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ORIGINAL PAPER

Effect of Processing Conditions on the Crystallization Behavior and Destabilization Kinetics of Oil-in-Water Emulsions

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Abstract The objective of this research was to systematically study the effect of processing conditions on the crystallization behavior and destabilization mechanisms of oil-in-water emulsions. The effect of crystallization temperature (T_c) and homogenization conditions on both thermal behavior and destabilization mechanisms were analyzed. Results show that the crystallization of lipids present in the emulsions was inhibited when compared with bulk lipids as evidenced by a lower onset and peak temperature (T_{on} and T_p, respectively) in differential scanning calorimetry crystallization exotherms. The smaller the droplet size in the emulsion, the more significant the inhibition (lower T_{on} and T_p). Lower values of T_{on} and T_p were not necessarily indicators of emulsion stability. Homogenization conditions not only affected the T_{on} and T_p of crystallization but also the crystallization profile of the samples. Lipids present in emulsions with small droplets were crystallized and melted in a less fractionated manner when compared to lipids in bigger droplets or even to the bulk lipids. The amount of lipid crystallized as evidenced by enthalpy values, did not have a direct relationship with the emulsions stability. Although enthalpy values increased as T_c decreased, the destabilization kinetics did not follow the same tendency as evidenced by back scattering measurements.

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Introduction

The last two decades have seen much controversy surrounding formulation of food products containing fats. The market for edible fats and oils has continually transformed as new processes are developed and health conscious consumers demand healthier foods. Many food products contain hard fats that impart particular sensory properties to food. In general these hard fats are formulated using saturated fats or *trans* fats. Although *trans* fats have clear advantages to food processors and impart desirable flavor and mouthfeel for consumers it is widely accepted that they have a negative impact on the human cardiovascular system [1]. Different strategies are used to replace *trans*-fatty acids in foods' formulations. Chemical and enzymatic interesterification, fractionation and the use of tropical fats are some of the options chosen by food industries [2, 3]. In particular, the use of tropical fats provides a quick and cheap solution for the food industry, however, they contain high amounts of saturated fatty acids such as palmitic and lauric which, although less severe, have similar anti-nutritional effects on the human body as do *trans* fats [4]. However, recent human studies show that not all saturated fats have a negative health effect. Mensink et al. [4] demonstrated that although lauric and palmitic fatty acids have a substantial negative effect by increasing the cholesterol ratio in blood, stearic fatty acids have a positive effect by decreasing it. A decrease in this ratio is associated with lower risk of cardiovascular disease in humans.

Anhydrous milk fat (AMF) has the potential to be used as a replacement for *trans*-fatty acids in the formulation of several processed foods. Its high content of stearic acid and relatively low content of palmitic fatty acids [5] makes AMF an ideal healthy alternative to improve the nutritional qualities of our foods. In addition, AMF can be blended with vegetable oils such as soybean oil (SBO) to decrease the saturated fatty acid content while maintaining some functionality. Among food products that might benefit from this lipid blend, emulsions are of especial interest due to their wide applications in foods such as dressings and mayonnaise. To use AMF and SBO in food emulsions, the effect of processing conditions, such as crystallization temperature and homogenization conditions on the stability of the emulsions needs to be studied.

Several studies have been reported during the last 30 years regarding the stability and characterization of food emulsions. The effect of lipid crystallization kinetics [6–16], pH, salt concentration, emulsifier type [17–20] and additives [21] on emulsions' stability has been previously studied. However, very little information on the effect of processing conditions on the physicochemical stability of emulsions was reported [22].

The objective of this research was to systematically study the effect of different processing conditions on the crystallization behavior and destabilization mechanisms of model emulsions formulated with a blend of AMF and SBO as the lipid phase. Processing conditions such as crystallization temperature and homogenization parameters on both the thermal behavior and destabilization phenomenon were analyzed.

Materials and Methods

Emulsion Formulation

Oil-in-water emulsions were formulated by mixing a 40% oil phase in a 60% water phase (40:60 w/w). A model emulsion containing an oil phase formulated with 50 wt% SBO in AMF was used. For the water phase, whey protein isolate (WPI) (Inpro 90: 90% WPI by Vitalus) was used as an emulsifier. Two percent of WPI was dissolved in water with sodium phosphate dibasic, 7-hydrate, crystal (0.268 g/100 mL solution) to obtain pH = 7.3 and stirred at room temperature until the proteins were completely dissolved. The solution was then filtered through Whatman 1 filter paper. The oil and water phases were then heated separately to 60 °C for at least 30 min prior to homogenization. These two phases were emulsified using two homogenization conditions. The first consisted of a high shear homogenization process (HS) using an Ultra Turrax (IKA T18 basic) at 18,000 rpm for 1 min; the second condition consisted of the HS followed by a high pressure homogenization step (HPH), using a Microfluidics Microfluidizer Processor Model M-110S, for one run through the system at 9,500 psi. To avoid crystallization of the emulsions, the microfluidizer was kept at 60 °C using a water bath. Emulsions formulated under HS conditions resulted in a larger droplet size [$d(3,2) = 14.2 \pm 1.9$ μm] when compared with HPH emulsions [$d(3,2) = 0.5 \pm 0.1$ μm]. Droplet sizes were determined using a Beckman Coulter particle characterization equipment (LS20 Version 3.19, Beckman Coulter Inc.).

Crystallization Conditions

After homogenization, samples were placed at a specific crystallization temperature (T_c = 10, 5, 0, −5 and −10 °C) and kept isothermally for 3 h. The crystallization and melting behavior of the emulsions was evaluated by differential scanning calorimetry (DSC). The physicochemical stability of the emulsions was analyzed using a TurbiScan equipment (see below).

Differential Scanning Calorimetry

The crystallization and melting behaviors of the bulk fat and emulsions were studied by DSC (TA Instruments, 2910). Five to fifteen mg of the emulsions was placed in a DSC pan after homogenization. Samples were cooled at 30 °C/min in the DSC to T_c and held there for 3 h. Samples were then heated at 5 °C/min to analyze the melting profile of the crystallized fat. Bulk fat (50% w/w SBO in AMF) was also crystallized in the DSC to evaluate the effect of emulsification on the crystallization behavior of the lipid phase. For bulk fat, a sample of 5–15 mg was placed in the DSC pan, heated to 80 °C for 15 min, and then cooled at 30 °C/min to T_c. Samples were held at T_c for 3 h, and then heated at 5 °C/min to 80 °C to evaluate their melting behavior. Crystallization and melting enthalpies, with peak and onset temperatures, were calculated for both emulsions (HS and HPH) and the bulk fat.

Physicochemical Stability

The physicochemical stability of the emulsions was studied using a vertical scan macroscopic analyzer (TurbiScan MA 2000). TurbiScan consists of a reading head moving along a flat-bottomed cylindrical cell while scanning the entire sample height. The reading head consists of a pulsed near infrared light source and two synchronous detectors: the transmission detector (T) picks up the light transmitted through the product; the backscattering detector (BS)

receives the light backscattered by the product at an angle of 135°. The reading head acquires transmission and backscattering data every 40 μm with a maximum height of 80 mm. The profile characterizes a sample's homogeneity, particle concentration, and mean diameter. A profile is represented by a curve showing the percentage of backscattered or transmitted light as a function of the sample height (in mm). The acquisition along the product is then repeated with a programmable or manually frequency, which superimposes readings of product fingerprints characterizing the stability or instability of the product. Since the emulsions analyzed in this study are opaque, only the BS profile was used to evaluate the physicochemical stability of the emulsions. Five to seven mL of the emulsions were placed in an test tube which in turn was placed in a water bath thermostatized at a specific T_c. Physicochemical stability was measured as soon as the emulsions were produced and during their crystallization at T_c for 3 h. Measurements were taken every 10 min for the first h and then after 15 min for the next 2 h. To perform the BS measurement, test tubes with the emulsions were taken from the water bath (set at T_c) and placed in the TurbiScan. After the measurement was taken (40 s) the assay tube was placed again in the thermostatized water bath. Back scattering profiles and kinetics were reported in the reference mode. The change in the thickness of the destabilization peak at half its height was used to follow the destabilization kinetics of the emulsions.

Statistical Analysis

Experiments were performed in duplicate or triplicate, as necessary. Data reported in this manuscript are the mean values calculated from the replicates. Results were analyzed for significant differences using a two-way ANOVA and a Bonferroni post-test ($\alpha = 0.05$).

Results

Effect of Homogenization Conditions on the Crystallization Behavior of Lipids

Bulk lipids and emulsions formulated under HS and HPH processing conditions were crystallized at different temperatures (−10, −5, 0, 5 and 10 °C) described in the "Materials and methods". The crystallization and melting behaviors were analyzed by DSC. Figure 1 shows the crystallization (Fig. 1a) and melting (Fig. 1b) profiles for each sample type (bulk, HS and HPH) at the T_c of −10 °C. In general, two crystallization peaks were observed for both bulk and HS samples. The first peak for the bulk samples crystallized at −10 °C shows an onset temperature (T_{on}) of

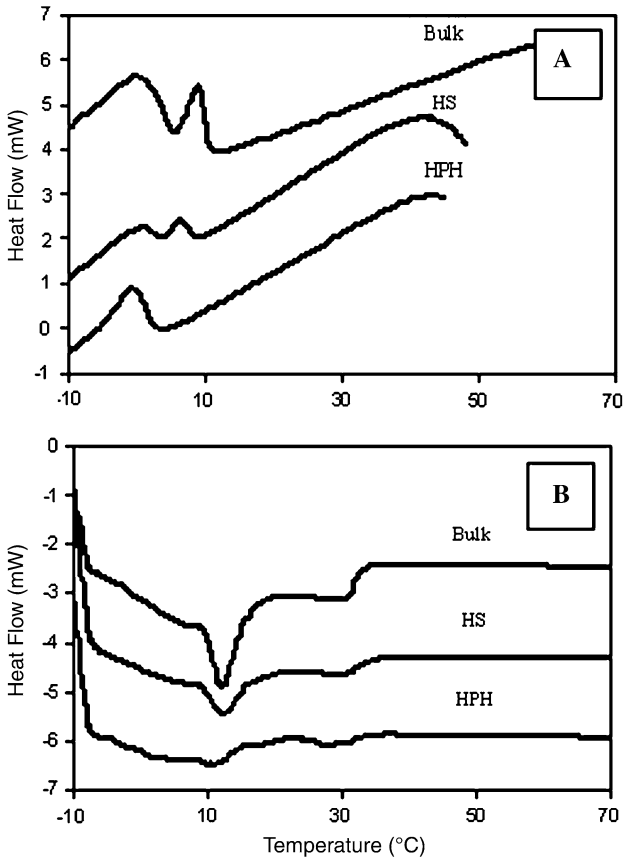

Fig. 1 Crystallization (**a**) and melting (**b**) behaviors of all samples (Bulk, HS and HPS) crystallized at −10 °C

10.24 ± 0.21 °C and a peak temperature (T_p) of 8.75 ± 0.29 °C. The T_{on} and T_p of the second crystallization peak were 4.71 ± 0.29 and −0.30 ± 0.39 °C, respectively. The T_{on} and T_p for the HS sample were 8.08 ± 0.34 and 6.18 ± 0.20 °C, respectively, for the first peak and 3.28 ± 0.13 and −0.68 ± 0.08 °C, respectively, for the second peak. The decrease in the T_{on} and T_p in the HS sample is in accordance with previous studies [6, 8, 9] and indicates that the lipid phase is completely homogenized in the emulsions. That is, there are no free lipids present after homogenizing and crystallizing the HS sample. The same behavior was observed with HPH; however, the decrease in T_{on} and T_p was more significant. In this case, the first crystallization peak shifted towards lower temperatures, with a T_{on} of 3.29 ± 0.22 °C and a T_p of −1.03 ± 0.59 °C. This same behavior was observed for all the crystallization temperatures analyzed in this study; for clarity, only the −10 °C profiles are shown in Fig. 1.

Effect of Homogenization Conditions on the Melting Behavior of Lipids

After 3 h at crystallization temperature, samples were heated at 5 °C/min to evaluate their melting profiles

(Fig. 1b). All samples showed two melting peaks. As an example, when crystallized at −10 °C, T_{on} and T_p for the first melting peak were 8.93 ± 0.04, 12.43 ± 0.27 °C, respectively, for the bulk sample; 7.66 ± 0.02 and 12.49 ± 0.02 °C, respectively, for the HS samples; and −4.38 ± 0.79 and 10.45 ± 0.37 °C, respectively, for the HPH samples. The T_{on} and T_p for the second melting peak were 24.19 ± 0.42, 30.46 ± 0.28 °C, respectively, for the bulk samples; 23.16 ± 1.56 and 30.19 ± 0.01 °C, respectively, for the HS samples; and 23.63 ± 0.79 and 27.96 ± 0.37 °C, respectively, for the HPH samples. The profiles shown in Fig. 1 suggest that the crystallization of triacylglycerides (TAGs) molecules present in the oil droplets occurs in different way depending on the homogenization conditions. When the lipid is crystallized as a bulk, that is when no water is present, the TAGs crystallize in a fractionated way as evidenced by the much defined peaks formed during the crystallization step (Fig. 1a). This means that TAGs with similar chemical composition co-crystallize resulting in different populations of crystals, each of which has similar crystallization and melting profiles. During melting, this fractionation is still present as evidenced by the small second peak at high temperatures in the DSC melting profile (Fig. 1b); however it is not as significant as the one observed during the crystallization process. The differences between the crystallization and melting profiles suggest that some molecular re-organization is taking place while the sample is held for 3 h at crystallization temperature, especially for the HS and HPH samples. Figure 1b shows that the second peak was more evident for the bulk lipid and decreased in size for HS and HPH emulsions suggesting that when lipids are present in smaller droplets they crystallize in a less fractionated manner. The same general behavior was found for all the temperatures studied (data not shown).

Comparing DSC Crystallization Parameters between Processing Conditions

Figure 2a–c compares the T_{on}, T_p and enthalpy values for the first crystallization peak for the bulk and emulsified lipids at different crystallization temperatures. Figure 2d–f shows the same parameters for the second crystallization peak. When bulk lipids were crystallized, they showed two crystallization peaks at temperatures between −10 and 5 °C and only one crystallization peak was observed at 10 °C. HS emulsions showed two crystallization peaks when crystallized at temperatures between −10 and 0 °C and only one peak was observed at 5 °C with no crystallization peak at 10 °C. HPH samples showed one crystallization peak for temperatures between −10 and 5 °C with no crystallization peak observed at 10 °C.

A decrease in the T_{on} of the first crystallization peak with emulsification conditions is observed in Fig. 2a. The T_{on} value observed for HPH samples was significantly lower for all crystallization temperatures when compared with HS emulsion and the bulk fat ($p < 0.001$). T_{on} values obtained for the HS emulsion was also significantly lower ($p < 0.05$) when compared with the bulk fat for all T_c excluding −5 °C. Even though the T_{on} was lower for HS, the difference was not significant. This behavior suggests that emulsification conditions result in a decrease of the T_{on}; the smaller the droplet size, the lower the T_{on} observed during the crystallization of the fat. For a specific sample (HS emulsion or bulk fat) T_{on} was constant for all the crystallization temperatures assayed. The only exception to this behavior was a significant increase in the T_{on} value for HPH emulsions crystallized at 5 °C ($p < 0.05$). When analyzing the second crystallization peak (Fig. 2d), T_{on} for the HS emulsions were significantly lower than the T_{on} observed for the bulk samples ($p < 0.05$) and these values were constant as a function of T_c ($p < 0.05$).

Figure 2b and e show the T_p of the first and second crystallization peak, respectively. Following the T_{on} tendencies, T_p values observed for the first crystallization peak decreased with emulsification conditions ($p < 0.001$). The smaller the droplet sizes, the lower the T_p. For both HS emulsions and the bulk fat, T_p was constant among crystallization temperatures. The T_p value observed for the HPH emulsions was constant for temperatures between −10 and 0 °C and significantly increased from 0 to 5 °C ($p < 0.001$). T_p values observed for the second crystallization peak were not significantly different between the bulk and HS samples; though a significant increase in T_p value was observed as the crystallization temperature increased (Fig. 2e). This increase in T_p at 5 °C might be a consequence of "incomplete crystallization". For high T_c, the crystallization process in HPH emulsions is not completed during the cooling of the sample and therefore a higher T_p is observed. Figure 2c and f show the enthalpies for the two crystallization peaks observed during crystallization of all the samples. The enthalpy values obtained for the emulsions are expressed in J/g of lipid. No significant differences were found in the enthalpy values of the bulk and HS samples. Significant differences ($p < 0.001$) were observed between HPH and the other samples especially at lower T_c (−5 and −10 °C). The highest enthalpy value for the first crystallization peak was observed for HPH emulsions crystallized at −10 °C and this value significantly decreased as T_c increased (Fig. 2c). This is an expected result since the lower the temperature, the higher the supercooling and therefore the higher the driving force for crystallization. However, no significant differences were found in the enthalpy values of the first crystallization peak of the bulk samples and HS emulsions as a function

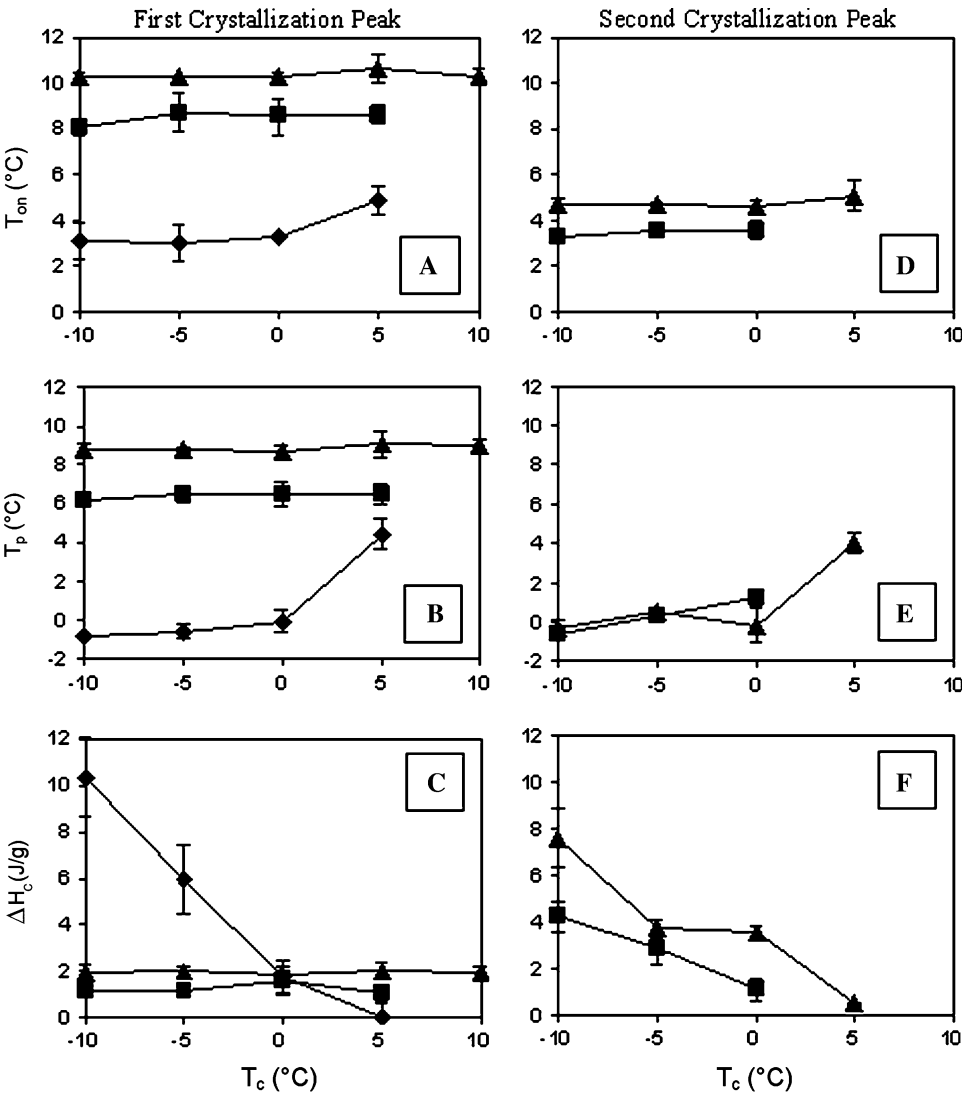

Fig. 2 Comparison of crystallization parameters among samples and crystallization temperatures. *Filled triangles* bulk sample, *filled squares* HS sample and *filled diamonds* HPH sample

of crystallization temperature. When enthalpies of the second crystallization peak for the bulk and HS samples are analyzed (Fig. 2f) significant differences for −10 and 0 °C were found and a decrease in enthalpies values with higher T_c was observed as described for the HPH first crystallization peak. These results, in combination with the decrease in the T_{on} with emulsification conditions, suggest that when the oil is entrapped in small droplets de crystallization of high melting point TAGs is inhibited.

Comparing DSC Melting Parameters among Processing Conditions

Figure 3 compares the melting T_{on}, T_p and enthalpies for all samples after being held at the given T_c for 3 h. Figure 3a–c shows the data obtained for the first melting peak and Figure 3d–f shows the data obtained for the second melting peak.

All samples exhibited two melting peaks at temperatures below 5 °C. For 10 °C, HPH samples did not show a melting peak, indicating that even after 3 h at T_c the lipid phase did not crystallize. Both HS emulsions and bulk lipids showed two melting peaks at 10 °C. For T_c below 5 °C HPH emulsions resulted in significantly lower T_{on} values when compared to HS emulsions and the bulk fat ($p < 0.001$). At 5 °C no significant differences were observed (Fig. 3a). In addition, the T_{on} observed for HS emulsions were also significantly different from the bulk T_{on} at 5, −5 and −10 °C ($p < 0.05$). The T_{on} values for HS and the bulk sample remained approximately constant for all T_c, however, the T_{on} for HPH sample increased linearly as crystallization temperature increased. For the second peak, the T_{on} did not show any significant difference among samples and a significant

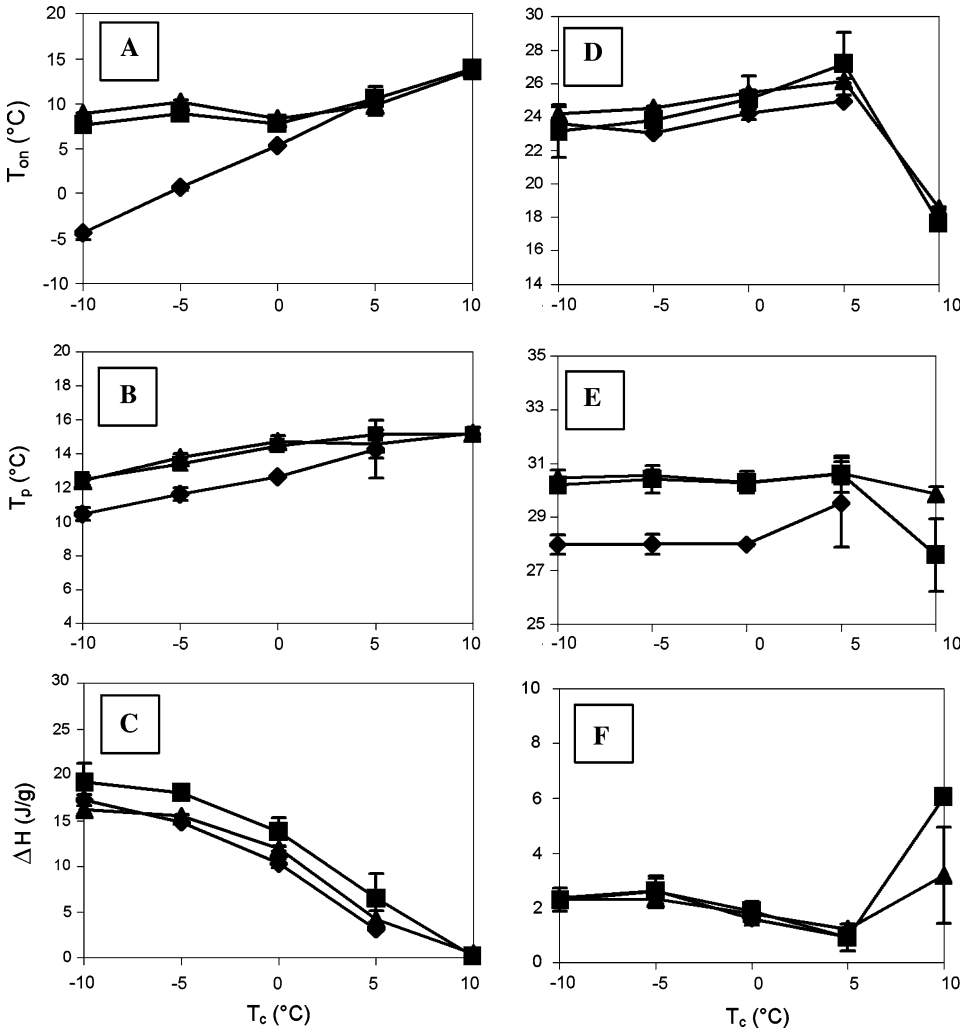

Fig. 3 Comparison of melting parameters among samples and crystallization temperatures. *Filled triangles* bulk sample, *filled squares* HS sample and *filled diamonds* HPH sample

difference was found when samples were crystallized at 5 and 10 °C ($p < 0.01$) (Fig. 3d).

Figure 3b shows the T_p values for the first melting peak for all samples. Only the T_p values observed when HPH emulsions were crystallized at −5 and −10 °C were significantly different from HS emulsions and the bulk fat ($p < 0.05$) and no differences were found between the T_p values of HS and bulk samples (Fig. 3b). In addition, T_p values increased as T_c increased, this tendency was more evident at lower T_c. The T_p values for the second melting peak were significantly lower for the HPH samples (Fig. 3e) and were not significantly different between the HS emulsions and the bulk fat. Melting enthalpies for both peaks were not significantly different between samples; however, as expected, a significant decrease ($p < 0.001$) was observed as T_c increased, especially for the first melting peak enthalpies.

In summary, the melting behavior of the lipid phase was mainly affected by the HPH emulsification condition, especially for the T_{on} of the first peak and on the T_p of the second peak. These differences became more important at lower crystallization temperatures (i.e. below 5 °C). The significant difference found for T_{on} and T_p values for HPH emulsions crystallized at T_c below 5 °C can be explained by considering the different crystallization behavior observed in HPH emulsions. That is, while crystallization is almost complete for the bulk samples and the HS emulsions during the cooling of the system, HPH emulsions continue to crystallize during the 3 h at T_c. Therefore, at lower T_c, TAGs of lower melting points crystallize during the isothermal period resulting in a lower T_{on} and T_p (Fig. 3a, b, e). The small differences observed among the processing conditions can be explained by considering that samples were kept at crystallization temperature for a long period of time (3 h), and therefore complete crystallization of the lipids present in the emulsion was achieved with the exception of HPH emulsions.

Physicochemical Stability of the Emulsions

The physicochemical stability of the HS and HPH emulsions was measured using light scattering equipment

(TurbiScan) as described in the "Materials and methods". Figure 4 shows the delta backscattering (ΔBS) profiles of HS (Fig. 4a) and HPH (Fig. 4b) emulsions during the crystallization process (3 h). A decrease in ΔBS values at the bottom of the tube indicates a clarification process that develops as a consequence of creaming destabilization, which is represented by an increase of ΔBS values at the top of the tube. Alternatively, when ΔBS values increase at the bottom of the tube, then the emulsion is undergoing destabilization by a sedimentation process causing clarification to occur (indicated by a decrease in ΔBS values) at the top of the tube.

Figure 4a illustrates a typical profile for HS samples. The destabilization process for these samples is creaming, which is shown by a large decrease in ΔBS values at the bottom of the tube (clarification) and a small increase at the top (creaming). In addition to the typical creaming and clarification peaks, HS samples show an additional clarification peak at the top of the tube (second clarification). In summary, three phases developed during the HS destabilization process: two clarification phases (one at the bottom and the other one at the top) and one creaming phase close to the top of the tube. However, for HPH (Fig. 4b), the destabilization process is radically different from HS. Instead of a clarification peak at the bottom, a sedimentation peak (note the increase of ΔBS values) is observed, and a very pronounced clarification peak at the top of the tube can be observed.

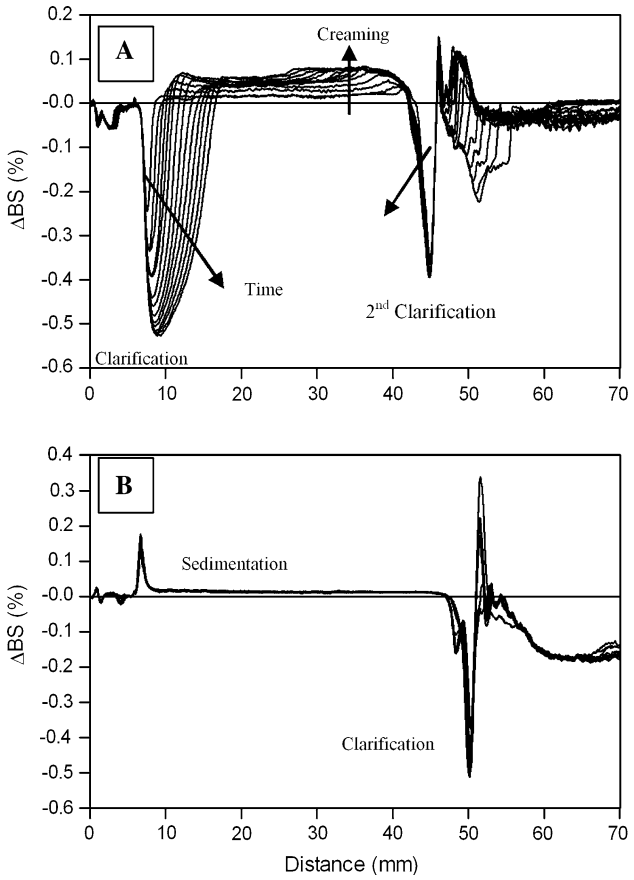

Fig. 4 Delta back scattering profiles of HS (**a**) and HPH (**b**) crystallized at −5 °C as a function of time

Effect of Crystallization Temperature on the Destabilization Kinetics of Emulsions

Figures 5 and 6 show the destabilization kinetics of HS and HPH emulsions, respectively, as a function of crystallization temperature. Figure 5a shows the clarification kinetics for HS samples. From this Figure the migration rate can be calculated as the slope of the first portion of the clarification kinetics. The migration rates obtained from the kinetics observed at the bottom of the tube (clarification) are: 0.062 ± 0.001, 0.043 ± 0.006, 0.027 ± 0.002, 0.041 ± 0.001 and 0.049 ± 0.001 mm/min for 10, 5, 0, −5 and −10 °C, respectively. Although these values are not significantly different ($p < 0.05$), trends show a minimum in clarification kinetics at 0 °C. The migration rate decreases between −10 and 0 °C and increases from 0 to 10 °C. When HS emulsions are crystallized at −10 °C, the clarification process reaches a plateau after 20 min at T_c, which means that at this temperature, the destabilization kinetics is fast (high migration rate) but is rapidly inhibited (low ΔBS value) by the low temperature. Alternatively, crystallization temperatures of −5 and 0 °C have approximately the same effect on the clarification kinetics; the sample gradually destabilizes during the 3 h period with a slower migration rate. The same behavior is observed for HS samples crystallized at 5 and 10 °C; however, the kinetics are faster (higher migration rates). Figure 5b shows the creaming kinetics for the HS emulsions. In accordance to the migration rates, the creaming kinetics are faster for lower crystallization temperatures however, these differences are not significant. When the second clarification peak was analyzed in Figure 5c, no significant differences were observed in the clarification kinetics, with only HS emulsions at 0 °C being slightly less stable than the rest. HS second clarification kinetics were very quick, reaching a plateau approximately 10 min after the sample was placed at T_c. This data suggests that the destabilization mechanism of HS emulsions involves several steps. The first and fastest phenomenon is separation of the phases at the top of the tube through creaming and clarification. This phenomenon is independent of the crystallization temperature and is probably dependent only of the droplet size. The second and slower mechanism is the clarification occurring at the bottom of the tube. From Fig. 5 we can conclude that the best way to study the destabilization kinetics of the oil in water emulsions studied in this work is

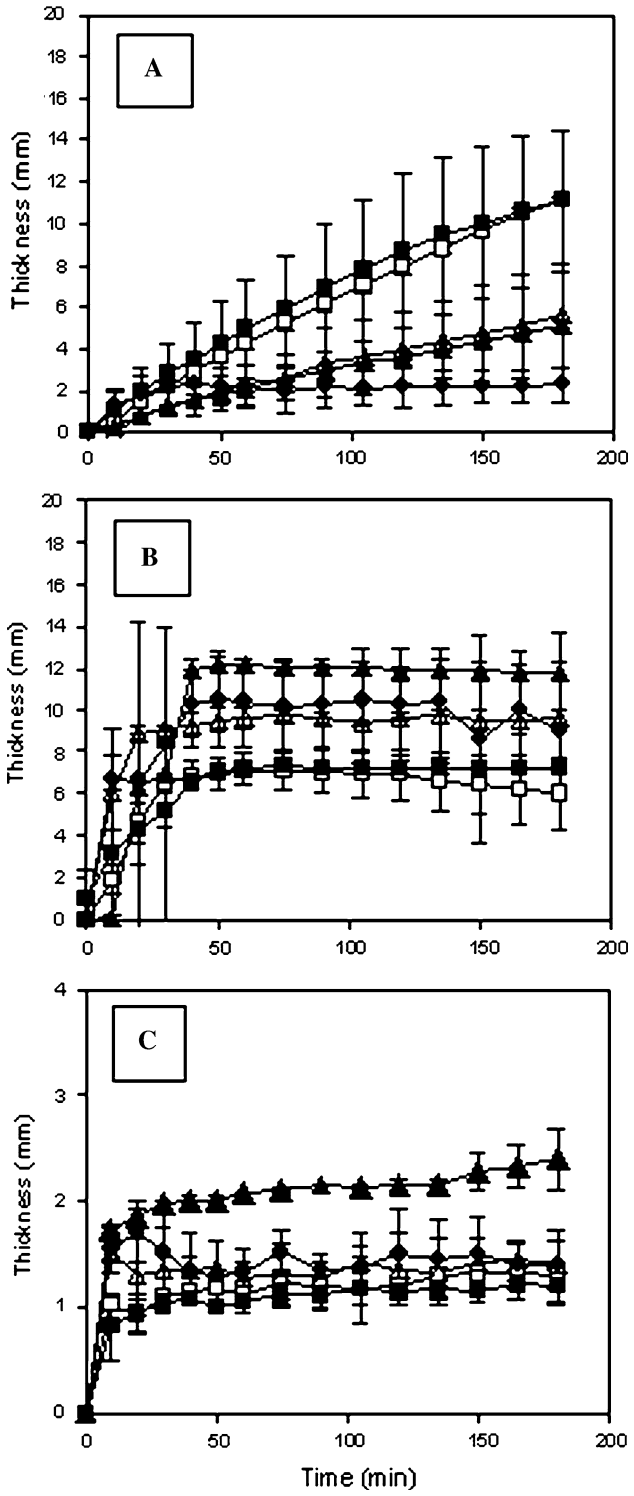

Fig. 5 Destabilization kinetics for HS emulsions (determined by BS measurements) as a function of crystallization temperature. **a** Clarification observed at the bottom of the tube, **b** creaming and **c** clarification observed at the top of the tube. *Open squares*, 10 °C; *filled squares*, 5 °C; *filled triangles*, 0 °C; *open triangles*, −5 °C and *filled circles* −10 °C

by using the clarification profile observed at the bottom of the tube since this is the slowest phenomenon and the one that shows more differences with processing conditions (Fig. 5a).

Figure 6 shows the destabilization kinetics of the HPH emulsions. Combining the profile shown in Fig. 4b with Fig. 6, it can be observed that HPH emulsions are more stable than HS emulsions. The migration rates calculated from Fig. 6a are: 0.012 ± 0.001, 0.012 ± 0.01, 0.034 ± 0.014, 0.066 ± 0.013 and 0.27 ± 0.21 mm/min for 10, 5, 0, −5 and −10 °C, respectively. A significant decrease in the migration rates values as a function of increasing T_c was observed ($p < 0.05$). No significant differences were found between these values and the values observed for HS. However, the destabilization profile is significant different between these two emulsions. Comparing Figs. 6a and 5a we can observe that for HPH the BS change reaches a plateau after 10 min at T_c; while for HS emulsions, the BS continuously increases during the crystallization period (Fig. 5a). In addition, the final relative thickness of the peak for the HPH emulsions is significantly lower than the one found in HS emulsions, indicating a more stable system. The increased stability observed for the HPH emulsions can be explained due to the smaller droplets generated during the high pressure homogenizer step. No significant differences were found for the clarification kinetics (Fig. 6b) for the different crystallization temperatures. However, it is important to note that emulsions crystallized at −10 °C show a significantly different behavior compared to other crystallization temperatures. When these samples were placed at $T_c = -10$ °C they froze after approximately 25 min. This freezing behavior is responsible for the high standard deviation and different destabilization kinetics. The presence of freezing in HPH emulsions observed at −10 °C and absent in HS emulsions suggests that small droplets, as the ones observed in HPH emulsions might act as nuclei for water crystallization, thereby inducing the emulsion's freezing. However, more research is needed in this area to understand the molecular mechanisms involved in this process.

Conclusions

The stability of oil in water emulsions formulated with a blend of SBO and AMF is strongly affected by processing conditions. Emulsions formulated using HS were significantly more unstable than HPH emulsions. They destabilized through a creaming phenomenon, while HPH destabilized through a sedimentation mechanism. In addition, HS

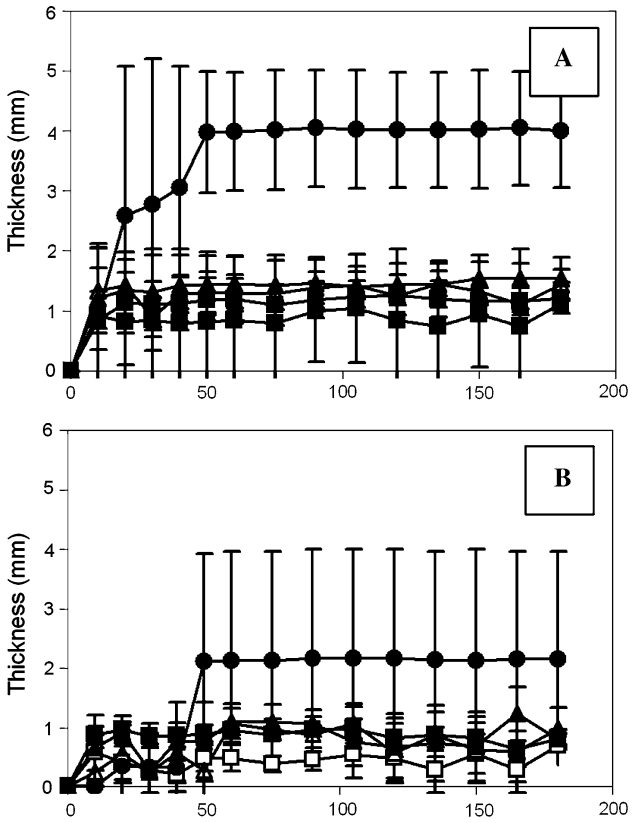

Fig. 6 Destabilization kinetics for HPH emulsions (determined by BS measurements) as a function of crystallization temperature. **a** Sedimentation observed at the bottom of the tube, and **b** clarification observed at the top of the tube *open squares*, 10 °C; *filled squares*, 5 °C; *filled triangles*, 0 °C; *open triangles*, −5 °C and *filled circles* −10 °C

stability was somewhat dependent on crystallization temperature while HPH emulsions' stability did not depend on crystallization temperature.

The crystallization behavior of SBO and AMF emulsions was also affected by processing conditions. Lipid crystallization in the emulsions was inhibited when compared with bulk samples. This inhibition is very significant in emulsions with small droplets ($\sim$0.5 μm). As expected, the amount of total lipid crystallized in the droplets, as evidenced by the enthalpies values, is dependent on the T_c: the lower the T_c, the more crystallized material found in the droplets. However, the amount of lipid crystallized in the droplet does not necessary correlate with the emulsion stability. This is very evident for emulsions with small droplets (HPH) since the stability of these systems was independent on the T_c. In addition, the crystallization profile of the lipid blend in the emulsions is affected by homogenization conditions. The lipid phase present in small droplets crystallizes in a less fractionated manner showing one broad crystallization peak. The bigger the droplet the more fractionated the crystallization and melting profile with more defined crystallization and melting peaks.

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