



Structure and rheology during catastrophic phase inversion of Pickering emulsions stabilized with fumed silica particles

Frederico Macedo Fernandes Barros, Christophe Chassenieux, Marli Miriam de Souza Lima, Lazhar Benyahia

► To cite this version:

Frederico Macedo Fernandes Barros, Christophe Chassenieux, Marli Miriam de Souza Lima, Lazhar Benyahia. Structure and rheology during catastrophic phase inversion of Pickering emulsions stabilized with fumed silica particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2020, 593, pp.124630. <10.1016/j.colsurfa.2020.124630>. <hal-03001459>

HAL Id: hal-03001459

<https://hal.science/hal-03001459v1>

Submitted on 22 Aug 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY-NC 4.0 - Attribution - Non-commercial use - International License

Structure and rheology during catastrophic phase inversion of Pickering emulsions stabilized with fumed silica particles

Frederico Macedo Fernandes Barros^a, Christophe Chassenieux^a, Marli Miriam de Souza Lima^b, Lazhar Benyahia^{a*}

* Corresponding author. E-mail: lazhar.benyahia@univ-lemans.fr

^a *Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS – Le Mans Université. 1, Avenue Olivier Messiaen 72085 - LE MANS cedex 9, France*

^b *Laboratório de Fotoquímica e Desenvolvimento Tecnológico - LAFITEC, Departamento de Farmácia - DFA, Universidade Estadual de Maringá-UEM, Maringá, Paraná, Brasil*

Abstract

Oil in water Pickering emulsions undergoing catastrophic phase inversion were investigated. Two polydimethylsiloxane (PDMS) oils of various viscosity have been emulsified in water and stabilized with fumed silica particles. The concentration of particles and the oil volume fraction were varied from 0.1 to 1 wt% and from 10 to 90 vol%, respectively. Upon increasing the oil content, a phase inversion occurred from oil-in-water to water-in-oil as evidenced from macroscopic and microscopic observations. At low concentration of particles, phase inversion occurred at lower oil volume fraction for the more viscous PDMS. Rheological measurements showed a strong increase of the elastic modulus of the emulsions with increasing the amount of oil up to a maximum value where the catastrophic phase inversion took place. The viscoelastic behaviour of the emulsions was discussed considering their structure but also the rheology of the particle suspensions that have been dispersed in both oil and water phases.

Key-Words

Pickering emulsions, catastrophic phase inversion, structure, rheology, fumed silica particles

1. Introduction

Emulsions are dispersions of one liquid into another and often require strong stirring conditions to be obtained. Despite the fact that they consist in metastable systems, they can exhibit some persistence against coalescence and phase separation upon addition of surface active agents such as surfactants, but also insoluble particles, starch microgels, proteins, considered individually or in combination [1]. The most common resulting morphologies encountered for emulsions are water-in-oil (W/O) and oil-in-water (O/W) but, multiple emulsions (also called double emulsions) can also be obtained. Several factors may alter the characteristics and then the properties of the emulsions, for instance, the physicochemical features of the ingredients such as the nature and composition of the surface active agents as well as the density and viscosity of both liquids[2].

Spectacular modifications of the characteristics of the emulsions can be achieved by a phase inversion where the dispersed phase converts to the continuous one and vice versa upon the modification of external parameters. The latter can either be related to the process conditions at play for obtaining the emulsions such as the energy input or to the ingredients such as the oil fraction[3, 4] or ionic strength of the water phase [3] not to mention the influence of external parameter such as the temperature [5].

Catastrophic phase inversion occurs when the volume fraction of the oil phase (ϕ_o) for example is increased above a critical value [4]. As a result both the size and the number of droplets of the emulsion increase with ϕ_o . This may force the interfaces to touch and the droplets to coalesce leading the initial internal phase to be turn into the new external phase [6]. According to some authors this process mimics a cusp catastrophe theory model [7, 8] as

supported by several observations such as the presence of bimodal morphologies. Thus, dispersed systems of phases A and B can either exist in A-in-B or B-in-A form. When such a phase inversion occurs, sudden changes in the physical properties of the emulsions are observed as, for example, the electrical conductivity [4, 9]. Another feature that corroborates the cusp catastrophe theory is the presence of hysteresis, meaning that the morphology can depend on the experimental path followed to process the dispersion [10]. However, when trivial modifications of this process occur, the cusp catastrophe theory fails at predicting behaviours that diverge from what is expected. Although the cusp catastrophe theory provides relevant information concerning the phase inversions, the kinetic approach appears as a relevant alternative to fully understand the inversion process [11, 12].

In the case of solid particle-stabilized emulsions, so-called Pickering emulsions, the wettability of particles plays a major role in achieving a given type of emulsions. The wettability is connected to the contact angle θ of the solid particles at the oil-water interface. Contact angles less than 90° are typical of hydrophilic particles and favour O/W emulsions whereas contact angles higher than 90° , related to hydrophobic particles, favour the formation of W/O emulsions [13]. Furthermore, the use of various types of particles allows to achieve different droplet size distributions resulting in various physicochemical properties [14]. The strong attachment energy of solid particles to the liquid interface confers to Pickering emulsions a high stability that makes them potential candidates for applications. For the specific case of PDMS, Simovic and Prestidge have described the behavior of hydrophilic and hydrophobic silica at PDMS/water interfaces[15]. They have carefully investigated the adsorption isotherms of silica particles and the structure of these particles at

interfaces. The authors have clearly shown that hydrophobic silica tend to form multilayers of particles at the PDMS/water interfaces which induces their armoring as well as some cross-linking between the droplets but they did not report on catastrophic phase inversion.

However, like surfactant-based emulsions, Pickering emulsions can exhibit catastrophic phase inversion. Binks and Lumsdon have described the features of the catastrophic phase inversion displayed by toluene-water Pickering emulsions stabilized with hydrophobic silica particles. They reported that phase inversion occurred from W/O to O/W for a volume fraction of water around 70% with no hysteresis that is no matter if ϕ_o was increased or decreased [4]. In the same work, the authors have varied the type of oil and the pH of the aqueous phase in order to modify the wettability of the silica particles but the phase inversion always occurred roughly with the same amount of water. However, PDMS oil appeared to be an exception as it was impossible to invert the W/O emulsions into O/W ones even at very high content of water ($\phi_o \approx 10\%$) with the hydrophobic silica particles that were used in this study. This result accounted for an increase in the hydrophobicity of the stabilizing particles upon adsorption of PDMS at their surface. For water and triglyceride oils based Pickering emulsions, Binks and Rodrigues have shown the paramount importance of the location of the solid particles into one of the phases prior to the emulsification step onto the phase inversion both in terms of type (from W/O to O/W or the revert) and critical volume fraction of water due to hysteresis in the contact angle value of the particles at the three line phase[16]. In order to overcome this last issue, the same group has proposed a new way for processing the emulsions where the particles were added in the powdered form at the top of the water phase and then covered with the oil

phase, the mixture being then thoroughly homogenised. By using the surface energy values at the different interfaces of the various ingredients of the emulsions to compute the contact angle of the solid particles, it has then been possible to qualitatively predict where the phase inversion from W/O to O/W occurred as a function of the hydrophobicity of the particles for perfume oils of various polarity[17]. In brief, the phase inversion for Pickering emulsions can then be achieved either by varying its composition, or the hydrophobicity of the particles or the process path which is followed to obtain them. Furthermore, it has been shown that such a phase inversion was useful for achieving high internal phase Pickering emulsions [18] as well as O/W/O double emulsions with fine-control of the fraction and number of droplets of the inner phase[19] or by increasing the time of the emulsification[20].

Here, we have achieved an extensive description of catastrophic phase inversion of Pickering emulsions based on PDMS and water and stabilized with industrial fumed silica particles. The structure of the emulsion has been investigated both at macroscopic and microscopic scales. The effect of the viscosity of the oil has been varied. The rheological properties of the emulsions have been investigated at each step of the catastrophic phase inversion and are discussed in the light of the emulsion structure.

2. Materials and methods

2.1. Compositions

Emulsions were prepared with Milli-Q water and two polydimethylsiloxane oils: PDMS 47V100 (Caldic Spécialités) and PDMS 47V20 (VWR) whose viscosity is respectively 0.1 and 0.02 Pa·s at 25°C. The Newtonian

viscosities communicated by the providers were confirmed within 10% by flow tests using a stress-controlled rheometer.

The particles used were hydrophobic fumed silica (Aerosil® R816), supplied by Degussa AG. These particles have been reported being amphiphilic despite the grafting of hexadecyl chains at their surface [21].

2.2. Emulsion preparation

Different emulsions were prepared by mixing the particles and the liquid phases with an ultrasound Vibra Cell 75115 (Bioblock Scientific, Illkirch, France) during 3 minutes. The amplitude was fixed at 24% with 3 seconds of pulsation and 2 seconds of pause. An ice bath was used to avoid overheating of samples. The particle and oil contents were varied from 0.1 to 1wt% and from 10 to 90 vol% respectively. Then, the emulsions were centrifuged for 1 min at 1000 RPM. The macroscopic, microscopic and rheological behaviour were investigated one week after sample preparation to achieve a steady state.

2.3. Suspensions preparation

Each suspension was prepared by adding 1 to up to 5 wt% of Aerosil® 816 particles to oil or water. Afterwards, ultrasound mixing was applied for three minutes as described for the emulsions. Samples were placed under vacuum for about five minutes prior to rheological measurements to remove entrapped air bubbles.

2.4. Confocal laser scanning microscopy

CLSM observations were made with a Leica TCS-SP2 (Leica Microsystems Heidelberg, Germany) by using different fluorescent labelling. For each ml of water phases, 10 µl of aqueous solutions of rhodamine B (10ppm) and 20 µl of fluorescein (20 ppm) were added for labelling respectively the particles and

water. Images of 512×512 pixels were obtained at different magnifications with a water immersion objective: $20\times$ NA = 0.7. The incident light was emitted by a laser beam at 543 nm and/or at 488 nm.

To estimate the droplet diameter, several images were considered and more than one hundred droplets per image were monitored for each case. The mean diameter and the standard deviation were then calculated.

2.5. Rheology

Rheological measurements were performed with a stress-controlled rheometer DHR3 (TA Instruments, France). Excess of water and oil phase were carefully removed with a syringe and the rheological properties of the emulsions were measured at $20.0 \pm 0.1^\circ\text{C}$ using plate–plate geometry (diameter of upper plate = 40.0 mm, gap height = 1.0 mm). Stress sweeps were performed between 0.001 and 1000 Pa at a frequency of 1 Hz. Then, the frequency dependence of storage (G') and loss (G'') moduli were measured by fixing a stress in the linear regime and by varying the frequency between 10 and 10^{-3} Hz. For particle suspensions, oscillatory measurements were carried out using cone-plate geometry (diameter = 60 mm, angle = 1°) at a temperature of $20.0 \pm 0.1^\circ\text{C}$. The same geometries were used for steady-state flow measurements where the viscosity was obtained versus shear rate in the range between 10^3 and 10^{-3} s^{-1} . Rheological measurements were repeated at least 3 times assessing a reproducibility within 10%.

3. Results

3.1. Phase diagram and emulsion structure

With less than 1 wt% of particle, the emulsions were stable over months. Fig. 1, shows an example of the macroscopic behaviour of the emulsions

obtained with 0.5 wt% of particles and PDMS 47V100 when increasing the volume fraction, ϕ_o , of the latter. The turbid phase represents the emulsion. After stopping the ultrasound process, no modification of the emulsions with time was observed.

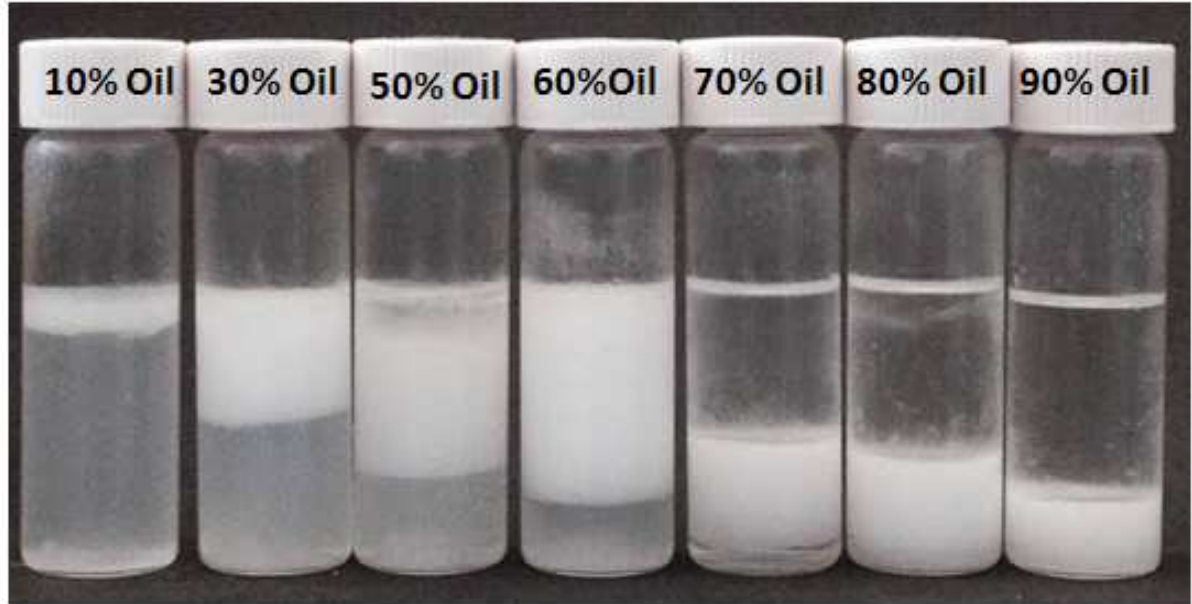


Fig. 1. Visual aspect of PDMS 47V100-water emulsions with 0.5 wt% of particles for different volume fraction of oil as indicated in the figure.

As seen from Fig. 1, for a given particle concentration, macroscopic changes occur depending on ϕ_o . With 0.5 wt% of particles, the emulsion is located at the top when ϕ_o is smaller than 60 %wt. Above this value, the emulsion is preferentially located at the bottom of the tubes which hints at the presence of a phase inversion.

The volume fraction of the emulsion (ϕ_e) increases with ϕ_o up to $\phi_o = 60\%$. Then ϕ_e decreases in big extent upon increasing further ϕ_o . ϕ_e is calculated considering the volume of the effective emulsion, i.e. the turbid phase, compared to the total volume.

Fig. 2 shows the evolution of ϕ_e as a function of ϕ_o for the two PDMS oils and with 1 wt% of particles. For $\phi_o \geq 70\%$, the turbid phase is located at the bottom and the volume fraction of the emulsions decreases whatever the viscosity of the oil. When the emulsion is located at the top, ϕ_e is much bigger for the less viscous oil especially at low ϕ_o . The difference fades away for ϕ_o comprised between 50% to 70%. When $\phi_o \geq 80\%$, ϕ_e is relatively much bigger for the more viscous oil.

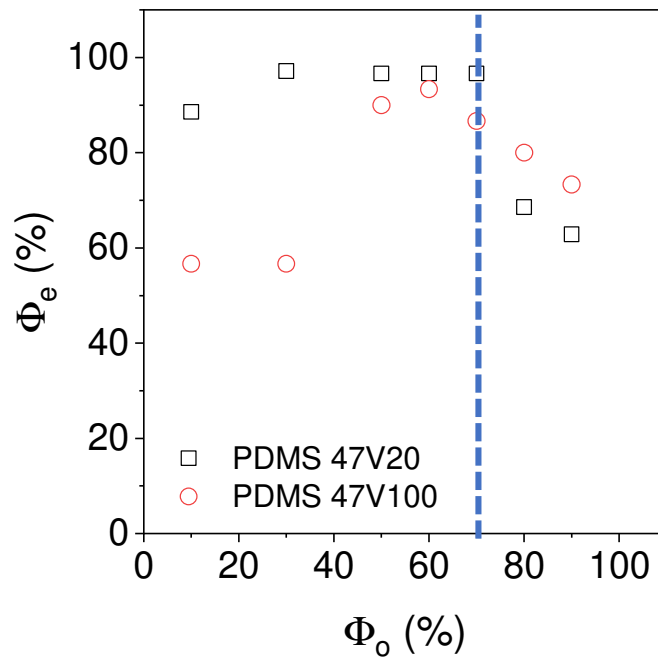


Fig. 2: Volume fraction of emulsions ϕ_e as a function of ϕ_o for two PDMS oils having different viscosities and stabilized with 1 wt% of particles. The dashed lines correspond to phase inversion which appears to be at the same value of ϕ_o for both oils with 1 wt% of particles.

CLSM images reveal that these macroscopic changes are related to a phase inversion phenomenon as shown in Fig. 3 for the same emulsions. For both oils the emulsions present similar structures. When $\phi_o \leq 50\%$, the continuous phase is water and turns out to be oil for $\phi_o \geq 70\%$ whatever the viscosity of oil. One could see, at this oil volume fraction, the formation of a

multiple emulsion, more clearly evidenced with the more viscous PDMS. It is worth mentioning that at higher ϕ_o , it is not possible to obtain larger volume fraction of emulsion even by further increasing the concentration of the particles.

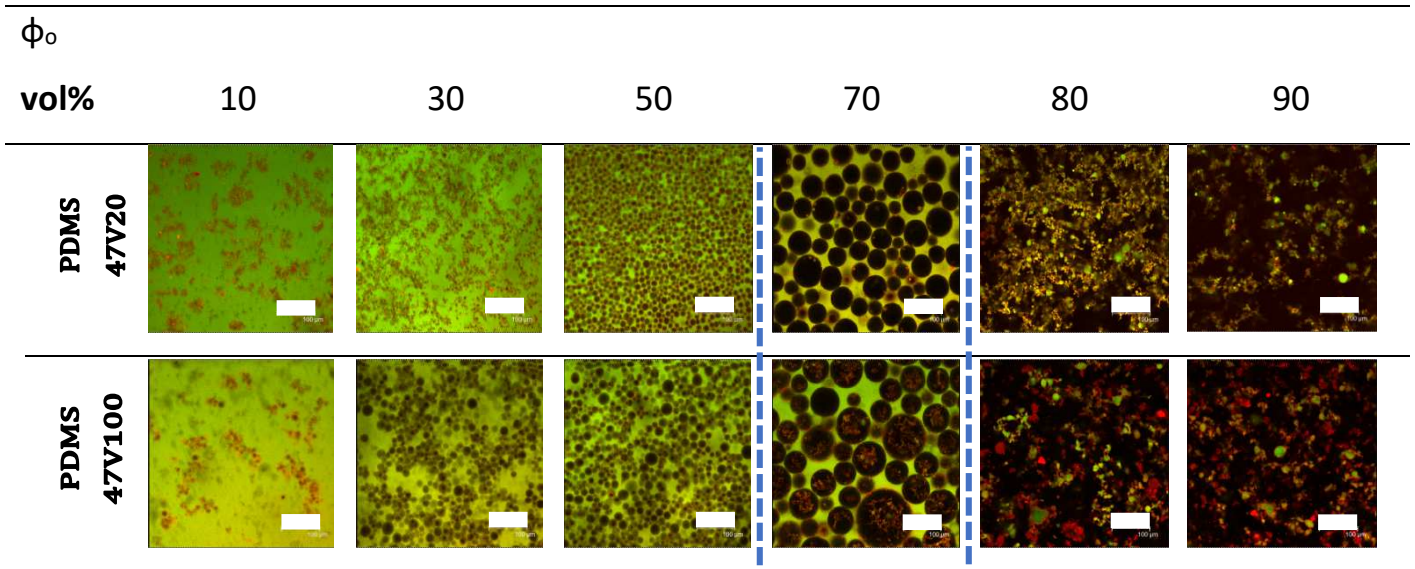


Fig. 3: Confocal laser scanning microscopy images of PDMS 47V20-water (top) and PDMS 47V100-water (bottom) emulsions with 1 wt% of particles for different volume fraction of oil as indicated in the figure. The water phase appears in green, the oil phase in black and the particles in red. The scale bar represents 100µm. The dash lines correspond to the composition zone where the phase inversion occurs and to the formation of multiple emulsions.

The number of droplets and their size do depend on the oil fraction as evidenced from Fig.4 where the average diameter of droplets is plotted as a function of ϕ_o . The size of the droplet increases with ϕ_o and is slightly bigger for the more viscous oil. The number of droplets increases also as more oil is added and at $\phi_o = 50\%$ the emulsion reaches a close packing configuration. For O/W emulsions, the droplet shape becomes more irregular and connections

within the dispersed phase can be visualised (Fig. 5). The size of the droplets is then difficult to determine.

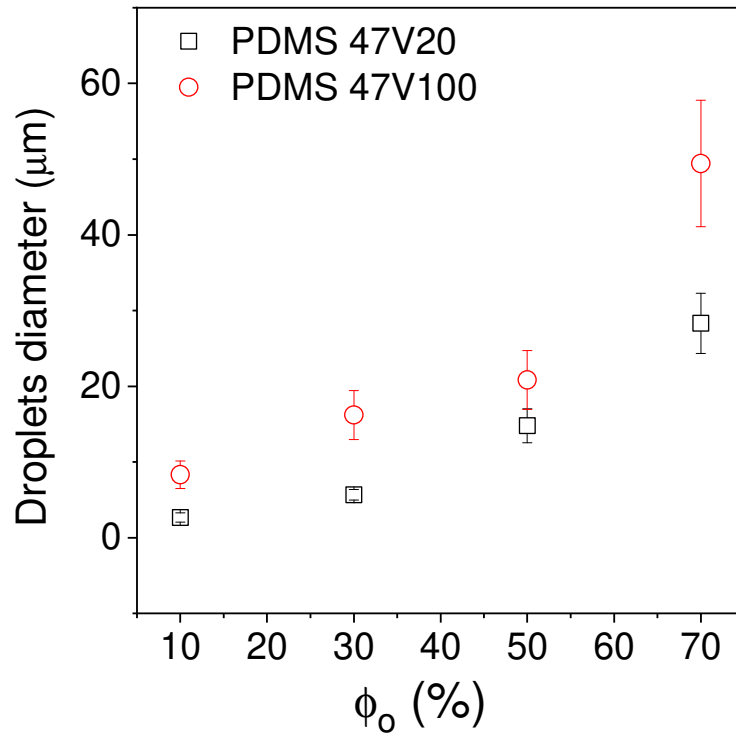


Fig. 4: Evolution of the droplet diameter with the volume fraction of oil for emulsions stabilised with 1 wt% of particles.

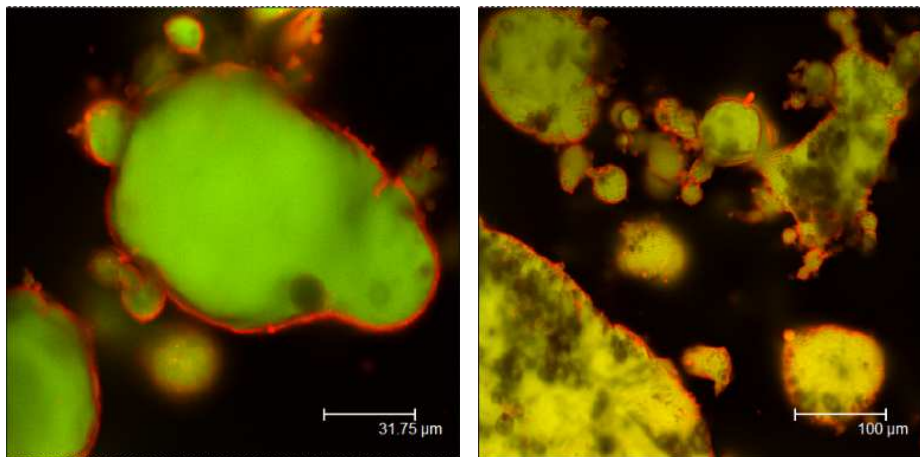


Fig. 5: Confocal images of W/O emulsions with irregular droplet shapes obtained for PDMS 47V100 (ϕ_o = 80% and 1 wt% of particles).

Macroscopic and CLSM observations were combined to determine the phase diagram of the catastrophic phase inversion as a function of ϕ_o , the particle concentration and the oil viscosity as shown in Fig. 6. For a given particle concentration, the phase inversion from O/W to W/O occurs when ϕ_o increases. On the contrary, for a fixed volume fraction of oil, the phase inversion from W/O to O/W occurs when the particle concentration increases. The viscosity of the oil phase has no influence when the concentration of particles is higher than 0.6 wt%. Below this value, the phase inversion takes place at lower ϕ_o for PDMS 47V100 compared to PDMS 47V20.

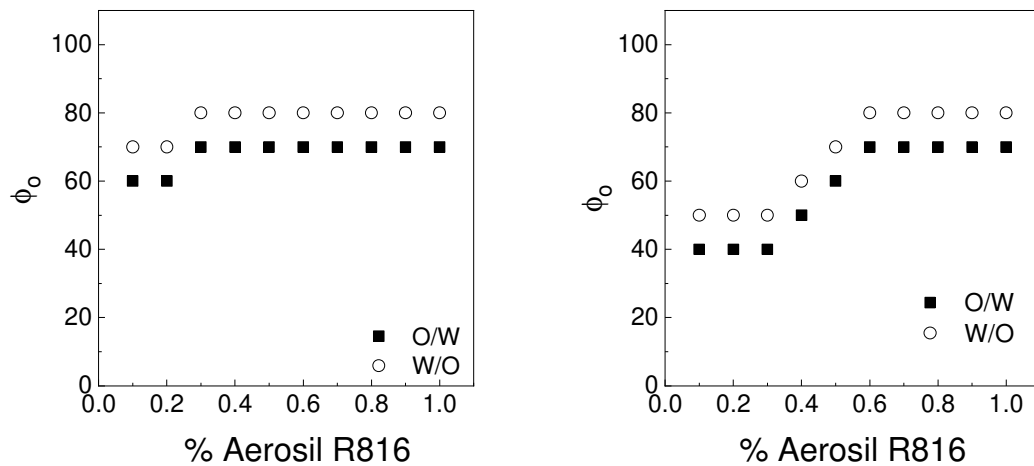


Fig. 6: Phase diagram of PDMS 47V20/water (left) and PDMS 47V100/water emulsions (right) for different oil fraction and particle concentration ranging from 0 to 1% wt.

The corresponding fraction of the dispersed phase (ϕ_d) within the emulsion is plotted in Fig. 7. ϕ_d increases almost linearly with ϕ_o below the phase inversion point. There is no significant difference in ϕ_d between the two oils. Furthermore, ϕ_d is much bigger for O/W than for W/O emulsions.

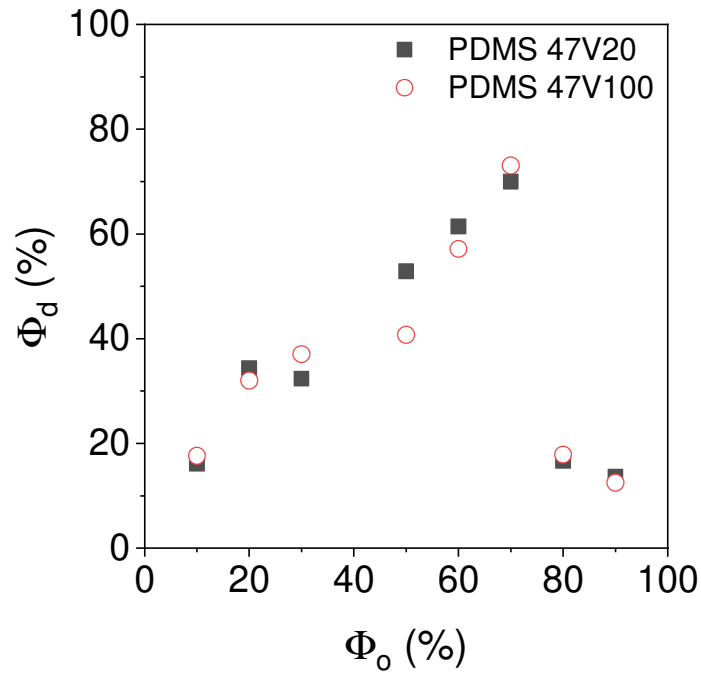


Fig. 7: Volume fraction of the dispersed phase of the emulsions as a function of the oil fraction for both oils with 1 wt% of particles.

3.2. Rheological behaviour

The viscoelastic properties of emulsions prepared using 1 wt% of particles and with ϕ_o from 10% to 90% are shown in Fig. 8.

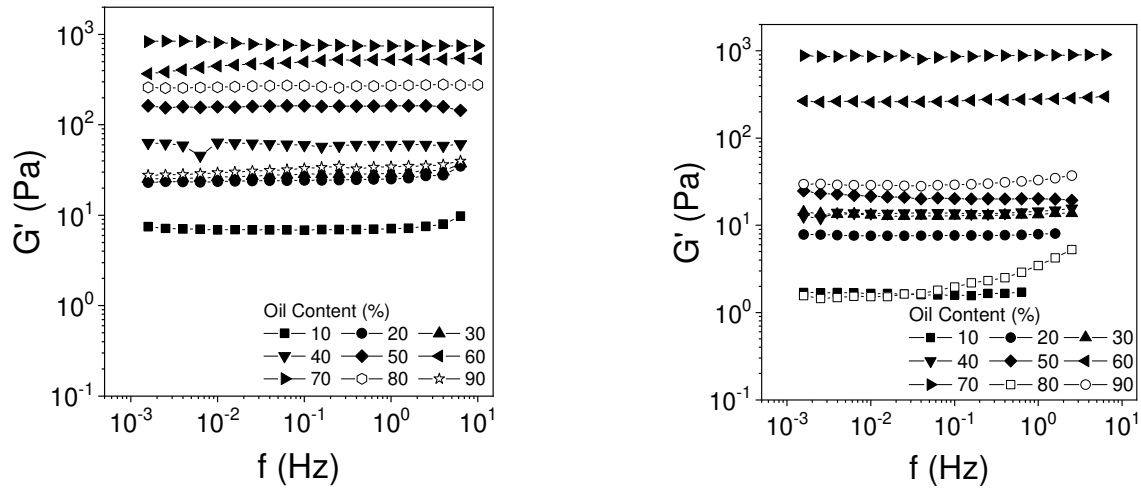


Fig. 8: Elastic modulus G' as a function of frequency for PDMS 47V100 (left) and PDMS 47V20 (right)-based emulsions made with various oil fractions as indicated in the figure and with 1 wt% of particles. The close symbols represent O/W emulsions and the open symbols W/O emulsions.

Since all the emulsions, that have been investigated, display an elastic modulus higher than the viscous one, we will focus on the former. The frequency dependence of G' is almost negligible within the measured frequency range for all the emulsions. Fig. 9 represents the value of G' as a function of ϕ_o for both oils. Qualitatively, upon increasing ϕ_o , G' increases until reaching a maximum value at roughly $\phi_o = 70\%$. At higher value of ϕ_o , G' starts to decrease when the dispersed phase becomes water. The same tendency is observed for both PDMS oils, though the emulsions made with the less viscous one present higher values of G' . The magnitude of the elastic modulus is almost one order of magnitude higher for emulsions based on the less viscous PDMS at low ϕ_o but the difference vanishes for $\phi_o > 60\%$.

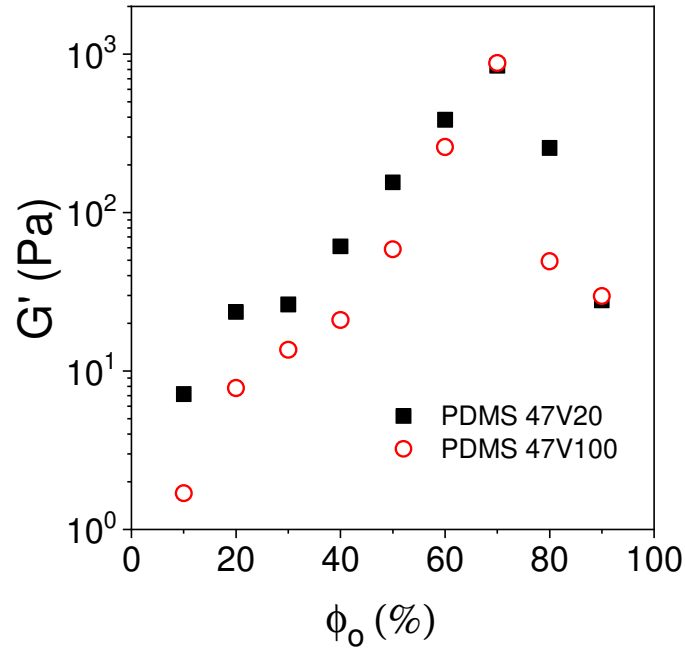


Fig. 9: Elastic modulus dependence on the oil fraction for emulsions made with 1 wt% of particles and both PDMS oils.

4. Discussion

4.1. Origin of the phase inversion

For emulsions stabilized either by surfactants or particles, increasing the amount of dispersed phase favours the droplet coalescence and thus the phase inversion [4, 22-24]. When using ionic surfactant, the phase inversion occurs from O/W to W/O when ϕ_o increases. Similar observations were reported for emulsions stabilized with non-ionic surfactant although the inversion occurred from W/O to O/W. The presence of a double O/W/O emulsions have also been reported in this case[25]. Binks and Lumsdon observed a similar behaviour for Pickering emulsions [4]. A catastrophic phase inversion was observed for water-toluene emulsions stabilized by hydrophobic silica and a transition from W/O to O/W upon increasing ϕ_o has been reported. For surfactant-based emulsions the viscosity is a key trigger that influences the catastrophic phase

inversion. When the viscosity ratio between the dispersed phase to the continuous one decreases, a phase inversion, from W/O to O/W, is favoured as documented for various systems [26, 27]. Similarly, for W/O Pickering emulsions, an increase of the oil viscosity has been reported to induce an inversion at ϕ_o that increases when decreasing the viscosity of the oil [28, 29]. Furthermore, it was found that the droplets were smaller and more regular in shape when using an oil of low viscosity rather than with a more viscous one for which polydisperse distributions of droplet sizes have been encountered.

In this work, we observe the phase inversion from O/W to W/O when ϕ_o increases. This may be related to the incomplete hydrophobic nature of the particles used as stabilizers. Indeed, despite their hydrophobic surface treatment, Aerosil® R816 particles were developed for rheological applications in water-based systems like coatings and cosmetics [21]. Furthermore, Yan et al. [30] reported a contact angle of these particle of about 60° which confirms our own observations regarding the rheology of these particles suspended in oil or in water [31]: the elastic moduli of Aerosil® R816 suspensions in oil were higher than in water indicative of a better dispersibility of them in water. Particles that prefer the water phase clearly promote O/W emulsions as it was predictable.

The phase inversion happens no matter the viscosity of the oil. However, below 0.6 wt% of particles, the phase inversion takes place at lower value of ϕ_o for PDMS of higher viscosity. This fact may originate from the difficulty for particles to reach and anchor to the interface due to viscosity constraints as it was suggested in the literature [32-34]. This could be also related to the higher stability of Pickering emulsions made with oils having lower viscosities that may enhance the probability for collision and adsorption of particles at the interface

[35]. The same effect may occur at higher particle concentrations leading to a fast and full interface coverage without an appreciable influence of the oil viscosity. All these possibilities support the lowering of the onset of catastrophic phase inversion in terms of oil fraction when decreasing the viscosity of the oil phase and when the concentration of particles remains below 0.6wt%.

4.2. Mechanical properties of the emulsions

The elastic moduli reflect the storage energy in the sample and is somehow related to the formation of a network. In a first approximation, G' may account for the strength of the strands and the nodes of the network. For these emulsions, the network is a complex structure composed of the droplets, the interfaces and the continuous phase. Indeed, it is clear that the droplets are connected in a complex way and form a connected network otherwise the emulsions at low ϕ_o would not exhibit a gel-like behaviour. To account for this effect, the elastic modulus of the emulsions has been plotted as a function of the volume fraction of the dispersed phase in Fig. 10.

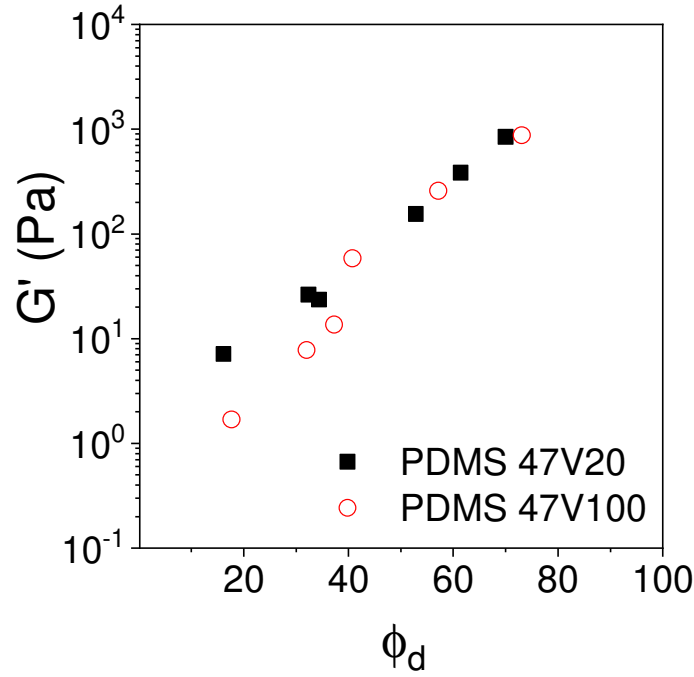


Fig. 10: The elastic modulus (G') of the emulsions as a function of the volume fraction of the dispersed phase below the phase inversion and at 1 wt% of particles.

As mentioned before, ϕ_d increases almost linearly with ϕ_o below the phase inversion with no significant influence of the viscosity of the oil (Fig. 7). Therefore, ϕ_d is much higher for O/W than for W/O emulsions. It follows that for both oils, the elastic modulus increases with ϕ_d until a maximum value of 70% and then collapses when ϕ_d drops dramatically after the phase inversion. Thus, the increase of G' is the consequence of the increase of ϕ_d with ϕ_o . Indeed, below the phase inversion, increasing the oil fraction leads to higher ϕ_d with more and bigger droplets that promote both a close packing configuration and connections between droplets.

When $\phi_d > 50\%$, i.e. for close packing configuration, one may assume that the elastic modulus depends on the compressibility of the droplets forming the network. As suggested in the literature [36, 37], this feature could be

quantified by the Laplace pressure of the droplet which equals $\gamma/2R$, where R is the radius of the droplet and γ the interfacial tension between PDMS and water (41 mN/m according to Ismail et al. [38]). From the CLSM images, we determined R (fig.4) and the elastic moduli normalized by the Laplace pressure are plotted as a function of ϕ_d in Fig. 11. It can be seen that $G'/(\gamma/R)$ is not sensitive to the viscosity of the oil as no substantial difference was noticed between them. Furthermore, $G'/(\gamma/R)$ exhibits an exponential dependence on ϕ_o : $G'/(\gamma/R) \approx e^{0.1\phi_o}$.

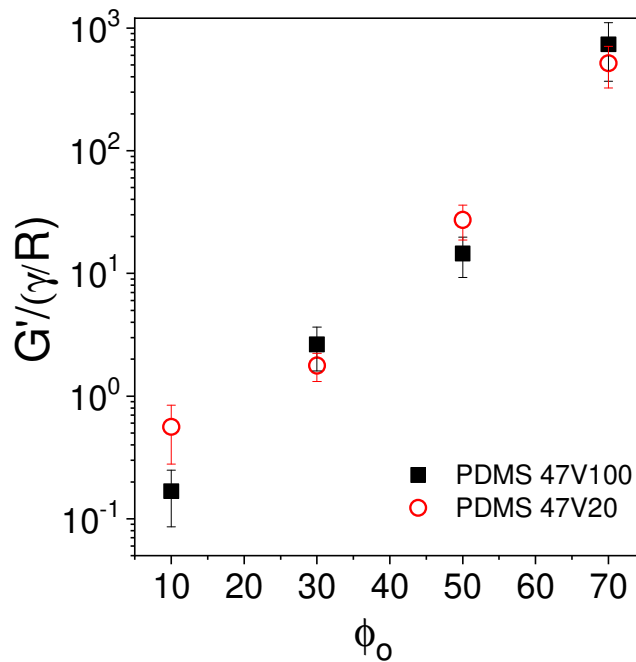


Fig. 11: The normalized elastic modulus by the Laplace pressure as a function of the volume fraction of the oil below the phase inversion.

However, G' is not simply related to the volume fraction of the dispersed phase since at low ϕ_d (below 50%), the elastic modulus is bigger for the emulsions made with the less viscous oil. In fact, as shown by the CSLM images (Figure 12), although most of the particles go to the interface, some may still be present in the oil and/or water phases. Their presence in the continuous phase

is likely to affect its rheology and thus to impact the over whole viscoelastic behaviour of the emulsion.

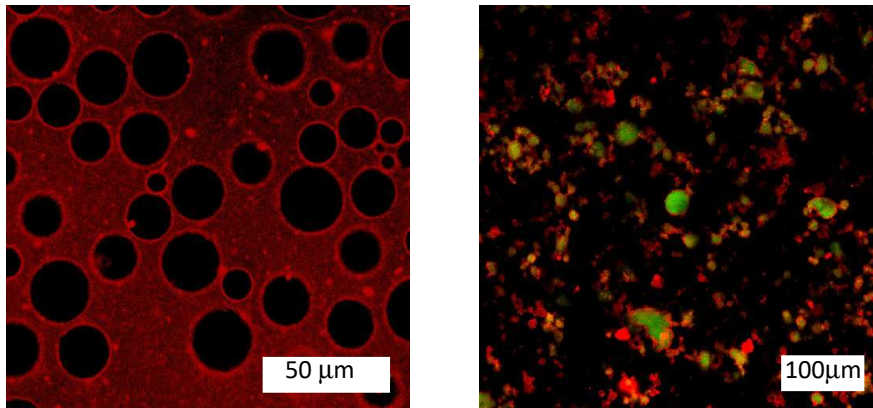


Fig. 12: CLSM images of emulsions made with 1 wt% of particles and $\phi_o = 70\%$ (a) and $\phi_o = 80\%$. One can see particles sitting at the interface as well as located within the continuous and dispersed phase.

That is why we have performed rheological tests on dispersions of particles in oil and aqueous phase to quantify their contribution to the bulk rheology of the emulsions. Figure 13 shows the elastic modulus for different concentrations of particles dispersed in both PDMS oils and water.

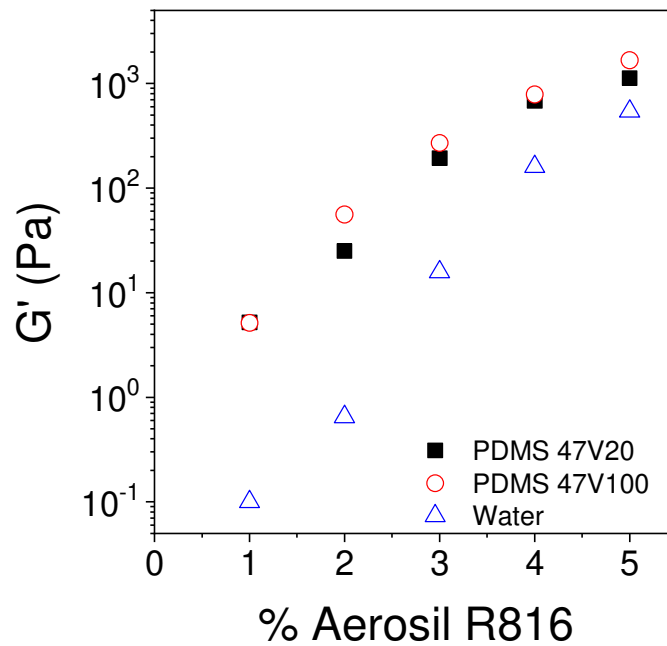


Fig. 13: Elastic modulus (G') of dispersions of particles in PDMS 47V20, PDMS 47V100 and water as a function of the concentration.

G' is higher than G'' (not shown) over the entire frequency range investigated implying a gel-like behaviour of the suspensions. As expected, the elastic modulus increases as the particle concentration increases, but no significant influence of the viscosity is observed between the oils. However, G' of aqueous dispersions are smaller than for the oil-based dispersions.

However, the magnitude of G' for the dispersions at low particle concentrations are not high enough to account for the elastic modulus of the emulsions. As evidenced from confocal images, most of the particles remain attached to the interfaces, as a result the effective concentration of particles remaining in oil and/or water phases is low. We can infer that the high elastic modulus of emulsions results from the synergic effect between the structuration of particles at the interfaces and the organisation of the latter in a connected network throughout the particles remaining dispersed in the

continuous phase. The increase in ϕ_d promotes interactions between the droplets, especially for high oil fractions close to the phase inversion point where the close packing configuration is observed.

Conclusion

By using relatively small concentrations of fumed silica particles, it is possible to emulsify PDMS oil with water. The emulsions present a long-term stability. By increasing the amount of oil, a catastrophic phase inversion occurs but less oil is needed to promote it with an oil displaying a higher viscosity. Confocal microscopy reveals no influence of the oil viscosity on the emulsion structure but smaller droplets are present for the less viscous PDMS oil. Increasing ϕ_o leads to an increase of the dispersed phase ϕ_d . The elastic modulus increases with ϕ_o as ϕ_d increases up to a maximum where the phase inversion takes place.

Rheological measurements emulsions reveal a gel-like behaviour for the emulsions with small influence of the oil viscosity in particular when ϕ_o is close to the phase inversion point. The results imply that the elastic modulus of emulsions originates mainly from the armoured interfaces due to the strong attachment of particles to them as well as from the connection between the interfaces and the droplets surrounding them like what has been reported by Simovic and Prestidge[15].

This phase inversion can be suitable for encapsulating hydrophilic active molecules. Initially they will be localised in the aqueous continuous phase but upon increasing the oil content, the phase inversion will take place and the hydrophilic active molecules will then be compartmentalized within water droplets embedded in a continuous oil phase. The resulting W/O emulsions can

then be spread easily due to its low viscosity and upon shearing the water droplets can be disrupted for delivering their actives. Furthermore, the use of PDMS as an oil allows to achieve several chemical modifications such as cross-linking reactions.

Acknowledgments

We acknowledge the Brazilian funding agencies CNPq (Conselho Nacional de Pesquisa). Frederico M. F. Barros has a doctoral scholarship from CNPq – Brasil (process n° 246416/2012-2).

References

- [1] B.P. Binks, *Modern Aspects of Emulsion Science*, Cambridge, 1998.
- [2] J.-L. Salager, L. Márquez, A.A. Peña, M. Rondón, F. Silva, E. Tyrode, *Current Phenomenological Know-How and Modeling of Emulsion Inversion*, *Industrial and Engineering Chemistry Research*, 39 (2000) 2665-2676.
- [3] R.K. Thakur, C. Villette, J.M. Aubry, G. Delaplace, *Dynamic emulsification and catastrophic phase inversion of lecithin-based emulsions*, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 315 (2008) 285-293.
- [4] B.P. Binks, S.O. Lumsdon, *Catastrophic Phase Inversion of Water-in-Oil Emulsions Stabilized by Hydrophobic Silica*, *Langmuir*, 16 (2000) 2539-2547.
- [5] K. Shinoda, H. Arai, *The effect of phase volume on the phase inversion temperature of emulsions stabilized with nonionic surfactants*, *Journal of Colloid and Interface Science*, 25 (1967) 429-431.
- [6] E. Tyrode, I. Mira, N. Zambrano, L. Márquez, M. Rondón-Gonzalez, J.-L. Salager, *Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 3. Conditions for Triggering the Dynamic Inversion and Application to Industrial Processes*, *Industrial and Engineering Chemistry Research*, 42 (2003) 4311-4318.
- [7] E. Dickinson, *Interpretation of emulsion phase inversion as a cusp catastrophe*, *Journal of Colloid and Interface Science*, 84 (1981) 284-287.
- [8] G.E.J. Vaessen, H.N. Stein, *The Applicability of Catastrophe Theory to Emulsion Phase Inversion*, *Journal of Colloid and Interface Science*, 176 (1995) 378-387.
- [9] D.H. Smith, K.H. Lim, *An experimental test of catastrophe and critical-scaling theories of emulsion inversion*, *Langmuir*, 6 (1990) 1071-1077.
- [10] D.H. Smith, K.H. Lim, *Morphology and inversion of dispersions of two fluids in systems of three and four thermodynamic dimensions*, *The Journal of Physical Chemistry*, 94 (1990) 3746-3752.
- [11] A. Gilchrist, K.N. Dyster, I.P.T. Moore, A.W. Nienow, K.J. Carpenter, *Delayed phase inversion in stirred liquid—liquid dispersions*, *Chemical Engineering Science*, 44 (1989) 2381-2384.
- [12] G.E.J. Vaessen, M. Visschers, H.N. Stein, *Predicting Catastrophic Phase Inversion on the Basis of Droplet Coalescence Kinetics*, *Langmuir*, 12 (1996) 875-882.

- [13] T. Sakai, Surfactant-free emulsions, *Current Opinion in Colloid & Interface Science*, 13 (2008) 228-235.
- [14] A. Saha, A. Nikova, P. Venkataraman, V.T. John, A. Bose, Oil emulsification using surface-tunable carbon black particles, *ACS Appl Mater Interfaces*, 5 (2013) 3094-3100.
- [15] S. Simovic, C.A. Prestidge, Nanoparticles of varying hydrophobicity at the emulsion droplet-water interface: adsorption and coalescence stability, *Langmuir*, 20 (2004) 8357-8365.
- [16] B.P. Binks, J.A. Rodrigues, Types of Phase Inversion of Silica Particle Stabilized Emulsions Containing Triglyceride Oil, *Langmuir*, 19 (2003) 4905-4912.
- [17] B.P. Binks, P.D.I. Fletcher, B.L. Holt, P. Beaussoubre, K. Wong, Phase inversion of particle-stabilised perfume oil–water emulsions: experiment and theory, *Physical Chemistry Chemical Physics*, 12 (2010) 11954-11966.
- [18] D. Zang, P.S. Clegg, Relationship between high internal-phase Pickering emulsions and catastrophic inversion, *Soft Matter*, 9 (2013) 7042-7048.
- [19] S. Kim, K. Kim, S.Q. Choi, Controllable one-step double emulsion formation via phase inversion, *Soft Matter*, 14 (2018) 1094-1099.
- [20] L. Sawiak, K. Bailes, D. Harbottle, P.S. Clegg, Mixing Time, Inversion and Multiple Emulsion Formation in a Limonene and Water Pickering Emulsion, *Frontiers in Chemistry*, 6 (2018).
- [21] Degussa AG Product information, 2005.
- [22] Y. Nonomura, N. Kobayashi, Phase inversion of the Pickering emulsions stabilized by plate-shaped clay particles, *J Colloid Interface Sci*, 330 (2009) 463-466.
- [23] A.N.I. Anisa, A.H. Nour, Catastrophic and transitional phase inversion of water-in-oil emulsion for heavy and light crude oil, 2010, pp. 3076-3076-3083.
- [24] F. Bouchama, G.A. van Aken, A.J.E. Autin, G.J.M. Koper, On the mechanism of catastrophic phase inversion in emulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 231 (2003) 11-17.
- [25] B.W. Brooks, H.N. Richmond, Phase inversion in non-ionic surfactant—oil—water systems—III. The effect of the oil-phase viscosity on catastrophic inversion and the relationship between the drop sizes present before and after catastrophic inversion, *Chemical Engineering Science*, 49 (1994) 1843-1853.
- [26] J. Galindo-Alvarez, V.r. Sadtler, L. Choplin, J.-L. Salager, Viscous Oil Emulsification by Catastrophic Phase Inversion: Influence of Oil Viscosity and Process Conditions, *Industrial and Engineering Chemistry Research*, 50 (2011) 5575-5583.
- [27] M. Rondón-González, L.F. Madariaga, V. Sadtler, L. Choplin, L. Márquez, J.-L. Salager, Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 6. Effect of the Phase Viscosity on the Inversion Produced by Continuous Stirring, *Industrial and Engineering Chemistry Research*, 46 (2007) 3595-3601.
- [28] V. Malhotra, R. Pal, S. Alhassan, Catastrophic Phase Inversion of Emulsions Stabilized by Amphiphilic Nanoparticles, *Journal of Nanofluids*, 7 (2018) 30-36.
- [29] S.B. Ogunlaja, R. Pal, K. Sarikhani, Effects of starch nanoparticles on phase inversion of Pickering emulsions, *The Canadian Journal of Chemical Engineering*, 96 (2018) 1089-1097.
- [30] N. Yan, Y. Maham, J.H. Masliyah, M.R. Gray, A.E. Mather, Measurement of Contact Angles for Fumed Silica Nanospheres Using Enthalpy of Immersion Data, *J Colloid Interface Sci*, 228 (2000) 1-6.
- [31] F. Macedo Fernandes Barros, C. Chassenieux, T. Nicolai, M.M. de Souza Lima, L. Benyahia, Effect of the hydrophobicity of fumed silica particles and the nature of oil on the structure and rheological behavior of Pickering emulsions, *Journal of Dispersion Science and Technology*, (2018) 1-10.

- [32] M.J. Hey, J.G. Kingston, Maximum stability of a single spherical particle attached to an emulsion drop, *J Colloid Interface Sci*, 298 (2006) 497-499.
- [33] K. Golemanov, S. Tcholakova, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, Latex-particle-stabilized emulsions of anti-bancroft type, *Langmuir*, 22 (2006) 4968-4977.
- [34] C.O. Fournier, L. Fradette, P.A. Tanguy, Effect of dispersed phase viscosity on solid-stabilized emulsions, *Chemical Engineering Research and Design*, 87 (2009) 499-506.
- [35] E. Tsabet, L. Fradette, Effect of the properties of oil, particles, and water on the production of Pickering emulsions, *Chemical Engineering Research and Design*, 97 9-17.
- [36] S. Arditty, V. Schmitt, J. Giermanska-Kahn, F. Leal-Calderon, Materials based on solid-stabilized emulsions, *Journal of Colloid and Interface Science*, 275 (2004) 659-664.
- [37] S. Arditty, V. Schmitt, F. Lequeux, F. Leal-Calderon, Interfacial properties in solid-stabilized emulsions, *The European Physical Journal B - Condensed Matter and Complex Systems*, 44 (2005) 381-393.
- [38] A.E. Ismail, G.S. Grest, D.R. Heine, M.J. Stevens, M. Tsige, Interfacial Structure and Dynamics of Siloxane Systems: PDMS-Vapor and PDMS-Water, *Macromolecules*, 42 (2009) 3186-3194.

Graphical Abstract

Title : Structure and rheology during catastrophic phase inversion of Pickering emulsions stabilized with fumed silica particles

Authors : Frederico Macedo Fernandes Barros^a, Christophe Chassenieux^a, Marli Miriam de Souza Lima^b, Lazhar Benyahia^{a*}

