Formulation and processing of novel non-aqueous polyethylene glycol-in-silicone oil (o/o) phase change emulsions

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Abstract:

Oil-in-oil phase change emulsions, composed of phase change materials (PCMs) dispersed in a continuous oily medium, have never been reported in the literature. The current study involves the formulation, stabilisation and characterisation of novel anhydrous emulsions of polyethylene glycol (PEG4000) as PCM in silicone oil. Emulsions with different dispersed phase concentrations were evaluated by analysing the viscous flow properties, optical microscopy and modulated differential scanning calorimetry. The results evidence that the emulsions can be pre-stabilised at 80 °C, under high shear conditions, by selecting an adequate silicone surfactant but undergo a severe destabilisation after a cooling and heating cycle. Nevertheless, a post-processing protocol (low shear agitation at 80 °C for 24 h) leads to thermal cycle resistant and storage stable non-aqueous dispersions. This process gives rise to a reduction of the shear-thinning character of the emulsion, shifts the melting and crystallization temperature of the PEG4000 to lower values and reduce its crystallinity. This is attributed to partial compatibility of the crystalline fraction of PEG4000 with other compounds of the emulsion.

Keywords: viscosity, non-aqueous emulsions, silicone surfactant, Phase Change Material (PCM), stability.

1. Introduction

Non-aqueous emulsions, also known as oil-in-oil, anhydrous or waterless emulsions, have been rarely studied and with relatively few publications available, despite having many real and potential applications [1]. Since the first papers in the sixties [2,3], most of the studies on this topic have been focused on the research of cosmetic and pharmaceutical applications, mainly in the formulation of anhydrous dispersions used as controlled release vehicles of active principles, and as bases for topical applications or as emollients in formulations. Examples of potential therapeutic applications are occlusive preparations, oily depot emulsions for intramuscular or subcutaneous injections and preparation of oral controlled release dosage [4–7]. In the case of the preparation of porous materials, it has been also reported the development of some non-aqueous oil-in-oil High Internal Phase Emulsions (HIPE) emulsions and, more recently similar systems have been formulated with an ionic liquid as dispersed phase [8]. In another remarkable field of application, they are employed to replace the emulsions where there are water-sensitive reactions or where higher temperatures than the boiling point of water need to be reached [9–11] and in developing dispersions of water labile drugs i.e. where the water itself is undesirable.

Recently, enormous research interest has been drawn to the development of dispersions of Phase Change Materials (PCM) in a continuous low viscosity medium (mainly water) for thermal energy storage and transport, known as phase change emulsions or slurries. However, whereas most of the scientific effort has been driven to the development of encapsulated phase change materials [12,13], little work has been done in incorporating PCMs in water with the help of emulsifiers [14–18]. Besides, to the best of our knowledge, there are no reports so far studying non-aqueous dispersions with such application. This opens the door for a new field of scientific research and innovative applications for solar and geothermal thermal energy storage and industrial waste heat recovery to increase the energy storage capacity of conventional heat transfer fluids. These non-aqueous phase change emulsions would not only have the advantages that slurries bring to heat transfer applications such as the possibility of using the same medium for transport and storage or the high heat transfer rate due to the increase of the specific surface area of the PCM [19], but also all those of the use of oil phases, making a difference. Anhydrous emulsions would allow the transport of matter and heat in systems where the pressure and temperature conditions are more extreme [20], as well as, provide a better long term chemical stability.

On the one hand, the search for an appropriate pair of immiscible phases is a crucial point for formulating non-aqueous oil-based emulsions since they will restrain future applications of emulsions. The immiscibility of these phases is generally analysed using the Hildebrand solubility parameter (δ) [21] which provides a numerical estimation of the degree of interaction for nonpolar or slightly polar substances without hydrogen bonding. It is considered a good indication of the solubility since materials with different values of δ are likely to be immiscible. Examples of immiscible pairs that may be potentially emulsified are castor oil/silicone oil [5,7] and polyethylene glycol ($\delta = \sim 20$ MPa$^{1/2}$) and silicone oil ($\delta = 15.4$ MPa$^{1/2}$) [22]. The latter pair could be possibly used for PCM dispersions, given that different polyethylene glycols can be chosen with a wide range of melting temperatures, for example, with a working temperature between 20 °C and 60 °C to store energy for domestic hot water application [23–25].

And on the other hand, the major difficulty in formulating stable non-aqueous emulsions arises from the lack of data regarding the availability of suitable surfactants in such systems, especially for relatively high molecular weight polymerised compounds. Even though, several traditional ionic and non-ionic surfactants are effective to stabilize some non-aqueous dispersions of immiscible low molecular weight compounds (e.g. olive oil in glycerine or alkanes dispersed in formamide) they are not suitable for more complex systems [5]. However, recently, the works carried out by Atanase and Riess [4] and by Suitthimeathegorn [7] propose the use of block or graft copolymers as alternatives to low molecular weight surfactants. Chemically, they are formed by two or more segments of different monomers and molecular weights, which are selectively soluble in either of the immiscible phases and may achieve optimal orientation at the interface. Then, these macromolecular surfactants adsorb at the interface more strongly than monomeric surfactants and present the advantage of attaching to a surface via several segments. Thus, even though every segment presents a low free energy of absorption, the accumulative attachment of a number of segments brings about a higher total free energy. Consequently, the improvement in adsorption onto interfaces makes them more effective for emulsification mainly stabilizing droplets by a steric barrier to coalescence and depletion mechanisms [26].

The present work was aimed at formulating stable non-aqueous emulsions of two oily phases, using a PCM as the dispersed phase of the emulsion in order to explore the possibility of using such systems as novel phase change emulsion (PCE) for thermal energy storage and as a transport medium simultaneously [27–29].

A polyethylene glycol (PEG4000), with a melting peak temperature of 58-61 °C, has been chosen as disperse phase for the present study because of its chemical and thermal stability, nonflammability, non-toxicity, non-corrosiveness and inexpensiveness [30,31]. In addition, a silicone oil has been selected as continuous phase because it is highly stable (chemically and heat resistant) and presents a low viscosity [26]. Moreover, both phases are also interesting from the cosmetic and pharmaceutical points of view.

With this aim, the effect of formulation (using several non-ionic surfactants and mass fractions of dispersed phase), processing conditions and storage time were studied. To that end, a comprehensive characterisation has been performed on emulsions, assessing their thermal properties, morphology, rheology and stability.

2. Experimental

2.1. Materials

The two immiscible phases used to prepare the oil-in-oil emulsion were polyethylene glycol 4000 (PEG4000, with a melting point of 58-62 °C) and industrial silicone oil, ESQUIM FH-100, (polydimethylsiloxane, viscosity 0.1 Pa·s at 25 °C). PEG4000 was purchased from Panreac Química S.A. (Spain) and the silicone oil was supplied by Esquim S.A. (Spain).

Three high-performance silicone surfactants were kindly provided by Dow Corning Corporation (Midland, USA), namely DOWSIL™ ES-5300 (Lauryl PEG-10 Tris(Trimethylsiloxy)silylethyl Dimethicone; hydrophilic-lipophilic balance (HLB) calculated = 3), DOWSIL™ 5225C (Cyclopentasiloxane (and) PEG/PPG-18/18 Dimethicone; $HLB_{calculated} = 2$) and DOWSIL™ ES-5226 DM (Dimethicone (and) PEG/PPG-18/18 Dimethicone; $HLB_{calculated} = 2$). Another silicone emulsifier, ABIL CARE XL 80 (Bis-PEG/PPG-20/5 PEG/PPG-20/5 Dimethicone (and) Methoxy PEG/PPG-25/4 Dimethicone (and) Caprylic/Capric Triglyceride; $HLB_{calculated} = 11$) was kindly supplied by Evonik Nutrition & Care GmbH (Germany) and contains a mixture of about 82 % of silicone polyether-based emulsifiers and about 18 % of Caprylic/Capric Triglyceride. All these silicone surfactants are characterised by a comb-like structure where different pendant groups are attached along the polydimethylsiloxane main chain.

Finally, four conventional non-ionic surfactants, Span 20 (HLB = 8.6), Tween 20 (HLB = 16.7), Polisorbate 80 (HLB = 15), Cremophor® ELP (HLB = 12– 14) purchased from Sigma Aldrich, were also assessed in this work as stabilisers of the resultant o/o emulsion.

2.2. Sample preparation

Non-aqueous dispersions were prepared by mixing PEG4000 into silicone oil on a rotor-stator homogeniser at 80 °C using an emulsifier. The emulsions were prepared at different weight ratios of disperse phase/continuous phase (30/70, 45/55, 60/40), using 4 wt.% of surfactant with respect to the total weight of both phases, according to the following procedure. It's worth mentioning that such a concentration of surfactant was selected due to the good stabilisation properties it showed in all the emulsions after a pre-study.

Typically, 4 g of silicone surfactant was first dissolved in 70 g of silicone oil by magnetic stirring at 250 rpm over 5 min at 80 °C, to ensure homogeneity. Then, 30 g of PEG4000 (pre-conditioned at 80 °C to ensure its liquid state) was incorporated drop by drop, and emulsified under high shear conditions for 10 min. Emulsification was carried out in a homogeniser Ultra-Turrax T25 (IKA, Germany) at 20,000 rpm (see Fig. 1 (a)). The applied high shear enables the constant temperature of 80 °C without the need of an additional heater. This protocol allowed obtaining the so-called fresh emulsions, that were kept at 80 °C for less than 1 hour before being fully characterised and tested (Fig. 1 (b)). Finally, selected fresh emulsions were subjected to a postprocessing (or stabilisation) stage, keeping them under low shear agitation at 80 °C for 24 h, using a four-bladed stirrer rotating at 500 rpm that was attached to an IKA RW-20 stirring device (Germany).

The nomenclature of the samples includes the identification of the two phases involved in the emulsion (SO/PG), followed by a number indicating the nominal concentration (30, 45, 60) of disperse phase and finally, the processing conditions are included, F80 for fresh emulsions characterised just after their preparation and P80 for post-treated emulsions. A special case is for those emulsion stored under ambient conditions and characterised after one month of its preparation, in which it is added (1M) at the end of the nomenclature, SO/PG30-P80 (1M).

2.3. Material characterisation

2.3.1. Rheological characterisation

The viscous behaviour of the non-aqueous emulsions was analysed in duplicate with the help of 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). Steady state flow curves were carried out at two different temperatures, 20 and 80 °C. An equilibration time of 3 min was set at every shear rate applied, to achieve steady state conditions. No wall-slip phenomena were detected related to the use of a smooth-surface sensor system.

In addition, the presence of thermal phase changes affecting viscous behaviour were studied by of temperature sweeps between 20 to 80 °C, at a constant shear rate of 1 s^{-1}, using heating and cooling rates of 1 °C/min.

2.3.2. Optical microscopy

Optical microscopy was used to study the morphology of the emulsion and droplet sizes. Samples prepared by using standard microscope slides (76 x 26 mm) were studied under an optical microscope (Olympus BX51, Japan) coupled with an LTS-350 Heating-Freezing Stage controlled by a Linkam TP94, manufactured by Linkam Scientific Instruments (UK). Optical images of samples were obtained under ordinary and cross-polarised light at different temperatures, ranging from 20 to 80 °C. The droplet size of the emulsions was determined from the analysis of the diameter of 100 emulsion droplets using ImageJ software. These droplet sizes have been reported as means ± standard deviation statistically assessed by analysis of variance (ANOVA, $p < 0.05$) by means of the statistical package SPSS 18.

2.3.3. Modulated Differential Scanning Calorimetry (MDSC)

Emulsion samples and their pure components were subjected to Modulated Differential Scanning Calorimetry (MDSC) tests, carried out in a Q-250 DSC calorimeter (TA Instruments, USA). Tests were performed under N_2 atmosphere with a flow rate of 50 ml min^{-1}, using 10–20 mg samples sealed in hermetic aluminium pans. A heating rate of 3 °C/min was used and modulation consisted of an oscillation period of 60 s and ±0.5 °C amplitude. During the MDSC test, samples were first heated up to 140 °C in order to provide the same recent thermal history. Then, they were kept at 140 °C for 10 min, to reach the thermodynamic equilibrium. Subsequently, the samples were quenched down to -80 °C, kept for 10 min at this temperature to reach the equilibrium, and, finally, heated up to 140 °C again during the test. All thermal events, as well as the enthalpy values and apparent specific heat and capacities of the samples, were determined.

3. Results and discussion

3.1. Surfactant selection

As there are no guidelines for the selection of surfactants to stabilise the here selected immiscible non-polar oils, a preliminary study of the macroscopic emulsion stability was carried out to determine the effectiveness of the chosen surfactants. Therefore, emulsions were firstly prepared as described in section 2.1 with every surfactant, and then the dispersion stability was evaluated, at 80 °C, by visual inspection.

According to these initial tests, it can be clearly deduced that none of the non-ionic surfactants of low molecular weight (namely Span 20, Tween 20, Polisorbate 80 and Cremophor®ELP) was able to stabilise the PEG4000-in-silicone emulsion since a rapid phase separation occurred within less than 15 min, even though they have been proven to be very effective for an oil-in-water emulsion. On the other hand, the group of silicone surfactants with different pendant groups of different lengths (ES-5300, 5225C, ES-5226 DM and ABIL CARE XL 80) present different emulsifying capacity. Thus, whereas ES-5300 leads to a quick phase separation, 5225C and ABIL CARE XL 80 yield to stable emulsions over some hours before it appears a silicone oil clarification layer on the top of the sample. The best result was obtained with ES-5226 DM which provides stable emulsions for more than one month of storage at 80 °C (Fig. 2). Structurally, this surfactant presents a comb-like structure, where PEG and PPG pendant groups (of an average of 18 moles each) are grafted onto a polydimethylsiloxane backbone. Accordingly, it seems these silicone surfactants containing block sequences selectively soluble in either of the immiscible phases are the most interesting molecules for stabilising the present system. Actually, some research carried out in the last years [4,7] found a similar behaviour, showing that these block copolymers were far more efficient than low molecular weight surfactants, contrary to oil-in-water emulsions, which are mainly stabilised by electrostatic or electro-steric processes by the presence of surfactants of low molecular weight. Moreover, a large copolymer network would provide a big steric barrier that helps avoid the coalescence, favouring the stabilisation of the PEG4000-in-silicone oil emulsion. Therefore, the solubility of PEG/PPG groups in PEG4000 and bulky dimethicone chains in silicone oil allows stabilisation with ABIL CARE XL 80, 5225C and ES-5226 DM. Furthermore, since lauryl group was not soluble in the disperse phase, the system employing ES-5300 rises unstable. Consequently, ES-5226 DM which produces the most stable emulsions was the surfactant eventually chosen for the following experiences.

3.2 Influence of the dispersed phase concentration

Viscous behaviour and morphology of fresh PEG4000-in-silicone oil emulsions stabilised with ES-5226 DM were studied for different concentrations of disperse phase (Fig. 3 and 4). The emulsion viscous properties, as a function of the shear rate and temperature, has a practical interest since they affect their applicability and processing properties. In general, the flow behaviour of emulsions ranges from Newtonian to highly shear-thinning behaviours and it is closely related to some the emulsion individualities such as the disperse phase volume fraction, viscosities of the phases, droplet size or the properties of the surfactant employed to stabilise the system [32]. For that matter, the viscous flow behaviour of the PEG4000-in-silicone oil emulsion, at 80 °C (above the melting point of the dispersed phase) at different dispersed phase concentration, has been presented in Fig. 3. All the emulsions exhibited a pronounced non-Newtonian shear thinning behaviour, at low shear rates, characterised by a drop of two orders of magnitude in viscosity and a clear trend to reach constant values at higher shear rates. By contrast, pure silicone oil and PEG4000 present viscosity values independent of the shear-rate what evidences their Newtonian behaviour (Fig. 3). This pronounced shear-thinning behaviour have been also reported for other non-aqueous emulsions [4,33,34]. In general, it is usually attributed to a shear-induced deflocculation process, and the eventual droplet deformation or elongation along the shear direction [35–38]. Such behaviour can be described as highly structured systems due to the three-dimensional network formed by highly packed and flocculated droplets of the PEG4000, which may be observed by optical microscopy in Fig. 4. Thus, it is clearly observed the presence of interconnected small droplets (diameter of 1.8 ± 0.2 μm in SO/PG30-F80 and 3 ± 0.4 μm in SO/PG45-F80) forming a complex clustering microstructure.

As expected, larger volume fractions of the dispersed phase give rise to a proportional increase in the viscosity of the emulsion (see Fig. 3). This agreed well with the results observed in some others phase change emulsions [39,40]. However, it is important to mention that although Fig. 4 shows that droplet diameter slightly increases from 1.8 ± 0.2 µm to 3 ± 0.4 µm with the growth of the dispersed phase, which could result in a decrease in the emulsion viscosity, this does not happen because in this situation not only does the drop size increase but also the dispersed phase fraction. Nonetheless, the increase in the disperse phase concentration leads to a shorter separation between droplets and a significantly higher specific surface area, both enhancing the interaction between droplets and increasing emulsion viscosity [41,42]. Likewise, the higher volume fraction of the dispersed phase, enhanced by the aggregation/flocculation of droplets, would explain the apparent shear-thinning viscous behaviour observed in Fig. 3 [43]. In essence, the rheological behaviour of these highly concentrated emulsions is mainly due to a competition of hydrodynamic and Brownian forces where, at low shearing rate, the Brownian forces are stronger forming floccules/aggregates that lead to a higher viscosity and, as more shearing force is applied at higher shear rate, the aggregates break observing the decrease in viscosity [44].

3.3 Effect of cooling and heating cycles

Temperature sweep tests at a constant shear rate were also carried out to evaluate apparent viscosity variations during the phase change of the disperse phase. Thus, emulsion SO/PG30-F80 was submitted to cooling and heating cycle (ramps of 1 °C/min), while recording emulsion viscosity at 1 s^{-1} (Fig. 5). As can be seen, temperature exerts a significant influence on fresh emulsion viscosity probably due to the liquid-solid transition of the PEG4000 phase. Then, in the cooling ramp, the viscosity remains almost unaltered until around 40 °C, where viscosity sharply increases by two orders of magnitude and, downwards, continues almost unchanged again. In order to shed some light on the microstructural origin of this effect, optical microscopy observations were performed at the same cooling rate (microscope pictures at the bottom of Fig. 5). Initially, despite this important change in viscosity, unpolarized optical microscopy hardly shows any difference in the morphology of the samples during the cooling stage (Fig. 5 (a), Fig. 5 (b) and Fig. 5 (c)). On the contrary, cross-polarised light at 30ºC (Fig. 5 (d)) does show the appearance of birefringent bright regions that indicates the formation of crystals in the sample, in this case, due to the crystallisation of PEG4000. The appearance of these crystals in an unordered way and mostly in contact with each other (see Fig. 5 (d) again) causes the abrupt rise in the viscosity of the emulsion.

In the heating pathway, as temperature rises, viscosity is slightly reduced until the melting point of PEG4000 is achieved, where an abrupt viscosity drop happens, reaching values clearly below those observed in the cooling ramp, a fact that hints microstructural changes during heating. Then, unlike the cooling stage, the melting of the disperse phase gives rise to the destabilisation of the emulsion due to partial coalescence of the droplets at the beginning and droplet coalescence at the end, as can be clearly observed in Fig. 5 (e) and Fig. 5 (f), respectively.

Such phenomenon of destabilisation is probably related to a shear-induced deformation of the droplets and coalescence. However, destabilisation seems to begin at temperatures below PEG4000 melting point, being also affected by crystallisation of disperse phase. Thus, by observing the light-toned regions in Fig. 5 (d), attributed to the crystals of PEG4000, it is clear that the dispersed phase has not crystallised in small defined drops and the crystals are not uniformly distributed [45]. Those needle-like PEG4000 crystals, grown in a droplet, possibly protrude from the droplet surface into the continuous phase tearing the film between the droplets [46,47], initiating the partial coalescence of the dispersion and the complete destabilisation as the temperature rises (Fig. 5 (e-f)). Actually, there are different mechanisms of emulsion destabilisation during the solid-liquid-phase transition of the dispersed particles documented in bibliography where partial coalescence is taking place due to semisolid droplets [48]. A similar “pin effect” of the sharp particle edges, which facilitate the coalescence of liquid drops, is identified in several studies of food emulsions [47,49,50]. On the other hand, the aforementioned non-uniformity and the lower diffraction intensity areas of the cross-polarised picture suggest that the crystalline perfection of PEG side chains has been disturbed [51]. Below, this assumption will be tackled in more detail, analysing the thermophysical properties of these systems.

3.4 Stabilisation method to provide storage and thermal stability

To obtain stable systems to storage, shear and temperature, fresh PEG4000-in-silicone oil emulsions were submitted to a post-treatment that consisted of a low-shear agitation at 500 rpm and 80ºC, for 24 h, using a four-blade turbine.

The flow behaviour of fresh PEG4000-in-silicone oil emulsions together with the post-treated emulsions was compared at two different temperatures, 20 °C and 80 °C, before and after the melting point of PEG4000, respectively, as shown in Fig. 6. Upon being treated at 80 °C, all samples undergo a remarkable viscosity fall and a clear reduction the shear-thinning characteristics, probably due to a change in its microstructure [52]. In this sense, Fig 7 (b) in comparison with Fig. 7 (a) shows a microstructure with a higher particle size. Specifically, drop size has increased from 1.8 ± 0.2 µm in SO/PG30-F80 to 5.8 ± 0.9 µm in SO/PG30-P80. This result suggests that the droplet size is strongly affected by the post-treatment, and plays the most important role in the rheological response shown in Fig. 6. In emulsions with the same composition, an increase in particle size leads to lower viscosity, as it was aforementioned. Similar behaviour has been reported by several authors in other emulsions [16,53,54].

However, it is worth noting that this post-treatment enhances the emulsion stability against macroscopic phase separation as can be inferred by simple visual inspection. In addition, SO/PG30 emulsion remains stable to steady shear temperature sweeps, as can be deduced from Fig. 5. Then, after the post-treatment (SO/PG30-P80), both cooling and heating curves follow the same pathway, giving a clear indication of emulsion stabilisation and showing the mentioned viscosity drop with respect to the fresh emulsion. Surprisingly, none of these curves presents any sharp change of viscosity at the melting and crystallization points. This finding suggests that the crystallinity of the PEG4000 has been altered during the post-treatment and, will be further explored in the next section.

Following the above results, one of the main concerns during the development of emulsions with a certain application is their stability as it will significantly influence their suitability for a specific application. Thus, the emulsion stability during a long storage period and under thermomechanical variations or, at least, to recover the initial conditions after a slight agitation is a very interesting feature in an emulsion. Then, once the temperature stability of these processed emulsions is achieved, long-term static stability was also analysed at room temperature for a month. Visual inspection showed a small layer of oil appeared at the top, but the emulsion quickly recovers the initial look after a little shaking. In order to better studying their stability, viscous flow curves and optical microscopy were performed on the stored emulsions.

Fig. 6 shows that, after one-month storage, only SO/PG30 underwent a minor decrease in viscosity at low shear rates, whereas SO/PG45 remained unaltered. The slight increase in droplet size, showed in Fig. 7 (b-c) with droplets of 6 ± 0.9 µm of diameter in SO/PG30-P80(1M) in comparison to 5.8 ± 0.9 µm in SO/PG30-P80, would explain this change in the viscous properties [52,55]. As a whole, the emulsions were quite stable as there was neither distinct microstructural change nor phase separation occurred.

3.5 Thermophysical properties

As it was previously commented, the evolution of the viscosity with temperature seems to be strongly related to phase transitions of the dispersed phase. To shed some light on this issue, MDSC measurements of pure components and selected non-aqueous emulsions were portrayed in Fig. 8 and then, melting and crystallization temperatures and phase change enthalpies are summarised in Table 1. For the sake of comparison, all these values have been normalised by the weight fraction of the dispersed phase.

As illustrated in Fig. 8, MDSC scan of neat PEG4000 shows the endothermic (melting point) centred at 59 °C and an exothermic peak (crystallization point) at around 37 °C with related enthalpies of 165 and 161 J/g, respectively. These results indicate a large supercooling degree of PEG, being consistent with the data of literature [56,57]. In addition, this outcome would also explain the viscosity evolution reported in temperature sweeps of the fresh emulsion (Fig. 5). Silicone oil thermogram shows the complete melting peak at around -45 °C and the onset of the corresponding crystallization at -75 ºC.

On the other hand, it is important to note that processing, post-treatment and storage time significantly affect the profiles of emulsions. Thus, Fig. 8 and Table 1 point out that the melting and particularly the crystallization temperatures of PEG4000 of fresh emulsion (SO/PG30-F80) post-treated emulsion (SO/PG30-P80) and 1 month stored emulsion (SO/PG30-P80 (1M)) are progressively shifted to lower temperatures. This effect is especially significant for the cooling scans, where the crystallization of the dispersed phase is split into several peaks. On the one hand, fresh emulsion presents a main crystallization peak at 30 °C and secondary one at -22 °C while the melting peak has been only slightly shifted to a lower temperature. On the other hand, the post-treatment and storage of the emulsion seem to intensify all these effects since the phase change peaks have not only shifted to lower temperatures and become wider but also the mean peak around 20 °C tends to disappear.

Also, taking into account that both melting and crystallization normalised enthalpies of PEG in the emulsion undergo a notable reduction, it is clear that the total crystallinity is markedly reduced, pointing out partial compatibility with some components. In general, such a phenomenon could be explained by the migration of some components of the emulsion inside the crystalline fraction of PEG4000 droplets. Even though this issue needs to be examined more thoroughly, it seems that small low molecular weight chains of silicone oil and/or, more probably, surfactant molecules may diffuse into the PEG4000 droplets hinting the crystallization process. In fact, several studies have proven that deviations of melting and latent heat from the pure component in dispersions are mainly due to the influence of surfactant micelles [58]. This assumption would also explain why this phenomenon is intensified with the post-treatment of the emulsion. Then, the stirring of the emulsion (for 24 hours at 80 °C) favours the mass transfer of a greater amount of surfactant or silicone oil molecules into the PEG4000 drops [59].

Finally, regarding the application field of these emulsions, even though the reported decrease of crystallinity and so its melting and crystallization heats, may limit their use as phase change slurries, the treated emulsions still retain a latent heat similar to that of some novel phase change emulsions found in the literature [40].

The modulated DSC also allows the separation of reversing (related to the heat capacity component of the heat flow) and non-reversing (arising from kinetically hindered process) components, in the same experiment. The non-reversing component is negligible in the single-phase region because there are no kinetic events while the reversing one dominates, pointing out that the changes in signal are mainly due to heat capacity out of the phase change temperature range. Therefore, Table 2 gathers the specific reversing heat capacity of pure components and selected emulsions at temperatures where no phase change occurs. As can be seen, in general, all samples undergo a moderate increase of C_p with temperature, where values of pure compounds are in line of those reported in the literature [60,61]. Surprisingly, the heat capacity of the emulsions are slightly higher than individual heat capacities of the pure constituents and, in addition, increases with the post-treatment and storage time. Even though the origin of this effect is not clear and needs further studies, as this evolution is inversely proportional to the dispersed phase crystallinity (Table 1), this finding could partially be attributed to the lost crystallinity to the reversing heat flow.

4. Conclusions

Non-aqueous PEG4000-in-silicone oil (o/o) emulsions can be stabilized by the use of a silicone surfactant. A steric stabilisation mechanism would avoid the coalescence and favour the stabilisation of the emulsion. However, a complete destabilisation of the emulsion happens when they are submitted to subsequent cooling and heating cycles. This outcome is attributed to a needle-like crystallization of PEG4000 that protrude from the dispersed phase tearing the film between the droplets leading to coalescence.

All fresh emulsions are characterised by a pronounced non-Newtonian shear thinning behaviour, at low shear rates, and an apparent trend to reach constant viscosity at high shear. In general, the viscous flow behaviour depends on the disperse phase concentration, processing protocol and storage time.

Given the instability of the fresh PEG4000-in-silicone oil emulsions, a stabilisation method (called post-treatment) has been successfully applied, enhancing the emulsion macro and microstability preventing phase separation and also makes them resistant to heating and cooling cycles. The post-treatment also yields a notable modification of the viscous flow response, leading to lower viscosities and a change in its microstructure, formed by droplets of higher particle size.

Likewise, both post-treatment and storage time yield a remarkable change in thermal behaviour as reported in MDSC scans. As a result, melting and the crystallization temperatures are shifted to lower temperatures and, the corresponding phase change enthalpies are reduced (i.e. reducing the crystallinity of PEG4000). This outcome points out a partial compatibility among compounds which is attributed to the diffusion of surfactant molecules and maybe small low molecular weight dimethicone chains into the PEG4000 droplets hinting the crystallization process.

As a result, it is important to note that the success in stabilising this anhydrous PEG4000-in-silicone oil (o/o) emulsions also opens new fields of applications (e.g. for cosmetic and pharmaceutical formulations).

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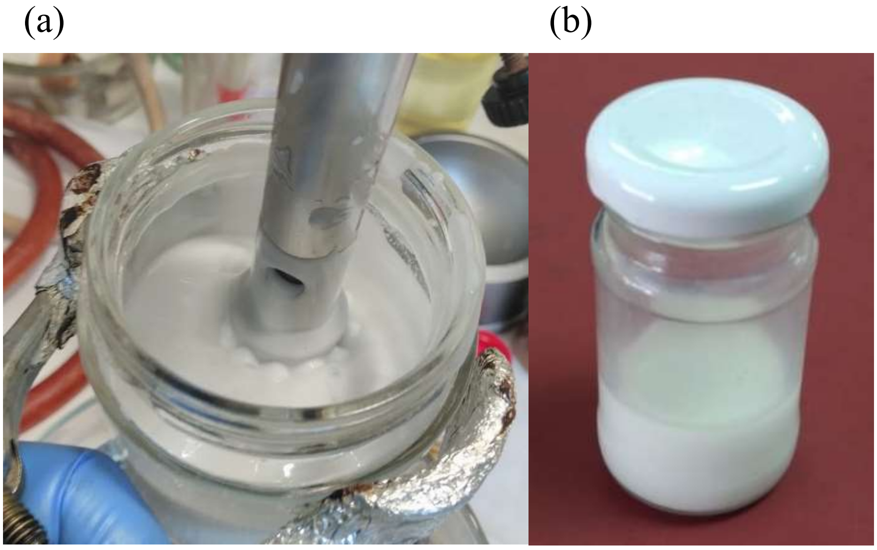

Fig.1. (a) Processing device of PEG4000-in-silicone oil emulsion and (b) fresh emulsion

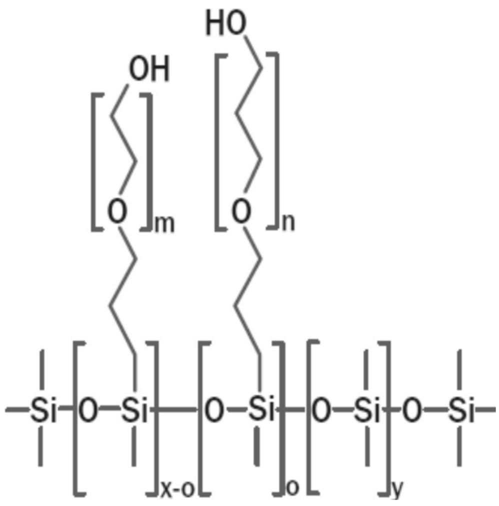

Fig.2. Example of the comb-like structure of silicone surfactants, with PEG and PPG groups grafted onto a polydimethylsiloxane backbone.

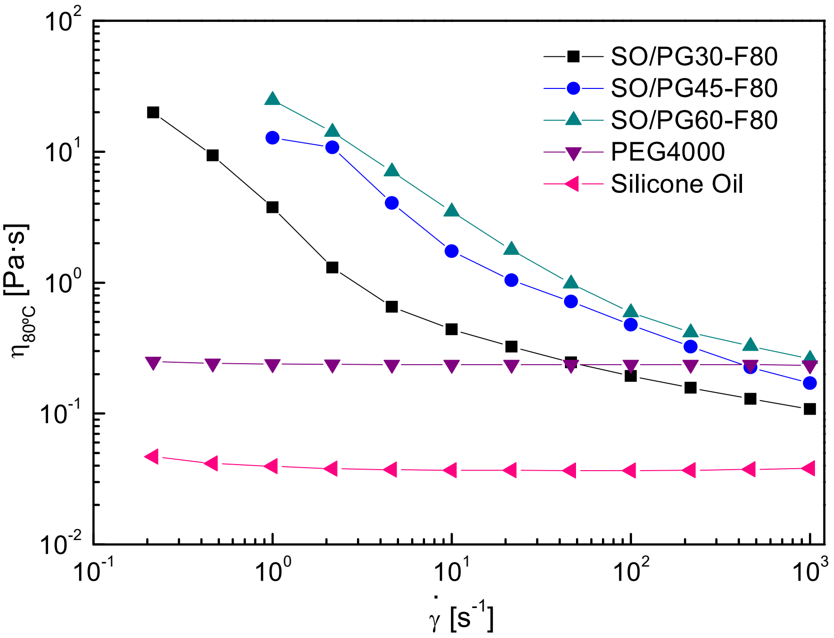

Fig. 3. Viscous flow curves of emulsions, at 80 °C, at different dispersed phase concentrations.

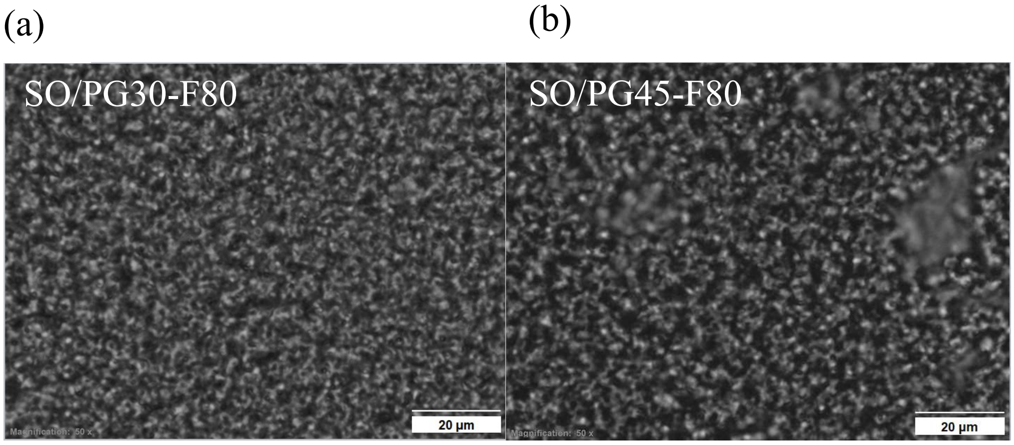

Fig. 4. Optical microscopy images of fresh emulsions.

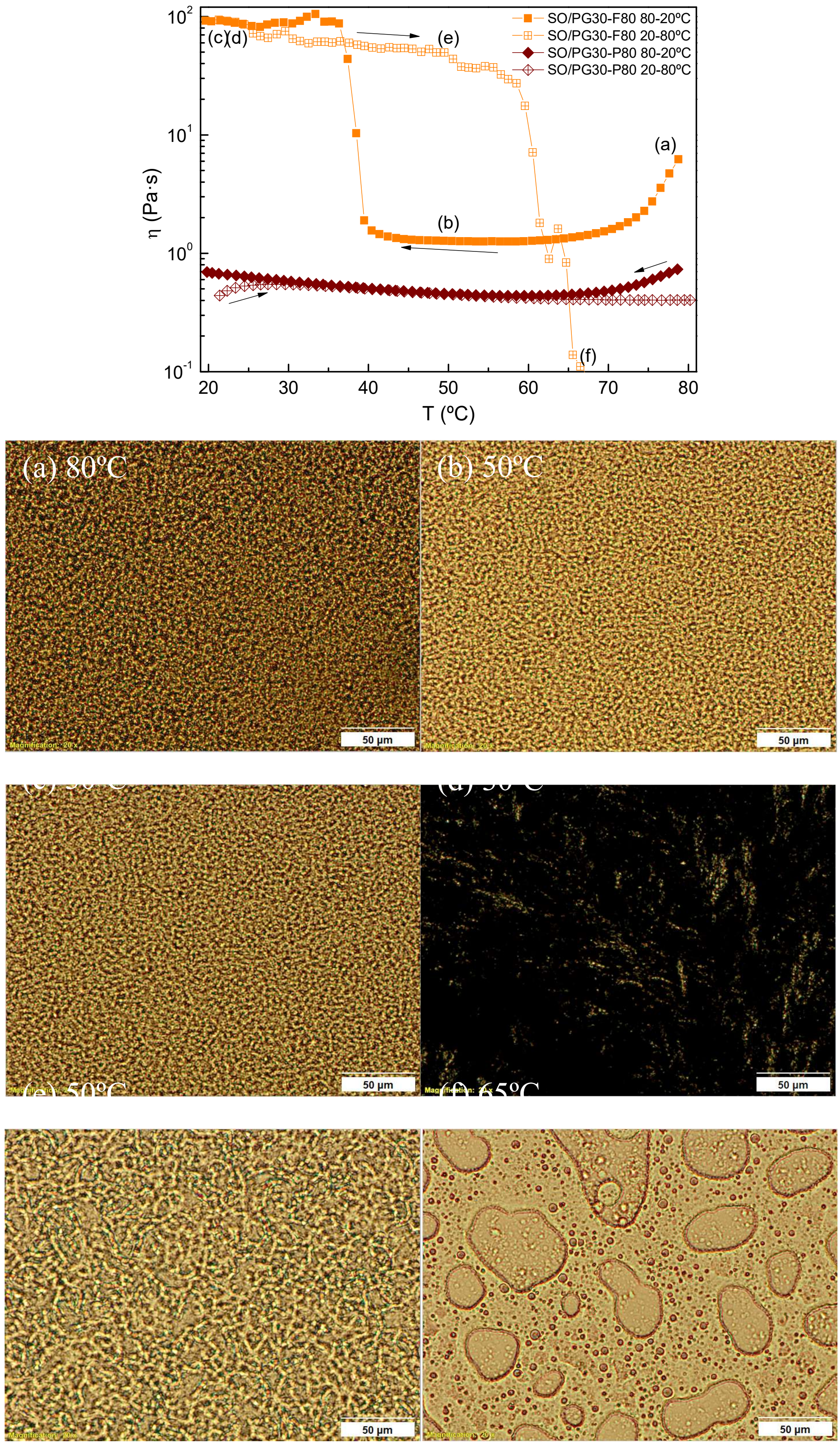

Fig.5. (At the top) Temperature sweep tests in steady shear (1 s^{-1}), at cooling and heating rates of 1 °C/min, of fresh and post-treated emulsions. (In the bottom) Corresponding optical

micrographs of the fresh emulsion at each point of its viscosity curves. Microphotograph (d) was taken under cross-polarized light.

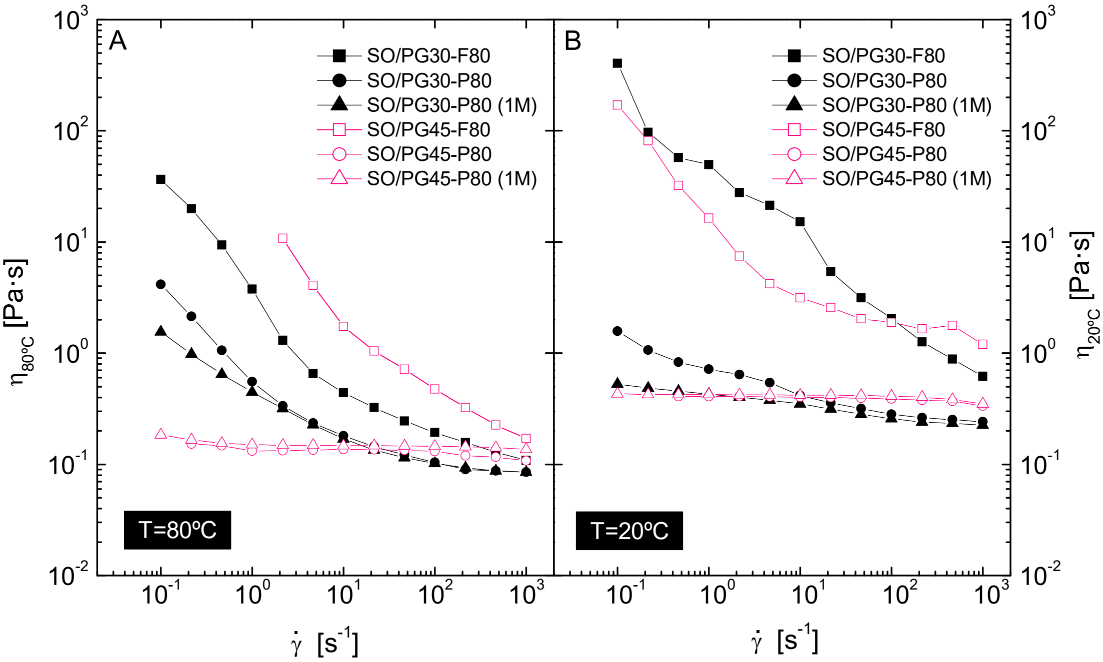

Fig.6. Viscous flow curves, at 20 and 80 °C, of selected fresh emulsions, after the post-treatment and after one-month storage.

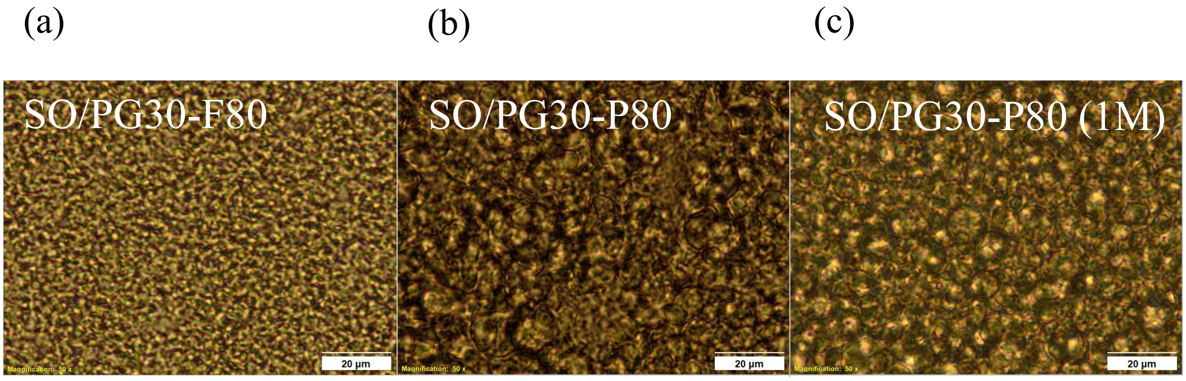

Fig.7. Optical micrographs of emulsions at 80 °C shown in Fig. 6.

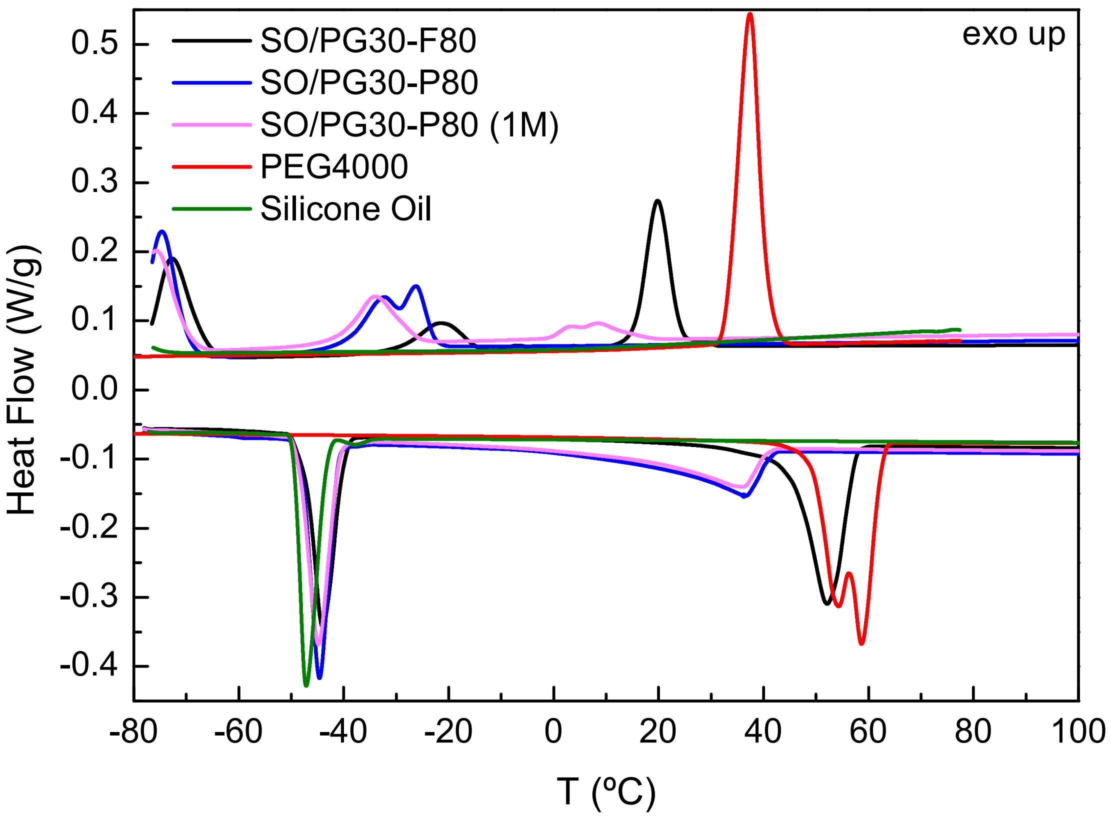

Fig. 8. MDSC cooling and heating scans of pure PEG4000, silicone oil and SO/PG30 fresh emulsion, after the post-treatment and after one-month storage. For the sake of compassion, curves of both pure components are normalised to the amount of them inside the emulsions.

Table 1. Phase-change temperatures and total latent heats of pure PEG4000 and PEG4000-in-silicone oil emulsions measured by the MDSC.

	CRYSTALLISATION		**MELTING**	
	ΔH_c (J/g of PEG4000)	T peak (°C)	ΔH_m (J/g of PEG4000)	T peak (°C)
PEG4000	160.71	37.4	165.42	58.7
SO/PG30-F80	109.30	19.8, -21.6	128.84	52.1
SO/PG30-P80	67.59	-26.3, -32.2	79.58	36.5
SO/PG30-P80-1M	57.68	8.5, -34.0	65.78	36.0

Table 2. MDSC reversing specific heat capacities for selected systems at -30, 30 and 80 °C.

	Heat Capacity (J/g·°C)		
	-30 °C	30 °C	80 °C
SILICONE OIL	1.56	1.62	1.68
PEG4000	0.93	1.45	1.85
ES-5226	1.36	1.44	1.53
SO/PG30-F80	1.42	1.62	1.68
SO/PG30-P80	1.68	-	1.90
SO/PG30-P80 (1M)	1.71	-	1.91