Role of crystallinity on the thermal and viscous behaviour of polyethylene glycol-in-silicone oil (o/o) phase change emulsions

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Abstract

Stable polyethylene glycol-in-silicone oil phase change emulsions were successfully prepared with a selected silicone surfactant. These oil-in-oil (o/o) emulsions have been scarcely examined up, despite the highly remarkable properties of both phases for energy recovery applications and cosmetic/pharmaceutical compositions. The objective of the present work was to study the effect of composition (surfactant and disperse phase concentrations) and the post-processing conditions (further agitation at the processing temperature for 24 h) on the final features of the emulsion. For this purpose, optical morphology, thermo-physical and the rheological behaviour of the emulsions and binary blends of their compounds were measured and analysed. Special attention has been paid to structural changes and crystallinity modifications of the emulsion disperse phase. The observed miscibility of the silicone surfactant and silicone chains with the disperse phase reduces its crystallinity degree and modifies in the crystallization mechanism of the polyethylene glycol, from heterogeneous to homogeneous nucleation. Interestingly, the change in the disperse phase crystallinity remarkably modifies final thermal and rheological properties of the emulsion.

Keywords: non-aqueous emulsion, phase change material (PCM), crystallisation, viscosity

1. Introduction

Anhydrous emulsions, also known as non-aqueous or oil-in-oil emulsions, have been rarely studied so that there is a lack of information about scientific background information and the technological developments on the subject [1–3]. 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. Since the first articles in the sixties [4–6] where olive oil-in-glycerine systems were studied, most studies on this topic have focused on the research of cosmetic or pharmaceutical preparations. On the one hand, systems comprising biocompatible oils such as polyethylene glycols, paraffins or glycerine esters stabilised with block copolymers have been prepared [7,8] being of great interest in these industries as bases for topical applications. Other castor oil/silicone oil emulsions are very interesting for their application in the pharmaceutical industry where they can act as solvents for drugs or as suspension vehicles [9–11]. In addition, emulsions prepared with soybean oil or sunflower oil dispersed in propylene glycol have been used in nutritional preparations with edible and non-toxic ingredients [12–14]. Besides, non-aqueous emulsions can replace conventional aqueous emulsions, with an undesirable presence of water, in water-sensitive reactions that do not allow the use of some catalysts or radical monomers. Likewise, other applications may demand temperatures higher than the boiling point of water, being non-aqueous emulsions, for example, an interesting alternative to obtain nanostructured polymeric materials [15–17]. However, the lack of basic scientific knowledge on these dispersions (formulation, physical-chemical properties or stabilization and destabilization mechanisms) greatly limits its extensive use in industrial processes, as well as the design of new products.

In this context, the present study aims to extend the field of o/o emulsions through the novel polyethylene glycol-in-silicone oil emulsions, only barely examined up despite the highly remarkable properties of both phases. Silicones, and, in general, polydimethylsiloxane polymers, are very interesting because of their unique physicochemical properties such as their low surface tension and their non-susceptibility to oxidation or thermal degradation. As for polyethylene glycol, it is used in a great variety of systems because of its solubility and viscosity properties. All of them are widely used in pharmaceutical and health care applications not only for the above-mentioned characteristics but also for their lack of toxicity [18–21]. However, there is very little literature and limited experience in developing those particular emulsions. As far as the authors know, there is only one study reporting anhydrous emulsions of a polyol with a silicone oil [17] to be employed for cosmetic and medical uses because some of their components (e.g. DeoxyArbutin) were found to be water sensitive. Likewise, few research studies developed polyol-in-silicone formulations for cosmetic or dermatological applications such as hair growth shampoo [22] or personal-care products [23]. Finally, it is worth mentioning that most of the studies carried out in this area are patents of topically applicable cosmetic and pharmaceutical compositions [24–26].

Recently, Delgado-Sánchez et al. [27] have managed to develop a long-term stable polyethylene glycol-in-silicone oil emulsion, facing the challenge of finding a suitable surfactant. Thus, stable emulsions of dispersed semicrystalline polyethylene glycol PEG4000 (with a melting point of 58−61 °C) in a silicone oil continuous phase were stabilized by a silicone surfactant containing comb-like structure, where PEG and PPG pendant groups are grafted onto a polydimethylsiloxane backbone. Such emulsions may lead to new fields of research since the use of phase change materials in the emulsions could be very worthwhile not only for energy

recovery applications but also for topically applicable cosmetic/dermatological compositions. Indeed, oil-in-water phase change emulsions have been proposed to improve the topical application in cosmetics [28–30] and for pharmaceutical delivery applications [31].

In general, it is well known emulsion disperse phase and surfactant concentrations affect its droplets size, rheological properties, stability, etc. [32]. However, when a phase change material is employed, emulsion compounds may also affect the crystallinity of the disperse phase [27,33] and, as a result of this, the bulk properties of the dispersion. On the other hand, features would depend not only on the formulation but also on the processing conditions (processing device, temperature, time, etc.) [34,35] and, specifically for phase change emulsions, resistance to sequential heating-cooling thermal cycles and heat storage stability have a crucial influence on the product performance.

For these reasons, a better and systematic understanding of the stability of the emulsion and the effect of formulation and processing parameters is required, to optimise the formulations, controlling their final characteristics and developing new materials and applications. Therefore, the objective of the present work was to examine the morphological, rheological and thermophysical characteristics of these non-aqueous emulsions as a function emulsion formulation (surfactant and PEG4000 disperse phase concentrations) and processing, putting special emphasis on the interaction among compounds, and the modification of crystallinity of the disperse phase.

2. Experimental

2.1. Materials

The two immiscible phases used to prepare the oil-in-oil emulsions were polyethylene glycol 4000 (PEG4000, average molecular weight 4000 g/mol, range: 3500–4500 g/mol) with a

melting point of 58-62 °C and silicone oil, ESQUIM FS-100, (polydimethylsiloxane, viscosity 0.1 Pa·s at 25 °C). PEG4000 was purchased from Panreac Química S.A. (Spain) and silicone oil for industrial use was supplied by Esquim S.A. (Spain). The emulsifier used for the stabilisation of the emulsion was a high-performance silicone surfactant, DOWSIL™ ES-5226 DM (Dimethicone (and) PEG/PPG-18/18 Dimethicone), kindly provided by Dow Corning Corporation.

2.2. Sample preparation

2.2.1. Emulsions preparation

Non-aqueous emulsions were prepared by high-shear mechanical stirring, mixing silicone oil as continuous phase with PEG4000 as disperse phase and DOWSIL™ ES-5226 DM as emulsifier, according to the method detailed elsewhere [27]. To sum up, in a typical experiment, 4 g of surfactant was first meticulously dissolved in 70 g of silicone oil by magnetic stirring RW 20 model (IKA, Germany) at 250 rpm at 80 °C, until a homogeneous mixture was obtained. Following, the disperse phase, 30 g of PEG4000 pre-conditioned at 80 °C in an oven, was added drop by drop to the mixture under high shear conditions using an Ultra-Turrax T25 (IKA, Germany) homogeniser at 20,000 rpm. Once all the disperse phase was added the stirring continued over 5 additional min at the same speed and keeping the temperature constant at 80 °C. The homogeniser enables maintain that constant temperature during the preparation of the emulsion, being not necessary to use any additional heater. Moreover, the high shear disperses homogenously PEG4000 in the silicone oil by providing the energy needed to form the droplets. The latters were stabilised thanks to the surfactant and, as a result, stable emulsions were obtained (the so-called fresh emulsions).

The above-described formulation of the fresh emulsion corresponds to a mass ratio of disperse phase/continuous phase of 30/70 and 4 wt.% surfactant over the total weight of both phases. However, in order to study the effect of disperse phase and surfactant concentration in the final properties, different mass ratios of disperse phase/continuous phase (30/70, 45/55, 60/40) and surfactant concentration (1, 4, 8 wt.% to the total weight of both phases) were also prepared.

On the other hand, selected fresh emulsions were post-processed at 80°C for 24 h in a cylindrical vessel (60 mm diameter and 140 mm height) with a four-bladed stirrer rotating at 500 rpm using an IKA RW-20 stirring device (Germany) before their characterisation. Based on this post-treatment, the effect of mixing time was studied by extending post-processing in a selected emulsion for 48h, at 80ºC.

Each sample was identified by the initials of the two phases involved PEG4000/Silicone oil (SO/PG), followed by a number indicating disperse phase fraction (30, 45 or 60), then the character F or P specifies whether the emulsion was characterised just after their preparation (Fresh) or post-treated (P), respectively. Finally, notation includes the processing temperature. As an example, the sample SO/PG30-P80 was prepared with 30 g PEG4000, 70 g silicone oil and 4 g surfactant and, afterwards, it was post-processed at 80 °C during 24 h. A special case in the labelling is for emulsions prepared with different surfactant concentrations to 4 wt.%, where surfactant content is added at the end (e.g. SO/PG30-P80-1%). The same applies for post-processing times longer than 24 h, in which this value is added at the end of the sample code (e.g. SO/PG30-P80-48h).

2.2.2. Binary mixtures preparation

Binary mixtures of all emulsion components (silicone oil, PEG4000 and surfactant) were prepared to analyse mutual interactions, independently. These samples were obtained using

similar mass ratios to those of SO/PG30-4%, following the same procedure as those for preparing fresh (SO/PG30-F80) and post-processed systems (SO/PG30-P80).

2.3. Material characterisation

2.3.1. Rheological characterisation

The rheological characterisation of the non-aqueous emulsions, blends and the pure components was carried out in a strain-controlled rheometer (ARES-G2, TA Instrument, USA) using a Couette geometry (cup of 30 mm diameter and bob of 27 mm diameter and 42 mm length). The rheometer was equipped with an Advanced Peltier System (APS) with a temperature range of -10 to 150 °C, with a maximum heating rate of 20°C/min and a temperature accuracy of +/- 0.1 °C (see in Fig. S1 of Supplementary Information). Steady-state viscous flow tests were performed on all samples at 80 °C. An equilibration time of 3 min was set at every shear rate applied, to achieve steady state conditions and all the measurements were performed in duplicate.

2.3.2. Optical microscopy

Optical microscopy was used to study the morphology and microstructure of the emulsions by means of an Olympus BX51 (Japan) microscope coupled to an LTS-350 Heating-Freezing Stage controlled by a Linkam TP94 (Linkam Scientific Instruments, UK). Hot samples were placed on standard microscope slides (76 x 26 mm) for observation at 80 °C. The whole setup can be observed in Fig. S2 in the Supplementary Information. The droplet size of the emulsions was determined from the analysis of the diameter of 100 emulsion droplets using ImageJ software. Droplet sizes values have been reported as means ± standard deviation statistically determined by analysis of variance (ANOVA, $p < 0.05$) employing the statistical package SPSS 18.

2.3.3. Differential Scanning Calorimetry (DSC)

Modulated Differential Scanning Calorimetry (MDSC) tests were performed on emulsions and the pure components in a Q-250 DSC calorimeter (TA Instruments, USA) to characterise their thermo-physical properties (phase change temperatures and latent heats during melting and crystallising process). Tests were carried out under N_2 atmosphere at a flow rate of 50 ml min^{-1} using 10–20 mg samples sealed in hermetic aluminium pans. The cycle of measurement was performed at an oscillation period of 60 s, with an amplitude of ± 0.5 °C, and a heating/cooling rate of 3 °C/min. During the MDSC, samples were first heated up to 120 °C to provide the same recent thermal history to all of them. Afterwards, they were kept at 120 °C, for 10 min, to reach the thermodynamic equilibrium. Subsequently, the cooling cycle was down to -80 °C, kept for 10 min at this temperature to reach the equilibrium, and, finally, heated up to 120 °C a final heating cycle. The DSC curves show the exothermic crystallisation process and the endothermic melting process. All thermal events, as well as the melting temperature and latent heat during melting, and the crystallisation temperature and latent heat during solidification, can be measured using DSC curves. The obtaining of these parameters is illustrated in Fig. S3 in the Supplementary Information.

3. Results and discussion

Emulsion properties are expected to be strongly affected by, at least, the following experimental parameters: disperse phase mass ratio, amount of surfactant, and processing conditions and, therefore, need to be investigated. In that sense, a viscous flow characterization, followed by a study of their morphology through optical microscopy and a thermo-physical characterisation by DSC analysis was carried out to determine the influence of each parameter. It is important to note that whatever the formulation, all emulsions were fairly stable and remained homogeneous after at least 30 days of static storage at constant temperature. Moreover, all

samples have been studied and characterised at 80 °C, above the crystallization temperature of PEG4000.

3.1 Effect of post-processing at different mass ratios

Fig. 1 shows the viscous flow behaviour of fresh and post-processed (24 h, at 80 °C) non-aqueous emulsions prepared at different mass ratios of PEG4000/Silicone oil. As can be noticed, whereas pristine phases present a Newtonian behaviour in the whole experimental window, all fresh emulsions develop a pronounced non-Newtonian shear-thinning behaviour, at low shear rates, followed by a trend to reach constant viscosity values at high shear rates. Such behaviour was found to be due to the shear-induced deflocculation process of a highly structured system, as shown by the optical images presented in Fig. 2, where fresh emulsions present a complex clustering microstructure network of interconnected small droplets [27]. In the case of fresh emulsions, as deduced from Fig. 1 and 3, the evolution of flow behaviour, and apparent viscosity at 1 s^{-1}, with the disperse phase concentration follows a logical sequence, i.e. a notable rise in viscosity with the higher amount of dispersed phase, as reported in the literature [36,37]. Thus, an increase in the disperse phase concentration leads to a shortening of the distance between droplets, together with a larger specific surface area that favour interactions among them and, therefore, giving rise to larger viscosities [38,39]. This was observed and verified in the previous work about PEG4000-in-silicone oil emulsion [27].

Surprisingly, Fig. 1 and 3 also point out that PEG4000 concentration does not affect emulsion viscosity following the same trend after the post-processing protocol (further mixing at 80 °C for 24 h). Thus, whereas the emulsion with the lowest disperse phase concentration (SO/PG30-P80) still presents a notable shear-thinning character, the other dispersions tend to develop an almost Newtonian viscous behaviour. This distinctive and apparently contradictory behaviour needs to

be analysed in detail since it is not only related to phase concentration but also to a complex process of structural modification during post-processing. In fact, when these emulsions are compared to the fresh ones, viscosity dramatically drops and flatter shear thinning profiles are clearly found (Fig. 1 and 3), being those changes more evident for samples SO/PG45-P80 and SO/PG60-P80.

Moreover, as calculated from the micrographs in Fig. 2, mean droplet sizes for post-processed emulsions are 5.8 ± 0.9 μm in SO/PG30-P80, 5.7 ± 1.7 μm in SO/PG45-P80 and 5.9 ± 1.9 μm in SO/PG60-P80. Therefore, an increase in the concentration of PEG4000 expectedly leads to larger volume fractions of the dispersed phase but does not seem to significantly affect the droplet size, even if the amount of surfactant per gram of PEG4000 decreases. However, the evolution of the emulsion viscosity for post-processed samples does not correspond to the increased dispersed volume fraction and reported microstructure, a fact that, again, hints complex processes during post-processing.

In order to understand the origin of these outcomes, phase transitions were analysed by MDSC measurements, since they are known to play a very important role in the properties of the emulsion when phase change materials are used [27]. Firstly, it is worth mentioning that, as shown in Fig. 4 (a), the melting peak associated with the silicone oil, which appears at around -45 °C, does not undergo any relevant modification with concentration changes. Neat PEG4000 thermogram is characterized by wide melting and crystallization peaks, centred at around 59 °C and 37 °C, respectively, pointing out a moderate supercooling degree, which is in line with other data previously reported [40,41]. However, after emulsion preparation, DSC curves reveal a significant modification of melting and, especially, crystallization events. Therefore, as shown in Table 1 the associated enthalpies of melting and crystallization per gram of PEG4000 in fresh samples undergo reductions of 22, 7 and 2 % for mass ratios of 30, 45 and 60, respectively, and

consequently, their crystalline fractions evolve similarly. In addition, all melting peaks are slightly shifted to lower temperatures (about 5 – 6 °C less) while crystallization temperatures lowered according to phase concentration, observing a shift of 17 °C for the major peak of SO/PG30-F80. This sample also shows a minor crystallization peak at much lower temperatures (≈ -22 °C), with a large supercooling degree. Similar crystallization processes in two steps with different supercoolings have been reported for PEG block copolymers and some polymer blends. Therefore, the appearance of a crystallization peak largely shifted to lower temperatures (large supercooling) has been related to the so-called homogeneous nucleation or homogeneous crystallization, caused by spontaneous aggregation of chain segments to form homogeneous nuclei [42]. As homogeneous crystallization involves the formation of new surfaces, it is usually difficult to attain because it requires overcoming a high energy barrier. Then, like most polymers, neat PEG4000 undergoes the so-called heterogeneous nucleation that happens on pre-existing surfaces that require a significantly lower energy barrier and, therefore, much lower supercooling. Thus, during the cooling of neat PEG from a molten state, heterogeneities (chain defects, catalytic debris, impurities, additives, etc.) serve as nuclei for crystal growth at temperatures close to the melting point.

In the case of emulsions, the appearance of homogeneous crystallization for PEG4000 is associated with a distinct change in the semicrystalline morphology of the disperse phase. Particularly, for polyethylene glycols, this has been often attributed to the formation of microdispersed crystallisable isolated domains with scarcer active heterogeneities, where the crystallization is initiated predominantly via homogeneous nucleation with a large supercooling [43]. Consequently, the reported evolution of DSC events in Fig. 4 (a), with a notable shifting of melting/crystallization peaks, hints that some silicone oil molecules are diffused into the dispersed phase, hindering the chain folding crystallization, depressing the crystalline perfection

and forming several small micro-domains that crystallize at much lower temperatures [44]. Therefore, as SO/PEG30-F80 undergoes a fractioned crystallization with an extremely large supercooling peak, its largest silicone oil content seems to promote the formation of dispersed isolated PEG4000 microdomains inside the droplets, by the migration of molecules from the silicone continuous phase.

Consequently, these outcomes reveal a partial compatibility among emulsion constituents that leads to a modification of the PEG4000 crystalline fraction within the dispersed phase. This assumption is consistent with the effects caused by the post-processing that clearly intensifies the reported modifications, as can be observed in Fig. 4 (b) and Table 1. However, the quantitative effect of post-processing is different depending on the formulation and, as in the case of flow curves, does not follow the expected evolution with silicone oil content. Thus, post-processing on SO/PG45-P80 and SO/PG60-P80 give rise to the practical disappearance of the melting/crystallization events, probably due to the diffusion of some poly(dimethylsiloxane) chains into the disperse phase, hindering the crystallization of PEG chains. By contrast, the sample with the highest content of silicone oil (SO/PG30-P80) still retains part of its crystalline structure after post-processing. Thus, this sample shows a notable drop of the melting temperature from 52 to 36.6 °C along with a reduction in its enthalpy of about 50 % in the heating scan (Table 1). In addition, its cooling cycle curve only displays two-merged peaks (at -26 and -32 °C) illustrating an extremely large supercooling effect, induced by the homogeneous crystallization, as a consequence of the mentioned development of PEG microdomains.

In this sense, DSC results may explain the observed evolution of viscosity values with post-processing (Fig. 1 and 3). Thus, it seems that a decrease in the crystallinity of the dispersed phase also yields a drop in the viscosity of the emulsion after post-processing, particularly when crystallinity disappears. This effect is also associated with the softening of PEG4000 by the

diffusion of emulsion compounds into the disperse phase that affects its contribution to the bulk viscosity [45].

On the other hand, it is noteworthy that, as these emulsions have been prepared with a constant total surfactant concentration (4 wt.%), an increase in the mass ratio of PEG4000/Silicone oil also leads to lower ratios of surfactant/PEG4000 (4/30, 4/45 and 4/60 respectively) i.e. lowering the amount of surfactant per gram of PEG4000. It could be therefore presumed from the data in Table 1 that as the amount of disperse phase ratio decreases (higher ratios of surfactant/PEG), the crystallinity is clearly affected, even though emulsions are highly structured and stable. Then, the surfactant may also alter the crystallization of the PEG4000.

Consequently, as previously commented, the complex physical processes involved in emulsion preparation and post-processing seem to be influenced by different factors such as disperse to continuous phase ratios, emulsifier content, and processing conditions, as will be discussed in the following sections.

3.2 Effect of the surfactant amount

In order to shed some light on this complex subject, the influence of the amount of surfactant on the emulsion properties was analysed in more detail. Emulsions were prepared using three different percentages of surfactant (1, 4 and 8 wt.%) over the total weight of disperse and continuous phases, keeping constant the disperse/continuous phase mass ratio (30/70) in all of them. This constant ratio was chosen since SO/PG30-F80 presents a typical viscous behaviour of complex structured materials and retains part of its crystallinity, even after the post-processing.

As portrayed in Fig 5(a) and the inset of Fig. 3, as surfactant content rises from 1 to 4 wt.%, the viscosity values of fresh emulsions were found to increase significantly, but a further increase to 8 wt.% hardly change emulsion viscous behaviour. Although many factors may have an

influence on emulsion viscosity, in a simple way, it can be said that the viscous properties are dependent on the continuous phase properties [46,47] and the contribution of the disperse phase [48,49]. Since the viscosity of the continuous phase is not significantly affected by the presence of surfactant (data that will be shown and analysed later in section "3.3 Microstructural considerations"), the impact of the dispersed phase seems to be the dominant factor affecting the rheological response. As such, the mean diameters of the droplets (5.4 ± 3.1 μm in SO/PG30-F80-1%, 1.8 ± 0.2 μm in SO/PG30-F80-4%, 1.3 ± 0.3 μm in SO/PG30-F80-8) strongly decrease with the amount of surfactant used to stabilise fresh emulsions. The higher the amount of surfactant, the lower the surface tension, giving rise to smaller droplets. Those smaller droplet sizes turn into higher viscosity because the mean distance of separation between the droplets decreases, leading to an increase in hydrodynamic interactions due to van der Waals attraction force, inducing depletion flocculation of the droplets causing an increase in viscosity [49]. However, even though for the largest surfactant concentration smaller particles are clearly distinguished, the viscosity does not experience the expected increase and, therefore, another factor may be affecting in the opposite way.

In this sense, DSC measurements may help to understand the phenomena involved in the disperse phase. Thus, Fig. 7 (a) and Table 2, show that an increase in the amount of surfactant leads to a proportional decrease of melting and crystallization enthalpies and, therefore, a gradual fall in the crystallinity of PEG4000. In addition, it is noteworthy the progressive disappearance of the heterogeneous crystallization peak (close to the melting temperature) with emulsifier content and the formation of the previously commented homogeneous crystallization peak (at large supercooling). Thus, these results seem to indicate that not only silicone oil but also surfactant molecules can penetrate the dispersed phase and modify the crystallinity of PEG4000. Thus, it can be stated that the surfactant effect is very important not only qualitatively but also

quantitatively since fresh emulsions components have only been processed for about 10 min in total, leading to a significant modification.

Following the same experimental methodology, the emulsions were post-treated (at 80 °C for 24 h) and compared to their precursors' fresh emulsion. Then, Fig. 5 (b) and inset in Fig. 3 show how, after the post-treatment, SO/PG30-P80-1% and SO/PG30-P80-8% exhibit practically Newtonian character, whereas, SO/PG30-P80-4% retains its shear-thinning behaviour. At high shear rates, all the emulsions tend to reach similar viscosity values.

Emulsion morphologies of shown in Fig. 6 can only partially explain the viscosity results since post-processing yields a less-structured system for every formulation. This effect becomes more intense for the sample with the highest surfactant content (SO/PG30-P80-8%) that has lost the three-dimensional network and presents a clear increase in droplet size. However, samples SO/PG30-P80-1% and SO/PG30-P80-4% still present a structured network but different viscous behaviour. In this sense, complex and kinetically-dependent diffusional effects on the dispersed phase could be behind this diverse rheological behaviour, as supported by DSC measurements. In general, post-processing intensifies the modification of the crystalline fraction of PEG4000 since the corresponding exothermic peaks of heterogeneous nucleated crystallization vanish after this process and total crystallinity is strongly reduced, in such a way that it completely disappears for SO/PG30-P80-1% and becomes residual for SO/PG30-P80-8%. By contrast, SO/PG30-P80-4% discloses an appreciable melting endotherm and a well-defined homogeneous nucleated crystallization event. Consequently, once again, the remained crystallinity of the dispersed phase after post-processing seems to produce a higher trend to develop a shear-thinning behaviour.

However, the reason why an intermediate surfactant concentration yields higher remaining crystallinity of the dispersed phase and larger viscosities need to be explored in more detail and will be discussed in next the section.

3.3 Microstructural considerations

According to the presented results, it seems that some emulsion compounds, silicone oil (probably small chains) and surfactant molecules, are likely to diffuse into the disperse phase during processing and post-treatment, affecting the crystallinity of the disperse phase.

With the aim of better understand these processes, binary mixtures between all emulsion compounds have been submitted to similar processing and post-treatment as emulsions to promote mass transfer processes, let them to phase-separate without surfactant, at 80 °C, and analysed by DSC and viscous flow measurements and compared to their neat counterparts (Fig. 8 and 9, respectively). According to this, pure surfactant does not show any relevant thermal event in the whole temperature interval and silicon oil only exhibits a single melting peak centred at –45 °C. In addition, as can be easily observed in Fig. 8 (a), the silicone oil thermogram is not affected after its contact with surfactant. By contrast, when analysing PEG4000 after mixing with surfactant (Fig. 8 (b)), it is clear that processing conditions used during the short emulsification step (F80, 80 °C for 10 min) yields a notable drop in melting and crystallization temperatures of approximately 20 °C, whereas further post-processing (at 80 °C, 24 h) leads to the complete disappearance of both thermal events. A similar effect is observed when PEG4000 is directly mixed with the silicon oil (without surfactant) and subsequent separated, as portrayed in Fig. 8 (c), but in this case, the effect is much more intense, since crystallinity completely disappears after 10 min processing, pointing out a faster mass transfer process. These outcomes confirm the partial compatibility of both silicone oil and surfactant with the crystalline fraction of PEG4000. Therefore, during processing and post-processing, these molecules diffuse into the crystalline phase and hinder the crystallization of the PEG moieties giving rise to its softening (Fig.9).

Consequently, the reported evolution of the thermal and viscous properties of emulsions, are mostly related to structural modifications in the dispersed phase. Thus, a higher retained crystallinity of the dispersed phase and especially larger heterogeneous-type crystallisable fractions (low supercooling) leads to an increase of the emulsion viscosity and favours the shear-thinning character.

However, the reason why SO/PG30 formulation presents the highest resistance to structural and rheological modifications remains to be unexplained. In general, it has been reported two structural effects that lead to a worsening in the rheological behaviour: reduction of PEG crystallinity by diffusion of other compounds and microstructural changes induced by post-treatment. As these interrelated effects are kinetically dependent processes, the global rate is enhanced by factors that promote the mass transfer (concentration of diffusing molecules, processing shear and time) and worsened by the transport resistances mainly due to the interfacial surfactant layer and the diffusion layer within the emulsion droplet [50].

Consequently, the formulation SO/PG30-F80-4% might contain the optimum surfactant concentration with a good compromise between both structuring and de-structuring effects, since it maintains a notable shear-thinning character after the post-treatment (SO/PG30-P80-4%). Thus, on the one hand, this quantity of emulsifier yields an optimal surfactant/PEG400 ratio that allows the emulsion to exhibit a 3-dimensional structure and the reported shear-thinning behaviour. On the other hand, this concentration is enough to develop an optimal interfacial surfactant layer, forming a protective barrier to mass transfer of compounds that alter the crystallinity of the dispersed phase. However, as mentioned before, the diffusion towards the dispersed phase is a time-dependent process so that this optimal formulation finally undergoes an apparent viscosity

drop after longer post-processing (see SO/PG30-P80-48h in Fig. 5 (b)), showing a similar viscous behaviour to those measured for the other surfactant concentrations.

Therefore, in the case of fresh emulsions with different surfactant concentration (see Fig. 5), 1 wt.% emulsifier is below the optimal value to develop a high viscosity and, probably, forms a weak protective interface barrier that does not prevent the quick diffusion of molecules into the disperse phase, after the post-treatment. Consequently, SO/PG30-P80-1% undergoes a notable drop in viscosity values and the disappearance of PEG4000 crystallinity. For the sample containing 8 wt.% surfactant, the slight worsening in the viscous behaviour for fresh emulsion (Fig. 5) is attributed to the excessive emulsifier content and the reported de-structuring of the emulsion with post-processing as well. Then, doubling the emulsifier concentration not only increases the number of available molecules to be diffused but also the driving force of mass transfer and, therefore, the diffusion rate. Consequently, both silicone oil and surfactant molecules diffuses into the PEG4000 droplets, hindering the crystallization and leading to a notable softening of the disperse phase that would explain the reported evolution of the viscous behaviour.

4. Conclusions

The obtained results demonstrate that stable polyethylene glycol-in-silicone oil (o/o) phase change emulsions can be successfully obtained by selecting an appropriate surfactant. However, their morphological, rheological and thermo-physical properties are greatly dependent on parameters such as surfactant concentration, volume fraction of the disperse phase and processing time. All of them ultimately affecting the crystallinity fraction and crystallization mechanism present into the disperse phase.

In general, all fresh emulsions show a notable non-Newtonian shear-thinning behaviour, which becomes more evident with the increase in PEG4000 concentration and with the amount of surfactant, reaching an optimum for 4 wt.% emulsifier. However, it was pointed out that the effect of those parameters on emulsion viscosity does not follow the same trend after the post-processing protocol (gentle mixing at 80 °C for 24 h), which has been attributed to mass transfer processes from the continuous silicone oil phase to the disperse phase, better understood thanks to the DSC measurements.

The results show that silicone oil and surfactant molecules may penetrate through the surfactant layer into the disperse phase, leading to a modification of the crystalline fraction of PEG4000. In fact, an increase of the surfactant content as well as of the silicone oil /PEG4000 ratio leads to a proportional decrease of melting and crystallization enthalpies and, therefore, a gradual fall of the PEG4000 crystallinity. In addition, it was also found a change in the crystallization mechanism of polyethylene glycol, as processing is more intense, characterised by a progressive disappearance of the heterogeneous crystallization peak (close to the melting temperature) and the formation of the homogeneous low temperature crystallization peak (at large supercooling). The latter is associated with an apparent alteration in the semicrystalline morphology of the dispersed phase due to some of those molecules diffused into the disperse phase, hindering the chain folding crystallization, depressing the crystalline perfection and forming several small micro-domains that crystallize at much lower temperatures. The disappearance of the crystallinity and, particularly, the decrease of heterogeneous-type crystallisable fractions lead to a much lower the emulsion viscosity and the loss of the shear-thinning character.

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