Processing effects on the nano-crystalline structure and mechanical properties of trans-fat free fats based from fully hydrogenated stock

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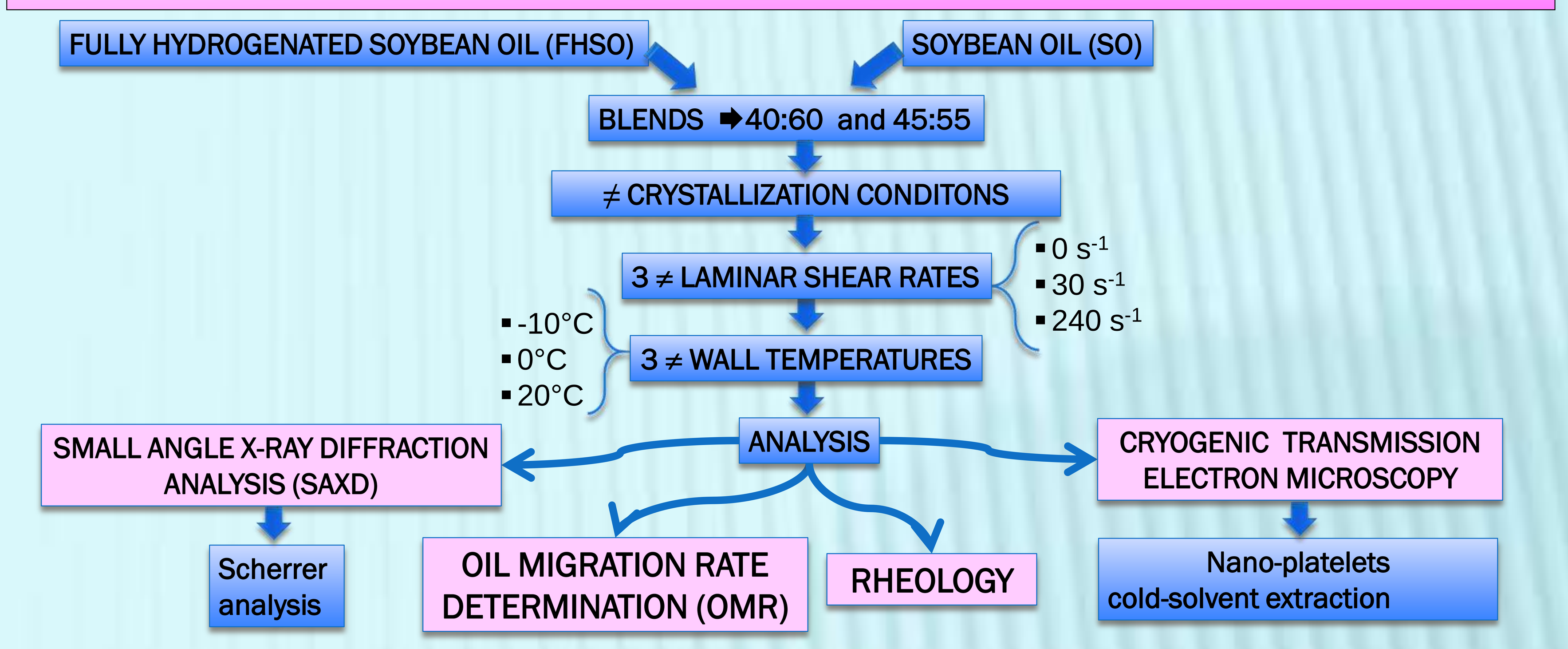
Introduction

Fat is a special class of plastic polycrystalline aliphatic soft matter. The crystallization behaviour of edible fats is greatly affected by external shear and temperature fields which can be manipulated through unit operations to tailor crystalline structure and physicochemical characteristics. The capacity of a fat crystal network to trap oil is an important material property that directly influences oil migration and can led to important changes in the structure and functionality of the product. The capability of fat crystals to bind and retain liquid oil within their crystal network is dependent on the composition, thermal properties, interactions and wetting properties of the fat crystals. However, particle size and interaction between them may act as important variables that affect oil migration in fat systems. Many studies have studied the effect of external fields on the structure and of fat crystal networks; however there is a lack of systematic studies on the effects of crystallization conditions on the nanostructure of plastic fats and its relationship with oil migration.

Objective

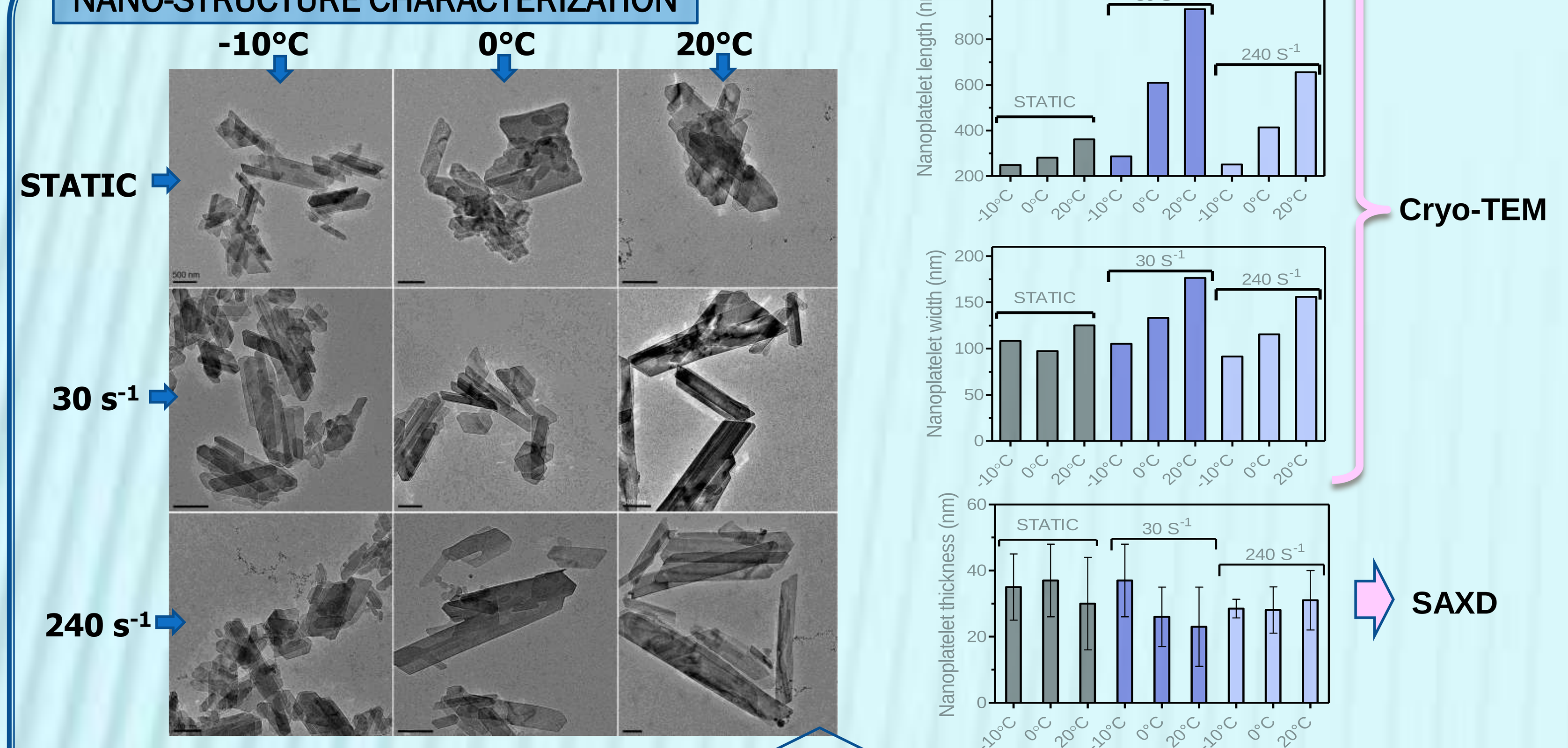
The purpose of this work was to determine the effects of laminar shear crystallization on the nano- and mesoscale structure and on the oil binding capacity of blends of fully hydrogenated soybean oil and soybean oil.

Materials and Methods



Results

NANO-STRUCTURE CHARACTERIZATION

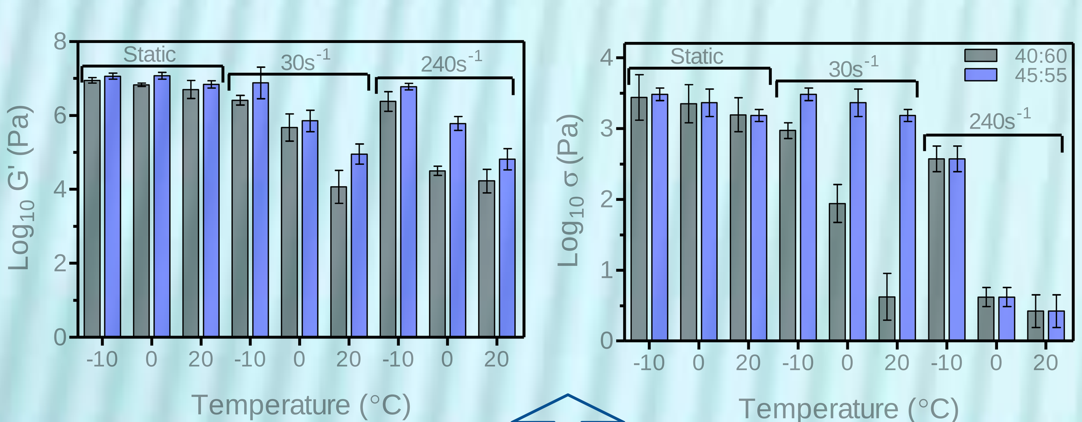


Cryo-TEM images of the nano-crystals formed under different shear/temperature conditions (left). Nano-platelet lengths, widths and thicknesses obtained by analysis of the Cyo-TEM images and Scherrer analysis of the SAXD data (right)

Aspect ratio L/W	
	$0\ s^{-1}$ = 2-3
	$30\ s^{-1}$ = 3-6
	$240 s^{-1}$ = 3-4

- Shearing caused a significant increase in nano-platelet size, in particular at 0 and 20°C.
- An **intermediate shear rate** increases sizes up to 3 times compared to those observed under static conditions.
- At **high shear rates** the sizes were twice of those in blends statically crystallized.
- Laminar shear induced the longitudinal growth of nano-platelets.

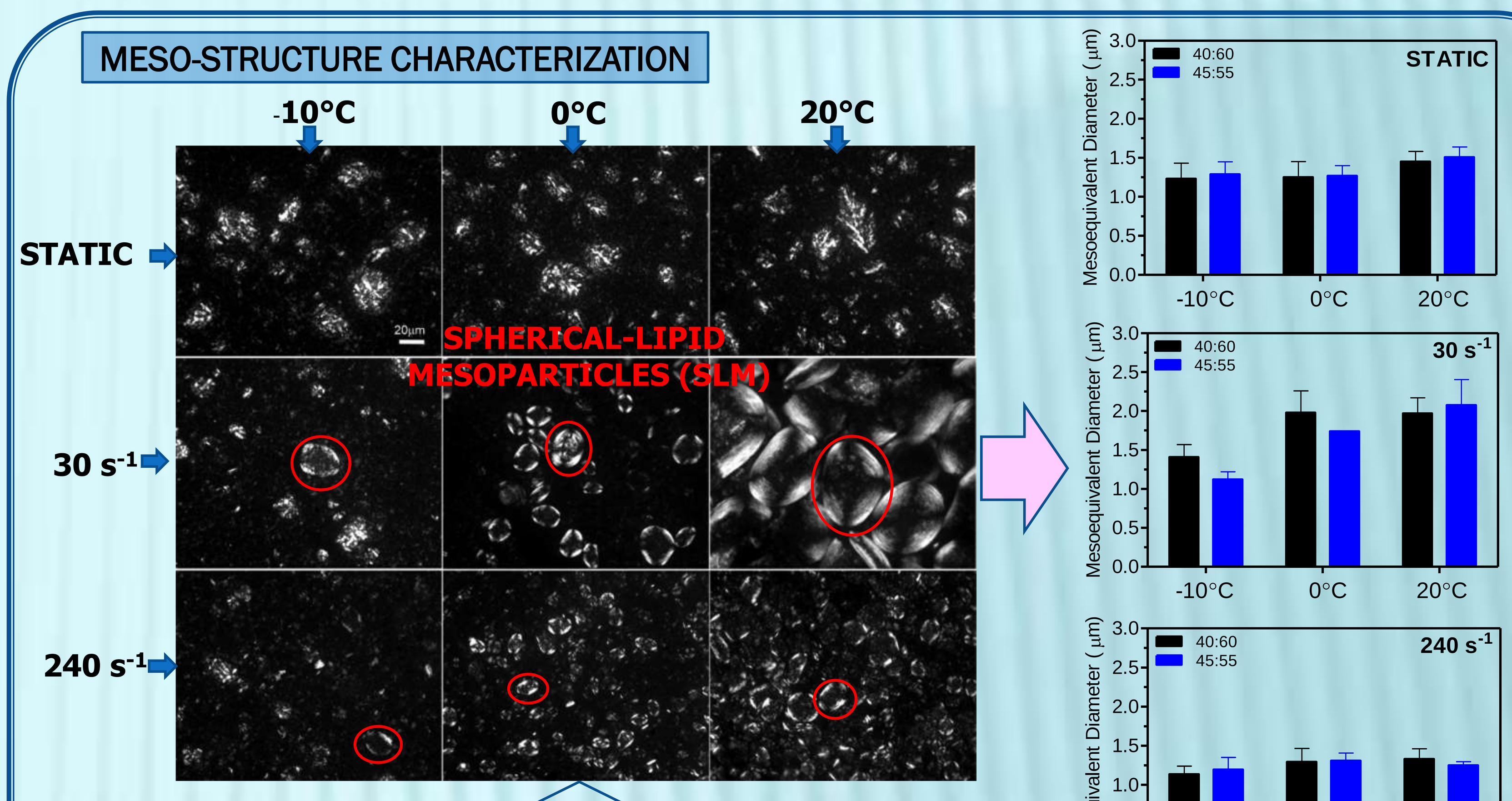
RHEOLOGICAL PROPERTIES



Rheological parameters obtained from blends crystallized at different shear/ wall temperature conditions

- Laminar shear induced a significant decrease in storage moduli (G') and yield stress (σ) values, in particular at higher wall temperatures.
- There are no significant differences between G' of blends crystalized at intermediate and high shear rates. However, σ values are significantly lower in blends crystallized at high shear rates.
- Yield stress is an important macroscopic property since it is strongly correlated to the hardness and spreadability of the material. σ is more sensitive to changes in concentration and processing conditions.

MESO-STRUCTURE CHARACTERIZATION

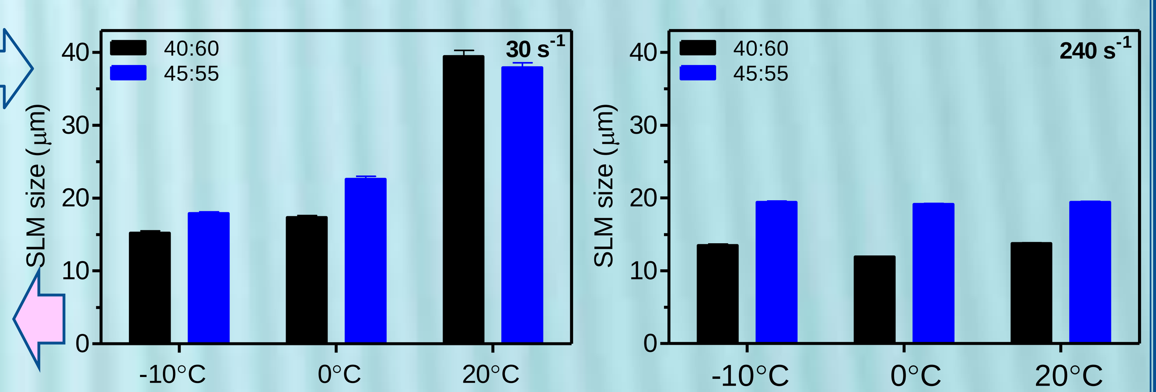


PLM images of 45:55 FHSO:SO mixtures crystallized in static and under different shear/wall temperature conditions

Equivalent diameters of the meso-structural elements obtained by PLM

- In the case of static crystallization a similar meso-structure was observed at any wall temperature used.
- Shearing greatly affected the structure at the mesoscale: laminar shear processing promoted the growth of **"Spherical-lipid particles".** Shear can break the crystals and led to an internal rearrangement of the fragments.
- Shear rate and wall temperature play a role on the sizes of these particles and it evident in these images that an intermediate shear rate generate the largest SLM.
- **Static crystallization:** no significant differences in meso-crystal size of blends with different supersaturation and crystallized at different wall temperatures.
- **$30 s^{-1}$:** Larger meso-crystal size, in particular at higher temperatures.
- **$240 s^{-1}$:** The smallest meso-crystal size compared to those observed in blends crystallized statically and under intermediate shear rates. High shear rates can fracture crystals.

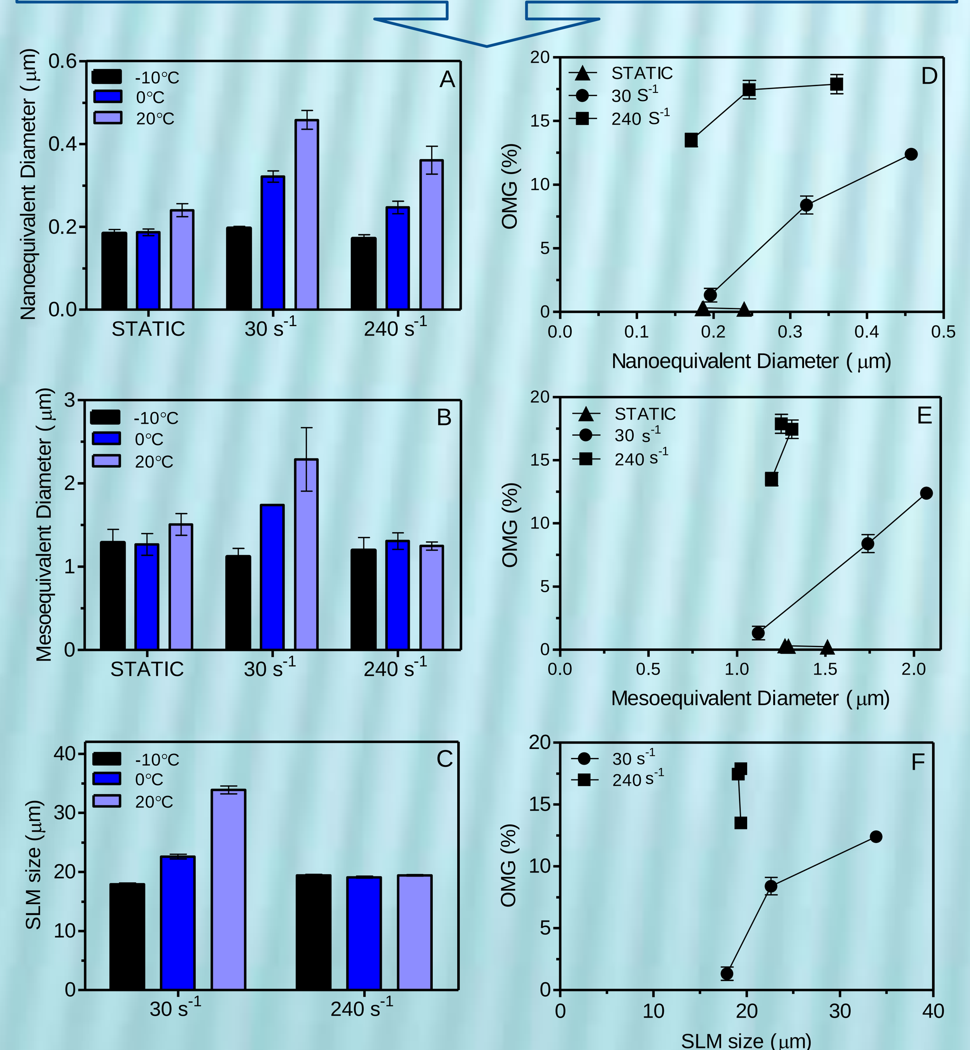
Mean diameters of SLMs observed by PLM in sheared blends



- SLMs are larger in blends crystallized at intermediate shear rates. In these blends SLMs are larger at higher wall temp.
- At high shear rates, wall temp. had not effect on SLMs sizes.
- Probably, there is a critical shear rate above which the development of SLM is no longer promoted.
- There are larger SLMs in blends with higher hardstock proportion, since the growth may be favoured by higher concentrations.

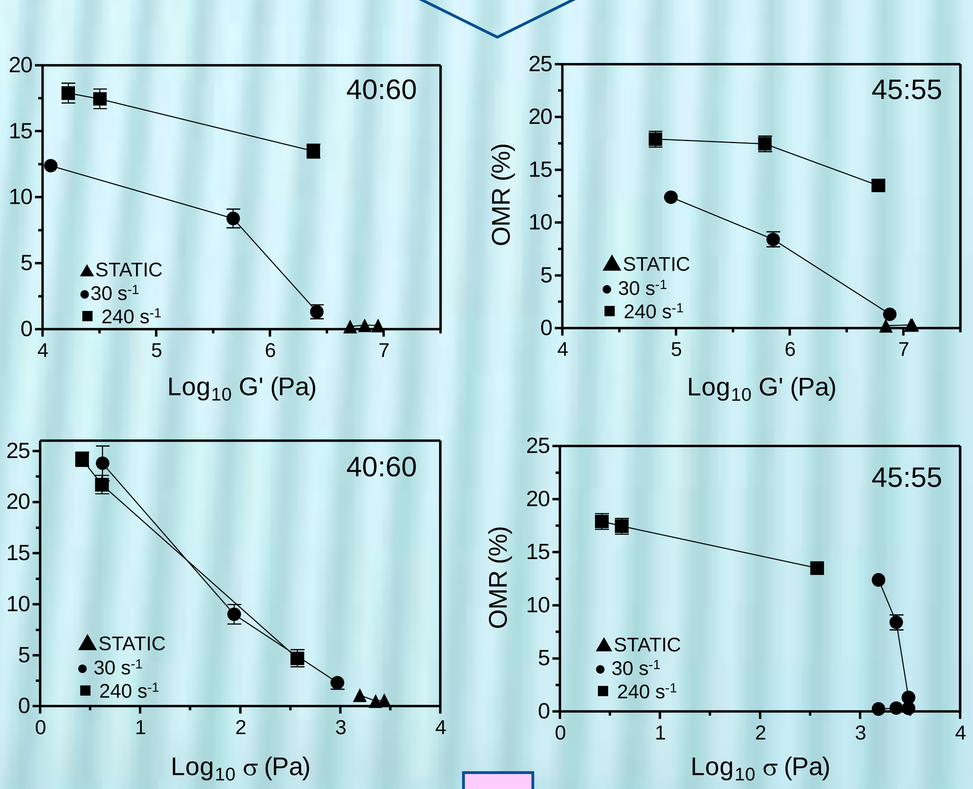
RELATIONSHIP WITH OIL MIGRATION RATE (OMR)

Changes in particle diamaters at the nano-(A), and micro-scale (B and C) induced by different processing conditions (left). Relation between oil migration rate values (OMR) and particle diameters [nano- (D); meso (E) and SPLM particles (F)] observed after crystallization at different combinations laminar shear/temperature (rigth).



- The higher the laminar shear rate used during crystallization, the greater the oil loss (OMR) in the blends.
- There is a good correlation between the increase in crystal size and the raise in OMR since permeability is dependent on crystal size.
- Similar trends were observed at both structural levels, the nano- and the meso-scale.

Relation between oil migration rate values (OMR) and rheological parameters fro blends with 40% (left) and 45% (right) of FHSO crystalized after crystallization at different combinations laminar shear/temperature.



- There is an inverse relationship of G' and σ with OMR which is indicative of the loss of structural integrity with laminar shear processing.
- In blends with 40% of hardstock high values of OMR (and therefore the lost of the structural integrity of the sample) are observed at both 30 and $240 s^{-1}$ shear rates, meanwhile in blends with 45% of hardstock the marked increase in OMR is shown only at $240 s^{-1}$.

Discussion and Conclusions

➢ Shearing greatly affected fat crystalline structure at the nano- and meso-scale.

1-Laminar shear processing promoted the growth of "spherical-lipid mesoparticles".

2-Laminar shear induced an important asymmetric growth of the nanoplatelets.

➢ Crystallization under laminar shear led to the formation of a weak network with low oil-binding capacity.

➢ Our results suggest that the observed increase in oil leakage from laminar sheared samples is a combination of both significant changes induced in the sample structure: the generation of solid spherical crystalline particles (rather than porous spherulites) with a resulting exclusion from their structure; and the increase in the size of the particles leading to a greater permeability of the system.

➢ Shear-temperature combinations could be successfully used to engineer oil binding capacity and structure fats at the nano- and meso-scale.

REFERENCES:

- Dibildox-Alvarado, E. ; Neves Rodrigues, J.; Gioielli, L.A.; Toro-Vazquez, J.F. and Marangoni, A.G. *Cryst Growth Des.* **2004**, 4, 731-736.
- Marty S. and Marangoni AG. *Cryst Growth Des.* **2009**, 9, 4415-4423.
- Mazzanti, G.; Guthrie, S.E.; Sirota, E.B.; Marangoni, A.G. and Idziak, S.H.J. *Cryst Growth Des.* **2003**, 3, 721–725.
- Mazzanti, G.; Guthrie, S. E.;. Sirota, E. B; Marangoni, A. G.; Idziak, S. H. J. *Cryst Growth Des.* **2004**, 4, 409–411.
- Ribeiro, A. P. B.; Grimaldi, R.; Gioielli, L. A.; Oliveira dos Santos, A.; Cardoso, L. P.; Goncalves, L. A. G. *Food Biophysics.* **2009**, 4, 106-118.
- West, A. R. In Solid State Chemistry and Its Applications; John Wiley & Sons, Chichester: West Sussex, England. **1984**; pp 174.