Polymorphic Stability of Hydrogenated Canola Oil as Affected by Addition of Palm Oil

P.H. Yap, J.M. deMan* and **L. deMan**[a]
Department of Food Science, University of Guelph, Guelph, Ontario N1H 2W1 and [a]deMan Food Technology Services, Inc., Guelph, ON N1H6B5

Palm oil was added to canola oil before and after hydrogenation and the effect of this addition on the polymorphic stability of the hydrogenated oils was investigated. Palm oil was added to canola oil at two levels to produce hydrogenated canola and palm oil blends containing 5 and 10% palm oil. The levels of palm oil added to hydrogenated canola oil were 5, 10 and 15%. Samples were subjected to temperature cycling between 5 and 20°C as well as storage at 5°C up to 56 days. X-ray diffraction and polarized light microscopy were used to follow the changes of polymorphic form and crystal growth, respectively, during cycling and storage. The β-crystal contents of the oils were quantified based on the relative density of the characteristic short spacings using a Soft Laser Scanning Densitometer. The delaying effect of palm oil on phase transition was observed using Differential Scanning Calorimetry. Palm oil showed no effect on the polymorphic stability of the temperature cycled selectively hydrogenated oil, however, it delayed the transition rate at a constant temperature of 5°C. Addition of palm oil at the 10% level before hydrogenation and the level after hydrogenation proved to be effective in delaying polymorphic instability of nonselectively hydrogenated canola oil. The β′ stabilization effect of palm oil on the polymorphic stability of hydrogenated canola oil is most likely due to a decrease of fatty acid chain length uniformity.

Canola oil has been widely used in various food products such as margarines, shortenings, salad oils and cooking oils. The oil is processed from the seed of the recently developed rapeseed cultivars (Canola), which are genetically low in both erucic acid and glucosinolates. It is well documented that hydrogenated canola oil has a tendency to recrystallize in the β-modification owing to its triglyceride homogeneity (about 95% of C18 fatty acids) (1,2). β-fat crystals are large, with sizes ranging from 5-25 micrometers. The formation of these large crystals results in a noticeable increase in graininess, which causes the products to be gritty and crumbly.

One way in which the β-crystal formation can be limited is by the addition of palm oil. Palm oil has the unique characteristic of having a high saturated acid content. The fatty acids located at the 2-position of the triglycerides contain 14% palmitic and 1% stearic acid. It also contains appreciable amounts of diglycerides (5-8%), which can have substantial effects on the physical properties of the oil (3,4). One of the important crystallization properties of palm oil is that its α-lifetime is extraordinarily long, which has been shown to be due to the high level of diglycerides (4). Blending of palm oil with hydrogenated canola oil thus may result in limiting or delaying the formation of β-form crystals. Since changes in physical properties take place during the hydrogenation process, the point at which palm oil is added to the oil can also affect the transition to the β-polymorph. The present study was undertaken to investigate the effects of the addition of different levels of palm oil to canola oil before and after the hydrogenation process on the polymorphic stability of the oil.

MATERIALS AND METHODS

Commercially refined and bleached canola oil was supplied by CSP Foods Limited and refined, bleached and deodorized palm oil was obtained from Palmco Inc. (Portland, OR). Canola oil and canola-palm oil mixtures of 95:5 ratio and 90:10 ratio were hydrogenated in a Parr pressure reactor with a 2L bomb and a charge of 1Kg oil. Hydrogenation conditions were 200°C and 48 kPa hydrogen pressure (selective), and 160°C and 303 kPa hydrogen pressure (nonselective). The nickel catalyst Calsicat E472F was used at a level of 0.2% by weight of the oil. Hydrogenations were carried out to yield products with I.V. of 68 ± 4. Palm oil was added at a level of 5, 10 and 15% by weight to the hydrogenated canola oils. The following designations were used for the selectively hydrogenated (SC) 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; SCP5% — Selectively hydrogenated canola oil containing 5% palm oil; SCP10% — Selectively hydrogenated canola oil containing 10% palm oil. For nonselectively hydrogenated NSC oils: 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; NSCP5% — Nonselectively hydrogenated canola oil containing 5% palm oil; NSCP10% — Nonselectively hydrogenated canola oil containing 10% palm oil.

Fatty acid composition of the oils was determined by transesterification and analysis of the methyl esters by gas liquid chromatography (GLC) using a Varian 1400 gas chromatograph with a 2 m column packed with 20% DEGS on Chromosorb 60-80 mesh operated at 170°C.

Iodine value was determined by the Wijs method (AOCS official method Cd 1-25). Dropping point was determined by the Mettler FP 3 automatic dropping point apparatus.

Trans isomer (T.I.) content was determined by AOCS method Cd14-61 using a Beckman model 4230 infrared spectrophotometer.

Solid fat contents (SFC) of all fat samples were measured by wide-line nuclear magnetic resonance. A Newport Analyzer Mark III and a sample temperature controller WR 2 MK II were used. Tempering and heating of the samples were done at five temperatures using a Praxis Model TU-900 tempering unit.

Diglycerides were determined by analysis of the TMS derivatives by GLC according to the method of Goh and

*To whom correspondence should be addressed.

Timms (5), using a Varian 3700 Chromatograph with a 0.5 m x 4 mm diameter glass column packed with 3% OV-1 on 80/100 Supelcoport (Supelco Inc., Toronto, Canada) (5). Internal standard was n-triacontan.

To study the polymorphic stability of the oil samples, all the oil samples in 6 cm long and 1 cm diameter tubes were heated at 70°C for two hours, to destroy any "memory" of earlier crystals, followed by crystallization at 0°C for one hour. The samples were then subjected to temperature cycling, initially at 5°C for one day followed by two days at 20°C; 5°C for one day; 20°C for two days; 5°C for one day; 20°C for two days; and, finally, 5°C for one day. For constant temperature-time studies, the tubes were stored at 5°C for up to 56 days. Crystal structures of the fat samples were visualized by polarized light microscopy using an Olympus model BH polarizing microscope with PM-6 camera attachment. A small amount of fat was spread on a microscopic slide which was mixed with mineral oil by means of a spatula, a cover glass was lightly pressed on top of this mixture before viewing. Photomicrographs were taken at 400 x magnification on Kodak Panatomic-X film.

The X-ray diffraction patterns of the samples were obtained with a 601 Diffractis X-ray generator and Guinier X-ray diffraction camera model FR552 (Enraf-Nonius, Delft, The Netherlands) with temperature controlled sample holder operated at 10°C. Short spacings on the X-ray film were measured with a Guinier viewer. The short spacings were visually judged to be of very strong (vs), strong (s), medium (m) or weak (w) intensity.

The β-crystal content of the fats was measured using a Zeineh soft-laser scanning densitometer model SLR-504-XL (Biomed Instruments Inc., Fullerton, CA). The quantification was based on the relative densities of the characteristic short spacings of β- and β'crystals at 4.6 and 4.2 Å, respectively. The following equation was used to determine the percent β- crystals:

$$\beta\text{- crystals} = \frac{\text{Peak area at 4.6 Å}}{\text{Total peak area at 4.6 and 4.2 Å}} \times 100$$

At the end of each cycle and specific storage time, approximately 30 mg of samples were taken from the tubes for differential scanning calorimetry (DSC) analysis. The DSC was carried out with a model 900 DuPont Thermal Analyzer. Samples were heated from 10 to 60°C at a heating rate of 5°C per min.

RESULTS AND DISCUSSION

The 12 selectively and nonselectively hydrogenated canola oil samples were analyzed for fatty acid composition, dropping point and *trans*-isomer content (Tables 1 and 2). Addition of 15% of palm oil increased the palmitic acid level to over 10%. The 18:2 content in the SC and NSC oils was virtually nil. The 18:2 fatty acids that some oils contained were derived from palm oil. Palm oil contained 11% of 18:2. The 18:1 content in the SC series was lower than that in the NSC series, and the 18:0 content was the reverse. *Trans* content was higher in the SC series than in the NSC series. These differences in fatty acid and *trans* content are reflected in the SFC curves (Figs. 1 and 2). The SC oils had much steeper curves (Fig. 1) than the NSC oils (Fig. 2). The SFC curve of SCP 10% was rather low (Fig. 1), the IV of this oil was highest in the SC series. The dropping points of all of the hydrogenated oils with palm oil added after the hydrogenation (except for SC + 15% P) were not affected. Dropping point of palm oil was 36°C, which is slightly lower than SC (Table 1). For the hydrogenated oils with palm oil added before hydrogenation, dropping points decreased as the level of added palm oil increased. It was also found that addition of palm oil before hydrogenation resulted in an increase of *trans*isomer content of the resulting hydrogenated oil.

Figures 3 and 4 show the diglyceride contents of the SC and NSC oils. The increase in the diglyceride content of SC and NSC oils was similar. At the same level of added palm oil, the diglyceride content of the samples with palm oil added before hydrogenation (SCP and NSCP series) were higher than that of the samples with palm oil added after the hydrogenation. This effect was particularly obvious in the SC oils. It was important to establish the diglyceride levels since recent studies (6) have indicated that diglycerides have a stabilizing effect on the β'-polymorphic form. The difference in diglyceride content between the hydrogenated oils containing no palm oil and those containing

TABLE 1

Fatty Acid Composition, Iodine Value, Dropping Point and *trans* Isomer Content of Selectively Hydrogenated Canola Oil Samples

Fatty acid	SC	SC + 5% P	SC + 10% P	SC + 15% P	SCP5%	SCP10%
14:0	—	0.1	0.1	0.1	0.1	0.1
16:0	4.5	6.6	8.7	10.7	6.6	8.3
18:0	19.1	18.7	17.6	16.3	14.4	9.0
18:1	74.0	72.3	70.9	70.1	76.6	80.4
18:2	—	0.2	0.5	0.7	—	—
18:3, 20:0	0.9	0.8	0.8	0.8	0.8	0.6
20:1	1.5	1.3	1.3	1.3	1.5	1.6
I.V.	66.5	65.4	65.3	64.8	67.9	70.5
D.P. °C	40.4	40.1	40.2	39.0	38.6	34.9
T.I. %	43.4	43.2	43.0	42.2	51.3	45.0

I.V. = Iodine value.

D.P. = Dropping point.

T.I. = *trans* isomers.

TABLE 2

Fatty Acid Composition, Iodine Value, Dropping Point and *trans* Isomer Content of Nonselectively Hydrogenated Canola Oil Samples

Fatty acid	NSC	NSC + 5% P	NSC + 10% P	NSC + 15% P	NSCP5%	NSCP10%
14:0	—	0.1	0.1	0.2	0.1	0.1
16:0	4.1	6.4	8.6	10.4	6.3	8.5
18:0	14.2	13.4	13.3	12.2	14.5	12.1
18:1	79.3	77.4	75.1	74.3	76.7	77.1
18:2	0.2	0.5	0.9	1.0	—	—
18:3, 20:0	0.6	0.7	0.7	0.7	0.8	0.7
20:1	1.5	1.5	1.4	1.3	1.6	1.5
I.V.	72.0	70.9	69.0	67.4	68.8	69.2
D.P. °C	35.3	35.6	35.3	35.2	38.2	36.4
T.I. %	30.1	29.8	28.4	27.9	30.7	33.3

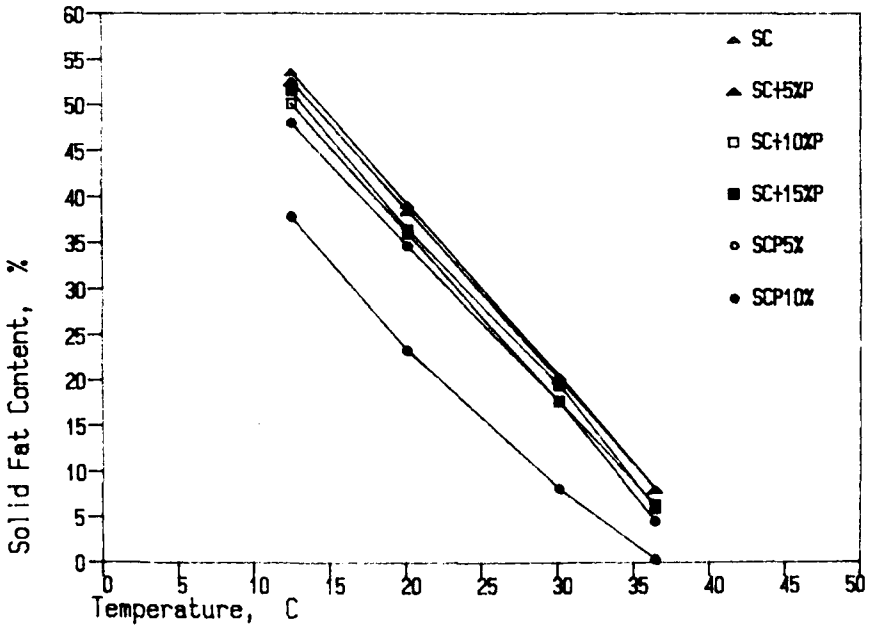

FIG. 1. Solid fat content of selectively hydrogenated canola oil and canola-palm oil blends.

the highest amount of palm oil was only 0.8%. It was doubtful that this slight increase had any influence on the polymorphic behavior of the fat crystals.

Microscopic study. When the fats were viewed under the polarizing microscope at cycle 1, all fats showed crystal agglomerates. Upon temperature cycling, the agglomerates in the SC series did not change much. The agglomerates in the NSC series became very small, and at the end of the fourth cycle the mixtures containing β-crystals developed small needles. The differences in solid fat between the cycling temperatures of 5 and 20°C in the SC series was 40% as calculated on the amount of solid fat present at 5°C, except for SCP 10%, which was 45% (Fig.1). These differences in the NSC series were between 58 and 65% (Fig. 2), which are much higher than in the SC series. This would explain the disappearance of the agglomerates in the NSC series. When the fat is originally cooled to 0°C the crystals are mixed crystals composed of high and low melting triglycerides. Upon tempering at 20°C, part of the mixed crystals melt into the liquid phase, and cooling will result in recrystallization of only the lower melting triglycerides. Recrystallization will take place in a more stable form (7,8). Percentage of solid fat present at 5°C was estimated to be more than 55% in the selective series, while in the nonselective series percentage of solid fat was 20% lower (35%).

X-ray diffraction analysis. Quantitation of the relative intensities of the short spacings at 4.6 Å (β) and 4.2 Å (β') as measured by the densitometer for the SC temperature cycled series is displayed in Figure 5. In the SC and NSC series the short spacings at the start of the experiment were 4.4 (m), 4.2 (s) and 3.8 Å (s). At the end of the SC temperature cycling study, short spacings—in addition to 4.6 Å for the β-form—appeared as follows: 5.1 (vw) and 4.0 (vw). In this series the β' form, which is evidenced by the short spacing of 4.2 Å, was the predominant polymorphic crystal form.

Figure 6 shows the development of β-crystals in the NSC series as measured by the densitometer. After storage for one day at 5°C all samples existed in the β' form.

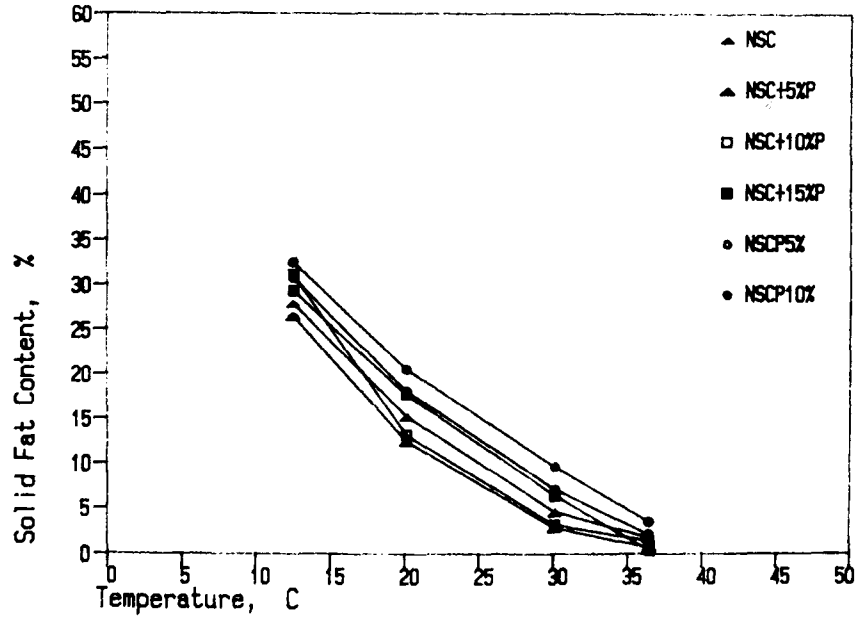

FIG. 2. Solid fat content of nonselectively hydrogenated canola oil and canola-palm oil blends.

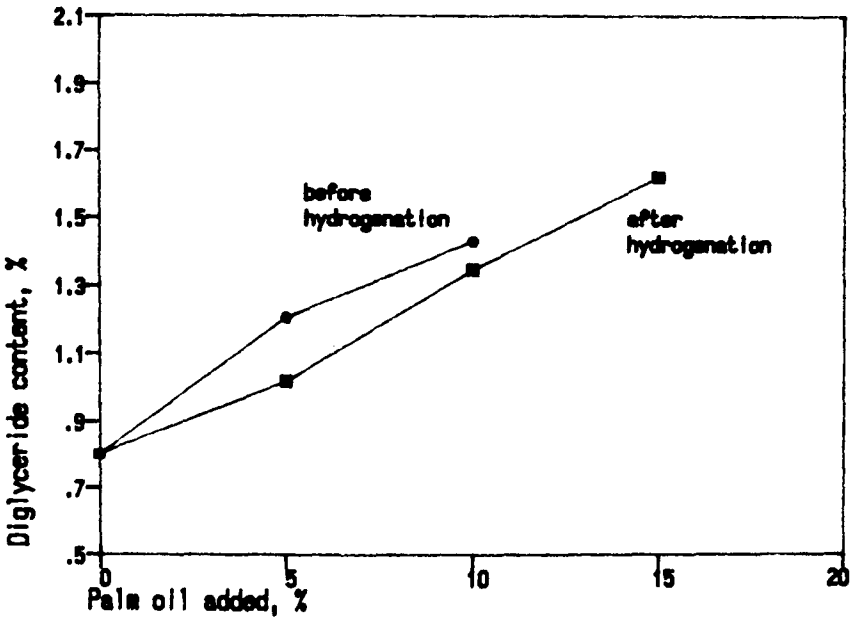

FIG. 3. Diglyceride content of selectively hydrogenated canola oil and canola-palm oil blends.

After the second cycle, β' to β-transition was observed in the control and the sample with 5% added palm oil. Repeated cycling resulted in the formation of β-crystals in all of the blends but the transition was greatly delayed by the addition of palm oil. Among the oil, NSC + 15% P and NSCP 10% contained the lowest amount of β-crystals. At the end of the experiment, additional short spacings appeared at 5.4 (w), 5.2 (w), 5.1 (vw), 4.9 (vw), 4.5 (s), 4.4 (m), 4.1 (w) and 3.9 Å (s). Figure 6 shows the development of β-crystals in the NSC temperature cycling series. The significance of the additional short spacings cannot be explained at present. They may suggest a more complex β-crystal structure.

In the constant temperature-time experiment no distinctive polymorphic transition was observed in the SC series. The crystal structure of the oils remained mostly in the β' form (Fig. 7) for up to 56 days of storage.

In the NSC constant temperature-time experiment, β-crystals developed by the third day of storage of the control, NSC + 5% P, NSC + 10% P and NSCP 5%. After 14 days of storage, all samples except NSCP10% contained β-crystals. At 28 days the β-crystals appeared in NSCP10%. The β-crystal content increased with time. At the end of 56 days of storage NSC + 15% P and NSCP10% had the lowest β content. The development of β-crystals is presented in Figure 8. Additional short spacings other than those specific for the β- and β' forms were less numerous in the constant temperature-time studies than in the temperature-cycling studies.

DSC analysis. Differential scanning calorimetry has

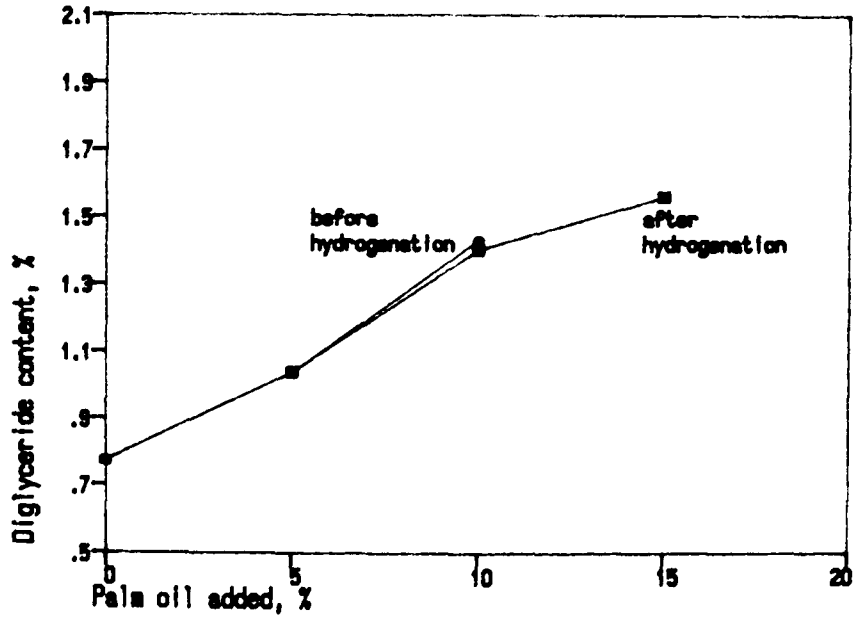

FIG. 4. Diglyceride content of nonselectively hydrogenated canola oil and canola-palm oil blends.

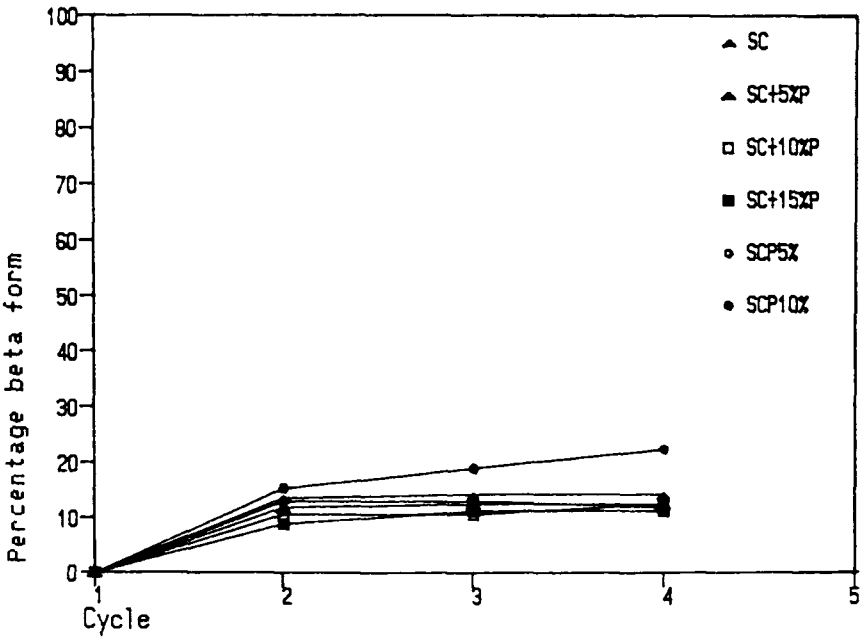

FIG. 5. Percentage of crystals in the β- polymorphic form during temperature cycling of selectively hydrogenated oils.

been found to be a useful technique for investigating the transition of crystal forms during melting of fats (8-10). It is recognized that when fat is being heated, it can exhibit multiple melting. Each recrystallization step represents a transition of a polymorph from its less stable form to a more stable form (11,12). Since the more stable crystal form has a higher melting point than the less stable crystal form, the transition peak temperature can serve as an important indicator of the polymorphic form of the crystals.

The DSC heating curves of the temperature cycled hydrogenated fats are presented in Figures 9 and 10. In the SC oils, a shoulder peak and two fusion peaks at 29.5°C, 39.8°C and 43.1°C were observed in the control after the first cycle (Fig. 9a). This indicated that transition had taken place. After the second cycle, the shoulder peak at 29.5°C and the peak at 43.1°C disappeared, and a major peak at 42.2°C and a small peak at 18.6°C became evident. Repeated cycling caused no change in the melting profile of the control. All of the selectively hydrogenated oils exhibited identical melting behavior as the control throughout the four cycles.

After one tempering cycle in the NSC oils (Fig. 10), the control showed a shoulder peak at 21.7°C and three fusion peaks at 34.0°C, 36.6°C and 37.5°C. Both NSC + 15% P and NSCP10% had a major peak at a slightly lower temperature (33-36°C), indicating that the transitions of lower melting crystals to higher melting crystals were

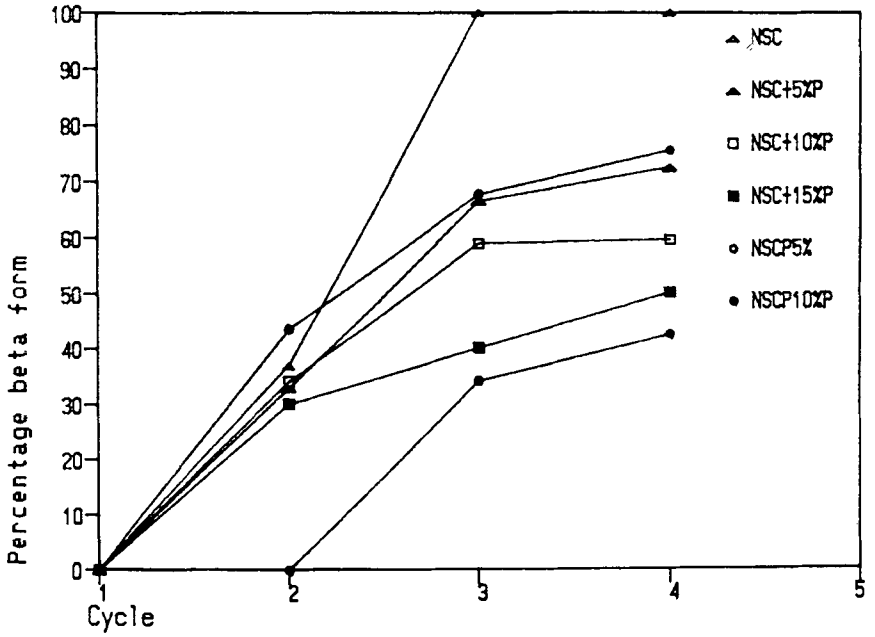

FIG. 6. Percentage of crystals in the β- polymorphic form during temperature cycling of nonselectively hydrogenated oils.

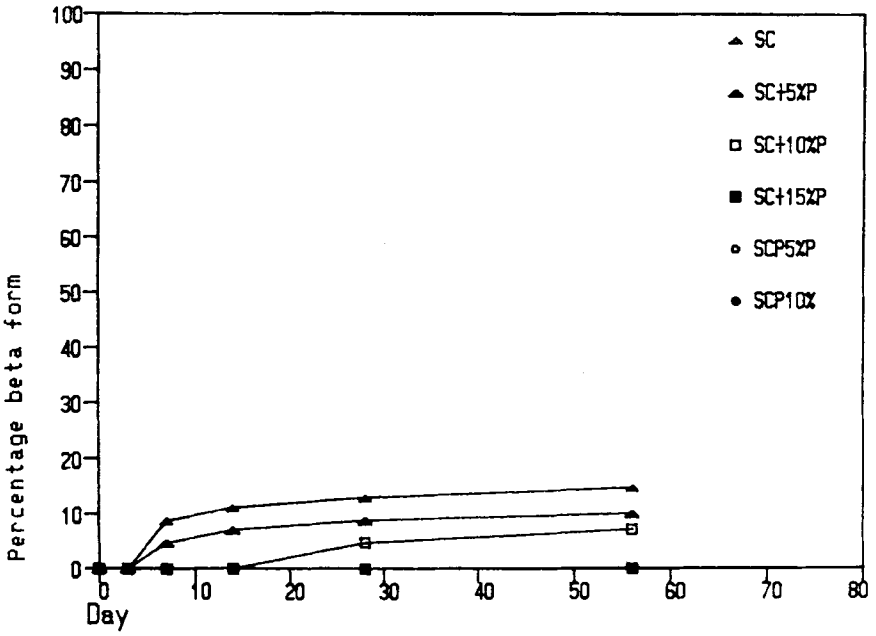

FIG. 7. Percentage of crystals in the β- polymorphic form during isothermic storage at 5°C of selectively hydrogenated oils (values for SCP 5%, SCP 10% and SC + 15% P were zero through the storage period).

greatly delayed in the two samples (Fig. 10a). After two cycles, the delaying effect was no longer in evidence. Continued cycling caused no change in the melting behavior of the samples.

Generally, the SC oils crystallized at higher temperatures. Shifting of the major transition peak temperature during temperature cycling was observed in all of the hydrogenated fats, except in the SC oil with palm oil added after hydrogenation. The increase in peak temperature was mainly due to the formation of a higher amount of high melting crystals as a result of polymorphic transition.

The DSC heating curves in the constant temperature-time studies in both SC and NSC studies exhibited mainly one melting peak, which corresponded in temperature to the last melting peaks of those of the temperature cycled studies. Although no partial melting of the crystals was possible during constant temperature storage, polymorphic transition to the β-form still took place, especially in the NSC oils.

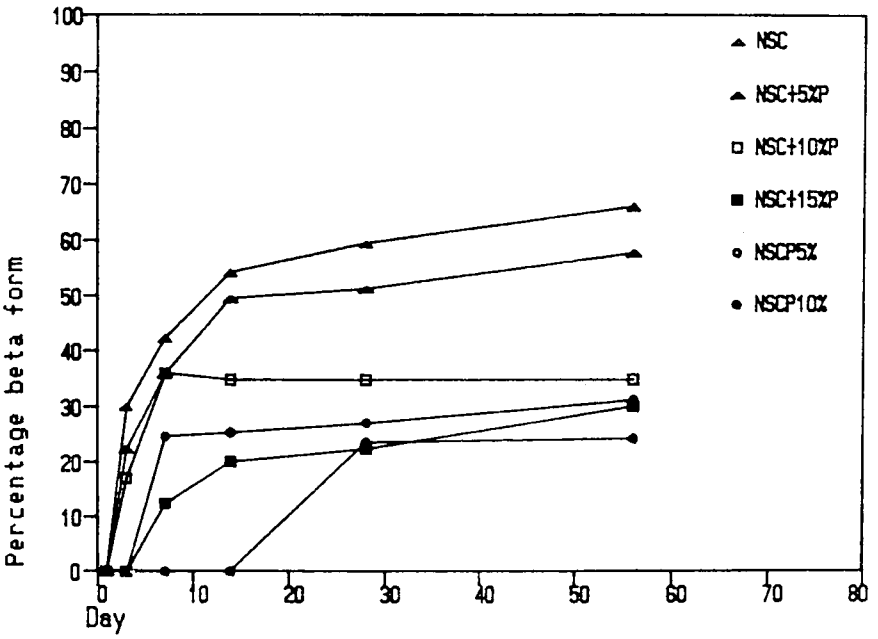

FIG. 8. Percentage of crystals in the β- polymorphic form during isothermic storage at 5°C of nonselectively hydrogenated oils.

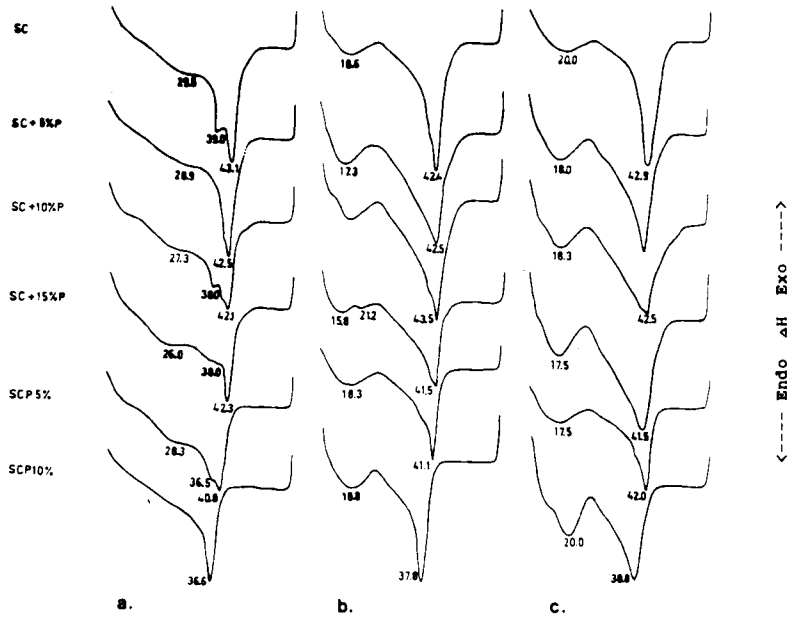

FIG. 9. DSC heating curves of selectively hydrogenated fats at (a) cycle 1, (b) cycle 2, and (c) cycle 4.

The NSC oils were more susceptible to phase transition than the SC oils under the experimental conditions used. The higher amount of solid fat at 20°C, average of 35% for SC against 16% for NSC oils, could be the reason that the SC oils were more stable.

Addition of palm oil at the 15% level after hydrogenation or the 10% level before hydrogenation was effective in delaying the phase transition in NSC oils upon temperature cycling. The phase transition in the NSC oils stored at 5°C could also be delayed by the addition of palm oil. The β′ stabilization effect increased as the level of added palm oil increased.

The β′stabilization effect of palm oil is most likely due to a decrease in fatty acid uniformity. Addition of palm oil increased the range of fatty acid chain lengths in hydrogenated canola oil, which, in turn, increased the irregularity in the crystal lattice, thus increasing the polymorphic stability of the oil.

Recent studies (13) have shown that a new type of canola oil containing high levels of palmitic acid possesses better β′ polymorphic stability in the hydrogenated form. It appears from the results presented in this study that the stabilizing effect of palmitic acid is related to its level in the solid fraction of the fat, which is increased by addi-

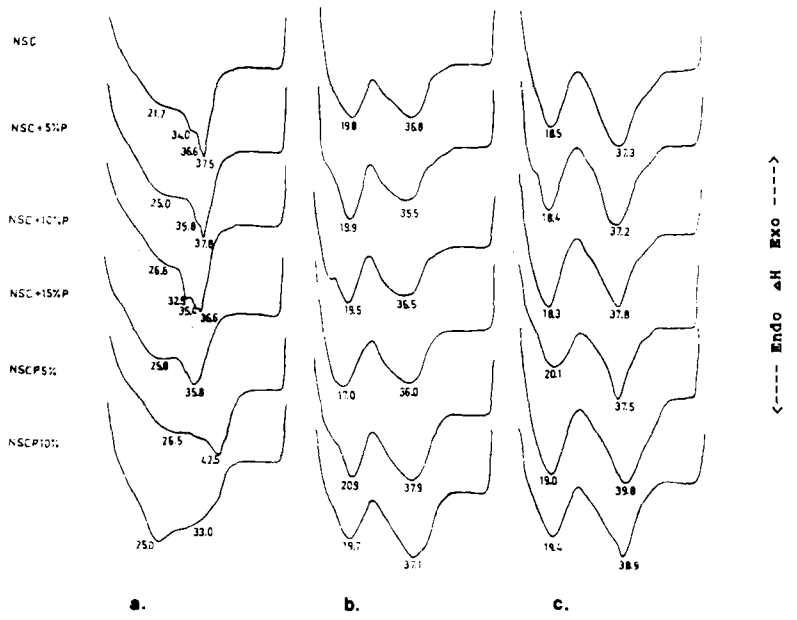

FIG. 10. DSC heating curves of nonselectively hydrogenated fats at (a) cycle 1, (b) cycle 2, (c) cycle 4.

tions of palm oil, or when the palm oil is partially hydrogenated and, therefore, not necessarily to its overall level.

Analysis of a number of North American margarines in this laboratory found stick margarines to contain between 14 and 17% solids at 22°C and between 25 and 35% solids at 10°C as determined on the separated fat. Solids content in these margarines and dropping points correspond to those in the NSC series. Therefore, in the manufacture of margarine from canola oil it is advantageous to incorporate palm oil at a level of at least 15% after hydrogenation of canola oil or at a level of 10% before hydrogenation of canola oil. Higher levels of palm oil will undoubtedly increase the stability of the hydrogenated canola oil.

Addition of palm oil to canola oil resulted in only a slight increase in total saturated fatty acid content and in some cases a reduced level of *trans*-isomers (Tables 1 and 2). The palmitic acid content of the canola-palm oil mixtures never exceeded the palmitic acid level of soybean oil (about 10.5%).

The crystallization characteristics of the hydrogenated oils described in this paper will be dealt with in a subsequent publication.

ACKNOWLEDGMENT

Financial support was provided by the Natural Sciences and Engineering Research Council of Canada and the Canola Council of Canada.

REFERENCES

1. Hernqvist, L., B. Herslof, K. Larsson and O. Podlaha, *J. Sci. Food Agric. 32*:1197 (1981).
2. Weinberg, B., *Can. Inst. Food Sci. Technol. J. 5*:A57 (1972).
3. Rossell, J.B., B. King and M.J. Downes, *J. Am. Oil Chem. Soc. 62*:221 (1985).
4. Timms, R.E., *Ibid. 62*:241 (1984).
5. Goh, E.M., and R.E. Timms, *Ibid. 62*:730 (1985).
6. Hernqvist, L., and K. Anjou, *Fette Seifen Anstrichmittel. 85*:64 (1983).
7. Chrysam, M.M., in *Bailey's Industrial Oil and Fat Product*, edited by T.H. Applewhite, John Wiley & Sons, New York, 1985.
8. Yap, P.H., J.M. deMan and L. deMan, *J. Am. Oil Chem. Soc. 66*:693 (1989).
9. Kawamura, K., *Ibid. 56*:753 (1979).
10. Kawamura, K., *Ibid. 57*:48 (1980).
11. Hoerr, C.W., and F.R. Paulicka, *Ibid. 45*:793 (1968).
12. Wilton, I., and G. Wode, *Ibid. 40*:707 (1963).
13. Hernqvist, L., O. Leissner and B. Peterson, *Food Sci. Technol. 5*:190 (1987).

[Received January 10, 1989; accepted July 6, 1989]
[J5635]