

The Influence of Chemical Interesterification on the Physicochemical Properties of Complex Fat Systems. 2. Morphology and Polymorphism

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ABSTRACT: Palm oil–soybean oil (POSBO) blends and lard–canola oil (LCO) blends were chemically interesterified with sodium methoxide. Changes in crystal morphology using polarized light microscopy and crystal polymorphic behavior using X-ray diffraction spectroscopy (XRD) were studied. Spherulitic crystalline particles, measuring 10–20 μm , were detected in palm oil (PO). These spherulitic particles were characterized by a dense core surrounded by a lower-density halo region. PO fat-crystal morphology was not greatly altered on addition of soybean oil (SBO), except for a gradual reduction in spherulite size as the amount of SBO in the blends was increased. Chemical interesterification (IE) did not alter PO or POSBO blend fat-crystal morphology significantly. Irregular particles and spherulites of different sizes and shapes were observed in lard, from small crystals to irregular, angular crystal aggregates. Changes in lard fat-crystal morphology due to the addition of canola oil (CO) were concentration-dependent. In general, spherulite diameter decreased with increasing CO addition. IE dramatically altered lard fat-crystal morphology—IE induced the formation of more symmetrical spherulitic crystalline particles, and the halo-to-core ratio was increased significantly. XRD spectroscopic analysis of POSBO blends revealed small changes in the long spacings of PO fat crystals with either blending or IE; all values were close to 45 Å. Short spacings of fat crystals in noninteresterified (NIE) POSBO blends suggested the predominance of β' polymorphs. IE led to an increase in the proportion of the β polymorph in PO and POSBO blends. Long spacings of NIE lard fat crystals suggested the presence of a bilayer structure in their unit cells (45 Å). Dilution with $\geq 10\%$ canola oil led to the appearance of a second reflection at 35 Å. β' polymorphs were predominantly detected in NIE lard and NIE LCO blends. The β polymorph became more evident with increasing addition of CO. Fat crystals in IE lard and IE LCO blends displayed a single long-spacing reflection at 40 Å. IE of lard and LCO blends induced the formation of β polymorphs.

KEY WORDS: Chemical interesterification, fat-crystal morphology, lard, palm oil, polymorphism.
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The major structural component of plastic fats is their crystal network. Fat crystals grow together to form aggregates that eventually associate to form a complex network. The proper-

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ties of fat crystals (i.e., polymorphic form, morphology) will influence the structure of this fat-crystal network which in turn will affect rheological behavior. Fat-crystal polymorphism is an important factor that greatly influences the rheological properties of fats. Of the main crystal polymorphic forms (α , β' , and β) (1), the presence of the β' form is most desirable in margarines, spreads, and shortenings, since it imparts a smooth texture to the product. Predominance of β -crystals in such systems results in a dull and brittle fat with a grainy texture. However, β polymorphs are desirable in chocolate products (2).

The objective of the present study was to assess the morphological and polymorphic modifications of lard and palm oil (PO) fat crystals following blending with vegetable oil and/or chemical interesterification. Modifications were assessed using polarized light microscopy (PLM) and X-ray diffraction spectroscopy (XRD).

EXPERIMENTAL PROCEDURE

Sample preparation and visual analysis. Blend preparation was performed as described in Marangoni and Rousseau (3). The method of chemical interesterification used was described in Marangoni and Rousseau (3). PLM used the method described in Rousseau and Marangoni (4).

X-ray diffraction spectroscopy. The polymorphic forms of all noninteresterification (NIE) and chemical interesterification (IE) blends ranging from 100% hardstock to 60% hardstock and 40% vegetable oil were examined. Samples were liquefied at 70°C for at least 10 min in a waterbath to remove crystal history. Using a pipette, 20 μL was put on the ridge of a curved glass plate ($r = 2.5$ cm, $l = 4$ cm). The sample solidified as a film on the ridge of the plate at room temperature. These were then refrigerated at 4°C for at least 24 h before analysis. Samples were held at 5°C in a temperature-controlled chamber while the diffraction pattern was collected.

The X-ray beam was generated by an Elliot GX6 rotating anode machine operating at 30 kV and 20 mA. A line focus was used, and the beam was 500 μm thick and approximately 0.5 cm wide. The monochromatic Cu-K α line was produced using a combination of a nickel-coated Franks mirror and a nickel filter. The line was oriented at a grazing angle with re-

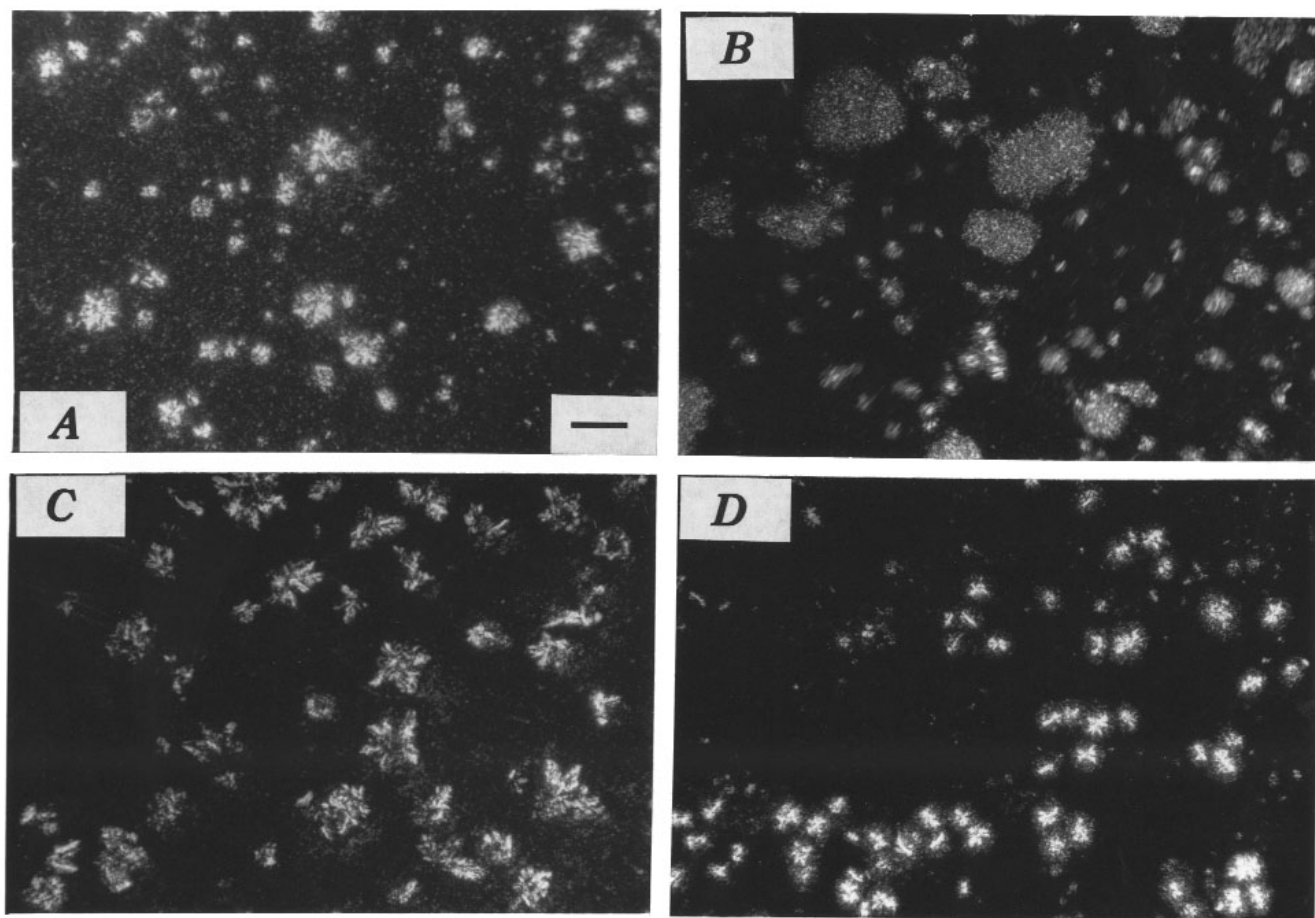


FIG. 1. Polarized light microscopy photomicrographs of lard–canola oil blends (LCO) tempered 24 h at 5°C; (A) noninteresterified (NIE) lard; (B) chemically interesterified (IE) lard; (C) IE80:20 LCO blend; (D) IE80:20 blend. The bar represents approximately 6 μm .

spect to the film on the curved glass plate. The diffraction patterns were recorded with a model B-OED-50S (M. Braun, GmbH, Munich, Germany) linear position sensitive detector that had an effective length of 50 mm and the appropriate timing electronics. The output from the timing electronics was from a time to amplitude converter. The diffraction pattern was obtained from this signal using a multichannel analyzer (Aptec Engineering, Mississauga, Ontario, Canada) housed in a microcomputer. The detector was filled with 95% Ar and 5% CH_4 at a pressure of 11.5 bar and held at a potential of 3.5 kV. The sample-to-detector distance was approximately 15 cm. The system was calibrated using crystalline potassium hydrogen phthalate; it was used because it has strong reflections at 1.34 and 0.498 nm. The samples were held in a specially constructed chamber. The temperature was controlled by a waterbath that circulated liquid through channels cut in the base plate of the sample chamber. The thick-walled brass chamber had 50 μm Mylar windows for the X-ray beam.

RESULTS AND DISCUSSION

PLM. Figures 1 and 2 show the effects of blending and IE on lard fat-crystal morphology. PLM examination of native lard

(Fig. 1A) shows that it consisted of dense, asymmetrical spherulitic particles and small crystals. Interesterification caused a decrease in the number of spherulites, and low-density aggregates of fine crystals were observed instead (Fig. 1B). The grainy texture of native lard is often attributed to the presence of large spherulites, or spherulitic aggregates, and more specifically to the presence of tristearin (SSS) (5). Many studies have shown that interesterification reduces the spherulitic nature of lard fat crystals (6–8).

Addition of 20% canola oil to lard led to the formation of larger and highly asymmetrical particles (Fig. 1C). Similar spherulitic size increases have been reported in butterfat–canola oil blends (9). IE of the 80% lard–canola oil (LCO) blend led to reduced spherulite size. Spherulites also became more symmetrical, and a distinct high-density core surrounded by a lower-density halo region became evident (Fig 1D). Addition of $\geq 30\%$ canola oil (CO) resulted in the formation of symmetrical spherulites (Figs. 2A and C). Reduced spherulite sizes resulted from IE; this was accompanied by an increase in the halo-to-core ratio within the spherulites (Figs. 2B and D). In general, incorporation of CO into lard led to a decrease in the spherulite size and the spherulitic particles became more symmetrical. IE led to a de-

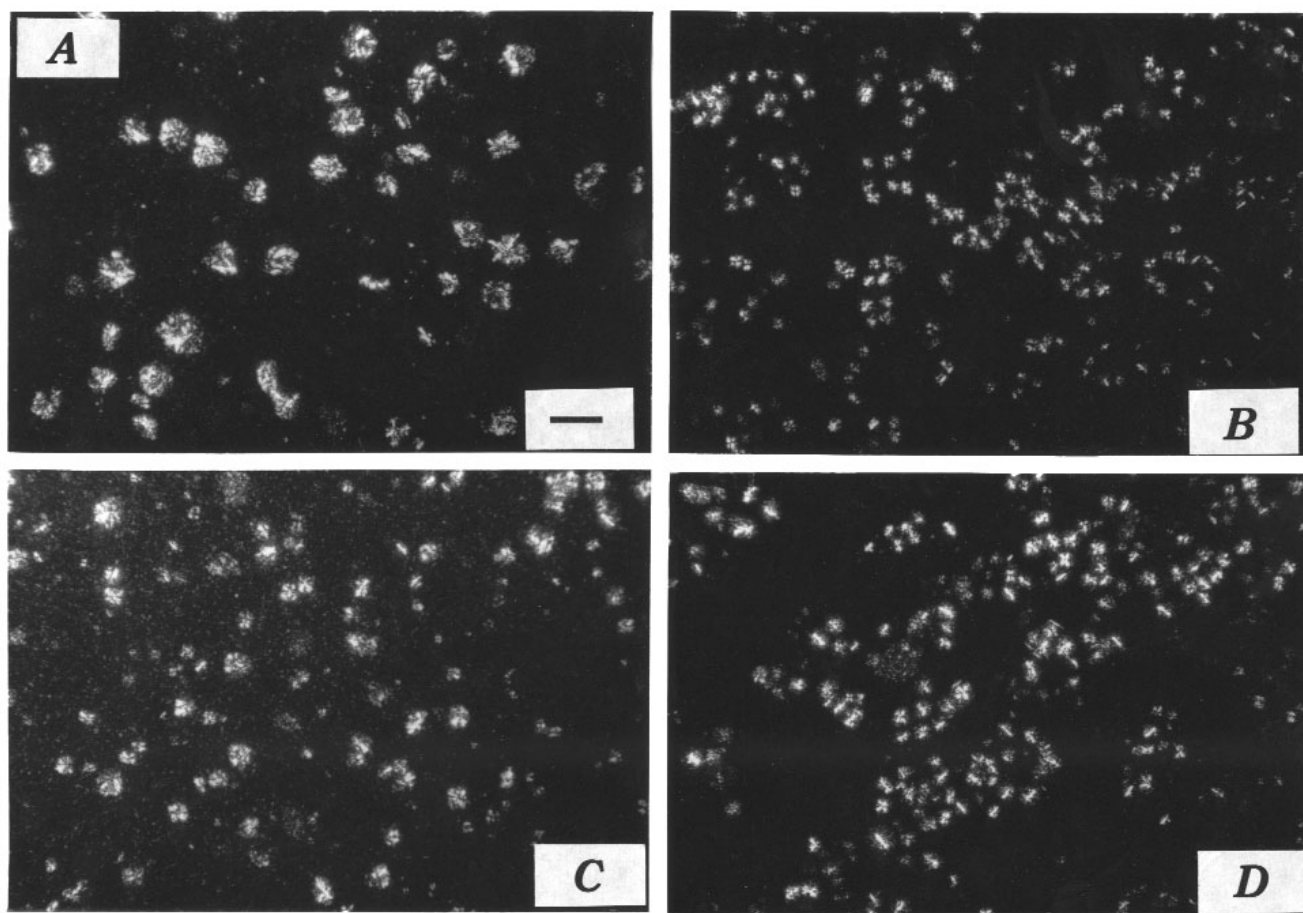


FIG. 2. Polarized light microscopy photomicrographs of LCO blends tempered 24 h at 5°C; (A) NIE70:30 LCO blend; (B) IE70:30 LCO blend; (C) NIE60:40 LCO blend; (D) IE60:40 LCO blend. The bar represents approximately 6 μm . See Figure 1 for abbreviations.

crease in spherulite size and to an increase in the halo-to-core ratio. Lard IE spherulites were also more symmetrical than their NIE counterparts.

Mulder and Walstra (10) have shown that fat-crystal morphology can substantially affect rheology. For example, they reported that slowly crystallized milk fat, with a solid fat content (SFC) over 20%, contained large spherulites and was pourable. On the other hand, acceptable spreads with SFC of ~10–15% can be manufactured (11,12). Hence, the formation of the fat-crystal network is strongly influenced by the structure of the individual crystals, or crystal aggregates (i.e., spherulites).

PO crystal morphology was not greatly altered by blending and/or IE (Figs. 3 and 4). PO spherulites were large, with a dense core and a lower-density halo region around the core. As for the LCO blends, incremental addition of soybean oil (SBO) to PO led to a decrease in the size of the spherulites. Interesterification of native PO and palm oil–soybean oil (POSBO) blends did not appear to alter crystal morphology significantly.

PO contains a high proportion of diacylglycerols (DAG) (~6%) (13,14) that influences its crystallization behavior (15).

Upon storage, PO develops a grainy texture that negatively impacts organoleptic properties, such as mouth feel. Watanabe *et al.* (16) found that PO granules predominantly consisted of POP (1,3-dipalmitoyl 2-oleoyl glycerol) in the β_1 form with a triple-chain-length structure. The main component of PO triacylglycerols (TAG) is POP, a symmetrical TAG (17). In a study of the kinetics of PO crystallization, Ng (18) discussed that the initial nuclei probably consisted of tripalmitin (PPP) and 1,2-dipalmitoyl-3-stearoyl glycerol (PPS). It is possible that this small fat fraction dictates the overall crystallization behavior. In complex fat systems, however, it is difficult to establish exactly which TAG, or other lipid components dominate the crystallization behavior (19).

In the NIE LCO blends, the interfacial boundary between the spherulites and liquid is much sharper than the NIE POSBO blends, in which spherulites consist of a dense core surrounded by a lower-density halo. The PO and POSBO spherulite boundary can be described as macroscopically diffuse. In practice, most of the available data on crystal-growth kinetics strictly considers sharp interfaces (20). This is at a microscopic level, however. Macroscopically, the presence of either sharp (lard) or diffuse (PO) interfaces may influence

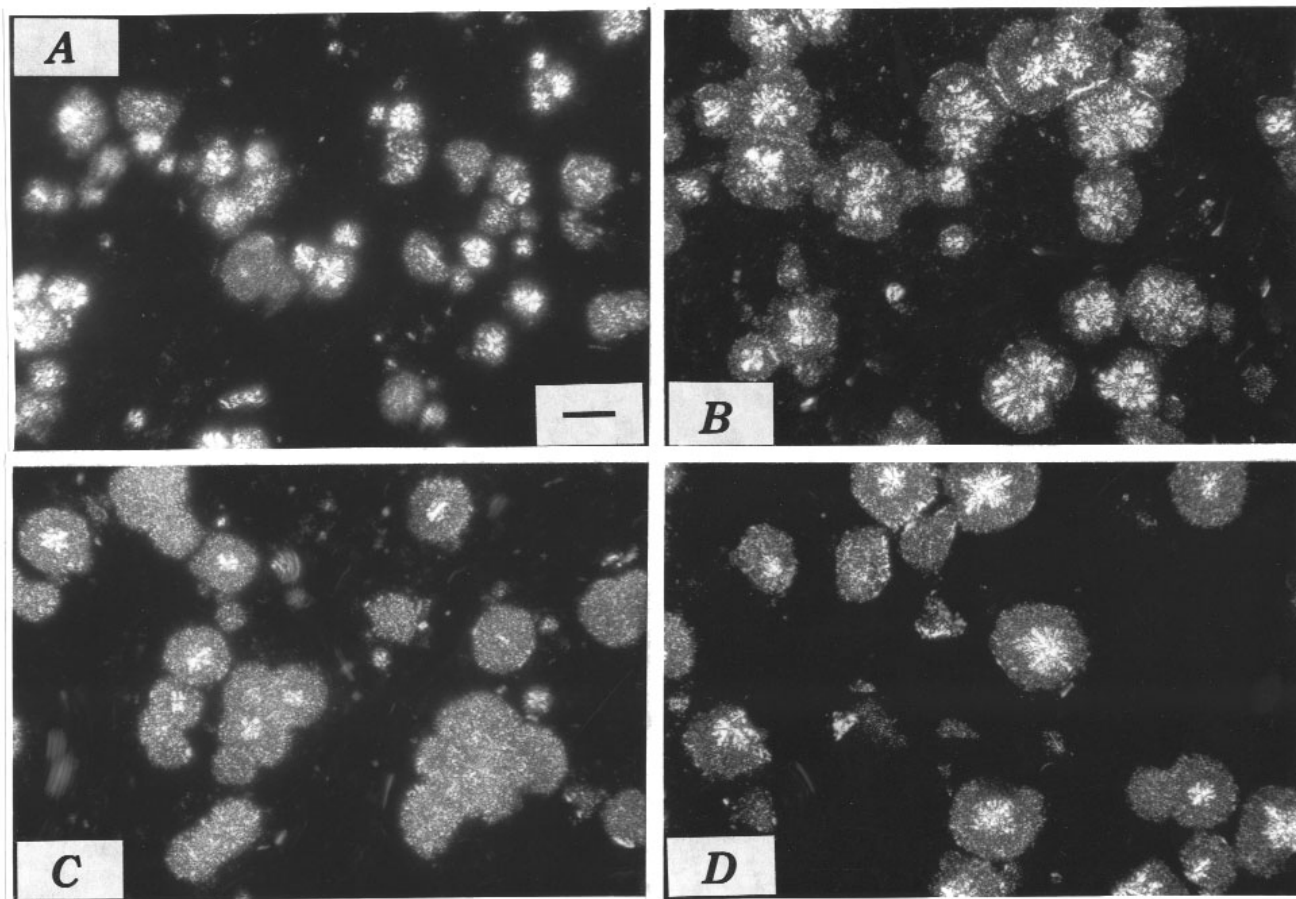


FIG. 3. Polarized light microscopy photomicrographs of palm oil/soybean oil blends (POSBO) tempered 24 h at 5°C; (A) NIE palm oil (PO); (B) IE PO; (C) NIE90:10 POSBO blend; (D) IE90:10 POSBO blend. The bar represents approximately 6 μm . See Figure 1 for abbreviations.

the interaction between spherulitic particles and affect the strength of the three-dimensional crystal network. The presence of greater halo-to-core ratios in the PO and POSBO spherulites relative to lard and LCO spherulites translates into a greater surface area available for spherulite-spherulite interactions and leads to a stronger network. The hardness index (HI) of PO and POSBO blends was much higher than the HI for lard and LCO blends, corroborating this hypothesis. Further support for this hypothesis comes from the fact that IE of lard and LCO blends led to the formation of more symmetrical spherulites with higher halo-to-core ratios, and the HI of lard and LCO blends increased.

In summary, our results suggest that fat-crystal networks composed of spherulites with high halo-to-core ratios are stronger than fat crystal networks composed on spherulites with low halo-to-core ratios. A potential strategy to modify the macroscopic physical properties of fat-containing products could involve altering the crystal morphology by blending or IE.

XRD. Long and short spacings of the NIE and IE LCO and POSBO blends were determined by powder X-ray diffraction. Diffraction patterns of natural fats produce broader peaks than

pure compounds (e.g., SSS) due to the presence of multiple fatty acid families within the unit cells (21) and the presence of oil. Lard has been previously reported to be a β -tending fat, whereas PO has been reported to be a β' -tending fat (22,23).

Table 1 summarizes XRD results on short and long spacings of fat crystals in the PO and POSBO blends. Short-spacing reflections of native PO fat crystals were centered at 4.46 \AA with shoulders at 3.92 and 4.30 \AA , and are characteristic of a mixture of β and β' polymorphs. Rapid cooling of PO results in the formation of β' crystals, while slow cooling at relatively high temperatures, giving rise to palm stearin, will result primarily in the crystallization of trisaturated TAG, and hence in the formation of β crystals (24). β crystal formation is promoted by the presence of trisaturates (e.g., PPP, SSS) containing fatty acids of similar chainlengths.

Upon dilution of PO with SBO, β polymorphs disappeared (Table 2). Chemically interesterified PO and IE POSBO blends contained mixtures of both polymorphs. Hence, the authors conclude that IE induced the formation of β polymorphs in PO and POSBO systems. Long spacings were not altered upon dilution of PO with SBO (Table 1). However, IE led to decreases of approximately 2 \AA in long spacings in PO

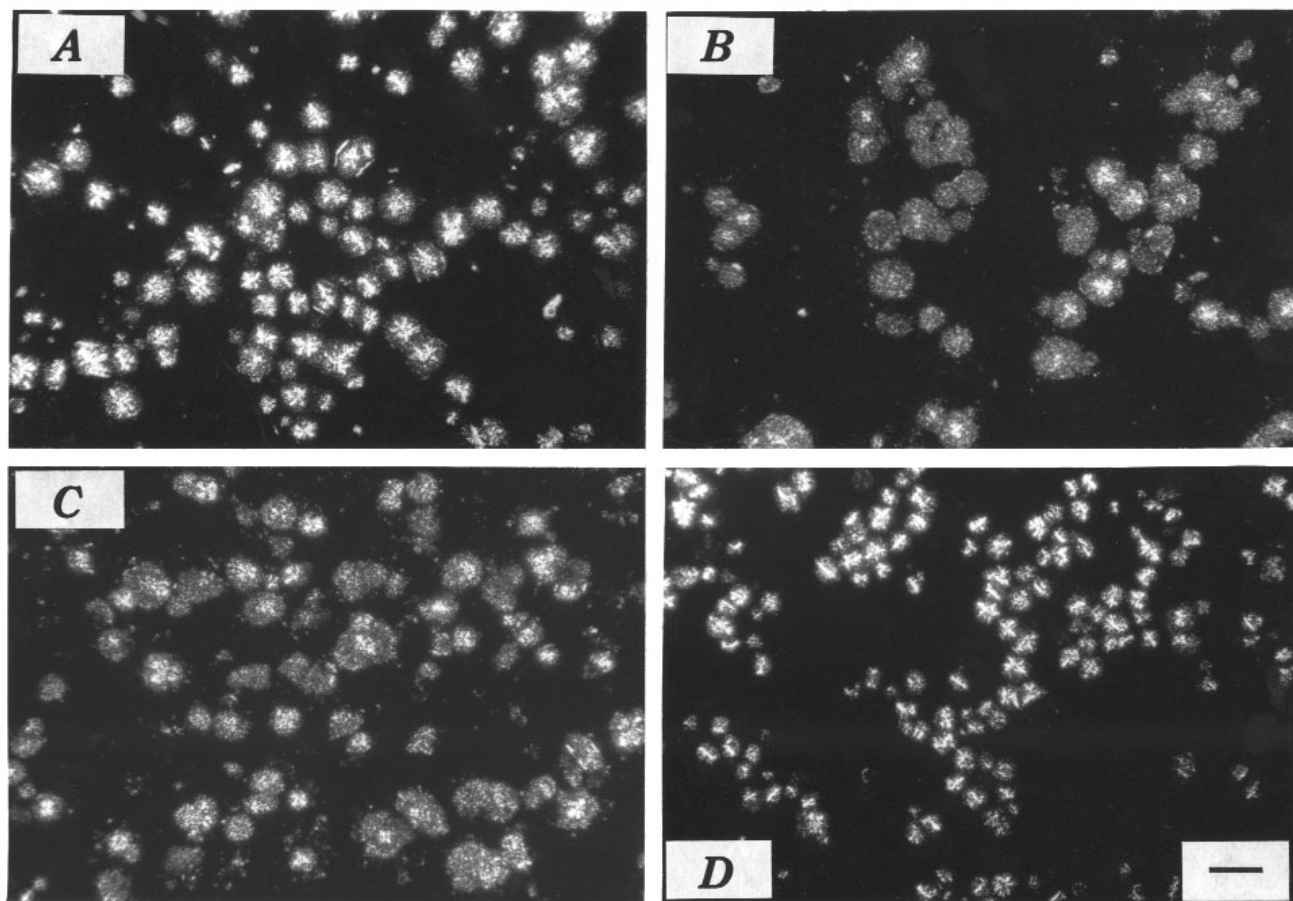


FIG. 4. Polarized light microscopy photomicrographs of POSBO blends tempered 24 h at 5°C; (A) NIE70:30 POSBO blend; (B) IE70:30 POSBO blend; (C) NIE50:50 POSBO blend; (D) CIE50:50 POSBO blend. The bar represents approximately 6 μm . See Figures 1 and 3 for abbreviations.

and POSBO blends (Table 1). These results agreed with short-spacing results that suggested the IE-induced transformation of some of the fat crystals to the β form. A transformation to a β form can be accompanied by a decrease in long spacings.

In this study, lard fat crystals were mainly β' tending (Tables 2 and 3). Incremental addition of vegetable oil led to an increased presence of β -crystals, and IE led to an increase in the proportion of β polymorphs in all blends (Table 2). Non-interesterified lard crystals had long spacings of 44.5 Å, while the crystals in the LCO blends with 10–30% CO had long spacings of 35.7 and 44.5 Å. The 44.5 Å spacing corresponds to a double-layer structure, and similar first-order long spacings have been observed in the past (6,25). The 35 Å spacing could correspond to the triclinic unit cell of an 18-carbon TAG bilayer tilted at 53.3° (26). This is surprisingly close to the tilt observed for an oleic acid bilayer triclinic unit cell (56.3°) (27). Another plausible explanation could be that addition of CO induced the formation of triple-chain unit cells in lard-fat crystals that has been observed in the past (6,25). In both cases, canola addition would have decreased system viscosity, permitting the crystallizing TAG to adopt a more thermodynamically favorable conformation.

Chemical interesterification of lard and LCO blends caused a large change in long spacings (Table 3). Only a single reflection at ~ 40 Å was observed after IE. Lutton (25) reported that hydrogenation or interesterification alone did not remove the triple structure of the unit cells of lard-fat crystals, but that a combination of both did. In double-layer structures, the odd-order long spacings are much stronger than the even-order long spacings (28–30) and such behavior has been observed in lard (25) and simple TAG (31). In triple-layer structures, the first-order spacing can be absent (32). Lutton (25) reported that only the second- and fifth-order reflections of a triple-layer structure were detected in lard-fat crystals. The authors observed this effect in this work as well. Singleton (33) explained this effect as acyl chains butting end-to-end, leading to decreased electron density between the layers.

As shown by deMan and deMan (24) and others (34,35), the more a fat is diluted down with liquid oil, the more likely is the formation of β -crystal polymorphs. This was generally the case in both fat systems.

Lutton (36) reported on the progressive decrease in long spacing of some saturated monoacid TAG crystals, in which a 1–2 Å decrease was generally associated with a transforma-

TABLE 1
Short and Long Spacings of Noninteresterified (NIE) and Chemically Interesterified (IE) Palm Oil–Soybean Oil Blends (POSBO)^a

Blend	Long spacings (Å)	Short spacings (Å)
NIE100	47.7(vvs), 14.4(vw)	3.92(w), 4.30(m), 4.46(s)
NIE90	46.8(vvs), 14.5(w)	3.90(m), 4.20(s)
NIE80	46.8(vs), 14.4(w)	3.89(m), 4.20(s)
NIE70	46.8(vs), 14.4(w)	3.90(m), 4.20(s)
IE100	45.0(s), 14.3(vvw)	3.90(m), 4.22(m), 4.46(s)
IE90	45.0(vvs), 14.3(w)	3.82(m), 4.2(s), 4.43(m)
IE80	41.9(vs), 13.7(w)	3.72(m), 4.10(s), 4.30(m)
IE70	45.0(vs), 14.5(w)	3.88(m), 4.25(m), 4.47(s)

^av, very; s, strong; w, weak; m, medium.

TABLE 2
Polymorphs of NIE and IE POSBO and Lard–Canola Oil Blends^a

Blend	Lard-canola oil blends		POSBO blends	
	NIE	IE	NIE	IE
100	$\beta' \gg \beta$	$\beta > \beta'$	$\beta' = \beta$	$\beta > \beta'$
90	$\beta' \gg \beta$	$\beta' > \beta$	β'	$\beta' > \beta$
80	$\beta' > \beta$	$\beta' = \beta$	β'	β'
70	$\beta' = \beta$	$\beta' = \beta$	β'	$\beta > \beta'$

^aFor abbreviations see Table 1.

tion of the β' to β polymorph. In the systems examined, a slight decrease in long spacings with increasing dilution was observed in NIE POSBO and IE LCO. The IE POSBO and NIE LCO systems, however, did not exhibit changes in long spacings as a function of dilution.

Attempts have been made since the 1950s to associate polymorphic form and morphology of fats (37). Hoerr (38) studied fat polymorphism and suggested that a specific crystal polymorphic form could influence the morphology of spherulites. However, it is virtually impossible to determine polymorphic form strictly by crystal morphology since a single crystal polymorph can exhibit multiple morphologies (39,40). Hicklin *et al.* (41) also observed such a lack of correlation with cocoa butter and vegetable fat blends. In this study, for example, 100% lard and the 70% POSBO blend both predominantly consisted of β' crystals. However, lard-crystal morphology was characterized by large, haphazard, irregular spherulites, while that of the POSBO blends was characterized by small, round spherulites with a dense core and a lower-density halo region. Likewise, in this study, the IE POSBO blends all had similar morphologies, yet the proportions of each polymorph within each blend differed appreciably.

TABLE 3
Short and Long Spacings of NIE and IE Lard–Canola Oil Blends

Blend	Long spacings (Å)	Short spacings (Å)
NIE100	44.5(vvs), 22.7(vw), 14.4(w)	4.08(m), 4.41(s), 4.64(vw)
NIE90	44.5(vs), 35.7(s), 22.7(vw), 14.3(w)	4.02(m), 4.35(s), 4.63(m)
NIE80	44.5(vs), 35.7(s), 22.7(vw), 14.1(w)	4.01(m), 4.39(s), 4.66(m)
NIE70	44.5(vs), 35.7(s), 22.7(vw), 13.6(w)	4.00(m), 4.36(m), 4.65(m)
IE100	39.9(vvs), 13.6(w)	3.84(s), 4.17(m), 4.44(vs), 5.15(mw)
IE90	39.6(vs), 14.2(w)	3.80(m), 4.19(s), 4.42(m)
IE80	40.2(vs), 14.1(w)	3.78(w), 4.21(m), 4.43(m)
IE70	39.0(vs), 13.8(w)	3.80(w), 4.21(m), 4.40(m)

IE led to changes in the crystal habit of lard and LCO blends—crystalline particles (spherulites) became more symmetrical, with a greater halo-to-core ratio, and the formation of β polymorphs was induced. These effects translated to a fat with a higher HI. IE did not lead to changes in the morphology of PO and POSBO blends, however, the formation of β polymorphs was induced in this system as well. The HI of PO and POSBO blends, however, did not change. Differences in the rheological properties between these two fats, and changes induced by IE, could be correlated to changes in crystal morphology, namely, a greater halo-to-core ratio in the spherulites that was associated with a harder fat.

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