

Effects of Sucrose Esters on Isothermal Crystallization and Rheological Behavior of Blends of Milk-fat Fraction Sunflower Oil

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ABSTRACT: Crystallization kinetics and rheological behavior of blends of high-melting milk-fat fraction (HMF) and sunflower oil (SFO) with and without addition of the sucrose esters P-170, S-170, and P-1670 were investigated. Addition of sucrose esters delayed crystallization, as was evidenced by the longer induction times of crystallization (τ) and the lower maximum solid fat content (S_{\max}). Values of penetration force and time corresponding to the 1st peak of curves force compared with time also diminished with addition of SFO. When sucrose esters were added, a solid fat content greater than 10% at the 1st crystallization temperature was necessary to give a stronger structure that could be noticed as higher yield point.

Keywords: high-melting fraction of milk fat, sunflower oil, sucrose esters, isothermal crystallization, rheology

Introduction

EMULSIFIERS ARE USEFUL FUNCTIONAL ADDITIVES WITHOUT WHICH many food products would be impossible to make. Emulsifiers typically act in multiphase systems in 2 main ways. The 1st is as an emulsifying agent to enable 2 distinct phases to be combined in a stable quasi-homogeneous state for an indefinite length of time. The 2nd function of an emulsifier is often to modify the behavior of the continuous phase of a food product so as to bring about a specific effect or benefit, for example, the use of lecithin in chocolate to reduce the viscosity of the product and improve the ease of handling and processability. Sucrose esters (SE) have a common feature that makes them suitable as emulsifying agents: they are amphiphilic, possessing both lipophilic and hydrophilic properties. The nature of this property is often expressed as the hydrophilic/lipophilic balance (HLB) on a scale of 0 to 20, with low numbers indicative of the oil-like tendency (Weyland 1997).

Rheological measurements of fats can be performed at low or high deformation. In the latter, the fat crystal network undergoes irreversible deformation, whereas in the former, viscoelasticity is measured below the yield point, and is reversible. For practical applications of solidified fat, mechanical properties related to large deformations are usually more important. These properties can be characterized by measurable quantities such as yield strain, yield stress, and apparent viscosity. An often-used and convenient method to characterize the firmness of semi-solid substances is penetrometry (Haighton 1959), which gives an apparent yield stress. It is called an "apparent" yield stress because during the measurement, the sample is strongly deformed locally. It is often found that apparent yield stress is proportional to other measures for firmness, such as apparent Young modulus measured by uniaxial compression (Kloek 1998) or an apparent elastic shear modulus (Narine and Marangoni 1999).

The rheological behavior of plastic fats is governed by interactions between fat crystals in an aggregated, 3-dimensional, solid-liquid fat matrix. The liquid portion of the fat, interspersed throughout the aggregated fat network, serves as a continuous

phase and, in conjunction with the solid fraction, is responsible for viscoelastic behavior. Of primary importance to the rheological behavior of fat is the amount of crystalline fat and the type of crystals present in the fat crystal network (deMan and Beers 1987). The control of fat crystallization and the resultant rheological behavior is very important for processing purposes. For example, in some products, such as ghee, fat is crystallized very slowly under well-controlled conditions to obtain large crystals and a grainy texture (Nasir 2001). There are very few reports about the effect of SE on crystallization processes and development of polymorphic forms of fats (Yuki and others 1990, Herrera and Rocha 1996, Nasir 2001). Recently, the effects of SE on crystallization in lipid emulsions were investigated (Awad and Sato 2001, Katsuragi and others 2001). However, the mechanism proposed in these reports for SE action was not reported to describe bulk systems (Garti and Yano 2001). It is of great interest to study the effects of SE on bulk fat systems, particularly in regard to their use in products such as chocolate and confections, since these esters are used as texturizers and film formers. The purpose of this work was to evaluate the effect of several SE with a range of HLB values on crystallization and rheological behavior of high-melting milk-fat fraction/sunflower oil blends and to interpret rheological behavior in terms of SFC and the information previously reported about crystal size, crystal morphology, and crystal-crystal interactions (Martini and others 2002).

Materials and Methods

Starting materials

High-melting milk-fat fraction (HMF) was obtained from Grassland Dairy (Greenwood, Wis., U.S.A.) and sunflower oil (SFO) from Molinos Rio de La Plata S.A. (Avellaneda, Buenos Aires, Argentina). Details of HMF manufacture were described elsewhere (Martini and others 2002). Three blends were prepared by mixing 10, 20, and 40% of SFO with HMF. Dropping points and chemical composition of the samples were reported elsewhere (Martini and others 2002). SE P-170, S-170, and P-1670 were supplied by Mitsubishi-

Kasei Food Corp. (Tokyo, Japan), Mettler dropping points of 58.0, 59.5, and 44.0 °C, respectively. The monoester content of S-170 and P-170 was 1 wt%, with di-, tri-, and polyesters comprising 99 wt%. P-1670 contained 80% monoester and 20% of di-, tri-, and polyesters. SE were added at concentrations of 0.1 and 0.5 wt% to HMF and the 3 blends with SFO.

Solid fat content determination

Solid fat contents (SFC) during crystallization of the samples were measured by pulsed nuclear magnetic resonance (p-NMR) in a Minispec PC/120 series NMR analyzer (Bruker, Karlsruhe, Germany; AOCs official method 1998). SFC was measured as a function of time for 90 min after sample temperature reached crystallization temperature (at time equal 0). Samples were melted at 80 °C for 30 min, after which were placed in NMR tubes, and first kept at 80 °C for 10 min before being placed in a water bath at crystallization temperatures of 10, 15, 20, 25, 30, 35, and 40 °C.

Data analysis

The SFC data were fitted to the Avrami equation (Avrami 1940):

$$-\ln(1-f) = k_n t^n \quad (1)$$

where, t is time, k_n is the rate constant, f is the fractional extent of crystallization at any time, and n represents the index of the reaction. The fractional extent of crystallization was taken as the SFC at any given time normalized by the maximum SFC (S_{\max}) obtained at that experimental condition (Ng and Oh 1994). To obtain the parameters that gave the best fit to Equation (1), a nonlinear regression procedure was used. Curves were evaluated after subtracting induction times for onset of crystallization. Statistical significance of differences in parameters k_n and n among samples and treatments was checked using the Student's t -test.

Two-stage crystallization

Samples were crystallized under the following thermal treatments: samples were melted at 80 °C for 30 min, and then immediately placed at crystallization temperature (T_c of either 35 or 40 °C) (fast rate) or cooled from 60 °C to T_c at 0.1 °C/min using a programmable bath (slow rate). Fast cooling rate was calculated from the slope of the cell temperature record. The results of several runs were averaged, with the average cooling rate being 5.5 °C/min. Samples were crystallized with agitation in an 80-ml crystallizer for 90 min, then the slurry was placed in plastic tubes of 20-mm height and 10 mm dia open on both sides. Samples were then cooled quiescently to 10 °C at 1 °C/min and held for 24 h prior to analysis by penetrometry and differential scanning calorimetry.

Penetration tests

Fat samples were analyzed by means of a TA-XT2i Texture Analyzer (Vienna Court, England), which measures force exerted on a probe as it penetrates the sample. Samples were penetrated to 75% of their original height (15 mm) with a stainless steel needle probe (SMSP/3), 3 mm dia, at a constant velocity of 1 mm/s. For each determination, 7 fat samples were used, and average values were calculated. The 1st peak appearing in the force-time curves is attributed to yield point (Y_p). Penetration force corresponding to the yield point and the time needed to reach the 1st peak maximum were determined from the force-time curves.

Differential scanning calorimetry

Melting profiles were measured in a Polymer Laboratories calorimeter (Rheometric Scientific Ltd.) driven with a Plus V 5.41 soft-

ware. Calibration was carried out at a heating rate of 5 °C/min by using indium proanalysis (p.a.), lauric acid p.a., and stearic acid p.a. as standards. From 5 to 9 mg of sample were placed in hermetically sealed aluminum pans, then kept at -10 °C for 5 min, prior to melting at a heating rate of 10 °C/min from -10 to 80 °C. A single empty pan was employed as a reference. Three replicates were performed for each sample and means and standard deviations are reported.

Results and Discussion

Isothermal crystallization by NMR

As a representative example, Figure 1 shows the increase in SFC with time for the 10% SFO blend crystallized at different temperatures (a) and with the addition of the sucrose esters P-1670 (b), P-170 (c, d), and S-170 (e, f). Curves obtained for P-1670 with only at 0.1 wt% are reported here, because this sucrose ester was not soluble in the fat systems used in this study at 0.5 wt%. Zero time was the moment at which the samples reached crystallization temperature.

To be an effective inhibitor of crystallization, a compound should have the ability to cocrystallize with the fat because of its similar chemical structure. It should also be structurally dissimilar enough that it delays nucleation and inhibits growth. In general, an emulsifier with high molecular weight and the above-mentioned chemical characteristics has potential to be a good inhibitor of crystallization (Garti 1988). According to our previous results, among the mechanisms described in literature, the cocrystallization hypothesis is the one that better described the effects of sucrose esters on crystalline microstructure in the systems used in this study (Martini and other 2002). The sucrose esters selected for this study are formed by interesterification of sucrose and the fatty acids, Palmitic (P) and Stearic (S), which are present in high proportions in milk fat. P-1670 has low affinity for hydrophobic compounds (HLB = 16). It may have been expected that P-1670 would not cocrystallize with the fat phase and may act as an impurity to accelerate crystallization (Garti and Yano 2001). However, for the highest selected crystallization temperature (40 °C) after 90 min, no crystallization was detected by NMR with addition of 0.1% P-1670. Compared to the control at 40 °C, 0.1% P-1670 slowed crystallization rate and diminished S_{\max} ; however, it had no effect at lower temperatures. Despite its hydrophilicity, P-1670 is soluble in the fat system at the concentration used in this study. Its melting point (44 °C) is lower than those of P-170 and S-170 but still high enough to cocrystallize with the fat. In addition, the presence of palmitic acid in P-1670, which is a main fatty acid in milk fat, made it efficient at delaying nucleation at low supercooling.

P-170 has high affinity for hydrophobic compounds (HLB = 1), and chemical groups similar to the fat system in which it was crystallized. P-170 also has a high melting point (MDP = 58 °C). Therefore, P-170 may be expected to co-crystallize with HMF/SFO blends and delay crystallization. At temperatures above 35 °C, this effect was confirmed by NMR, especially at the 0.5% addition level (Figure 1c, d); however, at crystallization temperatures lower than 35 °C, P-170 had no effect. S-170 has the same HLB value as P-170, but stearic acid is present at lower percentage than palmitic acid in milk fat. Thus, S-170 delayed crystallization to a lesser extent than P-170 at both levels (Figure 1e, f).

Mettler dropping points of HMF and the mixtures with 10, 20, and 40% SFO were 48.3, 46.9, 46.1, and 44.3 °C, respectively. Therefore, the corresponding thermodynamic driving force, or the supercooling defined as $\Delta T = T_m - T_c$ (with T_m melting point and T_c crystallization temperature), at 35 °C were 13.3, 11.9, 11.1, and 9.3 °C,

respectively. The effects of emulsifiers on induction times of crystallization (the time interval between the moment crystallization temperature was reached and the start of crystallization) and S_{max} were evident only at low supercoolings (values of ΔT below 15 °C). For high supercoolings, that is, high thermodynamic driving force, addition of the sucrose esters P-1670, P-170, and S-170 had no effect on crystallization kinetics at the selected concentrations. At crystal-

lization temperatures above 35 °C and at cooling rates of 0.1 or 5.5 °C/min, either the β' or β polymorph may be expected in fat systems (Sato 1988). For the 3 main polymorphic forms of fats, induction times for nucleation increase in the order of α , β' , and β polymorphs (α polymorph crystals most rapidly). It could have been expected that the longer induction times obtained with addition of sucrose esters corresponded to the formation of the β polymorph.

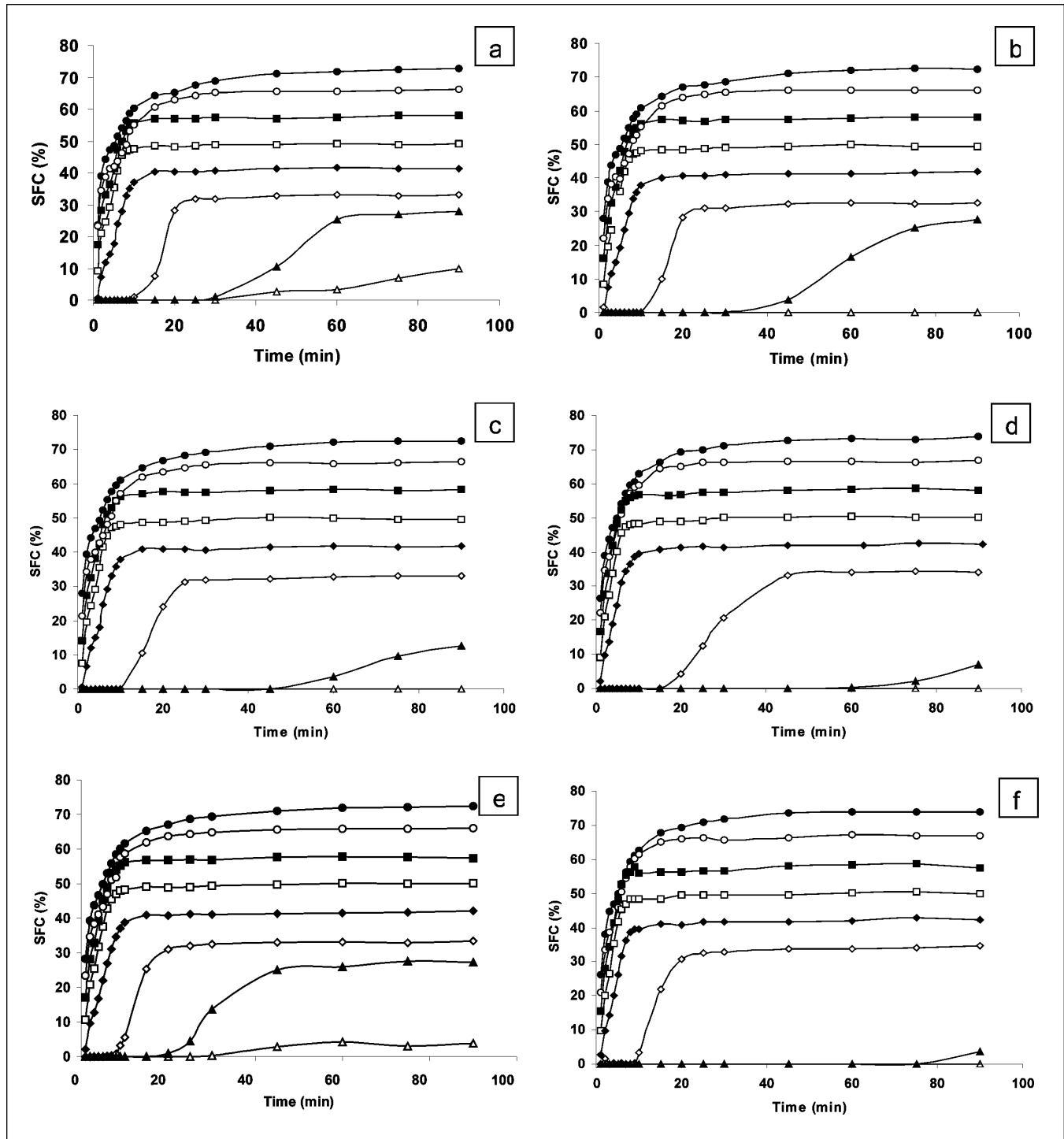


Figure 1—Solid fat content (SFC) with time for high-melting milk-fat fraction with 10% SFO oil crystallized at fast cooling rate (5.5 °C/min): (a) no emulsifiers added, (b) with P-1670 at 0.1 wt%, (c) with P-170 at 0.1 wt%, (d) with P-170 at 0.5 wt%, (e) with S-170 at 0.1 wt%, (f) with S-170 at 0.5 wt%. Δ , \blacktriangle , \diamond , \blacklozenge , \square , \blacksquare , \circ , \bullet are 40, 37.5, 35, 30, 25, 20, 15, and 10 °C, respectively. Standard deviations less than 1%.

However, X-ray diffraction analysis for all samples confirmed that in all cases, both with and without sucrose esters, samples crystallized in the β' polymorph (Martini and others 2002). No peak at 4.6 Å, characteristic of the β -form, was found. X-ray spectra for all samples were very similar, and, therefore, polymorphism was not responsible for differences in induction times.

Mathematical analysis

The SFC curves in Figure 1 were fitted to the Avrami model (Equation 1) by using a nonlinear regression package, with n values found to fall between 0.4 and 3.0. Table 1 shows, as a representative example, k_n values, n values and the correlation coefficients (r^2) at different temperatures for the mixture of HMF with 10% SFO with and without the addition of emulsifiers. For temperatures below 35 °C, a good fit to the Avrami equation was found over the rate of fractional crystallization from 0 to 0.7 ($r^2 > 0.9$ in all cases, Table 1). Crystallization curves above 35 °C were not included because they did not give a good fit.

For 10% SFO in HMF and with addition of P-170, S-170, and P-1670, k_n values were higher at lower temperatures ($p < 0.001$), indicating that crystallization proceeded more rapidly at higher driving force (lower temperature). In addition, values of k_n above 30 °C were considerably lower than at lower temperatures. According to Avrami, n is the reaction order and it describes the type of crystallization mechanism. The Avrami exponent is a function of the number of dimensions in which growth takes place, and reflects the details of nucleation and growth mechanisms (Graydon and others 1994). Christian (1975) has tabulated some values of n expected for various transformation conditions. For example, an n of 4 indicates heterogeneous nucleation and spherulitic growth from sporadic nuclei, whereas an n of 3 also indicates spherulitic growth but from instantaneous nuclei. An n of 2 represents high nucleation rate and plate-like growth, where growth is primarily along 2 dimensions. Fractional numbers for n indicate the contribution of more than 1 mechanism. The Avrami exponent, n , shown in Table 1, increased significantly above 30 °C for the sample with 10% SFO with and without addition of sucrose esters. According to the Avrami analysis, 2 different crystallization mechanisms would be expected below and above 30 °C. Below 35 °C, k_n and n showed no significant differences for addition of sucrose esters when mean values were compared using the Student's t -test ($p < 0.05$). At 35 °C, k_n decreased with addition of P-170 and S-170 at the 2 concentration used in this study. This indicates that, in addition to elongated induction times for crystallization, P-170 and S-170 inhibited growth. Moreover, n was close to 2 for all samples at 35 °C except for those with addition of P-170, where n was close to 3. This indicates that addition of P-170 probably produced a change in crystallization mechanism. k_n and n behaved in a similar way for all levels of SFO addition.

Addition of SFO substantially decreased k_n values ($p < 0.001$) at all T , with a greater decrease observed at higher T . For example, at 10 °C k_n values for HMF, 20, and 40% SFO were 0.434 ± 0.004 , 0.299 ± 0.006 , and 0.202 ± 0.005 , respectively, whereas at 35 °C, they were 0.0006 ± 0.0001 , 0.00015 ± 0.00001 , and 0.00005 ± 0.00001 , respectively. At 10 °C k_n values decreased by a factor of 2 upon addition of 40% SFO, whereas at 35 °C, k_n decreased by a factor of 8. The reaction index, n , was in the same order of magnitude for temperatures below 30 °C for HMF and HMF with SFO. However n increased significantly with SFO at 35 °C. n values for crystallization of HMF, and HMF with 20 and 40% SFO at 35 °C were 2.10 ± 0.09 , 2.62 ± 0.03 and 4.12 ± 0.04 , respectively. The changes in k_n and n indicated that addition of SFO substantially decreased the driving force for crystallization at 35 °C.

Table 1—Parameters (mean \pm standard deviation) of the Avrami Equation (Equation 1) obtained for high-melting milk-fat fraction with 10% sunflower oil crystallized at different temperatures with and without sucrose esters (P-170, S-170 and P-1670).

Sample	Temp. (°C)	k (min ⁻ⁿ)	n	r^2
No emulsifiers added	10	0.372 ± 0.045	0.45 ± 0.08	0.998
	15	0.296 ± 0.029	0.40 ± 0.04	0.999
	20	0.197 ± 0.019	0.64 ± 0.05	0.999
	25	0.110 ± 0.026	0.87 ± 0.14	0.998
	30	0.049 ± 0.022	0.94 ± 0.21	0.987
0.1% P-170	35	0.00027 ± 0.00002	2.18 ± 0.22	0.966
	10	0.380 ± 0.033	0.37 ± 0.01	0.999
	15	0.288 ± 0.035	0.43 ± 0.05	0.998
	20	0.184 ± 0.021	0.69 ± 0.07	0.999
	25	0.103 ± 0.021	0.89 ± 0.12	0.998
0.1% S-170	30	0.050 ± 0.024	0.94 ± 0.22	0.986
	35	0.00005 ± 0.000001	2.78 ± 0.29	0.973
	10	0.348 ± 0.018	0.44 ± 0.03	0.999
	15	0.295 ± 0.035	0.44 ± 0.05	0.998
	20	0.191 ± 0.018	0.70 ± 0.06	0.999
0.1 % P-1670	25	0.121 ± 0.016	0.84 ± 0.08	0.999
	30	0.040 ± 0.00876	1.13 ± 0.11	0.998
	35	0.00009 ± 0.00002	1.95 ± 0.18	0.926
	10	0.347 ± 0.021	0.43 ± 0.03	0.999
	15	0.274 ± 0.031	0.45 ± 0.05	0.998
0.5% P-170	20	0.193 ± 0.020	0.65 ± 0.05	0.999
	25	0.109 ± 0.022	0.88 ± 0.11	0.999
	30	0.051 ± 0.026	0.92 ± 0.23	0.984
	35	0.00029 ± 0.00031	1.98 ± 0.28	0.975
	10	0.353 ± 0.033	0.43 ± 0.04	0.999
0.5% S-170	15	0.297 ± 0.049	0.50 ± 0.08	0.997
	20	0.196 ± 0.029	0.72 ± 0.09	0.999
	25	0.118 ± 0.023	0.89 ± 0.12	0.999
	30	0.047 ± 0.001	1.09 ± 0.17	0.996
	35	0.00002 ± 0.000006	2.981 ± 0.20	0.997
	10	0.328 ± 0.028	0.48 ± 0.05	0.999
	15	0.248 ± 0.026	0.59 ± 0.06	0.999
	20	0.190 ± 0.028	0.74 ± 0.09	0.999
	25	0.111 ± 0.019	0.96 ± 0.12	0.999
	30	0.043 ± 0.001	1.19 ± 0.13	0.999
35	0.00002 ± 0.000004	1.91 ± 0.35	0.966	

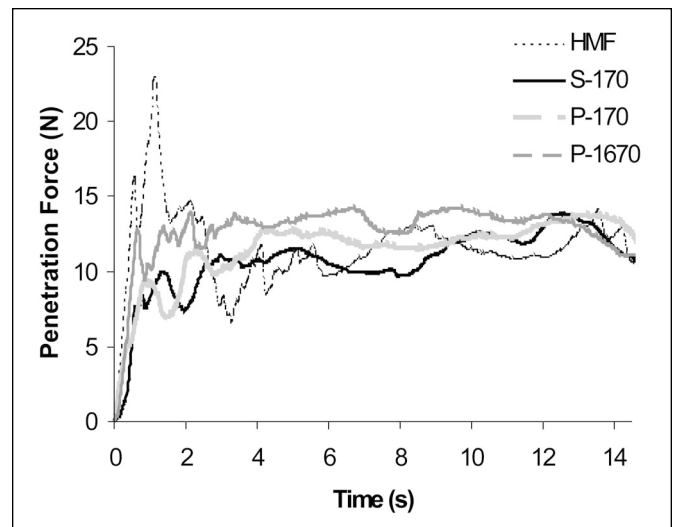


Figure 2—Typical force compared with time curves showing the effects of 0.1% sucrose esters (S-170, P-170, and P-1670) on samples of HMF crystallized at slow cooling rate at 40 °C followed by storage for 24 h at 10 °C.

Solid fat content (SFC)

Table 2 shows the SFC after 90 min at crystallization temperature ($T_c = 35$ and 40 °C) for crystallization with agitation and after being stored 24 h at 10 °C for all samples with and without the addition of P-1670 at 0.1%, and P-170 and S-170 at 0.1 and 0.5% levels. Samples were crystallized at 2 cooling rates: 0.1 (slow cooling) and 5.5 °C/min (fast cooling). Despite only small changes in MDP due to addition of SFO, a 4 °C decrease in MDP upon addition of 40% SFO, the SFC of the blends decreased substantially as SFO content increased. At 40 °C, HMF had SFC values of 12.7 and 13.4% for fast and slow cooling, respectively, whereas for the blend with 40% SFO, the SFC values were 0.4 and 5.3%, respectively. After crystallization at 35 °C and storage for 24 h at 10 °C, differences in SFC between blends also were very significant ($p < 0.001$). Slow cooling led to faster crystallization in some cases, but after 24 h at 10 °C, there were no differences in solid content based on cooling rates.

Penetration tests

Figure 2 shows the effects of emulsifiers on the force compared with time curve for samples of HMF crystallized at 40 °C (slow cooling rate) for 90 min with agitation followed by quiescent cooling and storage for 24 h at 10 °C. The 1st peak is attributed to the yield point. The penetration force and the time needed to reach the 1st peak maximum correspond to the point where the crystalline structure first begins to break. The shapes of those curves provide an indication of structural differences among sample. For HMF, force compared with time curve showed 2 sharp peaks the shape of which may be associate with hardness. When SE were added to HMF, the curves showed only 1 peak, which became broader with an increase in HLB value of the emulsifier. The loss of the 2nd peak probably indicated structural changes in the fat network due to emulsifier addition. When P-170 was added to HMF, a broader 1st peak was observed in the force compared with time curve, which is coincident with the results obtained by confocal microscopy (Martini and others 2002). Confocal images of microstructure of HMF with 0.1% addition of P-170 showed smaller differences in crystal size between the primary crystallization at T_c and the 2nd crystallization during storage at 10 °C than the ones found for HMF without emulsifiers. The same behavior was found for all blends.

Since fats do not undergo glass transition and therefore do not show great changes in viscosity above and below glass transition temperature (T_g) as do sugars and polymers, crystallization is mainly determined by the thermodynamic driving force, supercooling. However, kinetic factors may also influence crystallization behavior. It has been documented that cooling rate is one important parameter that influences crystallization of fats and leads to differences in physical properties of semi-solid fat products due to the effects on the crystal network (Herrera and Hartel 2000). Figure 3 shows the effects of cooling rate at different SFO addition levels on the penetration force corresponding to the yield point (Figure 3a) and time needed to reach the 1st peak maximum in the force-time curve (Figure 3b) for all samples crystallized at 40 °C without addition of SE. Cooling rate had no effect on yield point and time needed to reach the 1st peak maximum (means were compared using the Student's t-test at $p < 0.05$). The firmness depends in a complicated way on 3 main parameters: SFC, interaction between crystals, and structure of the crystal network. These 3 parameters depend on the crystallization process, which is in turn affected by the conditions during crystallization (Van Aken and Visser 2000). After 24 h at 10 °C, there were no differences in SFC due to cooling rate (Table 2). Surprisingly, there also were no differences ($p < 0.05$) in average crystal size for both rates (Martini and others 2002). In addition, no differences in microstructures of samples stored at 10 °C for 24h

were found when samples crystallized at both cooling rates were analyzed by confocal microscopy (Martini and others 2002). This behavior differed from that of blends of different milk-fat fractions (Herrera and Hartel 2000) and blends of HMF with SFO, (Martini and others 2001). In these previous studies, lower Mettler dropping points and a different chemical composition of the fats were used, perhaps indicating the relevance of TAG composition and interactions between TAG on crystallization and rheological properties. In agreement with the decrease in SFC with SFO addition, values of penetration force and time needed to reach the 1st peak maximum diminished with addition of SFO. Moreover, average crystal size determined just before storing samples at 10 °C also diminished with addition of SFO (Martini and others 2002).

Figure 4 shows the effects of SE addition on penetration force of HMF crystallized at 40 °C for fast (Figure 4a) and slow (Figure 4b) cooling. Addition of SE at 0.5% level delayed crystallization and even after several h at 40 °C, no crystals were formed. Emulsifiers significantly diminished the yield point when they were added to HMF; however, no significant differences in yield point were found due to addition of emulsifiers for samples containing any level of SFO. To understand the effects of SE on physical properties of fats, their effects on crystallization and crystalline microstructure must

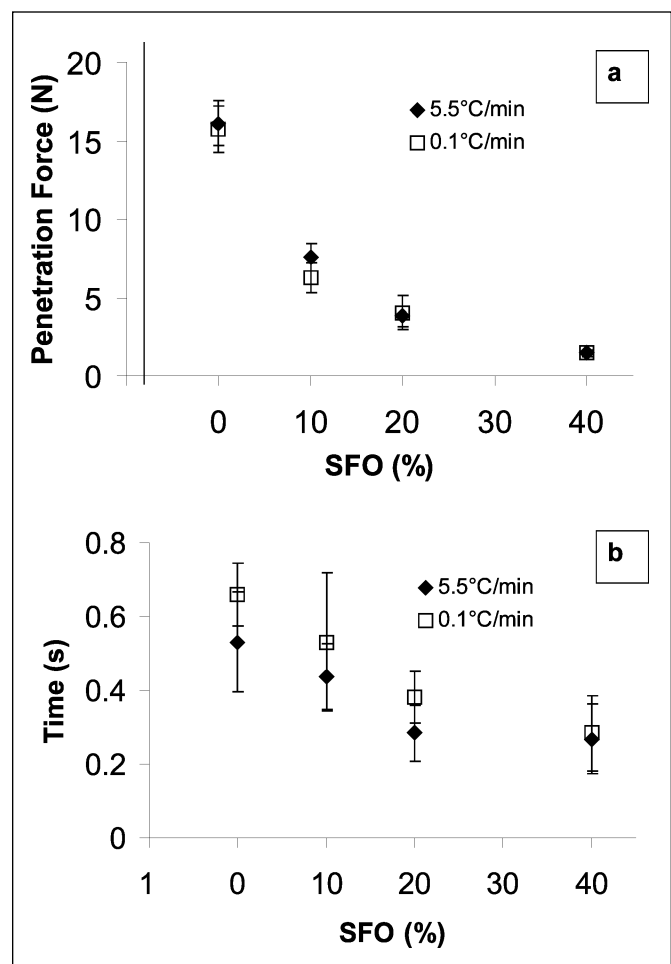


Figure 3—Effects of sunflower oil (SFO) addition and cooling rate on (a) penetration force and (b) time needed to reach the 1st peak maximum in the penetration curve for HMF crystallized with agitation at 40 °C for 90 min and quiescently at 10 °C for 24 h. Error bars represent standard errors of 7 replicates.

Table 2—Solid Fat Content (SFC) at different crystallization temperatures for high-melting fraction of milk fat (HMF) and its blends with sunflower oil (SFO) with and without addition of the sucrose esters P-170, S-170, and P-1670. Samples were crystallized with agitation for 90 min at 35 °C or 40 °C and then cooled quiescently to 10 °C and held 24 h prior to analysis.

Sample	35 °C		40 °C		10 °C	
	Cooling rate		Cooling rate		Cooling rate	
	5.5 °C/min	0.1 °C/min	5.5 °C/min	0.1 °C/min	5.5 °C/min	0.1 °C/min
HMF	37.4	37.0	12.7	13.4	80.8	82.1
HMF 0.1% P-1670	37.5	37.7	0.2	1.8	81.0	81.9
HMF 0.1% P-170	38.9	37.8	0.9	3.2	81.8	81.5
HMF 0.5% P-170	38.0	37.1	0.1	0.1	83.1	82.6
HMF 0.1% S-170	38.6	37.2	4.6	6.2	81.3	82.7
HMF 0.5% S-170	38.4	37.6	0.1	0.1	82.9	81.3
10% SFO	33.0	32.1	10.0	11.2	72.7	73.7
10% SFO 0.1% P-1670	32.7	33.1	0.2	0.4	72.9	73.5
10% SFO 0.1% P-170	33.2	32.4	0.4	0.9	72.6	72.8
10% SFO 0.5% P-170	34.0	33.0	0.1	0.1	73.8	73.0
10% SFO 0.1% S-170	33.4	32.4	3.8	5.1	72.4	73.9
10% SFO 0.5% S-170	34.8	33.2	0.1	0.1	73.8	72.5
20% SFO	27.6	27.1	4.2	8.5	64.0	63.9
20% SFO 0.1% P-1670	27.4	28.1	0.1	0.1	63.8	64.9
20% SFO 0.1% P-170	27.9	27.0	0.2	0.4	63.1	62.1
20% SFO 0.5% P-170	27.9	27.2	0.1	0.1	64.6	64.1
20% SFO 0.1% S-170	28.2	27.1	0.1	0.2	63.5	64.6
20% SFO 0.5% S-170	28.8	27.4	0.1	0.1	64.6	63.4
40% SFO	16.6	17.2	0.4	5.3	44.9	46.0
40% SFO 0.1% P-1670	17.6	18.1	0.2	5.1	45.2	44.8
40% SFO 0.1% P-170	12.1	13.7	0.1	0.1	44.9	45.1
40% SFO 0.5% P-170	0.2	1.6	0.1	0.1	46.2	44.8
40% SFO 0.1% S-170	17.7	18.5	0.8	0.2	46.4	46.0
40% SFO 0.5% S-170	4.4	6.7	0.1	0.1	45.9	45.3

Standard Deviation < 1% for all measurements

be understood. As previously reported (Martini and others 2002), primary crystals were formed under agitation at either 35 or 40 °C. After 90 min, samples were cooled to 10 °C, where crystallization continued without agitation. Confocal images of these samples showed larger primary crystals formed at T_c , surrounded by small and somewhat diffuse crystals in the background, which most likely were formed during storage (Martini and others 2002). After 24 h at 10 °C, the SFC of all samples, both with and without the addition of sucrose esters, was within the experimental error of the method (1%). However, the average size of the primary crystals decreased significantly with addition of P-170 and S-170 and the microstructures of the final products were quite different (Martini and others 2002). So, SE did not affect the final SFC of the fats, but had significant effect on the nature of the crystalline microstructure. The effect of SE on microstructure is related to their effects on crystallization kinetics. After 90 min at 40 °C, the pure HMF had SFC values of 12.7 and 13.4% for fast and slow cooling rate, respectively. This means that 12.7 or 13.4% of solids were formed at 40 °C, which were comprised of large crystals. The rest of the SFC, crystallized at 10 °C, were comprised of much smaller crystals. The addition of emulsifiers to HMF delayed crystallization (Table 2), reduced the amount of SFC formed at 40 °C. Therefore, much of the crystallization, when SE were present, occurred during cooling and storage at 10 °C. A similar effect was seen with addition of SFO to HMF. Most likely it is these differences in crystalline microstructure that were responsible for the differences in rheological behavior. A SFC after primary crystallization greater than 10% was necessary to give a microstructure that exhibited a sharp and high yield point. For this

reason, no differences in peak penetration force were found between the blends of SFO with HMF and these blends with addition of SE, (Figure 4).

Penetration forces for the 1st peak that appeared in force compared with time curves were 1.56 ± 0.48 , 1.62 ± 0.29 , 0.68 ± 0.17 , 0.74 ± 0.14 °C, 0.32 ± 0.11 , and 0.37 ± 0.19 N for the 40% SFO blend crystallized to 35 °C at 5.5 °C/min and with 0.1% P-1670, 0.1% P-170, 0.1% S-170, 0.5% P-170, and 0.5% S-170, respectively. All these samples had an SFC after being stored 24 h at 10 °C of around 45%. P-1670 did not modified crystal size when it was added to the 40% SFO blend at 35 °C. Therefore penetration force showed no significant differences with and without addition of P-1670 ($p < 0.05$). P-170 and S-170 significant diminished crystal size. SFC after 90 min at 35 °C were 12.1 and 17.7%, respectively. More than 10% of crystals were formed at 35 °C. Thus, addition of 0.1% of them significant diminished penetration force ($p < 0.05$). When P-170 and S-170 were added at 0.5% level, SFC levels were 0.2 and 4.4. This means that most of crystallization took place at 10 °C during cooling and storage. Very small crystals were formed in this condition and as a result penetration forces were very low. When sucrose esters diminished crystal size and at least 10% of crystals were formed at 35 °C, penetration force diminished due to addition of emulsifiers.

Thermal behavior

These samples were cooled (fast or slow) to crystallize with agitation at 40 °C for 90 min and then cooled quiescently to 10 °C and stored for 24 h. Samples were then heated at 10 °C/min in the DSC. Figure 5 shows the effects of addition of sucrose esters on melting

behavior for HMF crystallized in the 2-stage process with initial crystallization at 40 °C. For HMF, the melting curves showed a sharper and narrowed major melting endotherm for samples crystallized at both cooling rates, with a broader peak at slow cooling rate, as expected (Martini and others 2001). A smaller melting endotherm at lower temperature was observed, particularly when crystallization occurred at slower cooling rate, indicative of multiple components crystallizing independently. The addition of emulsifiers broadened the main melting endotherm, and in some cases, such as for the sample with P-170 at slow cooling rate, the endotherm even showed small shoulders. Melting temperatures of the main melting endotherm were 48.8 ± 0.1 , 49.4 ± 0.2 , 49.8 ± 0.9 , and 49.4 ± 0.1 °C for the HMF, and with S-170, P-170, and P-1670, samples crystallized at 5.5 °C/min, respectively, and 49.1 ± 0.1 , 49.7 ± 0.2 , 48.9 ± 0.9 , and 49.4 ± 0.4 °C for those samples cooled at 0.1 °C/min. Enthalpies of the high-temperature endotherm were 53.3 ± 1.0 , 53.82 ± 1.5 , 55.4 ± 6.2 , and 51.9 ± 0.7 J/g for the HMF, and with S-170, P-170 and P-1670, samples crystallized at 5.5 °C/min, respectively, and 61.2 ± 1.1 , 51.2 ± 0.8 , 55.4 ± 3.9 , and 59.8 ± 9.2 J/g for those samples cooled at 0.1 °C/min. Neither peak temperature nor enthalpy was different between cooling rate or with SE addi-

tion. However, DSC showed that sucrose esters caused a slight modification of the melting profiles of the fat samples even in the cases in which there were no differences in rheological behavior. Usually DSC heating curves are a combination of polymorphic transitions and melting of different solid solutions. However, in these systems, only the β' -form was observed (Martini and others 2002). The way in which the melting profile was modified suggests that the differences found in melting curves were most likely due to differences in chemical composition and phase behavior of the mixed TAG. Time scales for nucleation were different between the samples formulated with and without emulsifiers, and therefore TAG interactions and the melting profiles of the final products also were different.

Conclusions

MECHANICAL PROPERTIES OF FATS ARE RELATED TO THEIR SFC. However, samples with the same SFC can have different rheological behavior as a result of a different crystalline microstructure. Factors such as crystal size, crystal size distribution, density of crystal surface, primary and secondary structure, crystal interactions, and liquid dispersion can also impact rheological properties.

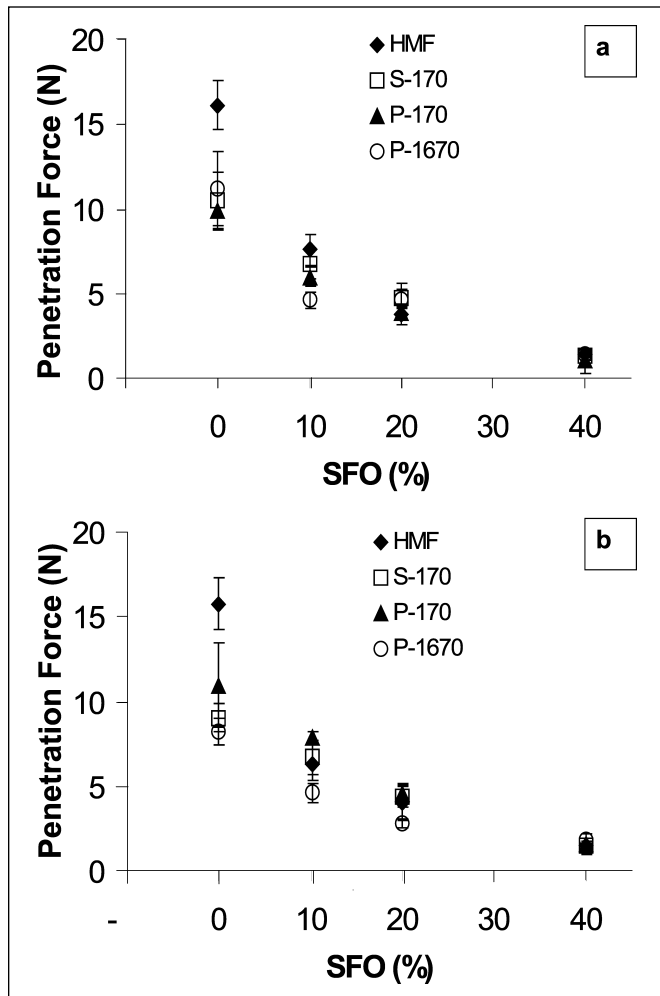


Figure 4—Penetration force corresponding to initial yield point for HMF crystallized at 40 °C with different levels of sunflower oil (SFO) and 0.1% sucrose esters (S-170, P-170, and P-1670). (a) Fast cooling (5.5 °C/min). (b) Slow cooling (0.1 °C/min). Error bars represent standard errors of 7 replicates.

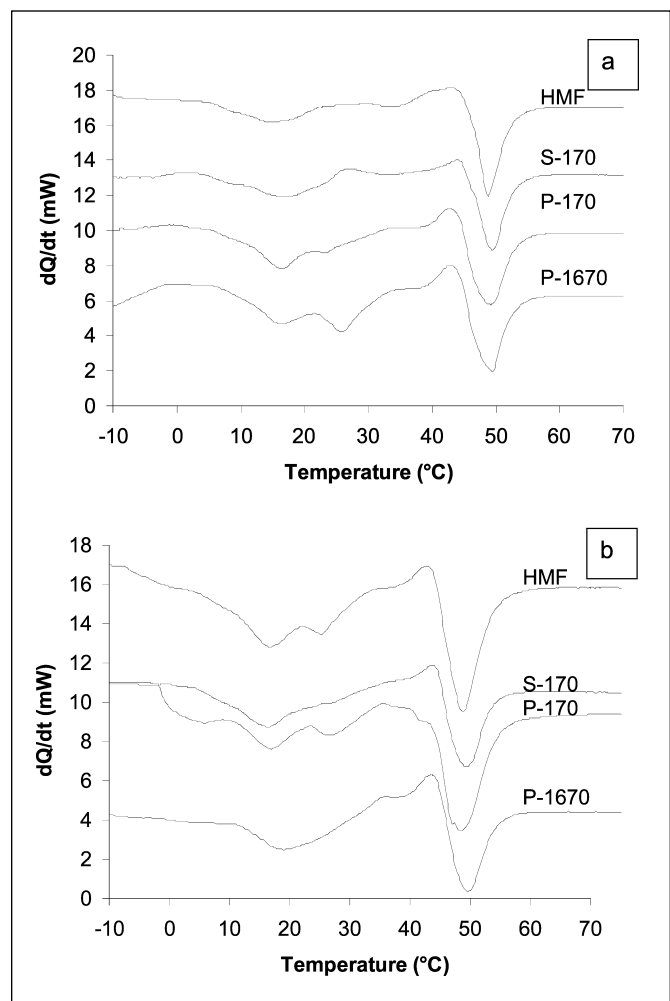


Figure 5—DSC melting curves for HMF with addition of sucrose esters (S-170, P-170, and P-1670) at 0.1% addition level. Crystallization by cooling at different rates: (a) 5.5 °C/min, (b) 0.1 °C/min to 40 °C for 90 min with agitation followed by quiescent cooling to 10 °C for 24 h.

Sucrose esters delayed crystallization of the HMF system, elongating induction times for crystallization and decreasing crystallization rate by a cocrystallization mechanism. After storage, SFC levels for samples with and without emulsifiers were within the experimental error. However, sucrose esters diminished the yield point of the semi-solid products made from a 2-stage crystallization process because their effect on crystallization kinetics also resulted in microstructural differences. The effect of emulsifiers on crystallization kinetics, rheological behaviors, and thermal behaviors was observed only at low supercoolings (values of ΔT below 15 °C). For high supercoolings, that is, high thermodynamic driving force, addition of the sucrose esters P-1670, P-170, and S-170 had no effect on the crystallization kinetics of the HMF system and did not affect the penetration force under compression.

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