Interesterification of Tallow and Sunflower Oil

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ABSTRACT: The objective of this study was to manufacture a shortening using chemical interesterification (IT) of tallow–sunflower oil blends to replace fish oil in the present formulation, which is now in short supply in Chile. The significant variables of the IT process were obtained by 2^{4-1} fractional factorial design. The proportion of tallow (T) in the blend, catalyst concentration, and reaction temperature had a significant effect on the melting point (mp) ($P \leq 0.05$). IT of tallow and sunflower oil blends (90:10 and 70:30) diminished the mp, dropping point, and refractive index compared to tallow. However, a noninteresterified 90:10 blend mp was not significantly different from tallow. IT produced a solid fat content (SFC) profile of IT90:10 blend that was appropriate for use in shortenings for the baking industry. Blending and IT of the 90:10 blend increased the melting profile of the tallow and the melting range from −40 to 60°C while the endotherms of the middle-melting triacylglycerols (TAG) decreased. The IT90:10 blend hardnesswas 70% lower than tallow hardness, and the crystal network was composed of large spherulites in a network. IT resulted in an appropriate method to improve physical properties of tallow, whereas blending did not significantly modify it. The interesterification changed the SFC profile of IT90:10, giving a more appropriate shortening for use in the baking industry.

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KEY WORDS: Blend, chemical interesterification, differential scanning calorimetry (DSC), fish oil, hardness, nuclear magnetic resonance (pNMR), polarized light microscopy (PLM), shortening, sunflower oil, tallow.

South American industrial production of shortenings and margarines provides blends of partially hydrogenated soybean, sunflower, fish, and other oils. However, fish oil has been in short supply since 1997 owing to environmental problems. Tallow is a poor replacement for fish oil in shortenings and margarines, because of its high melting point (mp) and narrow plastic range. “Plastic shortening” describes fats that are readily spread, mixed, or worked (1–3).

Effort has been made to improve textural and thermal behavior properties of tallow, including thermal fractionation and blending with a liquid oil (1,4,5). Deodorized and stabilized lard or beef tallow is a low-cost shortening for cookies (6). Another way to modify the composition and physical properties of fats is interesterification (1,3).

In interesterification, fatty acids are exchanged within (intraesterification) and among (interesterification) triacylglycerols until a thermodynamic equilibrium is reached (3,7,8). The objective of this study was to manufacture shortening by chemical interesterification (IT) of tallow–sunflower oil mixtures and to evaluate the physical, thermal, chemical, and textural properties for the purpose of finding a replacement for hydrogenated fish oil.

EXPERIMENTAL PROCEDURES

Source materials. A tallow high-mp fraction, a partially hydrogenated vegetable-animal (fish oil) shortening mixture for the baking industry, and a partially hydrogenated vegetable-animal (fish oil) shortening mixture used in cookies and ice creams were used (Tomás Castillo Co., Santiago, Chile). Sunflower oil (Malloa Co., Santiago, Chile) was obtained from a local supermarket. All chemicals were purchased from Merck Chemical Co. (Santiago, Chile). The catalyst, sodium methoxide (CH_3ONa), was stored at room temperature in a desiccator to avoid decomposition.

Experimental design. The experiments were performed with a 2^{4-1} fractional factorial design constituted by eight experiments (9–11). The independent variables considered were tallow fraction, catalyst concentration, reaction temperature, and reaction time (Table 1).

Blend preparation. Liquefied tallow and sunflower oil were mixed in proportions ranging from 50 to 90% (w/w) in accordance with Table 1. A ninth experiment was conducted at an intermediate level (70:30) to estimate the experimental error (9–11). The blends were identified by the tallow/sunflower oil mass ratio.

Chemical interesterification. Portions (100 g) of the blends were heated under vacuum to remove moisture and air. When the blend had reached the reaction temperature of 60–120°C, sodium methoxide, 0.4–1% (w/w), was added while the blend was vigorously stirred. The interesterification reactions were performed under constant vacuum and agitation for 15–60 min as shown in Table 1. To end the reaction, an excess of citric acid was added to neutralize the catalyst. The excess of citric acid and sodium methoxide was removed with warm water washes (3 × 150 mL), and the interesterified blends were vacuum-dried. Residual water was removed with an ex-

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TABLE 1
Response Data Obtained by Experimental Fractional Factorial Design 2^{4-1} for Interesterified Tallow and Sunflower Oil

	Independent variables				Response variables			
Assay number	Tallow (%)	Catalyst (%)	Temperature (°C)	Time (min)	Melting point[a] (°C)	Dropping point[a] (°C)	Hardness (N/cm^2)	Refractive index (n_D^{40}) ± 0.0005[c]
1	50	0.4	60	15	31.9 ± 0.8	38 ± 2	(—)	1.4623
2	90	0.4	60	60	41.3 ± 0.3	53 ± 3	3.5	1.4580
3	50	1.0	60	60	29.1 ± 0.5	31 ± 1	(—)	1.4615
4	90	1.0	60	15	40.3 ± 0.8	53 ± 7	2.55	1.4581
5	50	0.4	120	60	30.8 ± 0.3	36 ± 4	(—)	1.4621
6	90	0.4	120	15	41.2 ± 0.1	54 ± 1	3.38	1.4582
7	50	1.0	120	15	28.5 ± 1.7	25 ± 5	(—)	1.4612
8	90	1.0	120	60	37.3 ± 0.3	50 ± 4	1.94	1.4570
9	70	0.7	90	37	35.6 ± 0.8	49 ± 2	0.80	1.4605

[a]Values are reported as mean ± 95% confidence interval.
[b]Hardness was lower than 0.1 N/cm^2.
[c]Equipment error ≤0.00005; duplicate results equal in each case.

cess of anhydrous sodium sulfate, followed by filtration through Whatman #2 filter paper (Maidstone, England), before textural, thermal, chemical, and structural analyses (3).

The response variables considered for the chemical interesterification were mp (ºC), hardness (N/cm^2, dropping point (DP: °C), and refractive index (RI). The order in which the experiments were performed was randomized (9–11).

Physical-chemical data. Tallow, noninteresterified tallow/sunflower oil blend (NT), and IT samples were analyzed with respect to: mp (AOCS official method Cc 1-25), DP (AOCS official method Cc18-80), RI (AOCS official method Cc 7-25), free fatty acid (FFA: AOCS official method Ca 5a-40), peroxide value (PV: AOCS official method Cd 8-53), anisidine value (AV: AOCS Cd 18-90), saponification value (AOCS official method Cd 3-25), unsaponifiable matter (AOCS Ca 6b-53), and iodine value (IV: AOCS official method Cd 1-25) (12).

Pulsed nuclear magnetic resonance (pNMR). Solid fat content (SFC) was measured by pNMR in a NMR Minispec Analyzer (Bruker PC/20 Series, Milton, Canada) (AOCS official method Cd 16-81) (12).

Differential scanning calorimetry (DSC). Calorimetric evaluations of sample melting behavior were performed in a PerkinElmer differential scanning calorimeter (PE DSC 7, Norwalk, CT). Samples (9–10 mg) were loaded in hermetically sealed aluminum pans. All samples were refrigerated at 5°C for 24 h prior to measurements. DSC analyses were performed from 20 to −30°C and from −30 to 50°C at a scan rate of 5°C/min compared to an empty pan. Thermograms were analyzed from onset and end of melting and major peak maximum temperatures (°C). Data analysis was made with the DSC software (3).

Polarized light microscopy. A small amount of the fat was placed on a slide at 37°C and tempered at 5°C for 24 h prior to measurement. A cover slip was then placed on the slide. Magnification was 10× while photographic magnification was 100× (13). An Optiphot Nikon polarized light microscope (Tokyo, Japan) with a Microfelet Nikon 35-mm camera was used. Photomicrographs were taken on Fuji ISO100 film with an exposure time of 30–40 s. All handling was performed at 5°C.

Textural properties. A constant speed compression test was used to evaluate texture (6,14). Hardness and cohesiveness were determined from a stress-distance curve obtained from a Universal Testing Machine (Lloyd Instruments Limited, Lloyd LR-5K, Hampshire, England) with a 100-N load cell. Cylindrical samples (d = 2 cm; l = 2 cm) were tempered at 20°C for 24 h, and the tests were carried out at 20°C. Samples were compressed to 1.4 cm, and the crosshead rate was 70 mm/min. Six experiments were made. The Lloyd testing machine was connected to a computer, using data analysis software (Dapmat 40-0465, version 3.05, Lloyd Instruments Limited). The breaking force was calculated by dividing the maximum force (maximum peak) by the surface sample area (3.14 cm^2) (6,14)

Statistical analysis and experimental design. Experiments were duplicated, and triplicate analyses were performed on each replicate for each dependent variables. The 95% confidence intervals of each property and each analysis were calculated, taking into account the size of the samples (number of replications) and considering the standard deviation of each sample.

To determine the significant variables of chemical interesterification, an analysis of variance and multiple regression analysis were performed, applying Statgraphics version 7.0 (Manugistics Inc., Statistical Graphics Corporation, 1993, Rockville, MA).

RESULTS AND DISCUSSION

Blending and chemical interesterification effect on physical-chemical properties of tallow. Physical and chemical analysis of tallow and of NT and IT blends of tallow to sunflower oil (90:10 and 70:30) are shown in Table 2. Blending and IT of tallow and sunflower oil (90:10) and (70:30) blends diminished the mp. The mp decreased as the percentage of oil in-

TABLE 2
Physical and Chemical Analysis of Tallow, NT and IT of Tallow Blended with Sunflower Oil[a]

Analysis	Tallow	NT (90:10)	IT (90:10)	NT(70:30)	IT(70:30)
Melting point (°C)	44.0 ± 0.5	43.8 ± 0.2	39.2 ± 0.9	42.1 ± 0.2	34.9 ± 0.1
Dropping point (ºC)	63.2 ± 0.2	58.9 ± 0.8	50.1 ± 0.3	55 ± 1	43.2 ± 0.6
Refractive index,	1.4580	1.4585	1.4573	1.4608	1.4588
Free fatty acid (% oleic acid)	0.2 ± 0.1	0.2 ± 0.1	0.29 ± 0.02	0.2 ± 0.1	0.3 ± 0.1
Peroxide value (meq O_2/kg fat)	4.2 ± 0.1	4.2 ± 0.1	4.4 ± 0.1	4.2 ± 0.2	4.6 ± 0.2
Anisidine value	ND	5.7 ± 0.8	5.7 ± 0.5	ND	ND
Iodine value	38.3 ± 0.3	48.4 ± 0.1	49.02 ± 0.05	61.6 ± 0.2	60.8 ± 0.4
Saponification value (mg KOH)	193.3 ± 0.1	193.0 ± 0.1	193.2 ± 0.2	193.0 ± 0.2	192.2 ± 0.3
Unsaponifiable matter	0.6 ± 0.2	0.7 ± 0.3	0.7 ± 0.1	0.8 ± 0.4	0.8 ± 0.7

[a]Values are reported as mean ± 95% confidence interval. NT, nonesterified tallow/sunflower oil blend; IT, chemically interesterified blend. Values in parentheses indicate ratio of tallow to sunflower oil (w/w); ND, not determined.

creased, whereas that of the NT90:10 blend was not significantly different ($P > 0.05$) from tallow.

The DP of tallow and of noninteresterified and interesterified blends of tallow/sunflower oil (90:10 and 70:30) were significantly different from one another ($P \leq 0.05$). The proportion of tallow in the blend and interesterification had significant effects on the DP ($P \leq 0.05$). The DP of interesterified blends demonstrated big changes as the proportion of oil increased compared to NT samples. The DP decrease for NT and IT of tallow 90:10 and 70:30 relative to that of blends suggested a less structured, crystal network tallow.

The RI, FFA, AV, saponification value, and unsaponifiable matter were not significantly affected by blending and IT ($P \leq 0.05$), except for the saponification value of its blends ($P \leq 0.05$). FFA in the IT90:10 blend were higher than the NT90:10 blend. This could be due to the presence of citric acid residues.

Interesterification increased the PV. Blending and IT significantly increased the IV of the tallow/sunflower oil blend as the percentage of oil increased (1). The NT70:30 blend IV was higher than the NT90:10 blend due to the incorporation of unsaturated sunflower oil fatty acids, and blend hardness diminished.

Determination of significant variables of interesterification. The proportion of tallow in the blend, catalyst concentration, and reaction temperature significantly affected interesterification process variables ($P \leq 0.05$), but the reaction time did not produce significant changes in mp, DP, hardness, and RI (Table 1).

The proportion of tallow in the blend, catalyst concentration, and reaction temperature had a significant effect on the mp ($P \leq 0.05$). The mp increased with increasing tallow and decreased with increasing catalyst concentration and temperature ($P \leq 0.05$).

Interesterification effect on SFC of tallow. All blend SFC profiles were significantly different from each other ($P \leq 0.01$) (Fig. 1). Rouseau *et al.* (3) found that SFC was not significantly affected by chemical interesterification in the 25–30°C range ($P > 0.05$). The SFC profile showed that, at room temperature (21–25°C), tallow does not have optimal consistency for ready incorporation into leavened baked products. Only at high temperatures can tallow be incorporated.

The partially hydrogenated vegetable-animal mixture shortening (Tomás Castillo Co., Santiago, Chile) for the baking industry (S) had an SFC of 35–37% at 21°C and 28–30% at 25°C; the partially hydrogenated vegetable-animal mixture shortening (Tomás Castillo Co, Santiago, Chile) for cookies and ice creams had an SFC of 15–18% at 21°C and 9–14% at 25°C. DeMan *et al.* (6) found that SFC for vegetable-tallow shortening (Canada) was 28.3% at 25°C and 26.6% at 30°C, and vegetable-tallow for frying fat (Canada) was 29.1% at 25°C.

Addition of 10% sunflower oil to tallow (NT90:10) decreased the SFC in the temperature range of 10 to 35ºC. The short plastic range of NT90:10 SFC profile could be due to higher-melting glycerides that predominate over those of low mp. Interesterification of tallow and sunflower oil to NT90:10 blend caused a decrease in SFC profile. The IT90:10 blend

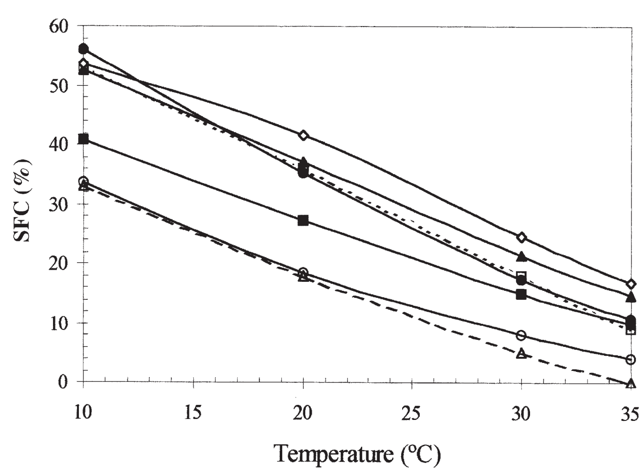

FIG. 1. Solid fat content (SFC) evolution of tallow, (w/w) noninteresterified (NT) and interesterified (IT) tallow/sunflower oil blends (w/w) as a function of temperature (°C); tallow (◇), NT90:10 (▲), IT90:10, (●), partially hydrogenated vegetable-animal (fish oil) mixture shortening for the baking industry (□), NT70:30 (■), IT70:30 (○), partially hydrogenated vegetable-animal (fish oil) mixture shortening for use in cookies and ice creams (△).

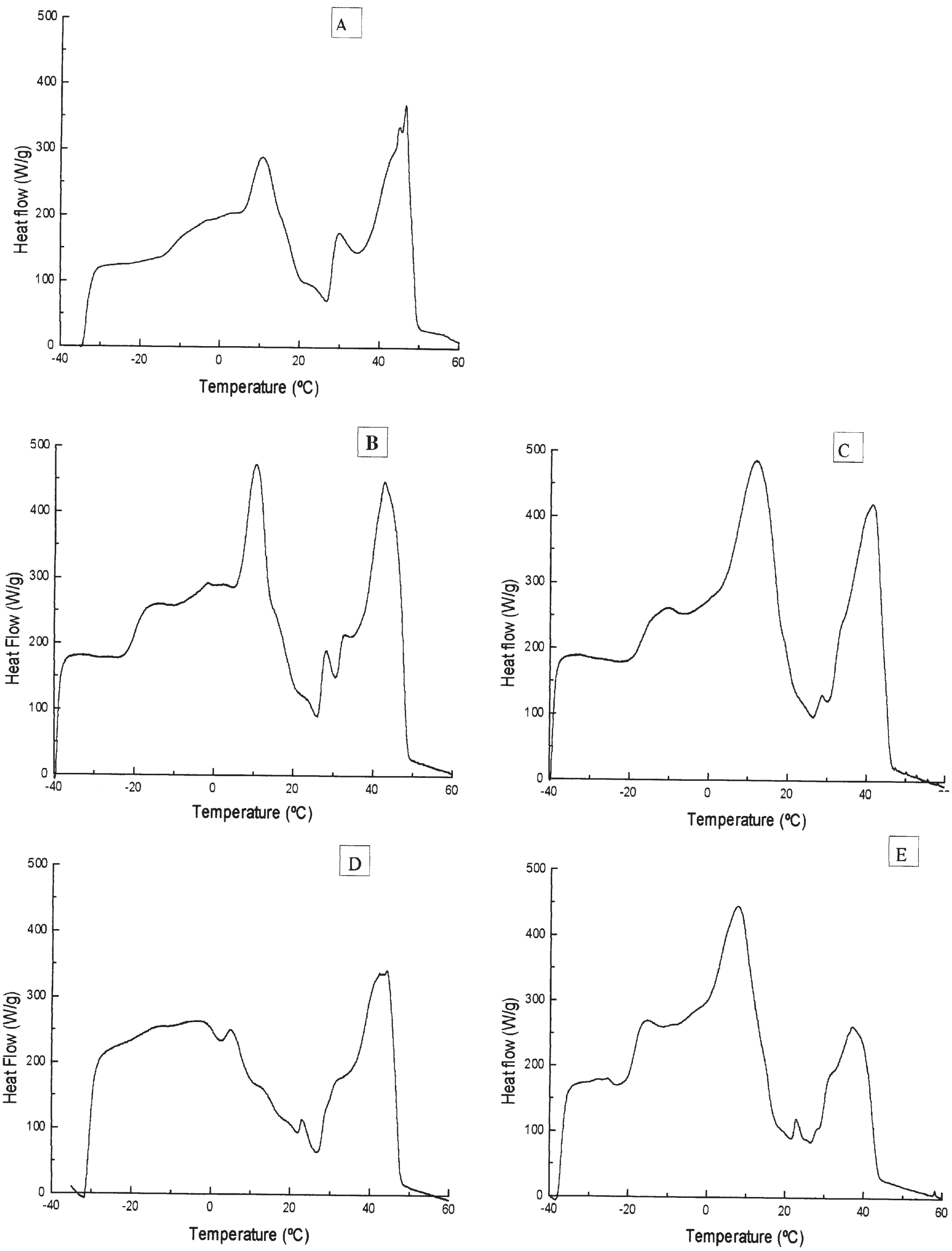

FIG. 2. Differential scanning calorimetry melting thermograms of noninteresterified (NT) and interesterified (IT) blends of tallow and sunflower oil (w/w): A, tallow; B, (NT90:10); C, (IT90:10); D, (NT70:30); E, (IT70:30).

was more appropriate for baking. The SFC profile of IT70:30 blend was always lower than the tallow and the NT70:30 blend. In all cases, NT and IT 70:30 blends had a lower SFC than NT and IT 90:10 blends owing to a major increase in liquid oil content. Interesterification of the IT70:30 blend produced a shortening that was more adequate to be used in cookies and ice creams.

Interesterification effect on tallow DSC. DSC thermograms, representative of tallow, NT and IT blends of tallow/sunflower oil (90:10 and 70:30) are shown in Figure 2. Blending and IT of tallow and sunflower oil (90:10) and (70:30) blends produced changes in the tallow melting profile.

Tallow contains numerous triacylglycerols (TAG) with a melting range from −35 to 60°C (Fig. 2A). These results agree with those of Rousseau *et al.* (3), who found that butterfat exhibited a melting range from –40 to 40°C. Butterfat was composed of the low-melting TAG (LMTAG), middle-melting TAG (MMTAG), and high-melting TAG (HMTAG). The tallow thermogram shows that LMTAG melted at 21°C, the MMTAG fraction at 34°C, and the HMTAG at 47°C. At refrigerator temperature, tallow was composed of all three fractions, whereas at room temperature, the solid tallow contained mainly the MMTAG and HMTAG fractions. Three steps were detected: at 10.8, 29.8, and at 46.7°C, the main peak.

Addition of 10% sunflower oil (NT90:10) increased the melting profile of tallow and the melting range from –40 to 60°C, whereas the profile of onset temperature and the endotherms of MMTAG decreased (Fig. 2B). The peak maximum values for MMTAG and HMTAG fractions decreased as the sunflower oil content increased. Interesterification of the 90:10 blend (IT90:10) (Fig. 2C) increased the LMTAG and HMTAG fractions, while the MMTAG fraction shifted a few degrees lower. In the results of Rousseau *et al.* (3), the IT of butterfat and canola oil to the NT90:10 blend created a much-altered thermogram. In their study, the MMTAG fraction also diminished, while the HMTAG fraction shifted a few degrees lower and the LMTAG became more pronounced.

Addition of 70% sunflower oil NT70:30 decreased (Fig. 2D) the LMTAG and MMTAG fractions, while the HMTAG fraction increased. The peak maximal values for LMTAG, MMTAG and HMTAG fractions decreased as the sunflower oil content increased, whereas the onset of melting temperature was not changed in comparison with the onset of tallow melting.

Interesterification effect on crystal morphology of tallow. Crystal network density, crystal size, and crystal morphology of tallow were heavily influenced by blending and IT of tallow and sunflower oil. Figure 3A reveals that the tallow crystal network consisted of a dense network of spherulites (globular collections of clustered crystals) and small needles with no evident regular pattern (13,14). Most structural elements measured 11–23 μm in size. Figure 3B shows that the addition of 10% sunflower oil to tallow (NT90:10) resulted in a dilution of the tallow structure (spherulite sizes, 11–17 μm) which varied in concentration but without substantial change in morphology. Figure 3C shows that the morphology of the interesterified tallow and sunflower oil (IT90:10) crystal network changed substantially. The crystal network was composed of large spherulite (size 15–46 μm) "stars" in a lacy network. These results agree with those of Rousseau *et al.* (13), who found that blending butterfat with canola oil [80:20 (w/w) blend butterfat/canola oil] and subsequent IT modified the crystal morphology of butterfat. Crystal size properties are essential for final product consistency and acceptability. Smaller crystals lead to firmer products, whereas large crystals produce a sandy mouthfeel (1,14).

Addition of 30% sunflower oil to tallow (NT70:30) (Fig. 3D) led to dilution of the tallow structure and fewer large crystals were visible. Instead, the majority measured 2–8 μm. Interesterification of the 70:30 blend (IT70:30) (Fig. 3E) caused an increase in the size of the crystal and changed the morphology with a stranded network of small crystals, measuring 7–14 μm. In this case the crystal sizes were less than those of IT90:10 (Fig. 3C).

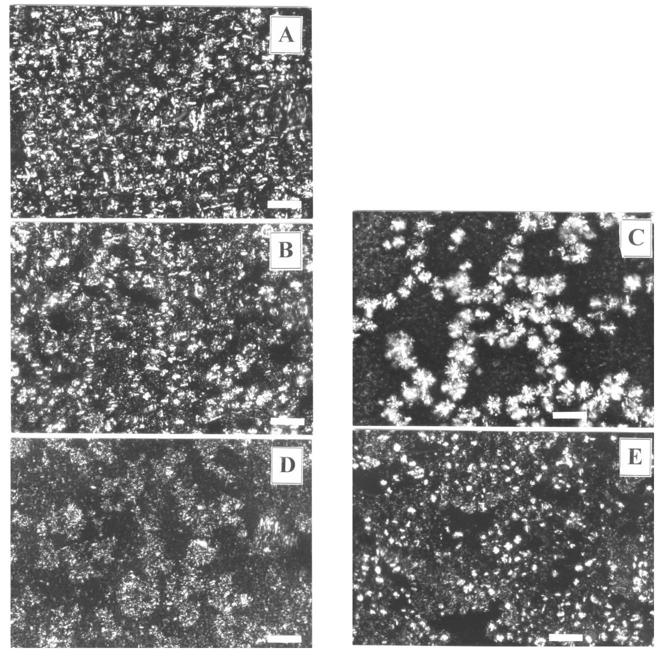

FIG. 3. Polarized light microcoscopy photomicrographs of samples tempered 24 h at 5°C of noninteresterified (NT) and interesterified (IT) blends of tallow and sunflower oil (w/w): A, tallow; B, (NT90:10); C, (IT90:10); D, (NT70:30); E, (IT70:30). The bar represents 50 μm.

Textural parameter. The hardness of tallow, NT, and IT of tallow blends (90:10 and 70:30) and a commercial shortening (S) were significantly different from one another ($P \leq 0.05$) (Table 3). The tallow hardness was higher than the S, NT and IT blends. The tallow breaking force appeared early during compression at small deformation and the tallow was disintegrated into small pieces indicating a brittle structure (14). The tallow hardness decreased as the oil percentage increased. However, the NI90:10 blend was not significantly affected ($P \leq 0.05$). Rousseau *et al.* (15) found out that replacement of 10% butterfat with canola oil did not substantially decreased the hardness index. The IT90:10 blend hardness was 70% lower than tallow and NT90:10. The breaking force appeared later during compression at large strains, and a diagonal or a V-like crack was observed in the fat cylinder indicating a more soft and pliable structure.

Addition of 30% sunflower oil produced a decrease in tallow hardness. This was interpreted as a structurally weaker network, producing a decrease in SFC (15). For the IT blends, the dilution effect of blending was compounded by the incorporation of unsaturated sunflower oil fatty acids into tallow TAG, resulting in hardness decrease. The hardness of shortening for use in the baking industry was 79% lower than the tallow. According to DeMan *et al.* (14) the breaking forces of tallow and tallow-vegetable shortenings (Canada) were 1.61 and 1.24 N/cm^2, respectively. The IT90:10 blend hardness was significantly higher than the S.

TABLE 3
Textural Parameters of Tallow, NT and IT of Tallow to 90:10 and 70:30 Blends and Shortening (S) for the Baking Industry

Textural parameter	Tallow	NT (90:10)	IT (90:10)	NT (70:30)	IT (70:30)	S
Hardness, N/cm^2	6.37	6.10	1.94	2.55	0.80	1.34
Cohesiveness, mm	0.97 ± 0.43	1.1 ± 0.5	13.99 ± 0.02	1 ± 1	13.97 ± 0.03	14.0 ± 0.01

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