Crystallization Characteristics of Hydrogenated Canola Oil as Affected by Addition of Palm Oil

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Addition of palm oil at levels of 5, 10 and 15% to selectively and nonselectively hydrogenated canola oil increased the time of isothermal crystallization at 20°C and delayed the appearance of the isothermal crystallization peak as determined by DSC. The degree of supercooling was also increased. Addition of palm oil to canola oil before selective or nonselective hydrogenation decreased the time of the appearance of the isothermal crystallization peak. Rates of crystallization were determined in selectively hydrogenated canola palm oil mixtures which followed first order kinetics.

Palm oil and hydrogenated palm oil are used as components of shortenings and margarines. In North America fully hydrogenated palm oil is used to extend the plastic range and stabilize the β′-crystal form of soybean and canola based shortenings (1-4). Palm oil is incorporated in canola based stick margarines mainly to stabilize the β′-crystal form and prevent β-recrystallization (5-7). It has been shown in a previous communication (8) that addition of palm oil at a level of 10% to canola oil before hydrogenation or 15% after hydrogenation greatly delayed polymorphic transition of the β′- to the β-form. This stability effect was especially pronounced in nonselectively hydrogenated canola oil containing about 30% solid fat at 10°C. Palm oil is generally considered to be a "slow crystallizer", giving rise to the post hardening effect (9).

This paper reports on a differential scanning calorimetry study of the effect of palm oil addition to canola oil as it influences the crystallization rates of these products.

MATERIALS AND METHODS

Canola oil was hydrogenated under selective (200°C and 48 KPa) and nonselective (160°C and 303 KPa) conditions as previously described (8). Palm oil was added to selectively and nonselectively hydrogenated canola oil at levels of 5, 10 and 15%. Palm oil was also added to the liquid canola oil at levels of 5 and 10%, and was then hydrogenated selectively and nonselectively. The following designations were used for selectively hydrogenated oils: SC — Selectively hydrogenated canola oil (Control); SC + 5% P — Control + 5% palm oil; SC + 10% P — Control + 10% palm oil; SC + 15% P — Control + 15% palm oil; SCP 5% — Selectively hydrogenated canola oil containing 5% palm oil; SCP 10% — Selectively hydrogenated canola oil containing 10% palm oil.

For nonselectively hydrogenated (NSC) oil the designations were: NSC —Nonselectively hydrogenated canola oil (Control); NSC + 5% P — Control + 5% palm oil; NSC + 10% P — Control + 10% palm oil; NSC + 15% P — Control + 15% palm oil; NSCP 5% — Nonselectively hydrogenated canola oil containing 5% palm oil; NSCP 10% — Nonselectively hydrogenated canola oil containing 10% palm oil.

Palm oil was also hydrogenated to evaluate its crystallization properties.

Iodine value, dropping point, fatty acid composition, *trans* isomer content and solid fat content were determined as previously described (8). Differential Scanning Calorimetry (DSC) was used to determine crystallization temperature, ΔH of crystallization and rate of crystallization. For the DSC analyses, a model 900 DuPont thermal analyser was used. Weighed samples (8-10 mg) were heated at 70°C for five minutes to destroy crystal nuclei before cooling began. Rate of cooling was 5°C/min from 60 to 20°C, followed by isothermal holding at 20°C for a total of 30 minutes.

Starting time is defined as the time when cooling began, which is indicated by the first exothermal deflection, which represents the specific heat (Figs. 1-3). The second exothermal deflection (peak I) represents the heat of crystallization during cooling, and the third exothermic deflection (peak II) represents the heat of crystallization during isothermal holding at 20°C.

The rate of crystallization during cooling was determined by calculation of ΔH of the crystal fraction, X, at a given time, t, as follows:

$$X_t = \frac{\frac{d\Delta H_{dt}}{dt}}{H}$$

where ΔH is the latent heat of crystallization during cooling. The crystallization rate constant was defined as:

$$K = \frac{\text{change in crystal fraction}}{\text{change log t}}$$

A straight line obtained from a plot of the data is indicative of first order kinetics.

The crystallization temperature is the temperature at the start of the exothermal deflection of crystallization.

Supercooling is defined as the difference in temperature between the dropping point and crystallization temperature.

RESULTS AND DISCUSSION

Cooling curves for SC fats are displayed in Figure 1, for NSC fats in Figure 2 and palm oil and hydrogenated palm oil in Figure 3.

SC + P and NSC + P. Addition of palm oil to hydrogenated canola oil in the SC + P and NSC + P series progressively decreased the iodine value and increased the saturated fatty acid content. Crystallization temperatures decreased with each addition of palm oil, but dropping points were affected to a minor ex-

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TABLE 1

TABLE 1. Composition and Properties of Palm Oil, Hydrogenated Palm Oil and Canola-Palm Oil Blends

Sample	Iodine value	Total saturates + *trans*	Dropping point °C	Crystallization temp °C	Supercooling[a] temp °C	Solids at 20°C %	Total ΔH of crystallization J/g	ΔH isothermal/ΔH total %	Rate of crystallization during cooling k	Time of isothermal crystallization peak (min)
Palm oil	51.5	48.7	38.5	22.0	16.5	16	20.2	59	8.0	10.2
Hydrogenated palm oil	27.5	66.0	54.9	39.5	15.4	85	108.2	0	4.6	—
SC	66.5	67.1	40.4	27.5	12.9	40	38	63	4.3	4.7
SC + 5% P	65.4	68.6	40.1	25.5	14.6	39	38	64	6.1	5.1
SC + 10% P	65.3	69.3	40.2	24.5	15.7	38	35	66	6.6	5.6
SC + 15% P	64.8	69.3	39.0	24.0	15.0	37	31	70	7.2	6.0
SCP5%	67.9	72.3	38.6	24.5	14.1	36	29	70	6.2	4.0
SCP10%	70.5	62.3	34.9	20.5	14.4	24	18	89	[b]	3.3
NSC	72.0	48.4	35.3	22.0	13.3	14	14.1	86	3.7	6.5
NSC + 5% P	70.9	49.6	35.6	21.5	14.1	12	12.5	90	[b]	7.7
NSC + 10% P	69.0	50.3	35.3	20.5	14.9	14	17.7	95	[b]	9.2
NSC + 15% P	67.4	50.5	35.2	20.0	15.2	17	17.4	97	[b]	10.5
NSCP5%	68.8	51.5	38.2	23.5	14.7	21	22.0	78	3.9	4.5
NSCP10%	69.2	53.9	36.4	21.5	14.9	17	18.0	75	[b]	3.5

[a] Temperature difference between dropping point and crystallization temperature.

[b] Insufficient fat had crystallized to determine K.

tent. The degree of supercooling was greater with increasing amounts of added palm oil and increased from 12.9 to 15.0°C in the SC + P series and from 13.3 to 15.2°C in the NSC + P series (Table 1). During the isothermal crystallization at 20°C the peak of the exothermal was delayed with increasing addition of palm oil (Figs. 1 and 2). In the SC + P series, the delay is from 4.7 min in SC to 6.0 min in SC + 15% P, and in the NSC + P series from 6.5 min in NSC to 10.5 min in NSC + 15% P (Table 1). The percentage of fat crystallization at isothermal holding at 20°C (ΔH isothermal/ΔH total) increased in both series with increased palm oil addition. This percentage in the SC + P series went from 63% in SC to 70% in SC + 15% P, and in the NSC + P series from 86% in NSC to 97% in NSC + 15% P (Table 1).

Addition of palm oil in the SC + P series decreased the solid content at 20°C from 40% in SC to 37% in SC + 15% P (Table 1). Total ΔH also decreased. The opposite was true in the NSC + P series. Solid fat increased from 14% in SC to 17% in NSC + 15% P. Total ΔH increased. Palm oil contains 16% solids at 20°C as compared to 40% in SC and 14% in NSC, therefore, solid fat content is decreased in the SC series and increased in the NSC series by palm oil addition. The correlation coefficient between solid fat content and total ΔH of crystallization was 0.9687. The rates of crystallization in the SC + P series is given in Figure 4. It appears that the rate of crystallization (K, as previously defined) increased during cooling with increasing additions of palm oil (Table 1). The value for K of SC is 4.3 and that of SC + 15% P is 7.2. Crystallization was insufficient during cooling in the NSC + P series, and this prevented calculation of the K values. The shape of the curves as plotted in a semi-logarithmic scale are indicative of first order kinetics (Fig. 4).

SCP. In SCP5% and SCP10% palm oil was added before hydrogenation of the canola oil and, therefore, was also hydrogenated. In selective hydrogenation the more unsaturated fatty acids are hydrogenated first. Palm oil contained 9.5% of 18:2 fatty acid and it is difficult to know how much of the palm oil itself was hydrogenated. It is difficult to hydrogenate to a specific iodine value. The iodine value of SCP10% (70.5) was a little too high to compare with the characteristics of fats of the SC + P series (IV 66:5–64.8). However, it did show that when palm oil is added before hydrogenation the onset of the peak of the isothermal

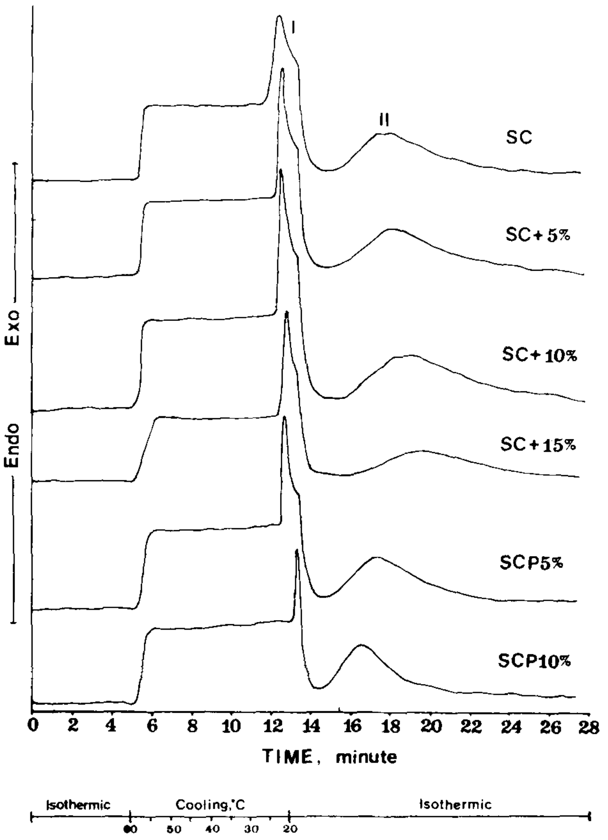

FIG. 1. DSC crystallization curves of selectively hydrogenated canola with palm oil additions. SC = selectively hydrogenated canola (control), SC + 5% P = control + 5% palm oil, SC + 10% P = control + 10% palm oil, SC + 15% P = control + 15% palm oil, SCP 5% = canola oil + 5% palm oil selectively hydrogenated, SCP 10% = canola oil + 10% palm oil selectively hydrogenated.

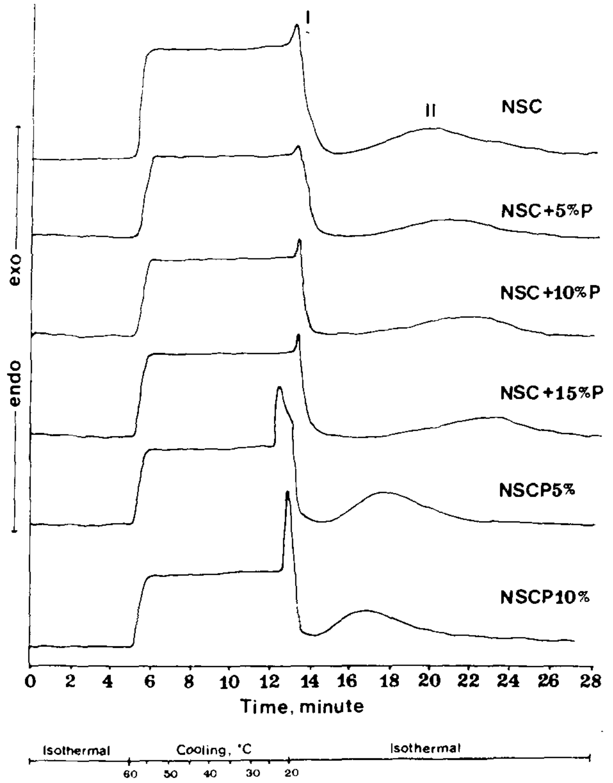

FIG. 2. DSC crystallization curves of nonselectively hydrogenated canola oils with palm oil additions. NSC = nonselectively hydrogenated canola (control), NSC + 5% P = control + 5% palm oil, NSC + 10% P = control + 10% palm oil, NSC + 15% P = control + 15% palm oil, NSCP 5% = canola oil + 5% palm oil nonselectively hydrogenated, NSCP 10% = canola oil + 10% palm oil nonselectively hydrogenated.

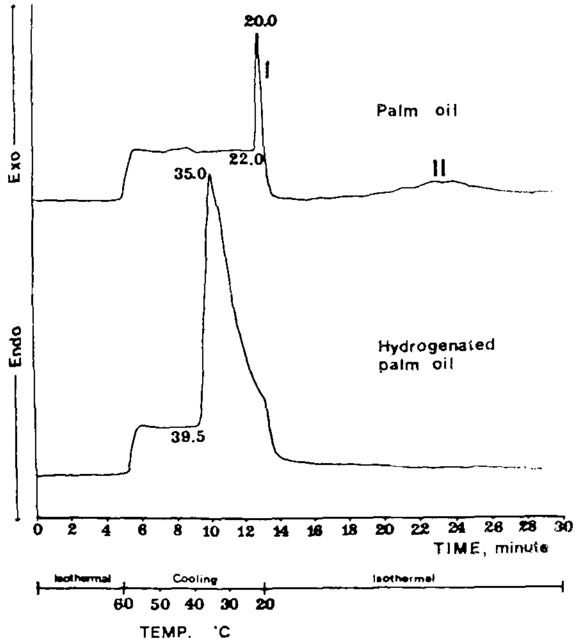

FIG. 3. DSC crystallization curves of palm oil and hydrogenated palm oil of IV 27.5.

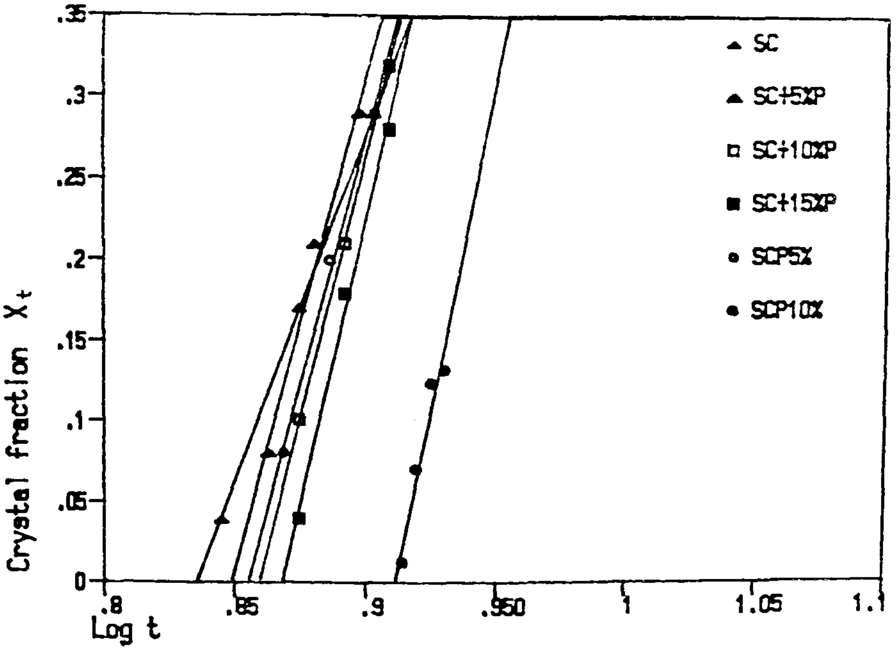

FIG. 4. Development of crystal fraction X_t during cooling of selectively hydrogenated canola oil.

crystallization takes place sooner, which means that post-crystallization time is shortened with increasing additions of palm oil (Fig. 1, Table 1).

NSCP series. In nonselective hydrogenation, unsaturated fatty acids are randomly hydrogenated without regard to their degree of unsaturation. Addition of palm oil before hydrogenation increased the saturation and the solid content as compared with fats in the NSC + P series. Time of isothermal peak of crystallization was 4.5 and 3.5 min for NSCP5% and NSCP10%, as compared with 6.5 min for NSC and 10.5 min for NSC + 15% P, indicating that the post crystallization time was shortened (Fig. 2, Table 1).

Values for hydrogenated palm oil of IV 27.5 are included although it is doubtful that the added palm oil in the SCP and NSCP series was hydrogenated to the same degree. The crystallization curve (Fig. 3) illustrates that the hydrogenated palm oil crystallized completely before reaching 20°C with no post-crystallization. The rate of crystallization was lower than for palm oil (Table 1).

It can be concluded that addition of palm oil to hydrogenated canola oil increased the extent of isothermal crystallization and delayed the appearance of isothermal crystallization peaks at 20°C. It also increased the degree of supercooling. In the selectively hydrogenated canola oil the crystallization rates during cooling were increased with the addition of palm oil. Rates of crystallization followed first order kinetics. When palm oil was added before hydrogenation the time of appearance of the isothermal crystallization peak was shortened.

In the manufacture of margarines and shortening Differential Scanning Calorimetry could be a useful technique in estimating crystallization temperature, rate of crystallization and post crystallization of a particular formulation.

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[Received January 10, 1989; accepted July 6, 1989]
[J5636]