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Sandra Domenek, Nicolas Delpouve, Samira Fernandes Nassar, Alain Guinault, Cyrille Sollogoub. Multiscale analysis of the impact of the polymer morphology on the gas barrier properties of semi-crystalline polylactide. 46. Colloque National du Groupe Français des Polymères, GFP2017, Nov 2017, Paris, France. 2017. hal-01739305

HAL Id: hal-01739305

<https://hal.science/hal-01739305v1>

Submitted on 5 Jan 2024

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MULTI-SCALE ANALYSIS OF THE IMPACT OF THE POLYMER MORPHOLOGY ON GAS BARRIER PROPERTIES OF SEMI-CRYSTALLINE POLYLACTIDE

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Introduction

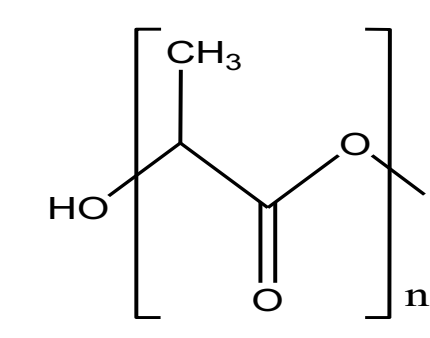
The optimization of the gas barrier properties of polylactide (PLA) is a pending issue for a number of applications. The crystallization of PLA is still the most relevant method from an industrial point of view. The objective of this work was the investigation of the impact of the crystalline morphology at the scales of the lamella and the spherulite, and the impact of the amorphous phase dynamics of PLA on its oxygen barrier properties. Therefore, sample films with controlled morphology were produced by a thermal annealing treatment. The sample size was designed to allow the multi-scale characterization of morphology and oxygen permeability on the same material. The results showed that the crystalline morphology and the mobile amorphous phase dynamics had negligible impact on the oxygen diffusion coefficient. It was however substantially increased by the presence of a rigid amorphous fraction (RAF) in the amorphous phase, which provides an accelerated pathway for diffusion. As a conclusion, for reaching optimal barrier properties, semicrystalline PLA should be pre-nucleated and quickly crystallized from the glass in α -form in the aim to reach a high crystallinity degree and decoupling of amorphous and crystalline phase.

Objective

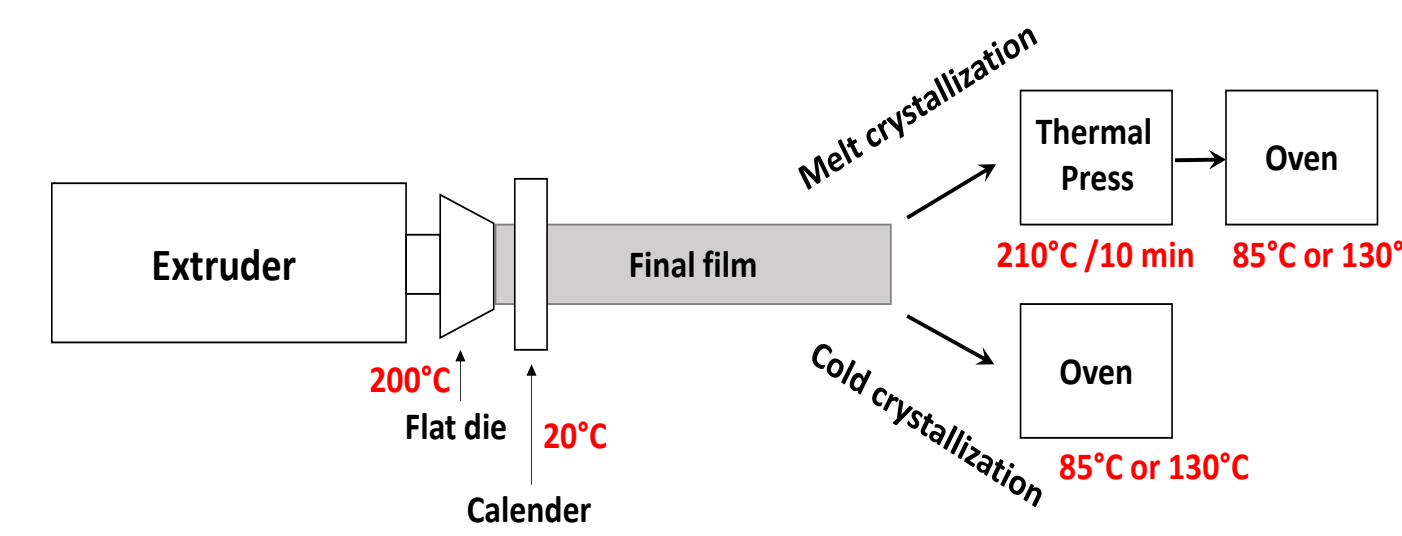
Investigation of the effects of the molecular mobility and dynamic heterogeneity in the amorphous phase of PLA on barrier properties

Material and Methods

PLA NatureWorks 2003D



Sample preparation



Analysis of crystallinity and molecular mobility

Temperature Modulated Differential Scanning Calorimetry (TM-DSC)

DSC Q100 (TA Instruments)

modulated mode for measurement of crystallinity and glass transition (heating rate 2 °C/min, amplitude 0.318 °C, period 60 s)

Analysis of crystalline morphology

WAXS and SAXS analysis was performed on the SWING beamline of Soleil (St. Aubin, France).

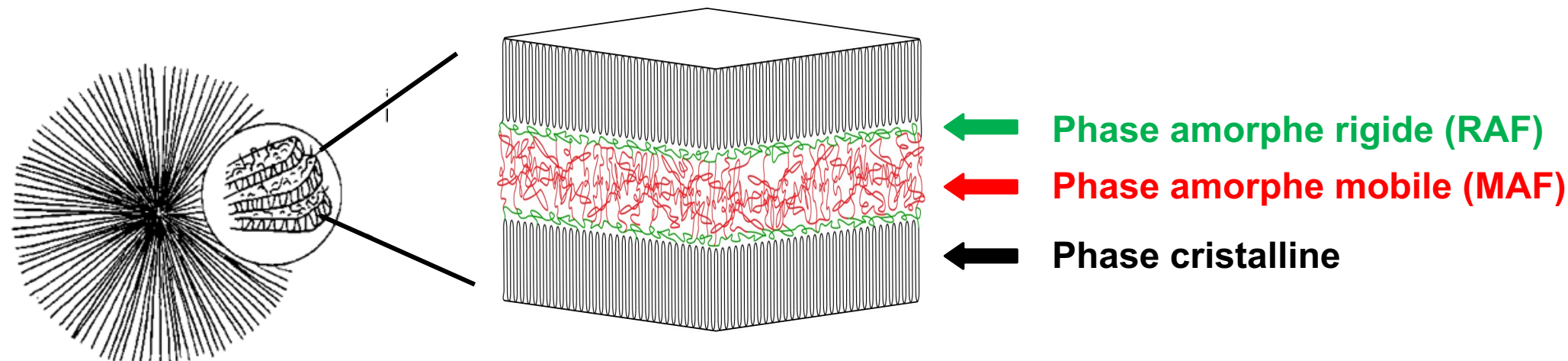
Analysis of gas permeability

Systec 8001 O₂ permeability analyser

23 °C, 0% RH

Molecular mobility of amorphous and annealed PLA

Three phase model - Rigid amorphous fraction (RAF)



$$X_c + X_{MAF} + X_{RAF} = 100\%$$

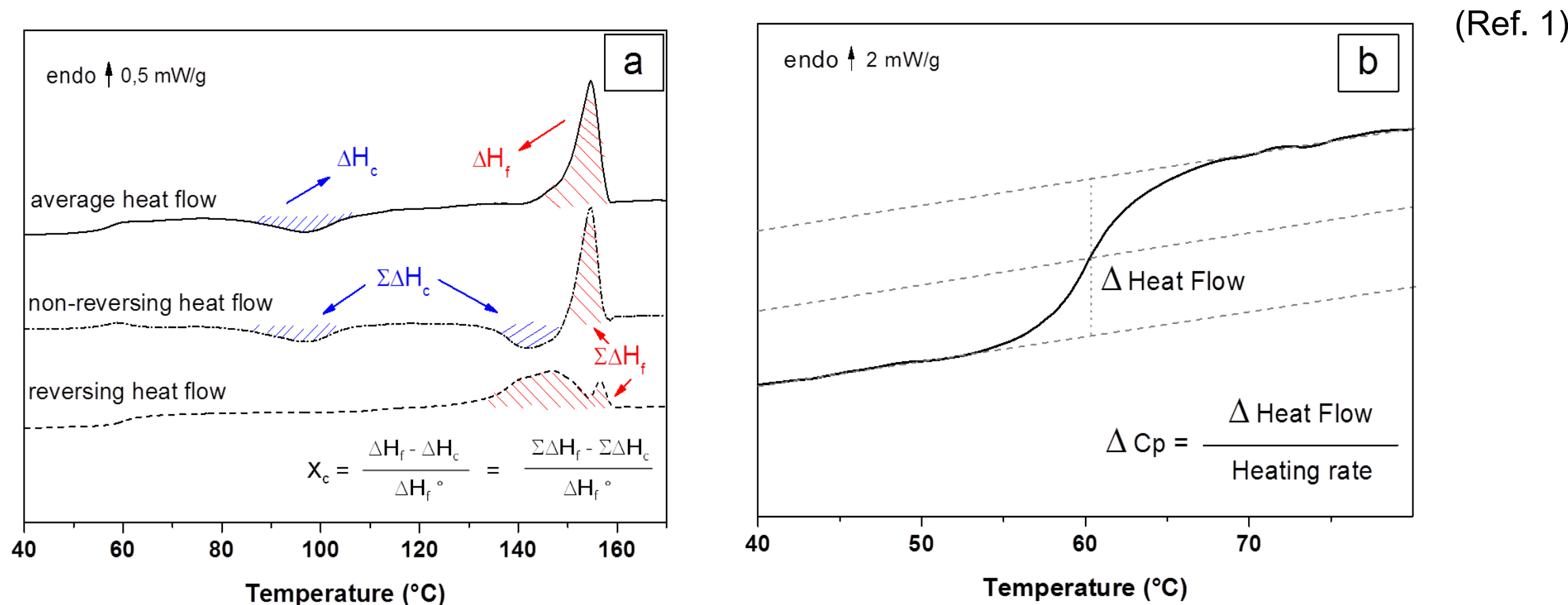
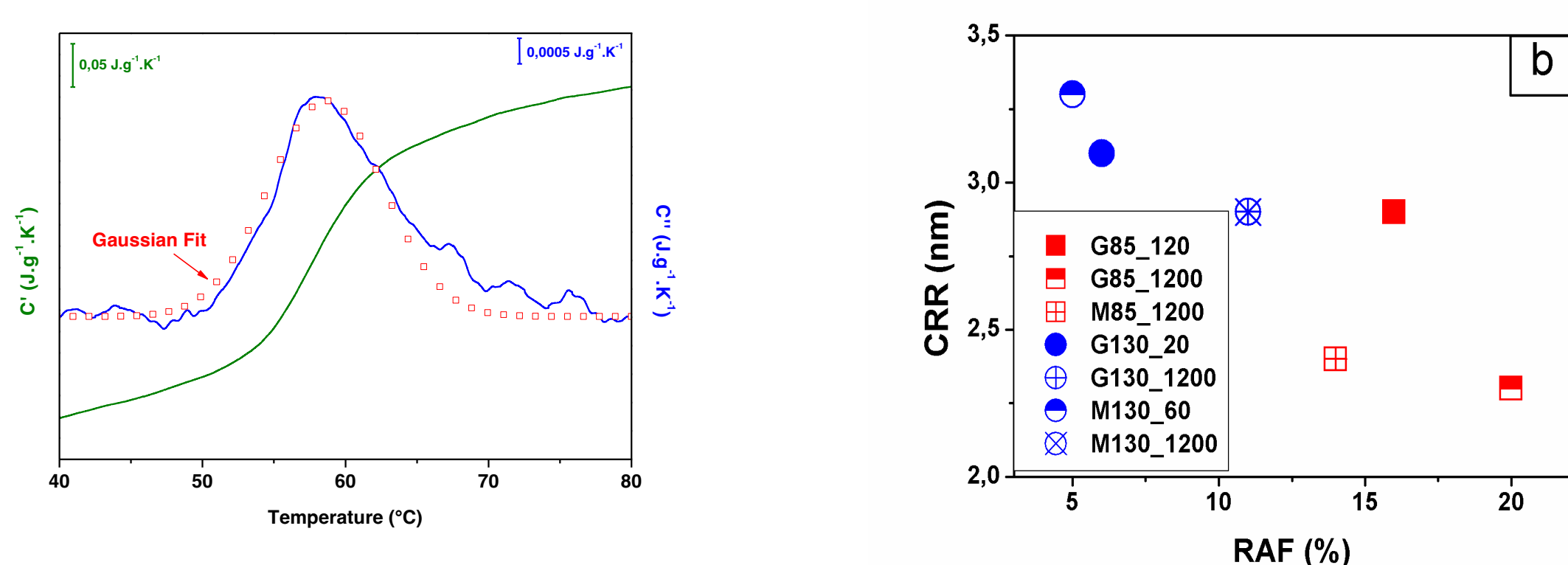


Figure shows the determination of the RAF by TM-DSC on the sample G85_60_17.

	T _g (°C)	χ(%)	MAF(%)	RAF(%)
amorphous	58,0	-	100	-
G85_60_17	57.2	27	17	75
G85_1200_39	56.1	39	40	21
G130_20_34	56.1	34	60	6
G130_1200_37	53.5	37	50	13
M85_60_24	56.9	24	73	3
M85_1200_47	54.8	47	38	15
M130_60_37	56.3	37	58	5
M130_1200_41	53.2	41	46	13

RAF develops at low crystallization temperature or long times

Size of Cooperative Rearranging Regions



$$\xi^3 \tau_c = V_a = \Delta \left(\frac{1}{C_p} \right) \frac{k_b T_g^2}{\rho (\delta T)^2} \quad \Delta(1/C_p) = (1/C_p)_{verree} - (1/C_p)_{liquide} = (1/C_v) - (1/C_l) \quad (\text{Ref. 2})$$

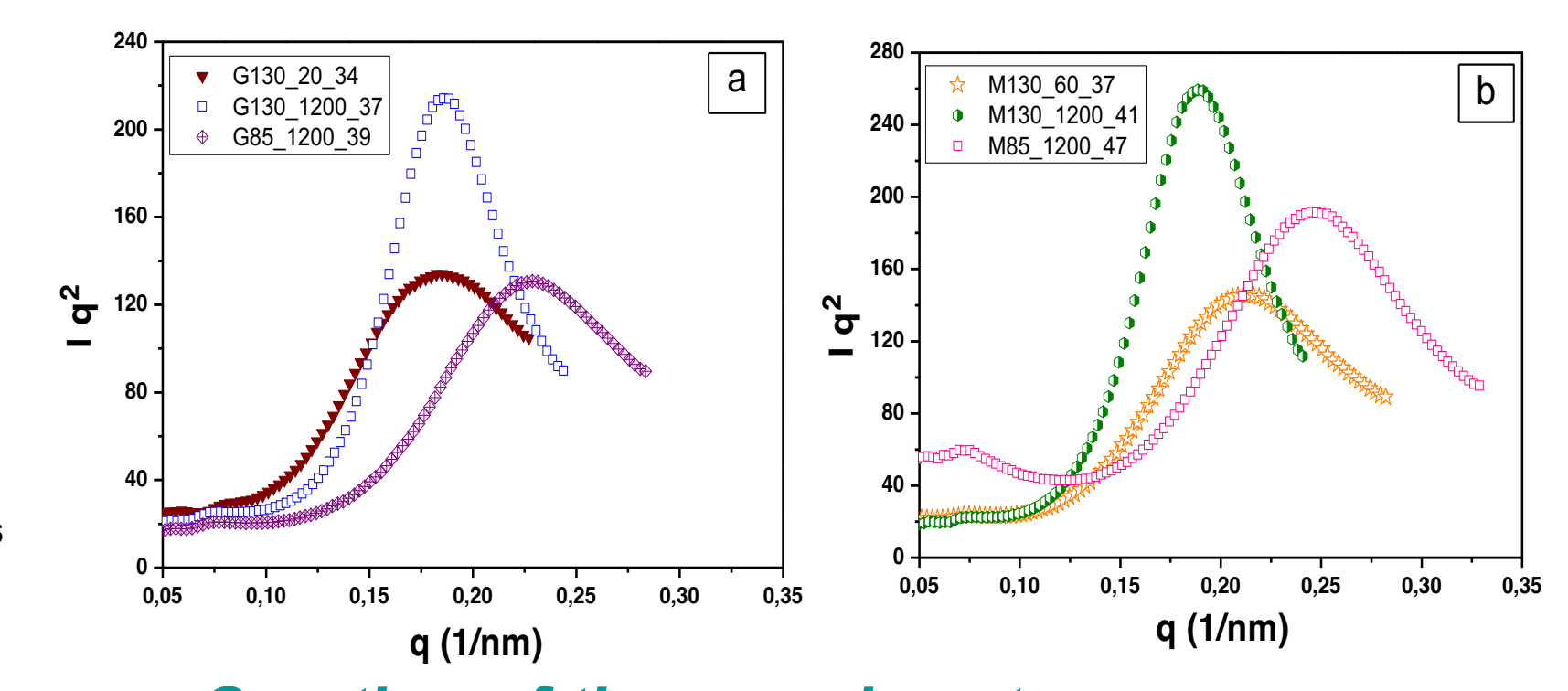
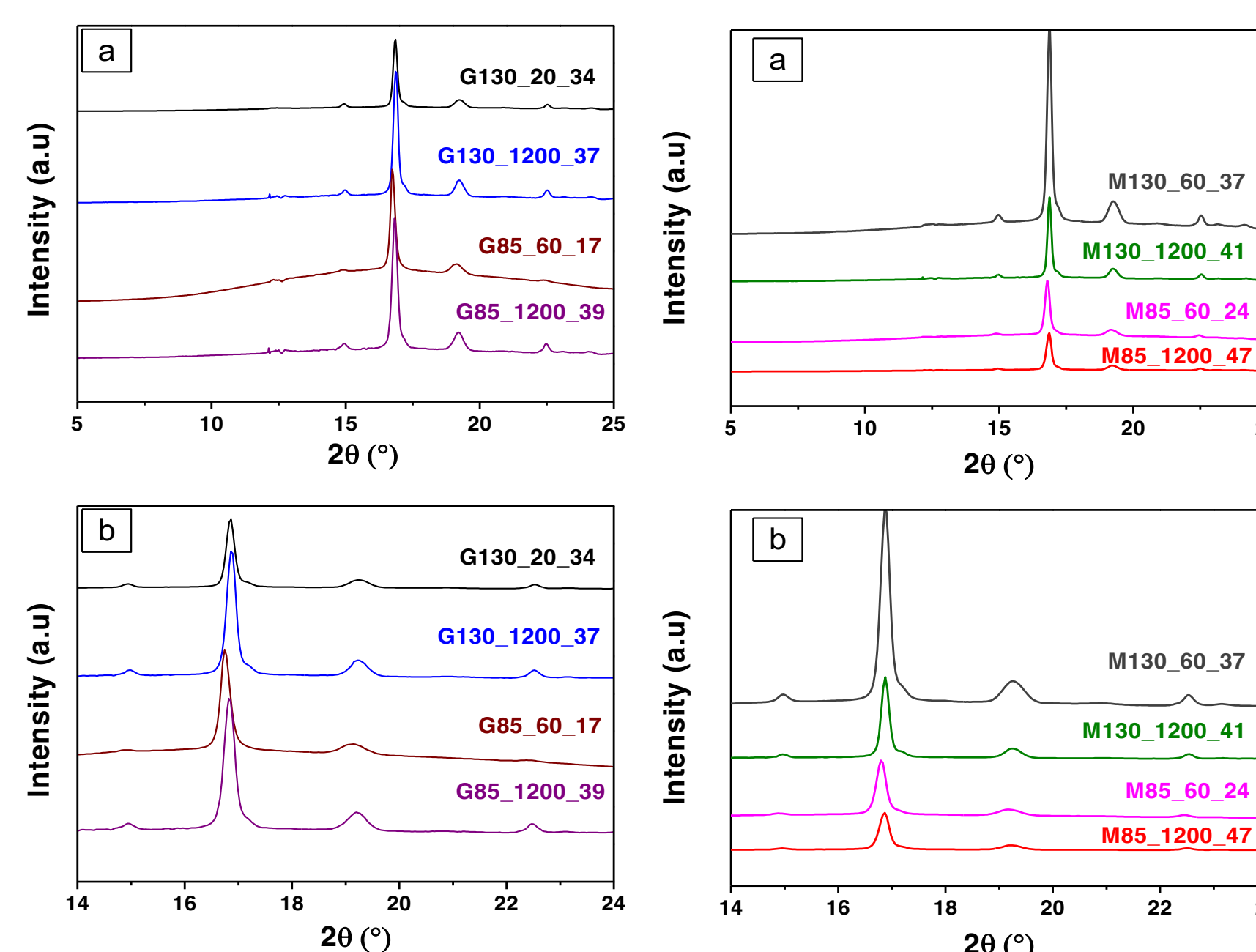
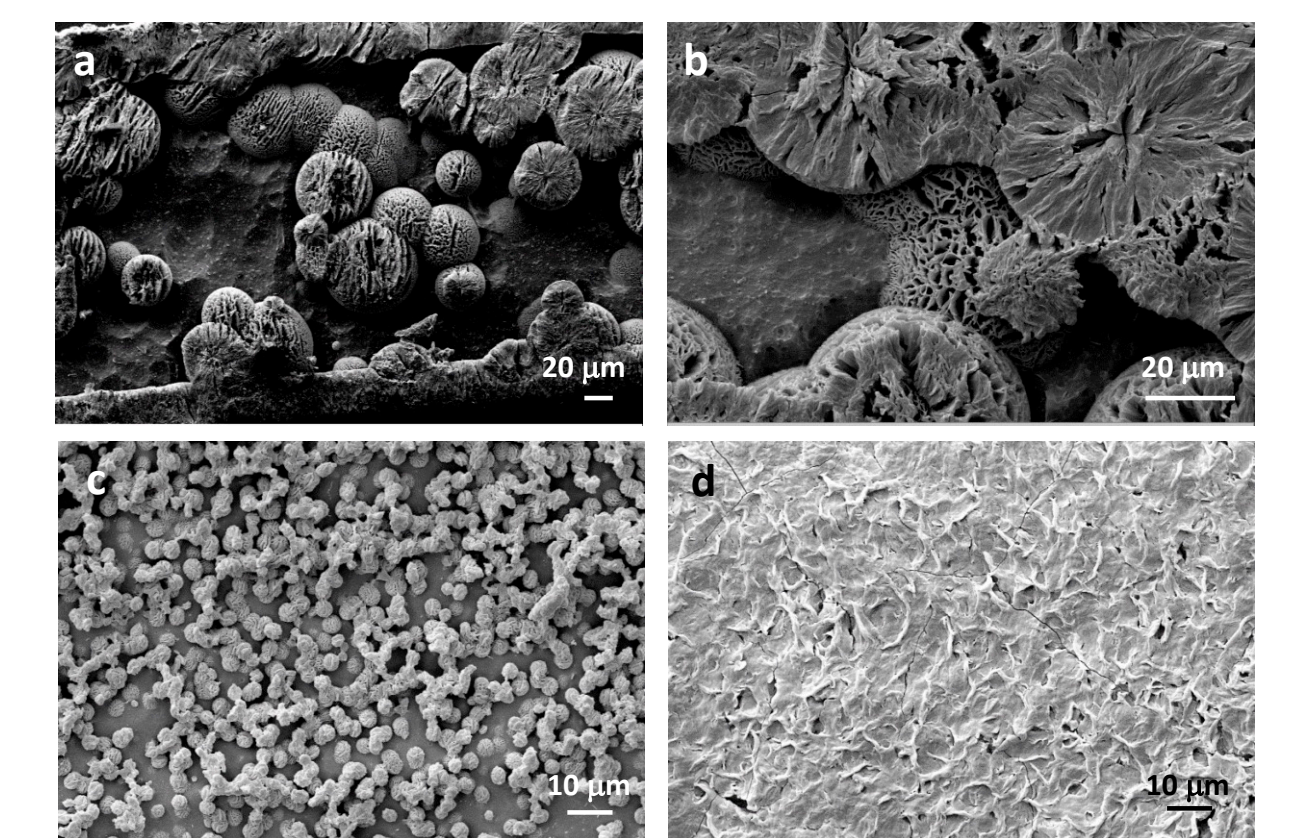
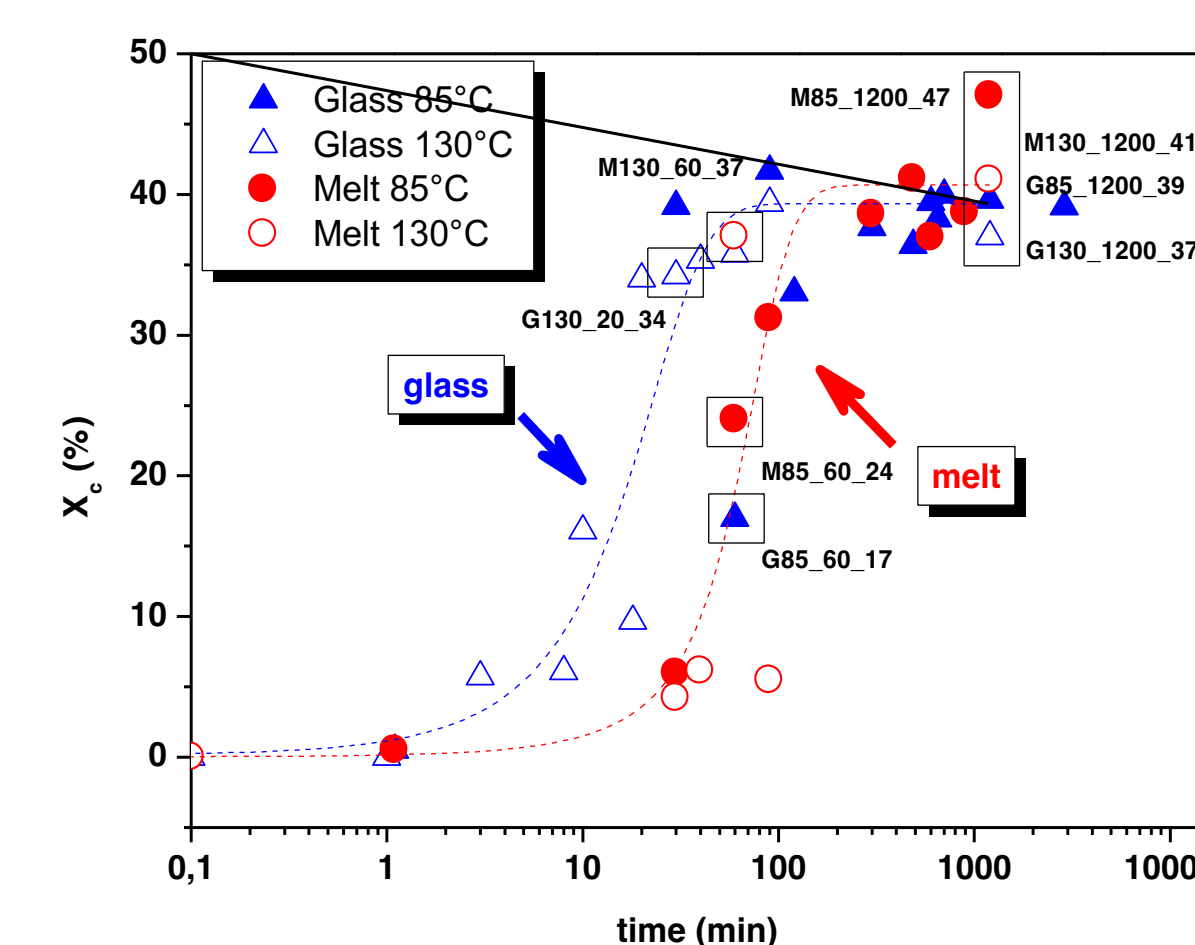
Decrease of CRR due to confinement caused by increasing crystallinity and RAF

References and Acknowledgement

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- E. Donth, J. Non-Cryst Solids 1982, 53, 325
- S. Fernandes-Nassar, Guinault, A., Delpouve, N., Divry, V., Ducruet, V., Sollogoub, C., & Domenek, S. Polymer 2017, 108, 163-172

The authors acknowledge the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES for the doctorate grant n° 9712-13-5 of Samira Fernandes Nassar.

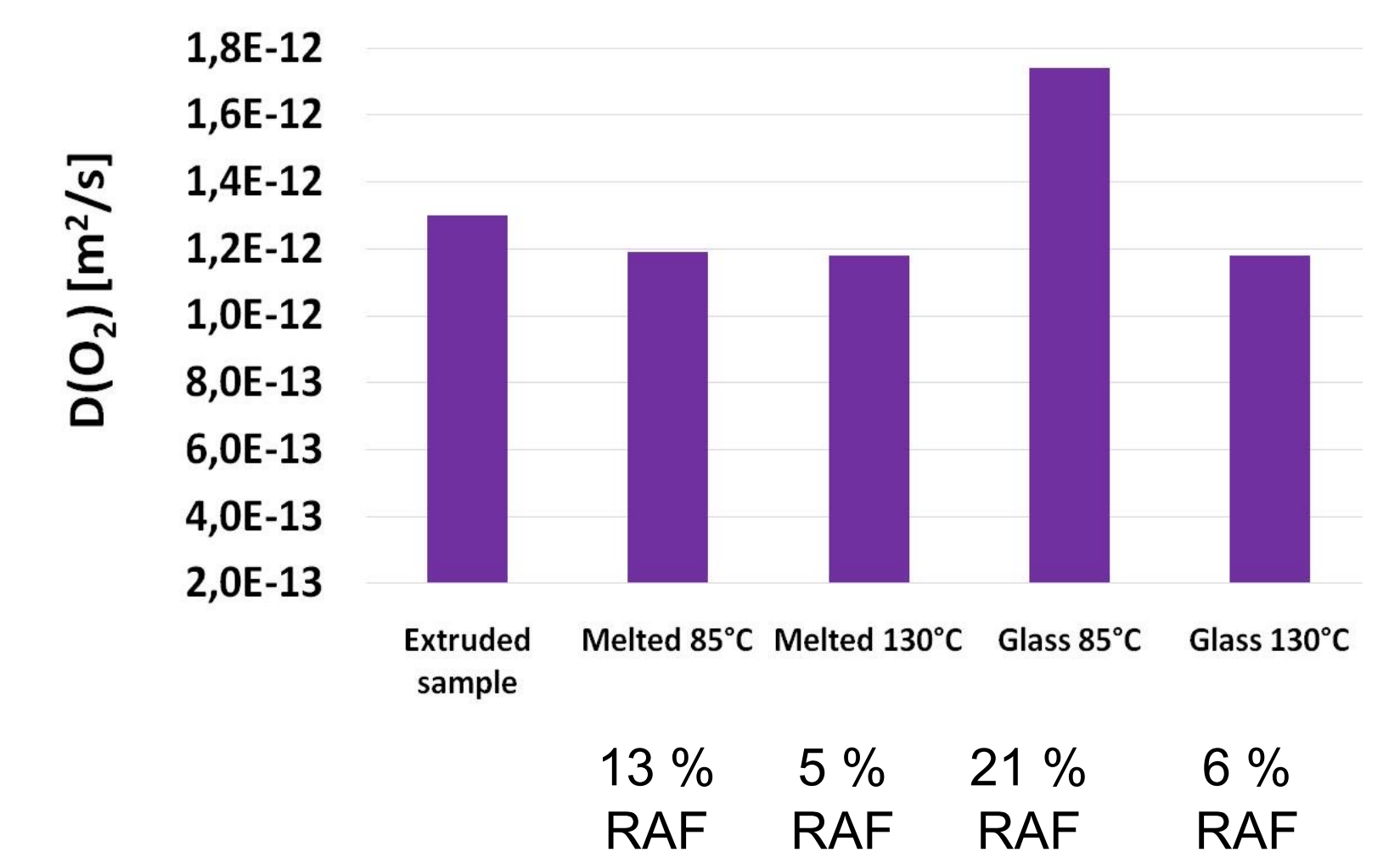
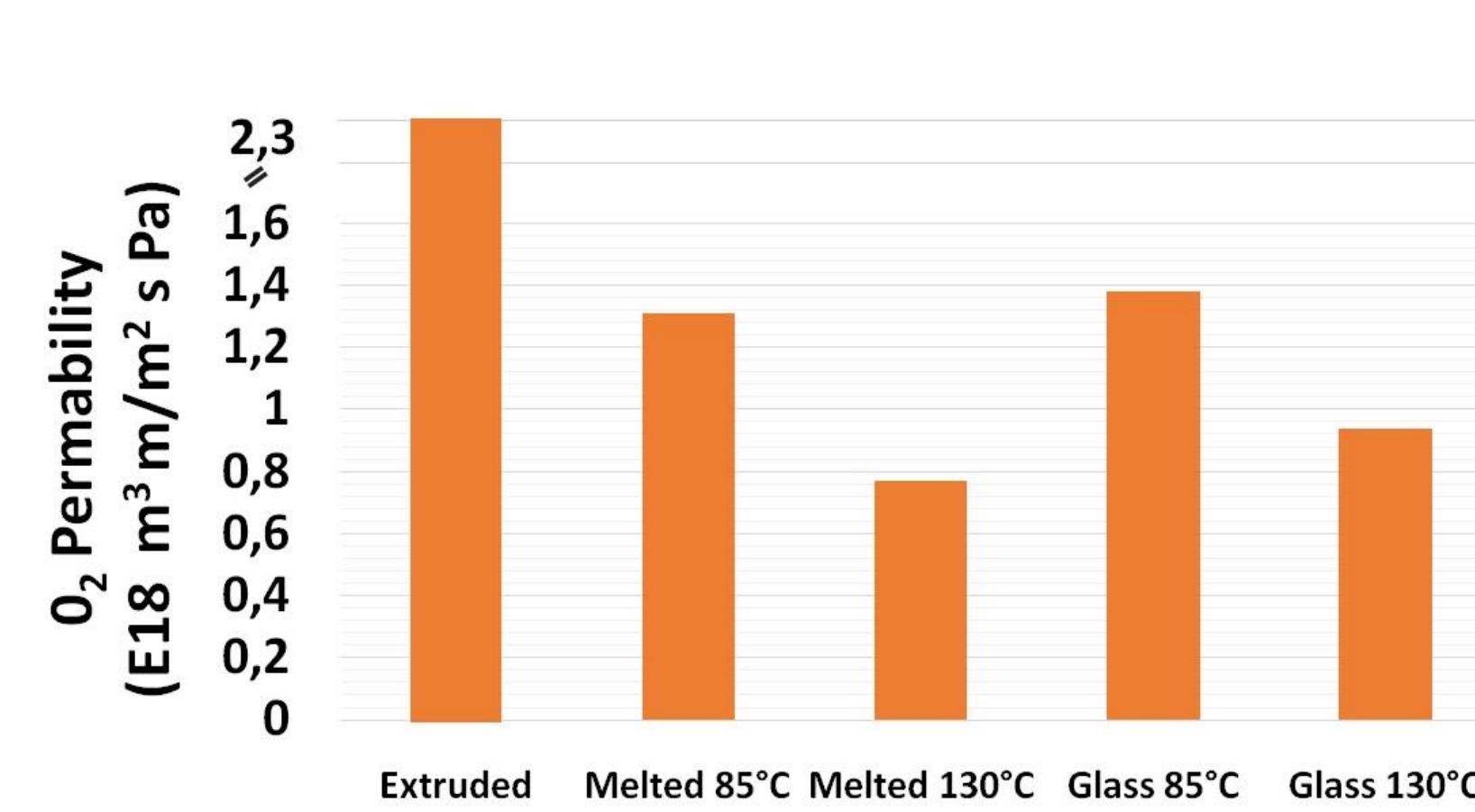
Crystalline structure of PLA



Creation of the sample set

- Use of samples with complete space filling
- For each crystallization temperature samples with big and small spherulites
- Lamella thickness correlated to crystallization temperature
- Crystalline polymorph of PLA → α -form

Oxygen transport properties



Conclusions

RAF rules barrier properties

	T (crystallisation) = 85 °C	T (crystallisation) = 130 °C
Glass	Amorphous phase dynamics	High coupling between amorphous and crystalline phase (RAF)
	Barrier properties	Low - 2.2 [SI]
Melt	Amorphous phase dynamics	Low coupling between amorphous and crystalline phase
	Barrier properties	High - 0,6 [SI]

CONTACT

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