Blending of Hydrogenated Low-Erucic Acid Rapeseed Oil, Low-Erucic Acid Rapeseed Oil, and Hydrogenated Palm Oil or Palm Oil in the Preparation of Shortenings

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ABSTRACT: Two ternary systems of fats were studied. In the first system, low-erucic acid rapeseed oil (LERO), hydrogenated low-erucic acid rapeseed oil (HLERO), and palm oil (PO) were blended. In the second system, hydrogenated palm oil (HPO) was used instead of PO and was blended with LERO and HLERO. The blends were then studied for their physical properties such as solid fat content (SFC), melting curves by DSC, and polymorphism (X-ray). HPO showed the highest melting enthalpy after 48 h at 15°C (141 ± 1 J/g), followed by HLERO (131 ± 2 J/g), PO (110 ± 2 J/g), and LERO (65 ± 4 J/g). Binary phase behavior diagrams were constructed from the DSC and X-ray results. Iso-line diagrams of partial-melting enthalpies were constructed from the DSC results, and binary and ternary isosolid diagrams were constructed from the NMR results. The isosolid diagrams demonstrated formation of a eutectic along the binary blend of PO/HLERO. However, no eutectic effect was observed along the binary lines of HPO/HLERO, PO/LERO, HPO/LERO, or HLERO/LERO. The same results were found with the iso-line diagrams of partial-melting enthalpies. As expected, addition of PO or HPO increased polymorphic stability in the β′ form of the HLERO/LERO mixture.

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KEY WORDS: Binary mixture phase, polymorphism, palm oil, rapeseed oil, shortening, ternary fat blends.

In product development work involving oils and fats, the solid fat content (SFC) profile of the oils and fats or their blends is of considerable importance. The SFC profile is used as a guideline in judging whether a certain oil, fat, or blend is suitable for a particular application (1). Physicochemical properties of a shortening influence its performance in the final products. For a cake shortening, a rather flat SFC curve with a tail at the end is desirable. The tail end indicates that some solids are present at high temperature (about 40°C), which is necessary to aid in the structural formation of the cake. One of the objectives in the manufacture of shortenings is to formulate a product that retains its plasticity over a wide temperature range (2). Typical plastic shortenings range between 15 and 30% in SFC and exhibit a relatively flat SFC profile over a temperature range from 15°C to their m.p. (3).

When fats of different compositions are mixed, they may show eutectic effects. This means that the m.p. of the SFC of the blend is lower than that of the individual components. Eutectic effects are usually undesirable, but in the case of margarines and shortenings, the effect can be beneficial (3).

The β′ form is preferred for margarines and for plastic bakery shortenings because the crystals tend to be small and uniform in size (4). The shortenings then provide good aeration for cakes. Shortenings that have the β-crystalline form aerate poorly but perform well in pie crust applications (5). For this reason, a β′-tending hard fat such as palm oil (PO) or hydrogenated palm oil (HPO) is usually incorporated into margarine and cake shortening formulations (3,6–8).

The objective of this work was to study the physical characteristics and interactions that occurred in a model of ternary systems involving PO or HPO, low-erucic acid rapeseed oil (LERO), and hydrogenated low-erucic acid rapeseed oil (HLERO) with respect to LERO-based shortening formulations. PO and HPO were chosen as the third component for their ability to stabilize β′-form crystals in soybean and canola margarines and shortenings.

MATERIALS

Commercial samples of LERO, HLERO (iodine value = 59), PO (iodine value = 51), and HPO (iodine value = 40) were obtained from Cargill N.V. (Izegem, Belgium).

METHODS

FA determination. FAME were prepared from crude lipids by boron trifluoride-catalyzed transesterification according to AOCS Method Ce 2-66 (9), which was slightly modified, and analyzed by GC on a Hewlett-Packard HP5880a apparatus fitted with a cold on-column injector and an FID (temperature 250°C). The operating conditions were as follows: 25 m × 0.32 mm CP-WAX-FFAP 58CB column from Chrompack (Middelburg, The Netherlands); film thickness, 0.2 μm; temperature program, from 55 to 150°C at 30°C/min and from 150 to 240°C at 5°C/min. Helium at 70 kPa was used as carrier gas. FAME were identified on the basis of their retention data compared with those of pure references.

Sample preparation. Various binary blends were prepared at composition intervals of 10 ± 0.1% by melting each type of oil or fat and mixing them in a glass vessel at the appropriate proportion. For ternary mixtures, fats were blended in

various ratios. All the blends were prepared according to Dan-thine and Deroanne (2). They were then stored at 15°C for 48 h in a room controlled at 15 ± 0.5°C.

Physical evaluation. (i) DSC. The DSC analyses were carried out using a 2920 Modulated differential scanning calorimeter (TA Instruments). Calibration was carried out using eicosane and dodecane. Blend samples were weighed after being crystallized and tempered in aluminum pans (TA Instruments) for 48 h at 15°C (see the previous paragraph). Samples were quickly frozen at –50°C in the DSC cell. The temperature was maintained at –50°C for 10 min to ensure complete crystallization. The melting curve was then obtained by heating the sample from –50 to 90°C at 15°C/min. Each analysis was run at least in triplicate. CV were all close to 5%.

(ii) X-ray diffraction analyses. The polymorphic forms of the blends were established by X-ray diffraction using a PW1710 Philips diffractometer (λ_{Cu} = 1.54178 Å, power = 1200 W) with a temperature control system (platinum probe). Short spacing was determined according to the Bragg relation. Each analysis was run twice. Analyses were performed isothermally at 15°C after samples were tempered for 48 h at 15°C.

(iii) SFC determinations. Samples were analyzed for their SFC after being crystallized and tempered (see the paragraph above on sample preparation). The NMR tubes were filled by means of a sampling device consisting of a glass tube with a tight-fitting plunger. The SFC in the products were determined after conditioning the samples for 10 min at temperatures of 15, 20, 25, 30, 35, 40, 42, 45, 47, 50, and 55°C. Each analysis was run at least twice. CV were all less than 5%.

(iv) Construction of phase diagrams. Binary-phase diagrams were constructed from the DSC results. The solidus and liquidus lines were fixed from DSC data. The liquidus line was recorded as the final melting temperature of the last peak, whereas the solidus line was recorded as the beginning temperature of the first peak. The low-temperature peaks corresponded to TG that were liquid at storage temperature. They were not ignored in this study because one of the blend components (LERO) was totally liquid at storage temperature (15°C) (2).

(v) Construction of iso-line diagrams. Binary and ternary diagrams of isosolid lines (compositions at which the SFC of a mixture is equivalent at a particular temperature) were constructed from the NMR data (10). Ternary diagrams of partial-melting enthalpies were constructed from DSC data. Partial-melting enthalpies, ΔH_i, were calculated by sequentially integrating the DSC melting curves and normalizing the values obtained (A_i) by the total surface included (A) by the DSC curves; the A_i to A ratios were then multiplied by the total melting enthalpy, ΔH_{tot}, of the sample (11):

$$\Delta H_i = (A_i/A) \times \Delta H_{tot} \qquad [1]$$

RESULTS AND DISCUSSION

Results from GLC analyses are shown in Table 1. The melting thermograms of the four fats after stabilizing for 48 h at 15°C are depicted in Figure 1. HPO showed the highest melting enthalpy

TABLE 1
FA Composition (wt%) of Hydrogenated Low-Erucic Rapeseed Oil (HLERO), Low-Erucic Rapeseed Oil (LERO), Hydrogenated Palm Oil (HPO), and Palm Oil (PO)[a]

FA	HPO	PO	HLERO	LERO
12:0		0.55	0.5	1.11
14:0	1.04	1.12		
16:0	42.68	44.56	6.61	4.57
16:1				
18:0	11.23	4.78	9.91	1.7
18:1	40.6	37.04	74.04	58.85
18:2	1.16	9.4	1.9	20.04
18:3				8.39
20:0		1.48		1.92
22:1			Traces	Traces

(141 ± 1 J/g), followed by HLERO (131 ±2 J/g), PO (110 ± 2 J/g), and LERO (65 ± 4 J/g). The higher-melting enthalpy of HPO compared to PO is related to its higher content of saturated FA. The same is true for HLERO compared with LERO.

Figure 2A shows a phase diagram of HLERO/LERO after tempering 48 h at 15°C. Figure 2B shows a phase diagram of HPO/LERO after tempering 48 h at 15°C. Figure 2C is a phase diagram of HPO/HLERO after tempering 48 h at 15°C.

The binary mixture of HLERO/HPO displays a typical continuous solid solution behavior after 48 h at 15°C. The binary mixtures of HLERO/LERO and of HPO/LERO display monotectic behavior after 48 h at 15°C. This type of behavior is characteristic of eutectic systems, which shift to monotectic systems when the difference in m.p. of the two components is 20°C or above (12). The m.p. of the components involved in the two blends studied are indeed different by more than 20°C.

Isosolid diagrams were constructed for binary and ternary blends from NMR data (10,12,13). The main use of these diagrams is for identification of eutectics in fat mixtures. If two fats are perfectly compatible and exhibit similar melting behavior, the points showing a constant SFC (isosolid lines) lie on straight horizontal lines and connect the melting temperatures of the individual fats. Two fats also can be compatible in phase behavior but have different melting behavior. In this case, the lines showing a constant SFC are straight and connect points for the two pure fats but exhibit a decrease in temperature from the harder fat to the softer fat. In this case, diluent softening of the hard fat occurs by addition of the softer fat. For extreme incompatibility between fats, eutectic crystallization effects cause significant depressions in SFC for mixtures of the two fats. On the isosolid diagram, this is seen as a compression of the lines, showing a constant SFC and a melting temperature below that of the individual fats. This procedure constitutes a useful way of rapidly judging the compatibility of fats qualitatively.

Binary isosolid diagrams. HLERO/HPO were compatible in phase behavior (straight lines; data not shown), whereas HLERO/LERO and HPO/LERO blends displayed monotectic behavior, as already seen in the phase behavior diagrams (data not shown).

Ternary isosolid diagrams. Figure 3A shows the isosolid diagram at 20°C for the ternary LERO/HLERO/HPO mixture
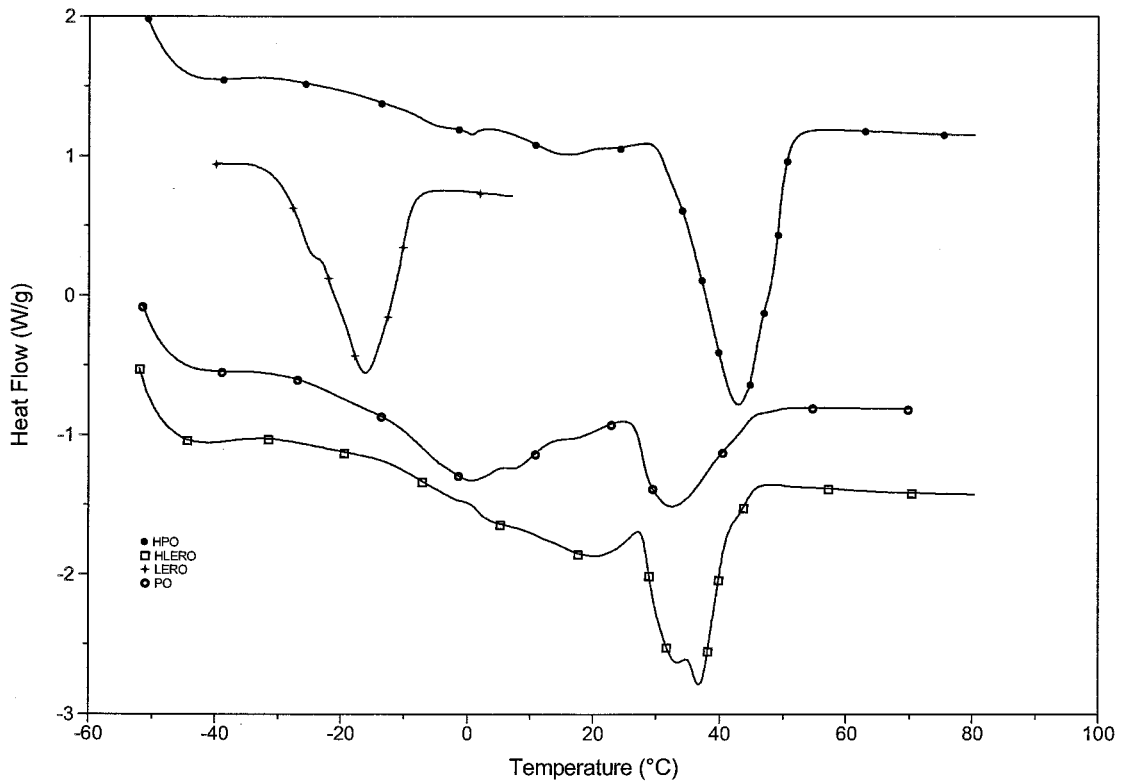
FIG. 1. Melting curves of hydrogenated low-erucic rapeseed oil (HLERO), low-erucic rapeseed oil (LERO), hydrogenated palm oil (HPO), and palm oil (PO) after tempering 48 h at 15°C.
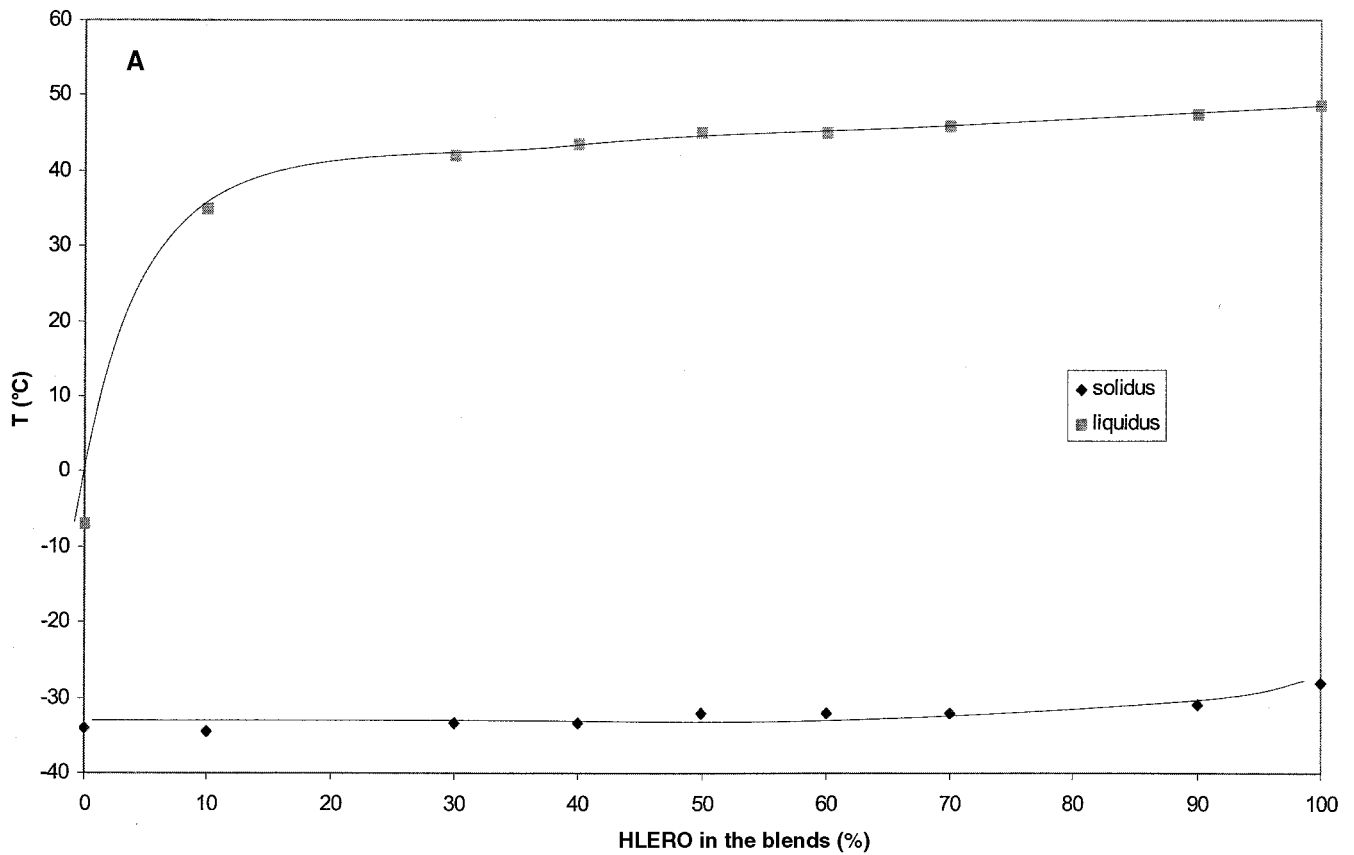

FIG. 2. Phase diagram after tempering 48 at 15°C. (A) HLERO/LERO blends; (B) HPO/LERO blends; (C) HPO/HLERO blends. T, temperature; see Figure 1 for other abbreviations.
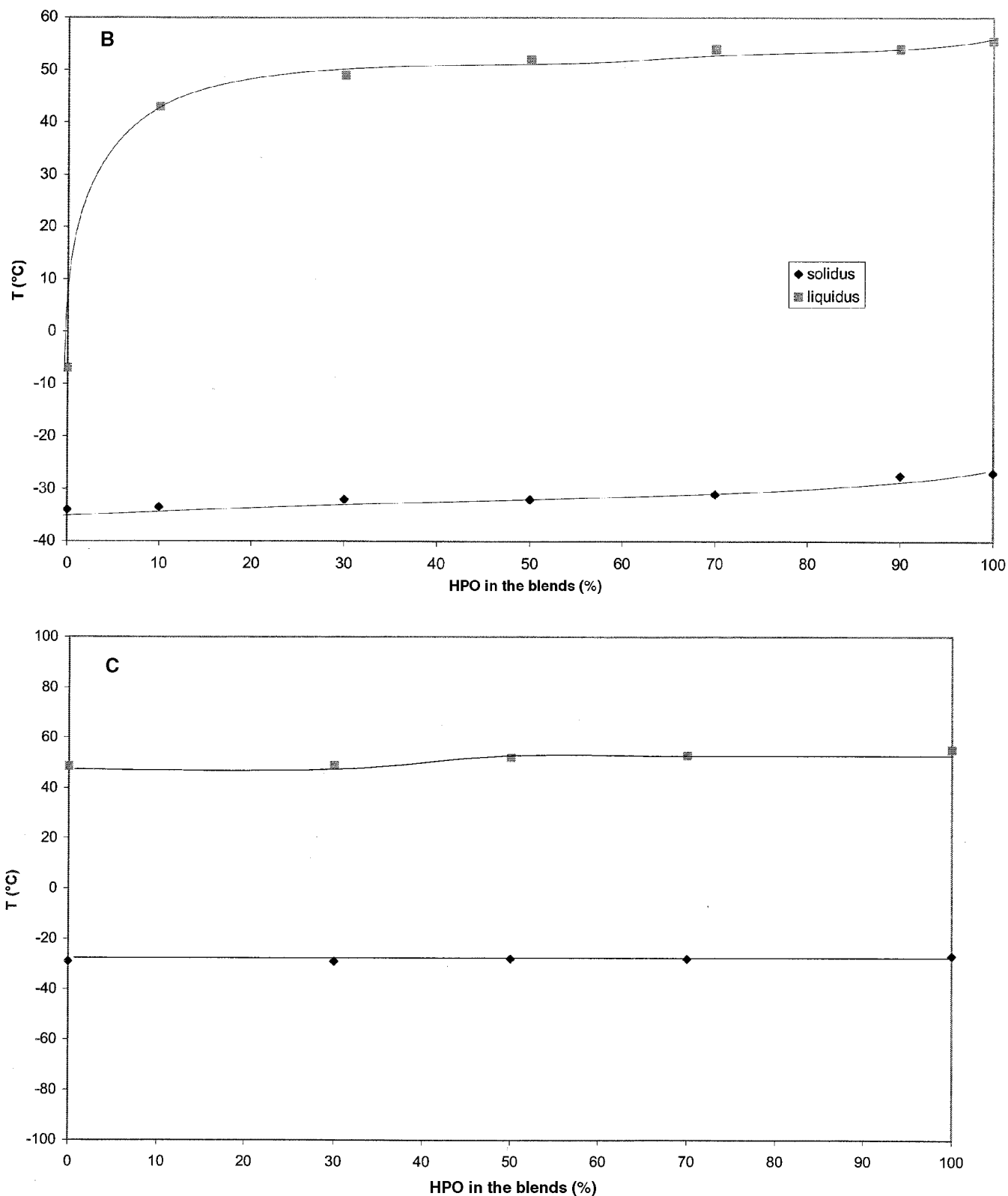
FIG. 2. (continued)

after tempering 48 h at 15°C. Figure 3B shows the isosolid diagram at 20°C for the ternary mixture LERO/HLERO/PO after tempering 48 h at 15°C.

Figures 4A and 4B show the isosolid diagrams at 30°C for the ternary blends LERO/HLERO/HPO and LERO/HLERO/PO. For ideal mixing behavior, a straight line would be
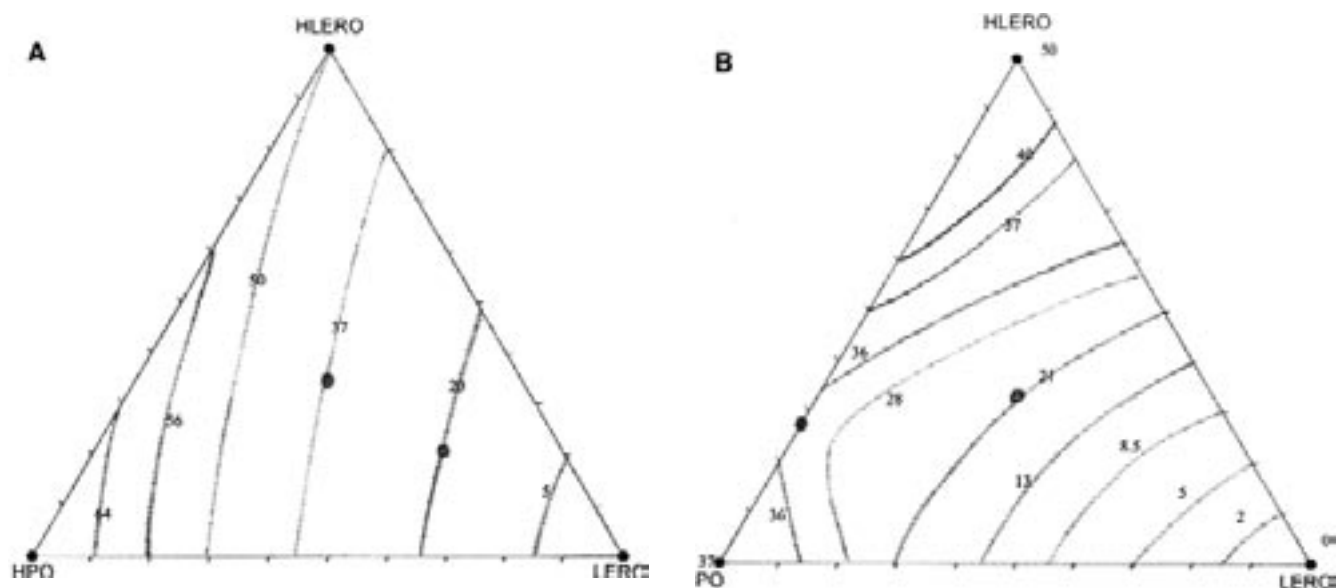
FIG. 3. Isosolid diagrams at 20°C for (A) LERO/HLERO/HPO and (B) LERO/HLERO/PO after tempering 48 h at 15°C. See Figure 1 for abbreviations.

observed for each iso-line at each temperature. However, this was not observed for many ternary combinations. Eutectic interaction, as indicated by a depression of the isosolid lines, was observed only along the binary lines of PO/HLERO. No eutectic effect was noted along the binary lines of HPO/LERO, HPO/HLERO, PO/LERO, and HLERO/LERO.

A partial melting enthalpy (ΔH_i) represents the energy that is necessary to bring the fat, oil, or blend from temperature i to a complete melt.

The iso-line diagrams of $\Delta H_{20°C}$ of HPO/HLERO/LERO and PO/HLERO/LERO are depicted in Figures 5A and 5B. HPO showed the highest $\Delta H_{20°C}$, followed by HLERO, PO, and LERO. The ternary diagram of HLERO/PO/LERO showed lower $\Delta H_{20°C}$ compared with HLERO/HPO/LERO.

For example, the $\Delta H_{20°C}$ for the blends coded X and X′, where all component fats were present in the ratio 1:1:1 (by wt), were 17 ± 1 and 50 ± 2 J/g, respectively. This is related to the higher content of saturated FA in HPO compared with PO.

Eutectic interactions, as indicated by the $\Delta H_{20°C}$ iso-lines, were observed only along the binary line of PO/HLERO (Fig. 5B). This was obvious for the blends coded A, B, and C (see Table 2 for ratios), in which $\Delta H_{20°C}$ were 70 ± 4, 55 ± 2, and 30 ± 1 J/g, respectively (binary line HLERO/LERO, Fig. 5A). Similar trends were observed for the blends coded D, E, F; G, H, I; and J, K, L (see Table 2 for ratios). Similar interaction trends were also observed in both $\Delta H_{30°C}$ systems (data not shown). The interactions between blends found by DSC were similar to those found by SFC analyses (NMR), where
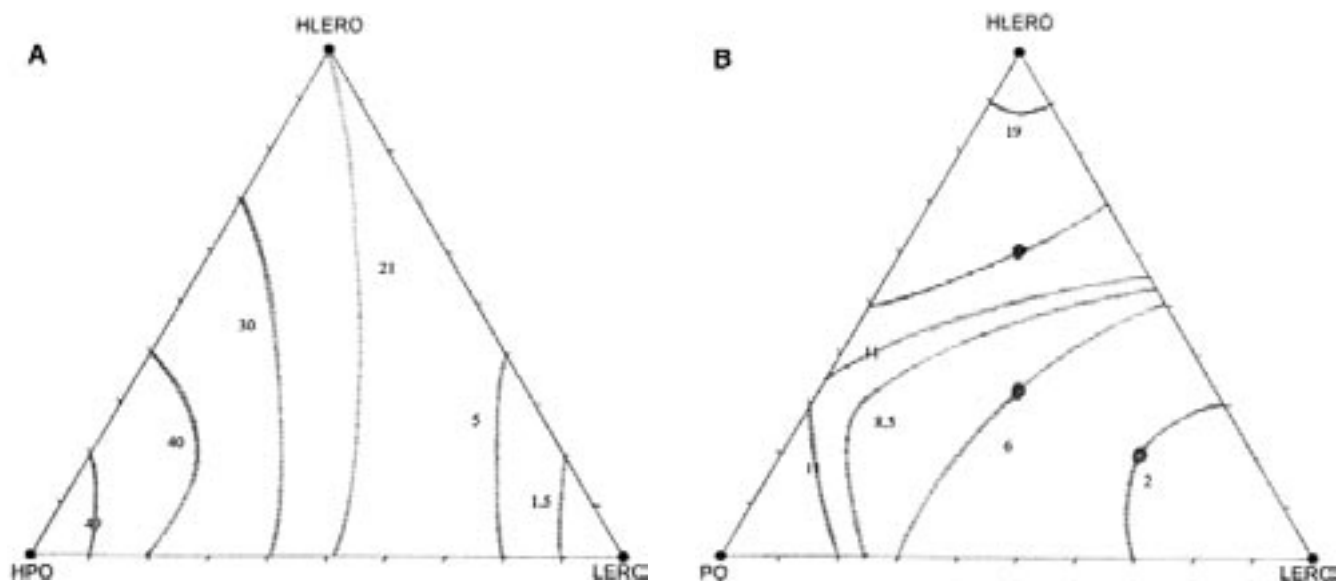

FIG. 4. Isosolid diagrams at 30°C for (A) LERO/HLERO/HPO and (B) LERO/HLERO/PO after tempering 48 h at 15°C. See Figure 1 for abbreviations.
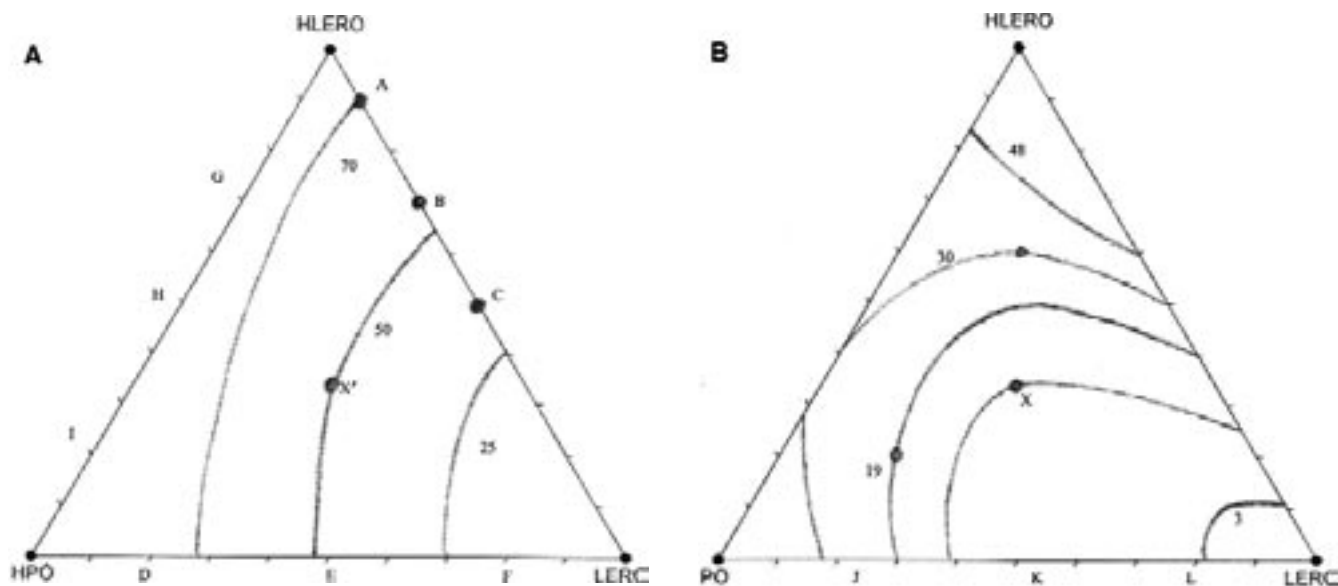
FIG. 5. Iso-line diagrams of partial melting enthalpy ($\Delta H_{20°C}$) for (A) LERO/HLERO/HPO and (B) LERO/HLERO/PO after tempering 48 h at 15°C. See Figure 1 for abbreviations.

eutectic formation was observed along the binary line of PO/HLERO.

Table 3 shows the X-ray diffraction patterns of several blends. As expected (3), the addition of HPO stabilized the β′ form of the HLERO/LERO/HPO blends. PO also delayed the formation of β crystals in the HLERO/LERO/PO mixture but was less effective than HPO.

As discussed in a previous paper (2), the mixture of 60% HLERO and 40% LERO is suitable to use as a plastic shortening. However, this blend is β-tending upon storage. The use of HPO to stabilize the β′ form, as recommended by deMan and deMan (3), is a way of using a blend of HLERO/LERO as a cake shortening.

The mixture of 50% HLERO, 45% LERO, and 5% HPO studied [with a composition similar to the blend studied previously (2) but more stable in the β′-crystalline form] displayed a flat SFC profile like a plastic shortening over the

temperature range of 15–25°C, with a small tail after 40°C, and was β′-stable upon storage at 15°C (data not shown). Such a blend could be used as a cake shortening.

ACKNOWLEDGMENTS

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TABLE 2
Composition of Several Blends Studied

Code	HLERO %	LERO %	PO %	HPO %
A	90	10		0
B	70	30		0
C	50	50		0
D	0	20		80
E	0	50		50
F	0	80		20
G	70	0		30
H	50	0		50
I	20	0		80
J	0	25	75	
K	0	50	50	
L	0	80	20	
X (ratio)	1	1	1	
X′ (ratio)	1	1		1

TABLE 3
Polymorphism Evolution During Storage of the Various Blends at 15°C[a]

Blend	1 h	16 h	48 h	7 d	1 mon	2 mon
LERO	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
HLERO	(α) + β′	β′	β′ ((+ β))	β′ + β	β + (β′)	β
PO	β′	β′	β′	β′	β′	β′
HPO	β′	β′	β′	β′	β′	β′
HLERO 90%/LERO 1%	α + β′	β′	β′ (+ psβ′)	β′ + β	β + (β′)	β
HLERO 70%/LERO 30%	α + β′	β′ + (β)	β + (β′)	((β′)) + β	β + ((β′))	β
HLERO 50%/LERO 50%	β′	β	β	β	β	β
HLERO 30%/LERO %	β′ + liquid	β + liquid	β + liquid	β + liquid	β + liquid	β + liquid
HPO 90%/LERO 10%	β′	β′	β′	β′	β′	β′
HPO 70%/LERO 30%	β′	β′	β′	β′	β′	β′
HPO 50%/LERO 50%	β′	β′	β′	β′	β′	β′
HPO 30%/LERO 70%	β′	β′	β′	β′	β′	β′
HPO 10%/LERO 90%	β′	β′	β′	β′	β′	β′
HLERO 20%/LERO 20%/HPO 20%	β′	β′	β′	β′		
HLERO 15%/LERO 15%/HPO 30%	β′	β′	β′	β′		
HLERO 20/LERO 20/PO 20	β′	β′	β′	β′ + (traces of β)		
HLERO 15/LERO 15/PO 30	β′	β′	β′	β′ + ((β))		

[a]Single parentheses mean few; double parentheses mean very few. ps, pseudo; for other abbreviations see Table 1.

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