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ORIGINAL PAPER

Influence of Different Factors on the Particle Size Distribution and Solid Fat Content of Water-in-Oil Emulsions

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Abstract The influence of the variation of different parameters on the particle size distribution and solid fat content (SFC) of water-in-oil emulsions was studied. The use of solid fat instead of liquid oil, higher polyglycerol polyricinoleate (PGPR) concentration, or higher homogenization energy led to smaller mean particle sizes. The decrease of the emulsifier/water ratio turned the particle size distribution of the emulsions from bimodal to trimodal. The increase of PGPR concentration increased the SFC of the fat in the absence of water, but it did not produce the same effect in the emulsion. This result suggested that the presence of dispersed aqueous phase prevented the modifying action of the emulsifier on the crystallization of the continuous lipid phase. The experimentation indicated that the adsorption of the surfactant at the interface would reduce its availability to affect crystallization in bulk fat, as the SFC in lipid phase decreased with increasing interfacial area.

Keywords W/o emulsions · Particle size distribution · Solid fat content · PGPR

Introduction

Water-in-oil (w/o) emulsions are characterized by having the aqueous phase dispersed in a continuous lipid phase, which in turn can be composed of liquid oil and/or solid fat. Fewer studies are dedicated to these systems in comparison to more common oil-in-water (o/w) emulsions, and particularly the particle size distribution (PSD) and solid fat content (SFC) of w/o emulsions have not been widely studied yet. These are important subjects that should be taken into account for the elaboration of food emulsions such as butter and margarine.

The emulsifiers employed for the preparation of w/o emulsions generally have higher hydrophobic than hydrophilic character (low HLB value). That is the case for lipophilic emulsifiers such as sorbitan esters (Spans), monoglycerides, and polyglycerol polyricinoleate (PGPR). The latter surfactant has been widely used during recent years for the preparation of w/o emulsions [1–6], mainly because of its high emulsifying properties attributed to the excellent water-binding capacity of the long hydrophilic polyglycerol chain [7]. The microstructure and stability of w/o emulsions prepared with PGPR as emulsifier and sunflower oil as continuous lipid phase have been previously studied by our research group [1], obtaining systems with smaller water droplet size and higher stability than those prepared with Spans under the same conditions [8]. Our new research is aimed to understand the PSD of w/o emulsions prepared with PGPR and including solid fat in the continuous lipid phase.

The use of solid fat instead of liquid oil for the preparation of w/o emulsions opens the door to questions regarding the effect of the emulsifier and dispersed aqueous phase on the crystallization of the continuous lipid phase. Previous studies indicated that when a surfactant is present in a

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fat system it usually plays an important role on nucleation, crystal growth, and/or polymorphic transitions [9–11]. It has been suggested that emulsifiers can promote crystallization of triglycerides by template effects or retard the same process by the disturbance of nucleation [12, 13]. With respect to emulsified systems, it has been reported that adsorbed surfactants can promote crystallization at the interface by heterogeneous nucleation because their hydrophobic tails are faced with fat molecules [2, 4, 10, 14]. In the present work, the effect of PGPR on the SFC of w/o emulsions will be analyzed in relation to the amount and distribution of dispersed aqueous phase.

The objective of this work is to study the effect of the lipid phase composition, emulsifier concentration, water content, and homogenization energy on the PSD and SFC of w/o emulsions prepared with PGPR and solid fats. In this way, the microstructure of the systems and its influence on the crystallization of the continuous lipid phase will be analyzed.

Experimental Procedures

Materials

The following fats were used as continuous lipid phase: low trans vegetable fat (LT), refined bovine fat (BF), partially hydrogenated soybean oil (HS), and refined sunflower oil (SO). PGPR 90 (Grindsted-Danisco) was employed as lipophilic emulsifier and distilled water was used as dispersed aqueous phase. LT, BF, HS, and PGPR were provided by CALSA (Lanús, Argentina) and SO (Molino Cañuelas SACIFIA; Cañuelas, Argentina) was purchased in a local market.

The melting temperature ranges of the fats, determined by differential scanning calorimetry (DSC), were: LT, from −50 to 50 °C; BF, from −40 to 50 °C; and HS, from −20 to 45 °C. LT was obtained by interesterification of natural fatty acids and fully hydrogenated fatty acids from vegetable oil (70 % cotton oil and 30 % soybean oil, approximately). BF corresponds to refined tallow obtained from bovine tissue. The fatty acid composition of the fats is shown in Table 1. PGPR is liquid at room temperature, its density at 25 °C is 0.96 g/mL, and its purity is given by a minimum content of 90 % total fatty acid ester.

Table 1 Fatty acid composition of different fats

Sample	Fatty acid types (%)			
	Saturated	Monounsaturated	Polyunsaturated	Trans
LT	48.86	12.83	37.49	0.83
BF	53.06	39.19	2.65	4.99
HS	28.15	29.46	0.45	41.91
SO	10.83	24.17	65.00	0

The composition of LT, BF, and HS was determined by gas chromatography [15] and the information corresponding to SO was obtained from the product label

LT low trans vegetable fat, *BF* bovine fat, *HS* hydrogenated soybean oil, *SO* sunflower oil

Preparation of Emulsions

A base w/o emulsion was prepared by the homogenization of 20 g of water and 80 g of lipid phase containing LT with 1.0 % w/w PGPR as lipophilic emulsifier, using a rotor–stator homogenizer Ultra-turrax T-25 (IKA-Labortechnik; Staufen, Germany) with a S25-20NK-18G rotor (IKA-Labortechnik) at 24,000 rpm for 2 min. The following parameters were varied keeping the other parameters equal to the base emulsion: lipid phase (LT, BF, HS, and SO); PGPR concentration (0.5, 1.0, 2.0, and 4.0 % w/w); water content (10, 20, and 30 % w/w); and homogenization speed (6000, 12,000, and 24,000 rpm). Previously, the lipid phase (fat with PGPR) was melted and the aqueous phase was heated (both over 75 °C) to avoid crystallization of the fat during homogenization; the temperature of the system immediately after concluding homogenization was superior to 55 °C. In order to obtain comparative results, fats were melted and mixed with PGPR without later addition of water.

PSD

PSD of the emulsions were obtained with a particle analyzer (Malvern Mastersizer 2000E, Malvern Instruments Ltd.; Worcestershire, UK). The De Brouckere, volume-weighted, moment mean diameter (d_{43}) was obtained from the volume PSD. In order to avoid crystallization of the fat during measurement, the emulsions were diluted in hot sunflower oil (1:5; ~70 °C) immediately after their preparation, and then they were diluted again in sunflower oil at room temperature (~21 °C) in the dispersion system (Hydro 2000MU, Malvern Instruments Ltd.) at a speed of 2000 rpm. The refractive indices applied were 1.33 for particle and 1.47 for dispersant, corresponding to water and sunflower oil, respectively.

Optical Microscopy

Micrographs of the emulsions were obtained immediately after their preparation with an optical microscope operating at 400× magnification and using an adapted digital camera (Canon A570 IS; Malaysia) at 4× optical zoom. A hot stage (~50 °C) was used to avoid crystallization of the fat, so that water droplets can be better appreciated.

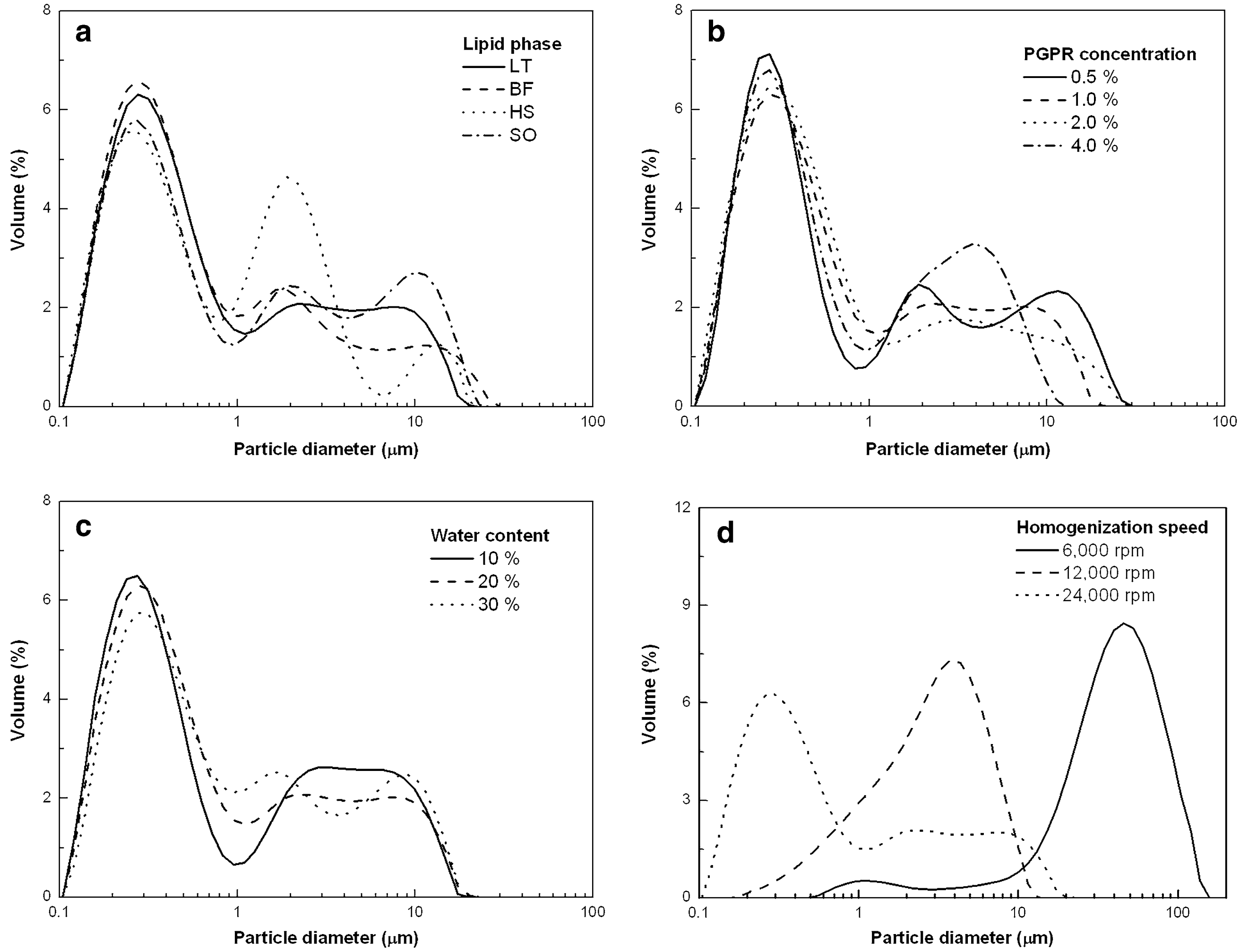

Fig. 1 Particle size distributions of w/o emulsions with variations from a base emulsion composed by low trans vegetable fat (LT), 1.0 % PGPR in lipid phase and 20 % water, homogenized at 24,000 rpm. **a** Lipid phase variation. **b** PGPR concentration variation. **c** Water content variation. **d** Homogenization speed variation

SFC and DSC

SFC of the emulsions and fats was calculated using a MDSC Q-200 instrument (TA Instruments; New Castle, DE, USA). Samples were enclosed in hermetically sealed aluminum pans immediately after their preparation and stored at 7 °C for 1 day. Then samples were cooled until 1 °C at 10 °C/min (with an isotherm at that temperature for 10 min) and heated until 70 °C at 5 °C/min. Measurements were performed with a modulation amplitude of ±1 °C every 60 s. The calculation of SFC was performed by a corrected method for SFC estimation by DSC, where melting energy is transformed into melted mass using a linear correlation between melting enthalpy and melting point of different triglycerides [16]. Because in the present work emulsions were only cooled to 1 °C to prevent freezing of the aqueous phase, a full thermogram to analyze crystallization of the fat phase was not obtained. Therefore, the method for SFC estimation was adapted using the following equation:

$$\mathrm{SFC} = \frac{\int_{T}^{T_f} m\,\mathrm{d}T}{M} \times 100 \qquad (1)$$

where m is the melted mass as a function of the temperature (T), T_f is the final temperature of melting, and M is the total sample mass weighted in the pan.

Statistical Analysis

The statistical analysis was performed by analysis of variance and test of least significant difference ($P < 0.05$) using the statistical program Statgraphics Plus 5.1. Two

Table 2 Effect of lipid phase, PGPR concentration, water content, and homogenization speed on mean particle diameter (d_{43}) of w/o emulsions

Lipid phase	PGPR concentration (%)	Water content (%)	Homogenization speed (rpm)	d_{43} (μm)[a,b]
LT	1.0	20	24,000	2.10 ± 0.14a
BF	1.0	20	24,000	2.08 ± 0.09a
HS	1.0	20	24,000	1.94 ± 0.30a
SO	1.0	20	24,000	2.71 ± 0.10b
LT	*0.5*	20	24,000	3.05 ± 0.20a
LT	*1.0*	20	24,000	2.10 ± 0.14b
LT	*2.0*	20	24,000	1.86 ± 0.25b
LT	*4.0*	20	24,000	1.74 ± 0.27b
LT	1.0	*10*	24,000	2.09 ± 0.13a
LT	1.0	*20*	24,000	2.10 ± 0.14a
LT	1.0	*30*	24,000	2.04 ± 0.30a
LT	1.0	20	*6000*	41.23 ± 1.84a
LT	1.0	20	*12,000*	2.84 ± 0.48b
LT	1.0	20	*24,000*	2.10 ± 0.14b

Italics indicates which factor is varied

LT low trans vegetable fat, *BF* bovine fat, *HS* hydrogenated soybean oil, *SO* sunflower oil

[a] Values are means of two replicates ± SD

[b] Mean values with different letters for each varied factor are significantly different ($P < 0.05$)

independent replicates were measured at least two times in each experiment.

Results and Discussion

PSD

Figure 1 shows the PSD, expressed as differential volume, of w/o emulsions with variations of different parameters. The effect of the variation of the continuous lipid phase can be observed in Fig. 1a, studying the use of different fats (LT, BF and HS) and liquid oil (SO). At the employed conditions of preparation, every lipid phase led to emulsions with trimodal distributions, with approximate modes at 0.3, 2, and 10 μm. In all cases the major population corresponded to 0.3 μm, without important variations in the volume percentage of droplets in that population. However, some differences were observed in the other two populations. The emulsion prepared with HS presented a population with higher volume of droplets with a diameter of 2 μm, while the system prepared with SO showed a higher volume of droplets of 10 μm. Furthermore, no significant differences were observed between the d_{43} values given by the fats, but the emulsion prepared with SO showed a higher d_{43} value (Table 2). This last result indicates that a higher proportion of unsaturated fatty acids leads to w/o emulsions with bigger water droplets. According to Israelachvili [17], the attractive force (A) between two water droplets in the continuous lipid phase is expressed as follows:

$$A = a\left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^2 + b\frac{\left(n_1^2 - n_2^2\right)^2}{\left(n_1^2 + n_2^2\right)^{3/2}} \tag{2}$$

where n_i and ε_i are the refractive index and the dielectric constant of phase i, respectively, and a and b are constants. This equation indicates that the attractive force is reduced when the difference between the refractive indices and/or the dielectric constants of the two phases is diminished. Because the refractive indices of saturated triglycerides are lower than the corresponding to unsaturated triglycerides (60 °C) [18], they are more proximate to the refractive index of water. And although the dielectric constant of the lipid phase tends to increase and be more proximate to water with increasing number of double bonds [18], this variation is relatively low and the dielectric constant of water is too high in comparison, so in this case the effect on the attractive force is insignificant. Thus, the use of a continuous lipid phase with higher content of unsaturated triglycerides would increase the attractive force between water droplets, producing a higher degree of coalescence during homogenization and/or immediately after preparation of the emulsion. This would explain the higher d_{43} value observed with SO in comparison to LT, BF, and HS. A similar effect was observed in a previous study of w/o emulsions prepared with PGPR as emulsifier and SO as lipid phase, where a lower d_{43} value was detected when the difference between the refractive indices of the two phases was diminished, but in that case it was attributed to the increase of the refractive index of the aqueous phase because of the addition of calcium salt [1].

The PSD observed at different PGPR concentrations in lipid phase are shown in Fig. 1b. The population at 0.3 µm did not present important changes with the variation of the emulsifier concentration. On the other side, the distribution corresponding to particle diameters higher than 1 µm was clearly affected by the increase of PGPR concentration. In that range, the emulsion with 0.5 % w/w PGPR showed two modes where the emulsion with 4.0 % w/w PGPR presented only one, observing intermediate situations at intermediate concentrations. Thus, the increase of PGPR concentration produced a change from trimodal to bimodal distribution. A similar effect was previously observed in w/o emulsions prepared with PGPR and SO as lipid phase, where the homogenization conditions produced two populations that tended to be less defined with the increase of emulsifier content [1]. Moreover, the d_{43} values showed a tendency to decrease with the increase of PGPR concentration, even though only the emulsion with 0.5 % w/w PGPR presented a significantly higher d_{43} value (Table 2). These results indicate that the capability to produce more interfacial area because of the higher emulsifier quantity tended to reduce the emulsion polydispersity at same homogenization conditions.

With regard to the effect of water content, the PSD presented similar changes to those produced by the variation of PGPR concentration (Fig. 1c). In point of fact, the increase of dispersed aqueous phase percentage from 10 to 30 % w/w turned the distributions from bimodal to trimodal. In this case, the increase of polydispersity would be attributed to the reduction of the emulsifier/water ratio, considering that the PGPR concentration was maintained. Thus, the effect produced by the increase of water content can be compared to the changes produced by the decrease of PGPR concentration, as less emulsifier quantity was available per volume unit of water. According to these results, the PGPR/water ratio where the modality of the PSD is changed would be slightly superior to 1:25 in emulsions prepared with LT at 24,000 rpm. The variation of water content, in spite of its effect on the PSD, did not lead to significant differences between the d_{43} values (Table 2).

The variation of the homogenization energy, at the selected speeds, produced the most notorious changes in the PSD of the emulsions (Fig. 1d). While the system homogenized at 24,000 rpm showed its major population with mode at 0.3 µm, the emulsions prepared at 12,000 and 6000 rpm presented their main populations at 4 and 50 µm, respectively. Consequently, a decrease of the d_{43} values was observed with the increase of the homogenization speed (Table 2), because of the generation of more interfacial area as a consequence of a higher energy input [19]. These results were confirmed by optical microscopy (Fig. 2); considerably bigger water droplets were observed in the emulsion homogenized at 6000 rpm.

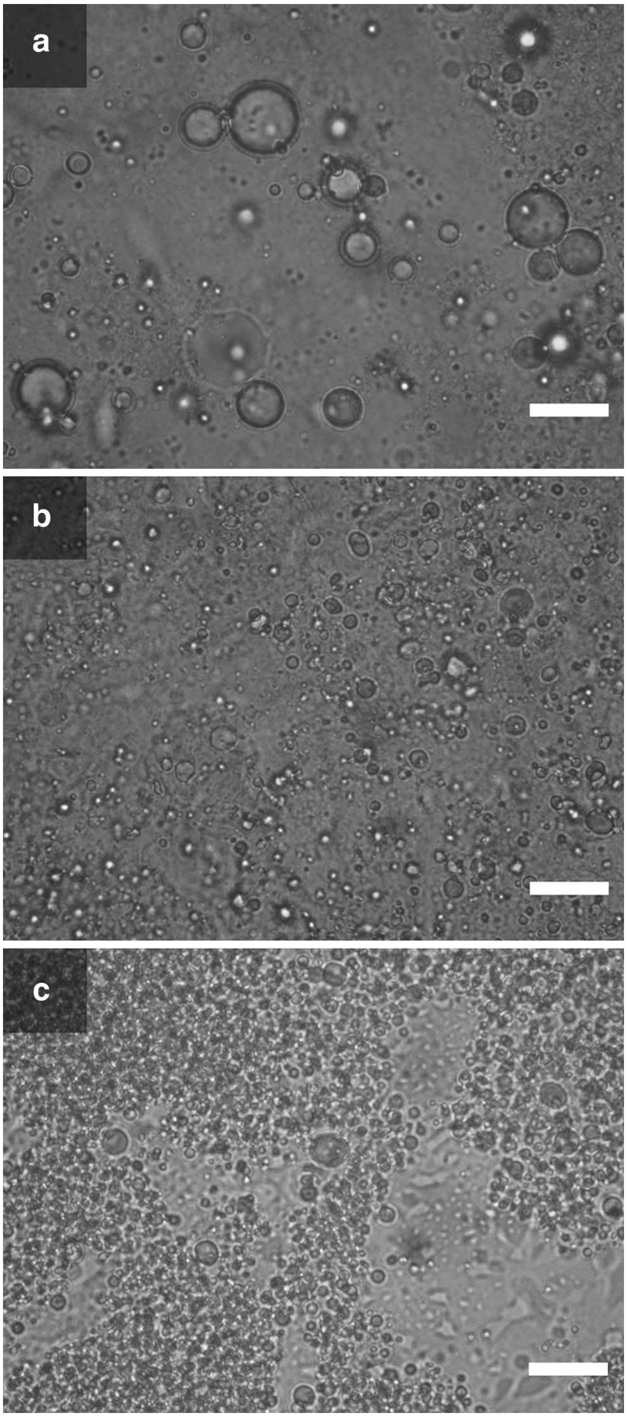

Fig. 2 Optical micrographs of w/o emulsions composed by low trans vegetable fat (LT), 1.0 % PGPR in lipid phase and 20 % water, homogenized at different speeds: **a** 6000 rpm; **b** 12,000 rpm; **c** 24,000 rpm. *Bar* 20 µm

SFC

The SFC of the w/o emulsions was clearly linked to the nature of the fat selected as lipid phase (Fig. 3a). At lower

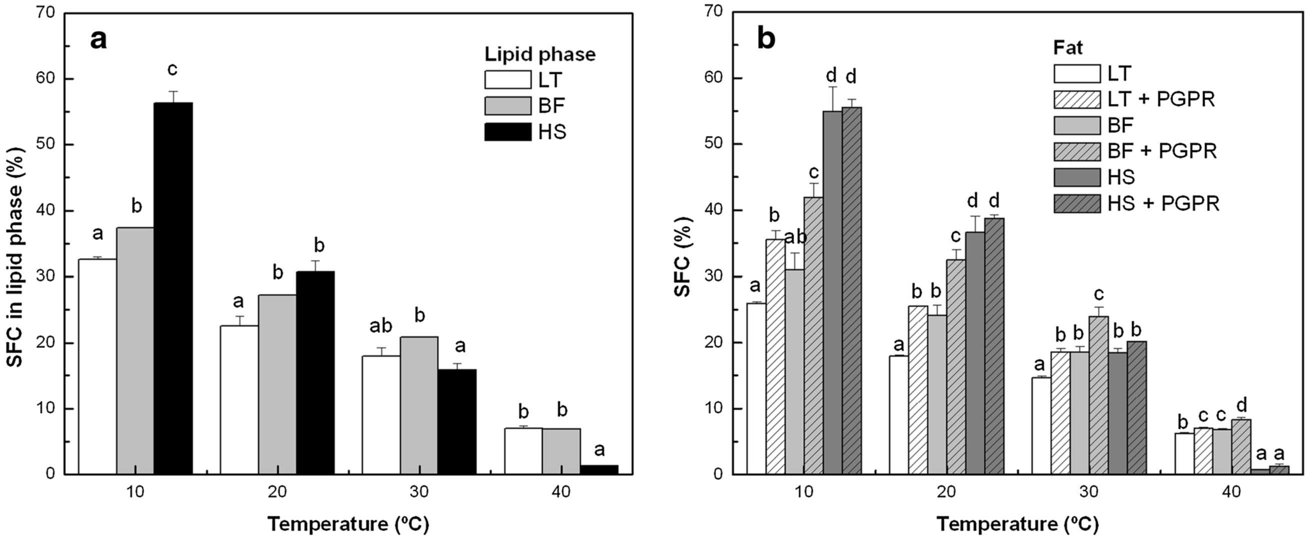

Fig. 3 **a** Effect of lipid phase variation on the solid fat content (SFC) of w/o emulsions with 1.0 % PGPR in lipid phase and 20 % water, homogenized at 24,000 rpm. **b** SFC of different fats without emulsifier or with 1.0 % PGPR. Values are means of two replicates and *error bars* indicate SD. Mean values with *different letters* for each temperature are significantly different ($P < 0.05$)

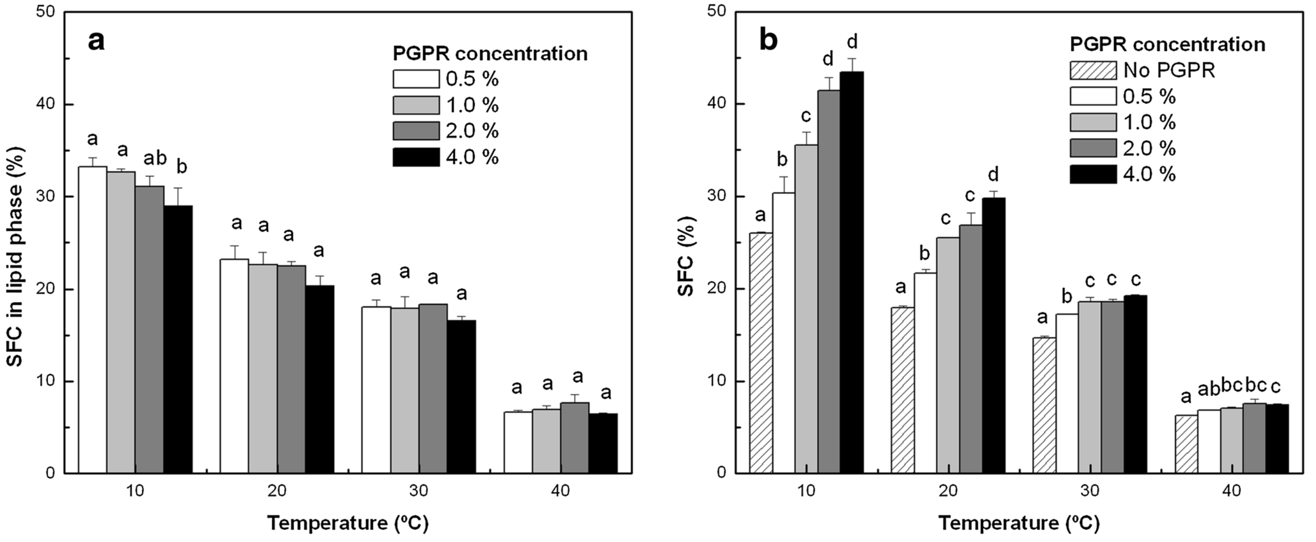

Fig. 4 **a** Effect of PGPR concentration variation on the solid fat content (SFC) of w/o emulsions composed by low trans vegetable fat (LT) and 20 % water, homogenized at 24,000 rpm. **b** Effect of PGPR concentration variation on the SFC of LT. Values are means of two replicates and *error bars* indicate SD. Mean values with *different letters* for each temperature are significantly different ($P < 0.05$)

temperatures (10–20 °C) the order of SFC in the lipid phase of the emulsions was HS > BF > LT, but at higher temperatures (30–40 °C) the emulsions prepared with LT and BF presented similar results while HS gave the lowest SFC value due to its lower melting point. The same relations between samples were observed when the SFC was analyzed on the fats with and without addition of PGPR and without added water (Fig. 3b). However, the presence of the PGPR led to higher SFC values in LT and BF in comparison to the same fats without emulsifier, an effect that is explained below. Nevertheless, this effect was not observed in HS, indicating that this increase of SFC depends not only on the presence of the emulsifier but also on the nature of the fat.

The variation of PGPR concentration in lipid phase did not seem to affect the SFC of the emulsions, except for a slight diminution of the SFC value observed at 10 °C with increasing emulsifier content (Fig. 4a). However, when the fat (LT) was analyzed in the absence of water, the increase of PGPR concentration produced an increase of the SFC values (Fig. 4b). The DSC thermograms indicated that the presence of PGPR in LT produced an increase of the total heat flow area between 25 and 40 °C, due to the higher non-reversible component in that range (Fig. 5a, b). A previous work reported that PGPR induces the formation of more stable polymorphs in tristearin during crystallization [9]. According to the authors, PGPR adsorbs onto the fat nuclei during cooling, favoring the formation of β’-form instead of α. It should be noted that the fat without emulsifier (Fig. 5a) presented a higher total heat flow area at lower temperatures (between 5 and 10 °C) in comparison to the fat with PGPR (Fig. 5b), probably because of a higher proportion of less stable polymorphs. Then, the addition of PGPR would lead to the formation of higher melting point crystals, enriching the 25–40 °C fraction because of the formation of more stable polymorphs. This would explain the increase of SFC with increasing PGPR concentration in the fat at the studied temperatures. Also, it should be considered that PGPR remains at liquid state at temperatures superior to 0 °C (confirmed by DSC), so the emulsifier would not contribute solid material to the fats. The contradictory results observed in the emulsions, where the increase of PGPR concentration did not produce an increase of SFC (Fig. 4a), may be explained by the emulsifier adsorption at the interface, reducing the amount of surfactant available to affect crystallization in bulk fat. Actually, the thermogram corresponding to the emulsion prepared with 4.0 % w/w PGPR (Fig. 5c) was similar to the thermogram of the fat without emulsifier (Fig. 5a), in both cases observing less crystallization in the 25–40 °C range than the fat with 4.0 % w/w PGPR (Fig. 5b). Moreover, as it was previously observed, the increase of PGPR concentration tended to decrease the d_{43} value of the emulsions (Table 2), indicating that more interfacial area was created, and thus higher emulsifier quantity would be located at the interface. This would explain the non-observation of SFC increase in the emulsions when PGPR concentration was increased. Although it has been stated that adsorbed emulsifiers (e.g. monoglycerides) can promote interfacial crystallization [4, 10, 14], this effect was not observed with PGPR as the only surfactant in previous studies, probably because its structure is incompatible with the aliphatic chains of the triglycerides [2]. The emulsion prepared with 4.0 % w/w PGPR even presented a significantly lower SFC value in comparison to 0.5 and 1.0 % w/w PGPR at 10 °C (Fig. 4a), but this result may be explained by the higher replacement of solid fat by liquid emulsifier in the lipid phase.

A significant diminution of the SFC in lipid phase was detected when the water content of the emulsion was increased (Fig. 6a). Specifically, the systems with 0–10 % w/w water showed higher SFC values in their lipid phase

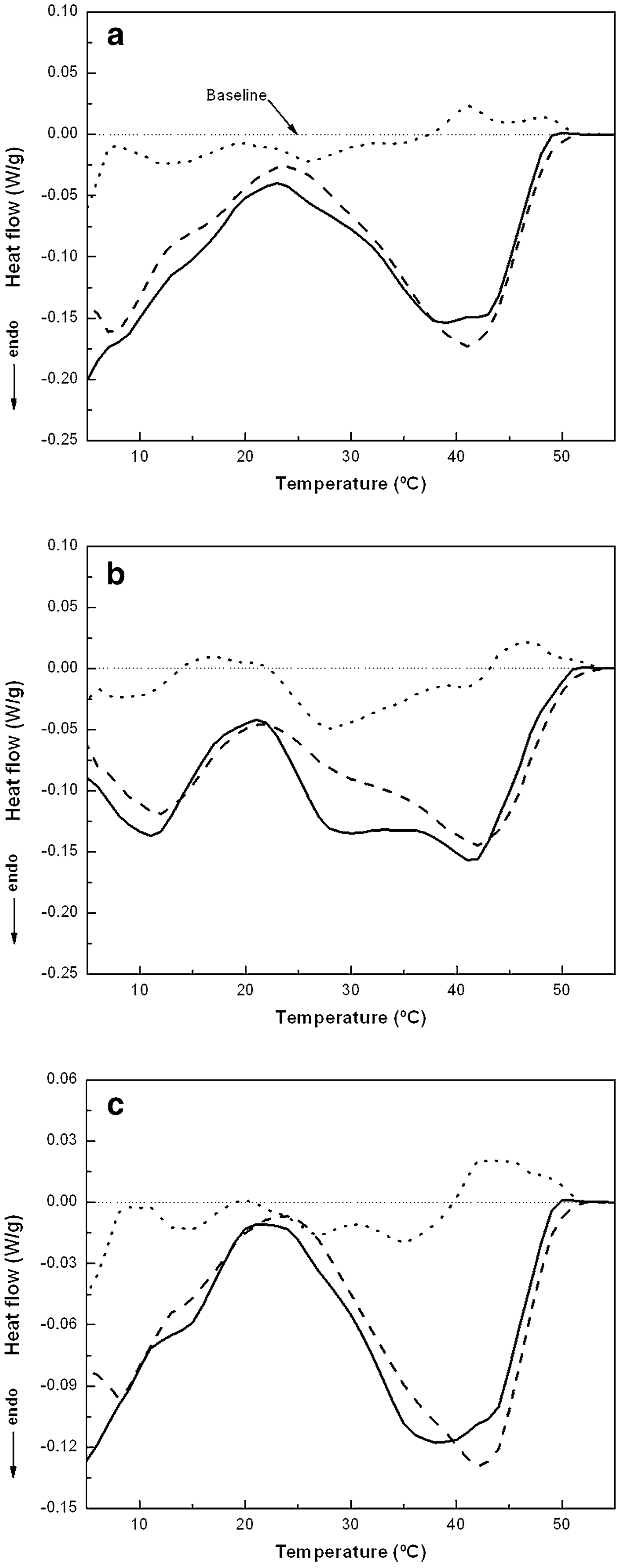

Fig. 5 DSC thermograms showing total heat flow (*solid line*), reversible heat flow (*dashed line*), and non-reversible heat flow (*dotted line*) as a function of temperature. **a** Low trans vegetable fat (LT). **b** LT with 4.0 % PGPR. **c** W/o emulsion composed by LT, 4.0 % PGPR in lipid phase and 20 % water, homogenized at 24,000 rpm

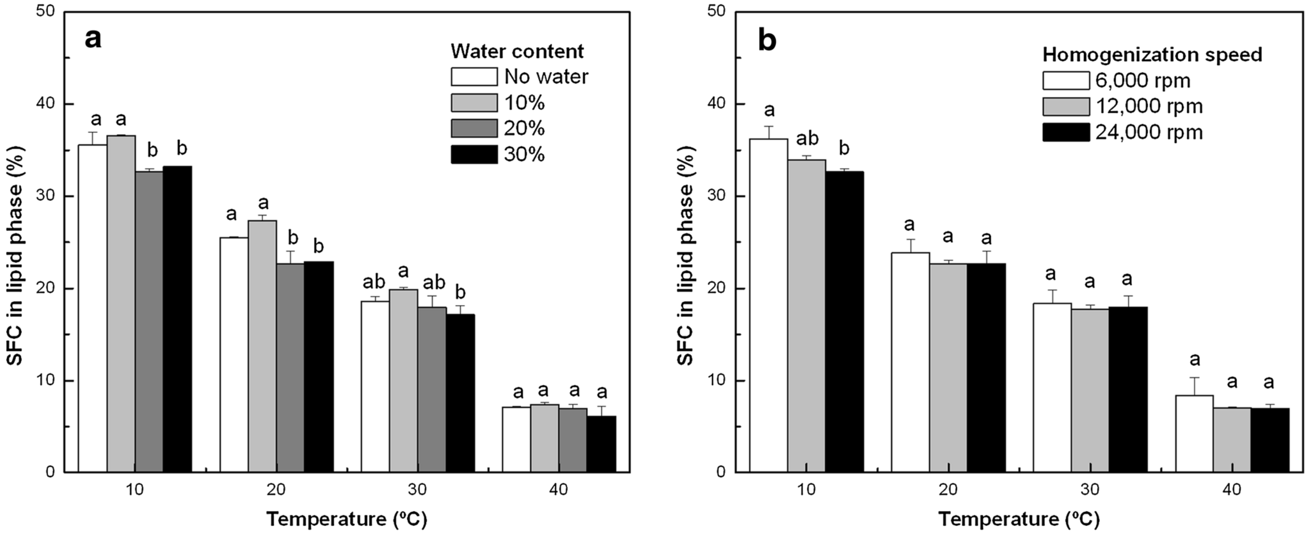

Fig. 6 **a** Effect of water content variation on the solid fat content (SFC) of w/o emulsions composed by low trans vegetable fat (LT) and 1.0 % PGPR in lipid phase, homogenized at 24,000 rpm. **b** Effect of homogenization speed variation on the SFC of w/o emulsions composed by LT, 1.0 % PGPR in lipid phase and 20 % water. Values are means of two replicates and *error bars* indicate SD. Mean values with *different letters* for each temperature are significantly different ($P < 0.05$)

than the emulsions with 20–30 % w/w water at 10–20 °C. Because the variation of water content did not produce significant changes in the d_{43} values (Table 2), it can be assumed that the increase of volume fraction of dispersed aqueous phase led to the formation of more interfacial area, demanding a higher emulsifier quantity at the interface. Taking into account that in this case the PGPR concentration in lipid phase (1 % w/w) was kept constant, it could be inferred that the amount of surfactant in bulk fat would be reduced with the increase of water content, producing a lower effect on the crystallization of the lipid phase manifested by a lower SFC value. Thus, these results confirm that the presence of dispersed aqueous phase reduces the effect of PGPR on fat crystallization, probably because of the adsorption of the emulsifier at the interface.

Finally, the increase of the homogenization speed produced a significant diminution of the SFC value at 10 °C (Fig. 6b). As it was previously observed, the d_{43} values decreased with increasing homogenization speed (Table 2), indicating an increase of the interfacial area because the dispersed aqueous phase percentage (20 % w/w) was not varied in this case. Because a higher emulsifier quantity would be required to cover the larger interfacial area, and considering that the PGPR concentration in lipid phase (1 % w/w) was also maintained, the amount of surfactant in bulk fat and its effect on the crystallization of the lipid phase would be diminished. This would explain the lower SFC value observed at higher homogenization speed, in agreement with the previous explanations regarding the reduced effect of PGPR on fat crystallization due to the presence of dispersed aqueous phase.

Conclusions

The results obtained in this work allowed to analyze the influence of the lipid phase, PGPR concentration, water content, and homogenization speed on the PSD and SFC of w/o emulsions. The use of different fats as continuous lipid phase produced slight changes in the PSD and naturally modified the SFC of the systems. The decrease of PGPR concentration or the increase of water content tended to increase the emulsion polydispersity, as this characteristic seems to be related to the emulsifier/water ratio. While the increase of PGPR concentration led to the increase of the SFC of LT fat in the absence of water, it did not produce the same effect in the presence of dispersed aqueous phase. This result was attributed to the location of the emulsifier at the interface, reducing the effect of the surfactant on the crystallization of the lipid phase. The SFC determination at varied water content or droplet size confirmed the last explanation, as the SFC value decreased with increasing interfacial area. This research could be useful for the design and preparation of food emulsions such as margarines, with the possibility of approaching the required characteristics by the control of different factors.

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