:79 Rashidi, Y., MN1:11 Rasteiro, M. d. G., IP22:75, PO166:132, SM15:61 Rathinaraj, J., EM20:83 Ratzsch, K.-F., EM6:49 Ravindran, P., SM25:91 Raymundo, A., FR3:50. FR10:68, FR16:104, FR19:105, PO57:122 Räz, L., BM1:8 Recktenwald, S. M., BM12:27, PO3:107 Redondo, R., PO26:113 Reichart, C., SG4:80 Reinwald-Jaksche, D., PO6:108 Rempfer, G., NF20:38 Renggli, D., EI20:100, PO17:110 Rev, J. M., GS20:41 Ribeiro, H., SP21:79, SP29:94 Richtering, W., EI21:31 Rio, E., EI10:29 Rissanou, A., SM30:93 Robert de Saint Vincent, M., EI25:101 Robisson, A., PO125:145, PO156:147, PO159:148 Rodríguez Agudo, J. A., IP21:75, PO31:114. PO32:115, SG13:97 Rodriguez Hakim, M., BM1:8 Rodriguez-Barroso, A., EM17:82, GS8:18, PO75:127 Rohringer, S., BM5:9 Röhrs, K., PO32:115 Puisto, A., EI10:29 Rojas, O. J., GS16:21 Py, C., PO102:134 Rolo, J., PO166:132

Roman, C., MN24:102, PO76:127 Romancer, R., FR19:105 Romano, A., EI9:29 Romano, S., MN11:33 Romero, A., BM19:70, GS12:19, PO1:107, PO86:131, SG7:95 Röpert, M.-C., PO142:140, SM7:44 Rosales-Romero, A., SP18:78 Rossi, E., NF17:37 Rousseau, F., FR17:104, Roussel, N., EM13:66 Roustaei, A., NF31:55 Roux, J.-N., SP16:7 Roy, S., NF24:53, Rubio, M. A., EI19:99, PO28:114 Rubio Hernández, F. J., PO157:148, PO163:149 Rubio-Hernández, F. J., PO152:146, PO153:147, Rubio-Valle, J. F., PO73:126 Rudolf, Ž., PO55:121 Rühs, P., GS21:41 Ruiz-Domínguez, M., PO53:121 Ruiz-López, J. A., PO75:127, SP7:22 Russo Spena, S., GS15:20 Rüther, M., PO91:141 Rüther, T. N., EM3:48 Ruymbeke, E. V., PO135:142 Rydval, M., PO90:131 Ryl, A., BM16:28 Sagis, L. M., PO20:112

Saintillan, D., MN7:32 Saiz, A., PO26:113 Sakellariou, D., GS13:20 Salmeron-Sanchez, M., GS20:41 Salonen, A., EI8:29. EI10:29 Salton, F., BM7:25 Salvador, A., PO15:110, PO25:117, PO29:114, PO30:117 Sammler, R. L., SM14:60 Sánchez, M. C., PO72:126, PO73:126 Sánchez Carrillo, M. d. C., PO138:143 Sánchez-Cid, P., GS12:19 Sánchez-Puga, P., EI19:99, PO28:114 Sanders, J., EM1:47 Sandino, C., IP10:62

Sandoval, A. J., PO131:142 Santamaria, A., GS27:57, IP8:61, PO131:142 Santana, I., PO119:138 Santelli, L., PO161:148 Santos, J., EI4:100, FR2:50, PO51:120, PO52:120 Santos-Ráez, I. M., PO152:146, PO153:147 Sanz, T., PO15:110, PO25:117, PO29:114, PO30:117 Saraiva, J., BM14:27 Sarrica, A., FR12:103 Sathvanath, R., EI23:101 Sattari, M., SM13:60 Saulnier, L., PO48:119 Schaub, E., EI12:30 Schmid, H.-J., EM3:48, PO91:141, SP25:93 Schmidt, D. S., GS36:88, SP17:79 Schmidt, M. M., EI21:31 Schneider, K., BM5:9 Schönhoff, M., PO70:125 Schöppner, V., PO91:141 Schuetz, D., SG4:80 Schußmann, M. G., PO142:140, SM7:44 Schütz, D., PO31:114 Schwarzenberger, K., EI17:98, GS37:88 Secchi, E., BM15:28 Seguin, A., SP26:94 Semenzato, A., PO16:110 Serial, R., EI3:10 Seth, L., SM21:77 Seto, R., PO161:148 Seuront, L., PO18:111 Shahriyar, K., MN10:33 Shekar, A., NF7:15 Shen, A. Q., IP4:46, MN3:12, MN9:32, NF14:17, NF26:54 Shin, S., PO147:146 Šijakovic Vujicic, N., PO71:126 Sijs, R., SM24:91 Silva, Â. D., PO118:138 Silva, M. M., PO118:138 Silvestri, B., PO66:124 Simionato, G., BM12:27, MN1:11, PO3:107 Simões, S., FR16:104 Sinha, S., NF24:53, PO107:135 Sirignano, M., PO151:146 Skocilas, J., PO67:125 Slemenik Perše, L., MN20:85 Smith, M. G., MN15:34

Smutny, S., PO6:108

Sneijders, S., NF18:38 Soares, P., BM17:69 Soares, Y., SP21:79 Sobral, R. G., BM14:27 Solange, M., GS14:20 Sonker, A., GS19:41 Sousa, H. C., IP22:75 Sousa, I., FR10:68 Sousa, I., FR3:50, FR7:51, PO42:117, PO44:118, PO57:122 Southern, E. J., NF15:17 Spanjaards, M., IP2:45 Stading, M., FR1:49 Stancl, J., PO67:125 Staropoli, M., IP12:63 Steeb, H., IP21:75, SG6:82 Stephanou, P. S., PO139:143 Stergiou, Y., GS37:88 Štípek, J., PO55:121 Stoiber, B., BM5:9 Stricker, L., BM1:8, GS6:5, PO17:110 Strugova, D., SG15:98 Suarez-Fernandez, W., GS22:42 Suc Sajko, J., PO71:126 Suman, K., GS34:87 Sun, J., PO18:111 Sun, Q., GS25:56 Sunder, J., EM22:84 Swan, J. W., EM4:48, PO112:136 Sztucki, M., IP12:63

Tafuro, G., PO16:110 Tajuelo, J., EI19:99, PO28:114 Talmon, Y., GS14:20 Talukdar, J., NF12:16 Tammaro, D., EI14:31, EI22:100, EM18:82, GS15:20, IP1:45 Tammisola, O., EM7:49, NF36:90 Tanguv, G., FR17:104 Tassieri, M., GS20:41, MN15:34 Tasso, A., FR16:104 Tedeschi, F., NF5:3 Tello-Rivas, P., PO51:120 Tenorio-Alfonso, A., IP20:74, PO19:111, PO23:112, PO83:130, PO123:139 Terkel, M., GS8:18, PO75:127 Terry, A. E., NF9:15 Tervoort, T. A., SM10:59, SM19:76 Thambi, A., MN22:85

Thielemans, W., GS30:58 Thokchom, A., PO147:146 Thompson, R. L., NF19:38 Thurber, C. M., SM14:60 Tomaiuolo, G., MN14:34, Topgaard, D., GS14:20 Torregroza Fuentes, E. E., PO64:124 Torres, L., EI2:10 Touil, I., PO85:130 Trappe, V., EI11:30, SP31:95 Trejo-Cáceres, M., PO72:126 Trofa, M., SP12:23 Troisi, E., SM19:76 Trolez, Y., IP10:62 Trujillo-Cayado, L. A., EI4:100, FR2:50, PO51:120, PO52:120 Truong, N. H., BM20:70 Truzzolillo, D., SG2:81, SG12:97 Tsalikis, D. G., PO139:143 Tsamopoulos, J., BM6:9, NF14:17, NF34:89

Urbano, J., IP16:64 Urtasun, L., PO46:119

Valencia, C., GS16:21, IP16:64, IP20:74, PO72:126, PO73:126, PO79:128, PO138:143, PO140:144 Valeria, G., GS4:4 Valette, R., NF21:39, SP14:24 van Berlo, F. A., NF26:54 Van Damme, L., GS13:20 Van den Evnde, M., EM15:66 van der Gucht, J., EI3:10 van der Linden, E., PO20:112, PO22:112, PO124:140 van der Sman, R. G., FR11:68 van Esbroeck, T., PO22:112 Van Puyvelde, P., EM15:66 van Ruvmbeke, E., PO141:144, SM8:59, SM16:61, SM18:76, SM23:90, SM27:92, SM28:92 Van Vlierberghe, S., GS13:20 Varchanis, S., IP4:46, MN3:12, NF14:17 Vargas Clavijo, J., SP15:24

Vasile, F. E., PO21:112 Vasisht, V., SP31:95

Vassalli, M., GS20:41 Vazquez-Perez, F., GS22:42 Vazquez-Quesada, A., NF17:37, SP18:78 Vázquez-Quesada, A., SP7:22 Vega, J. F., MN2:12, PO131:142 Vehres, G., IP12:63 Velázquez Navarro, J. F., PO157:148, PO163:149 Velu, N., SP2:6 Venezia, V., PO66:124 Vereda, F., PO75:127 Vereroudakis, E., GS29:57 Vermant, J., BM1:8, BM15:28, EI1:10, EI2:10, EI18:99, EI20:100, GS3:4, GS6:5, NF25:53, PO17:110, SM19:76 Vervoort, S., SM14:60 Villalba Chehab, M. E., NF27:54 Villone, M. M., MN11:33, NF4:2, NF16:17 Vilotte, A., GS18:40 Visani, D., PO40:116 Vitiello, G., PO66:124 Vlassopoulos, D., BM3:8, EI18:99, EM21:83, GS29:57, SM11:60, SM16:61 Voigtmann, T., PO113:137,

Wagner, C., BM4:8, BM12:27, MN1:11, PO3:107 Walluch, M., PO31:114, SG13:97 Wang, L., GS16:21 Wang, Q., PO15:110 Weeber, R., NF20:38 Weingrill, H. M., SG4:80 Westermann, S., IP12:63 Westman, G., GS19:41 Weyer, C., EI21:31 Wierschem, A., BM10:26, PO32:115 Wilhelm, M., EM6:49, EM10:65, EM22:84, IP5:46, PO142:140, PO146:145, PO162:149, SM7:44 Wilhelmsen, Ø., PO107:135 Willenbacher, N., MN21:85, SP19:79 Windberger, U., BM5:9, PO6:108 Windhab, E. J., FR5:51

Winter, H. H., SG1:80

Volkova, O., SP10:23 Vozikis, L., PO85:130 Wittemann, A., PO162:149
Wobill, C., GS21:41
, GS19:41
Wolf, B., FR18:104
Wood-Adams, P. M.,
SM13:60
Woolley, L. A., PO17:110
Wurm, C., EM19:83
Wyatt, T., PO18:111
Wyss, H. M., PO93:132

Yakubov, G., FR8:67, PO63:124 Yang, J., PO20 Yang, X., PO102:134 Yelash, L., NF5:3 Yokoyama, D., SP21:79 Yousfi, M., EI24:101 Yun, C., EI1:10

Zakhari, M. A., SP22:80 Zarandona, I., PO74:126 Zare, M., EM14:66, IP3:45 Zatloukal, M., SM3:43 Zhang, W., PO18:111 Zhao, J., SP28:94 Zhou, J., GS25:56 Zinelis, K., NF10:16 Zink, J., FR5:51 Zitny, R., PO67:125 Zografos, K., NF22:39

Paper Index

BM1, 8	EM14, 66	GS33, 87	NF7, 15	PO29-EI, 114	PO91-IP, 141		SP13, 24
BM3, 8	EM15, 66	GS34, 87	NF9, 15	PO30-EI, 117	PO93-MN, 132	SG1, 80	SP14, 24
BM4, 8	EM16, 67	GS35, 87	NF10, 16	•	PO94-MN, 132	SG2, 81	SP15, 24
BM5, 9	EM17, 82	GS36, 88	NF11, 16	PO31-EM, 114	PO96-MN, 133	SG3, 81	SP16, 7
BM6, 9	EM18, 82	GS37, 88	NF12, 16	PO32-EM, 115	PO97-MN, 133	SG4, 80	SP17, 79
BM7, 25	EM19, 83		NF13, 16	PO34-EM, 115	PO98-MN, 134	SG5, 81	SP18, 78
BM8, 26	EM20, 83	IP1, 45	NF14, 17	PO35-EM, 115	PO102-NF, 134	SG6, 82	SP19, 79
BM9, 26	EM21, 83	IP2, 45	NF15, 17	PO39-EM, 116	PO103-NF, 134	SG7, 95	SP20, 78
BM10, 26	EM22, 84	IP3, 45	NF16, 17	PO40-EM, 116	PO104-NF, 135	SG8, 96	SP21, 79
BM11, 26	21.122, 0 .	IP4, 46	NF17, 37	PO41-EM, 116	PO105-NF, 135	SG9, 96	SP22, 80
BM12, 27	FR1, 49	IP5, 46	NF18, 38	PO42-FR, 117	PO107-NF, 135	SG10, 96	SP23, 93
BM14, 27	FR2, 50	IP6, 46	NF19, 38		PO109-NF, 135	SG11, 97	SP25, 93
BM15, 28	FR3, 50	IP7, 47	NF20, 38	PO44-FR, 118	PO110-NF, 136	SG12, 97	SP26, 94
BM16, 28	FR5, 51	IP8, 61	NF21, 39	PO45-FR, 118	PO111-NF, 136	SG12, 97 SG13, 97	SP28, 94
BM17, 69	FR6, 51	IP9, 62	NF22, 39	PO46-FR, 119	PO112-NF, 136	SG14, 98	SP29, 94
BM17, 09 BM18, 70	FR7, 51	IP10, 62	NF23, 40	PO48-FR, 119	PO113-NF, 137	SG15, 98	SP30, 95
BM19, 70	FR8, 67	IP11, 63	NF24, 53	PO49-FR, 119	PO114-NF, 137	5015, 76	SP31, 95
BM20, 70	FR9, 68	IP12, 63	NF25, 53	PO50-FR, 120	PO117-NF, 137	SM1, 43	31 31, 93
DIVI20, 70	FR10, 68	IP13, 63	NF25, 55 NF26, 54	PO51-FR, 120	FO117-NF, 137	SM3, 43	
EI1, 10	FR11, 68	IP15, 64		PO52-FR, 120	PO118-SG, 138	SM4, 43	
EI1, 10 EI2, 10	FR12, 103	IP16, 64	NF27, 54	PO53-FR, 121	PO119-SG, 138	SM5, 44	
EI2, 10 EI3, 10	FR13, 103	IP17, 73	NF28, 89	PO54-FR, 121	PO120-SG, 138	SM6, 44	
EI4, 100	FR14, 103	IP18, 74	NF29, 55	PO55-FR, 121	PO121-SG, 139	SM7, 44	
EI5, 11	FR16, 104	IP18, 74 IP19, 74	NF30, 55	PO56-FR, 122	PO122-SG, 139	SM8, 59	
EI5, 11 EI6, 11	FR17, 104	IP20, 74	NF31, 55	PO57-FR, 122	PO123-SG, 139	SM9, 59	
	,	,	NF32, 56	PO58-FR, 122	PO124-SG, 140	SM19, 59	
EI7, 28	FR18, 104	IP21, 75	NF34, 89	PO59-FR, 123	PO125-SG, 145		
EI8, 29	FR19, 105	IP22, 75	NF35, 89	PO61-FR, 123	10120 00, 110	SM11, 60	
EI9, 29	GS1, 4	MN1, 11	NF36, 90	PO62-FR, 123	PO129-SM, 141	SM13, 60	
EI10, 29	GS3, 4	MN2, 12	DI 1 1	PO63-FR, 124	PO130-SM, 142	SM14, 60	
EI11, 30	GS4, 4	MN3, 12	PL1, 1	PO64-GS, 124	PO131-SM, 142	SM15, 61	
EI12, 30	GS5, 5	MN4, 12	PL2, 37	PO66-GS, 124	PO135-SM, 142	SM16, 61	
EI13, 30	GS6, 5	MN5, 13	PL3, 73	PO67-GS, 125	PO137-SM, 143	SM17, 76	
EI14, 31	GS7, 18	MN7, 32	DO1 DM 107	PO69-GS, 125	PO138-SM, 143	SM18, 76	
EI16, 31	GS8, 18	MN8, 32	PO1-BM, 107	PO70-GS, 125	PO139-SM, 143	SM19, 76	
EI17, 98		MN9, 32	PO2-BM, 107		PO140-SM, 144	SM21, 77	
EI18, 99	GS10, 19		PO3-BM, 107	PO71-GS, 126	PO141-SM, 144	SM22, 77	
EI19, 99	GS11, 19	MN10, 33	PO5-BM, 108	PO72-GS, 126	PO142-SM, 140	SM23, 90	
EI20, 100	GS12, 19	MN11, 33	PO6-BM, 108	PO74-GS, 126	PO143-SM, 144	SM24, 91	
EI21, 31	GS13, 20	MN12, 33	PO9-BM, 109	PO74-GS, 126	PO144-SM, 145	SM25, 91	
EI22, 100	GS14, 20	MN13, 34	PO11-BM,	PO75-GS, 127	PO146-SM, 145	SM26, 91	
EI23, 101	GS15, 20	MN14, 34	PO12-BM, 109	PO76-GS, 127		SM27, 92	
EI24, 101	GS16, 21	MN15, 34	PO14-BM, 109	PO77-IP, 128	PO147-SP, 146	SM28, 92	
EI25, 101	GS17, 40	MN16, 35	DO15 EL 110	PO78-IP, 128	PO150-SP, 146	SM29, 92	
E) (1 47	GS18, 40	MN17, 84	PO15-EI, 110	PO79-IP, 128	PO151-SP, 146	SM30, 93	
EM1, 47	GS19, 41	MN19, 84	PO16-EI, 110	PO80-IP, 129	PO152-SP, 146	CD1 5	
EM2, 47	GS20, 41	MN20, 85	PO17-EI, 110	PO81-IP, 129	PO153-SP, 147	SP1, 5	
EM3, 48	GS21, 41	MN21, 85	PO18-EI, 111	PO82-IP, 129	PO156-SP, 147	SP2, 6	
EM4, 48	GS22, 42	MN22, 85	PO19-EI, 111		PO157-SP, 148	SP3, 6	
EM5, 48	GS23, 42	MN23, 102	PO20-EI, 112	PO83-IP, 130 PO84-IP, 130	PO159-SP, 148	SP4, 21	
EM6, 49	GS25, 56	MN24, 102	PO21-EI, 112		PO161-SP, 148	SP5, 7	
EM7, 49	GS26, 57	NF1, 1	PO22-EI, 112	PO85-IP, 130	PO162-SP, 149	SP6, 7	
EM8, 64	GS27, 57	NF2, 2	PO23-EI, 112	PO86-IP, 131	PO163-SP, 149	SP7, 22	
EM10, 65	GS28, 57	NF3, 2	PO24-EI, 113	PO87-IP, 141	PO164-SP, 149	SP8, 22	
EM11, 65	GS29, 57	NF4, 2	PO25-EI, 117	PO88-IP, 131	PO165-SP, 150	SP9, 23	
EM12, 65	GS30, 58	NF5, 3	PO26-EI, 113	PO89-IP, 131	PO166-SP, 132	SP10, 23	
EM13, 66	GS31, 58	NF6, 3	PO28-EI, 114	PO90-IP, 131	, -	SP12, 23	