Relationship Between Cooling Rate and Crystallization Behavior of Hydrogenated Sunflowerseed Oil

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The relationship between cooling rate and crystallization behavior of hydrogenated sunflowerseed oil and its thermal properties during melting were investigated by differential scanning calorimetry and x-ray diffraction. At crystallization, temperature peaks and area percents of components with higher melting points were found to be greater when cooling rate was slower. When samples were melted, total enthalpies were similar at all rates. According to the chemical composition of the analyzed samples, the components with higher melting points were found in samples with a higher saturated fatty acid content. Changes in the profile of melting curves might be due to differences in triglyceride intersolubility.

KEY WORDS: Cooling rate, crystallization, differential scanning calorimetry, hydrogenated sunflowerseed oil.

Crystallization phenomena in fats and other lipids are fundamental subjects to elucidate their physical and chemical properties (1). Physical deterioration of fat products, such as margarine, shortening and chocolate, depends on size, morphology and polymorphic structure of fat crystals. All of them are primarily influenced by crystallization conditions and secondly by phase transformation (2,3). Cocoa butter and other fats, such as palm oil, have been reported as examples of polymorphic fats. Under proper crystallization and aging conditions, different crystal forms are obtained with characteristic melting points and x-ray diffraction patterns (4–7).

Hydrogenated sunflowerseed oil has been fractionated by crystallization, and the fractions obtained have been analyzed by differential scanning calorimetry and x-ray diffraction (8). The same temperature program was used to obtain all fractions. Under these conditions, x-ray patterns showed that samples were a blend of β' crystals. Melting diagrams of samples, after they were obtained without any additional treatment, corresponded with their chemical compositions. The experiments described below have been designed to understand how different temperature programs may modify crystallization characteristics. The aim of the present work is to study the effect of cooling rate on crystallization behavior of hydrogenated sunflowerseed oil and its thermal properties during melting, so that fundamental aspects of crystallization in relation to polymorphic behavior and chemical composition may be discussed.

MATERIALS AND METHODS

Starting oils. Samples were supplied by Molinos Río de La Plata S.A. (Capital Federal, Argentina). They consisted of five hydrogenated sunflowerseed oils whose compositions were determined by gas-liquid chromatography (GLC) (Table 1). Fatty acids were analyzed in a 5890 A chromatograph (Hewlett-Packard, Palo Alto, CA) with a column of 170 cm length and 0.3 cm internal diameter, packed with 10% SP 2330 on 100/120 WAW chromosorb. Methyl esters were prepared by transesterification with a mixture of methanol:benzene (3:1) and 3% wt/vol sulfuric acid.

Crystallization of samples. Crystallization of the samples was performed within the differential scanning calorimetry (DSC) (DuPont Co., Wilmington, DE) and in a Lauda UK 50 DW cryostat (Messgeräte-Werk Lauda, Lauda-Konigshofen, Germany). Crystallization at a linear rate (DSC) was performed after a 5-min isothermal stage at 80°C to ensure melting. Then, crystallization rates of 20°C/min, 10°C/min, 5°C/min, 2°C/min and 0.5°C/min from 80°C to −40°C were used. After 2-, 10-, 20- and 30-min isothermal staging, samples were melted at a heating rate of 10°C/min.

Crystallization at an exponential rate was performed with uncovered tubes, 6 mm diameter, and tubes covered with a gross gum (2 mm wall). The tubes were heated during 5 min at 80°C and put into the cryostat. Then, temperature was decreased from 80°C to 0°C. Thermal history of each sample was recorded in a 595 Omega recorder. Crystallization rates were calculated by the following equation:

TABLE 1

Fatty Acid Composition of Hydrogenated Sunflowerseed Oils (%)

Sample	C16:0	C18:0	C18:1	C18:2	Others	*trans* Acid content	Calculated iodine value
1	6.7	11.0	69.8	12.2	0.3	42.1	81.2
2	7.1	16.3	65.0	11.5	0.1	41.3	75.9
3	7.0	12.4	64.9	15.6	0.1	40.4	83.0
4	7.0	10.9	60.5	21.4	0.2	40.9	89.2
5	8.3	13.5	71.2	6.9	0.1	43.1	73.3

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$$\ln \frac{T_a - T_F}{T_i - T_F} = -K\, t_a \qquad [1]$$

where T_F is final temperature; T_i is initial temperature; T_a and t_a are the temperature and time anywhere in the curve. Rates were obtained for K values of 1.2×10^{-1} s^{-1} and 2.3×10^{-2} s^{-1}, respectively. Afterwards crystallization samples were melted at 10°C/min.

Differential scanning calorimetry. A programmed calorimeter (Du Pont 910) fitted to a cooling apparatus and a thermal analyzer (model 99) was used. Calorimetric diagrams were recorded with a Hewlett-Packard 7046B recorder. Then, samples ranging from 15 to 20 mg were placed in hermetically sealed aluminium pans and subjected to the mentioned temperature program. The equipment was calibrated with indium as standard. Diagrams dQ/dt (heat flow) were plotted as a function of time. Although the sensitivity used varied from 1.038 to 0.414 mJoule/s, based on the quantity and quality of the samples, diagrams fitted by computer were comparable because they were printed on the same scale and divided by mass. Calorimetric diagrams were measured as reported earlier (9), and fusion enthalpies were calculated (8). Samples were run in duplicate and dispersion was less than 1% in areas and 0.5°C in temperatures. Values given are the average of two thermograms.

X-ray diffractometry. Samples analyzed by x-ray diffraction were cooled at exponential rate in a Lauda UK 50 DW cryostat as described above (crystallization of samples). X-ray diffraction spectra were obtained with a Philips 1730 instrument fitted with a system for temperature control (Philips Argentina S.A., Capital Federal, Argentina). The temperature of the sample holder placed within the refraction chamber was controlled through a programmable Lauda UK-30 cryostat. Ethylene glycol in water (3:1) was used as refrigerant fluid. $K_{\alpha 1 \alpha 2}$ radiation from copper was used at 40 Kv, 20mA and a scanning velocity of 1°/min.

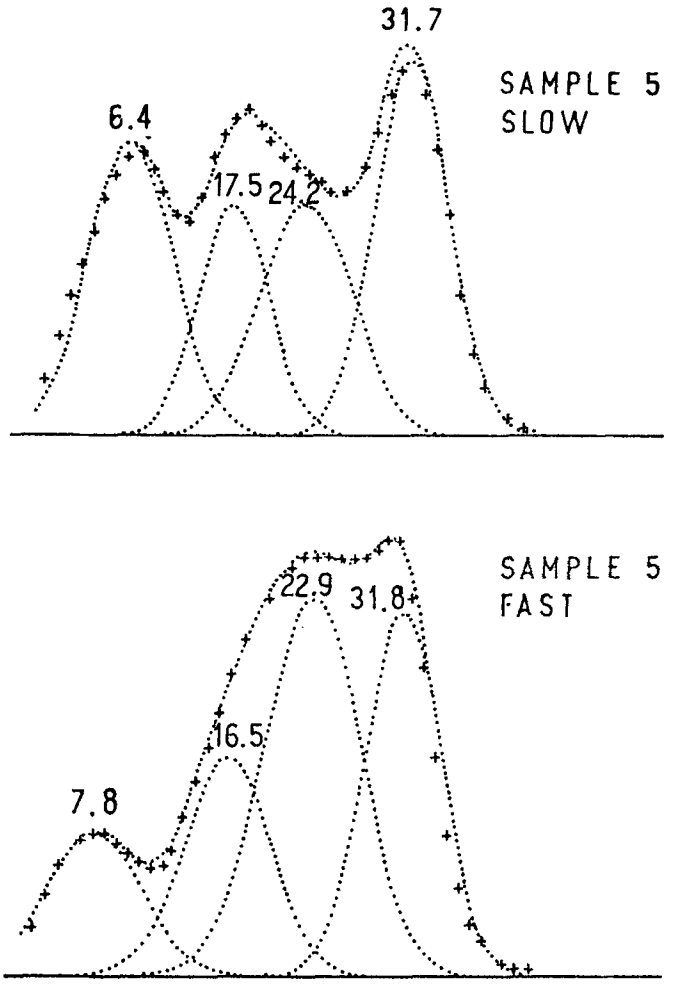

FIG. 1. Sample 5: calorimetric diagrams crystallized at slow and fast cooling rates (computer-fitted).

RESULTS AND DISCUSSION

Sample 5 was crystallized at an exponential rate and at the temperature program just mentioned. Figure 1 shows melting curve diagrams fitted by computer. There seem to be three endotherms but it was not possible to fit the curve with three peaks without making a big error. The second endotherm did not show a normal distribution. This means that there is more than one component in this peak, and temperature peaks are too close to each other to be resolved by differential scanning calorimetry. At the slow rate, the diagram was fitted with four components. Their temperature peaks are: 6.4°C; 17.5°C; 24.2°C and 31.7°C with area percents of 13.5%; 17.5%; 38.6% and 30.5%. At the fast rate, there were also four components with temperature peaks close to those reported for the slow crystallization: 7.8°C; 16.5°C; 22.9°C and 31.8°C. Although temperature peaks were similar, area percents were different: 26.8%; 18.8%; 24.0% and 30.4%, respectively. The total enthalpy calculated for this sample was 45.5 Joule/g at fast rate and 38.7 at slow rate. In both cases portions of the same sample were crystallized. However, the total enthalpy obtained had a 15% variation from one experiment to another and was smaller than that expected based on chemical composition of the sample [H = 91.5 Joule/g before melting and recrystallization (8,10)]. This could mean that crystallization was not complete. Thus, solid solutions with different triglyceride compositions and different specific heats could be formed. Samples must have been kept 30 min at 0°C to assure complete crystallization. X-ray diagrams of sample 5 that crystallized at fast and slow rates are shown in Figure 2. Both diagrams show three lines at 3.8–3.9A, 4.2A and 4.3A. These lines correspond to β' crystals. There seem to be no differences between diagrams, whereas the first and third components differ greatly in calorimetric runs. While the third component decreased at slow temperature, the first component increased, and the sum of the two areas stayed constant. This behavior was not always evident, but the fact that components with higher-temperature peaks had greater area percents in crystallized samples at fast rate is always true. At slow rates, their area percents decreased and all the components had a similar percentage of total area. It has been reported that triglycerides crystallize from the liquid phase into the α form, transform themselves more or less rapidly into β', and subsequently into the intermediate and/or the β modifications, if they are likely to exhibit these higher polymorphs. This sequence is irreversible. Once a transformation

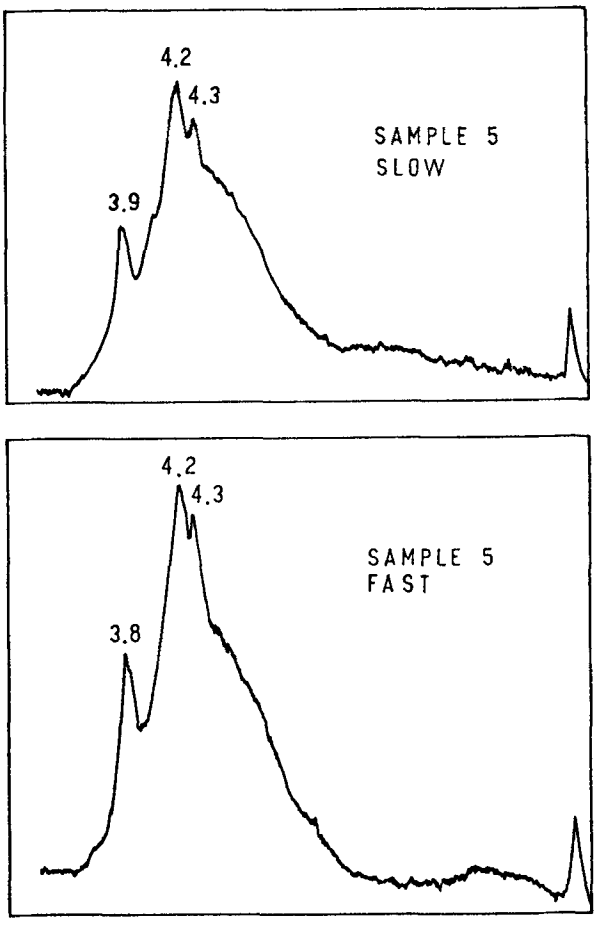

FIG. 2. X-ray diffraction spectra of calorimetric diagrams shown in Figure 1.

to a more stable form has occurred, lower polymorphs can be obtained again only by melting the sample, crystallizing the α form, and repeating the sequence of transformations (11). If a β polymorph had been formed during crystallization, a line at 4.6 A would have appeared in the x-ray diagrams. Also, DSC diagrams should have showed components with higher melting points at slow rate (12). β crystals were not found when sample 5 was crystallized at slow or fast rates.

Samples 1, 2, 3 and 4 were crystallized at a linear rate within the DSC. Figure 3 shows the exotherms corresponding to crystallization curves of sample 1 and Figure 4 shows the endotherms recorded in melting after the sample was kept for 2 min at −40°C. It was evident that temperature peaks of components were higher when the cooling rate was slower (Fig. 3). The area percents of components corresponding to samples crystallized at 20°C/min, 10°C/min, 5°C/min and 2°C/min are shown in Table 2. The amount of heat exchange during sample crystallization at 0.5°C/min was small, so the thermograms do not show well-defined peaks, even when the highest sensitivity was used. So, they were not included. Not only did the temperature peaks increase but the areas of peaks with high temperatures were greater. The total enthalpies calculated for the four cooling rates were 79.2, 73.1, 80.2 and 80.8 Joule/g at 20°C/min, 10°C/min, 5°C/min and 2°C/min, respectively. Melting curves (Fig. 4) were fitted by six components at all rates, with the exception of $\beta = 0.5$°C/min. This diagram was fitted with seven components. A component with a melting point of 40.1°C was found, which was not present in the diagrams corresponding to the other cooling rates. This was due to the fact that at 0.5°C/min there was more time for the sample triglycerides to interact with each other. Thus a more stable structure was formed that could not be obtained

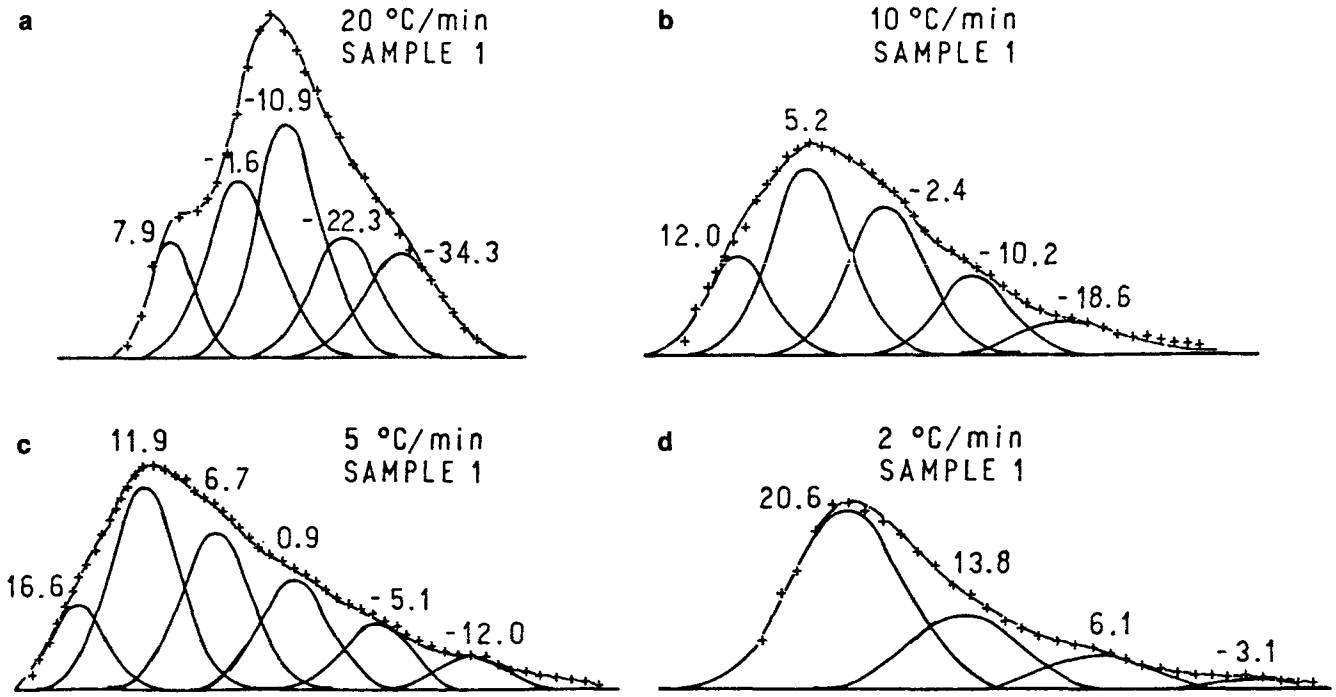

FIG. 3. Sample 1: calorimetric diagrams of crystallization at different rates (computer-fitted).

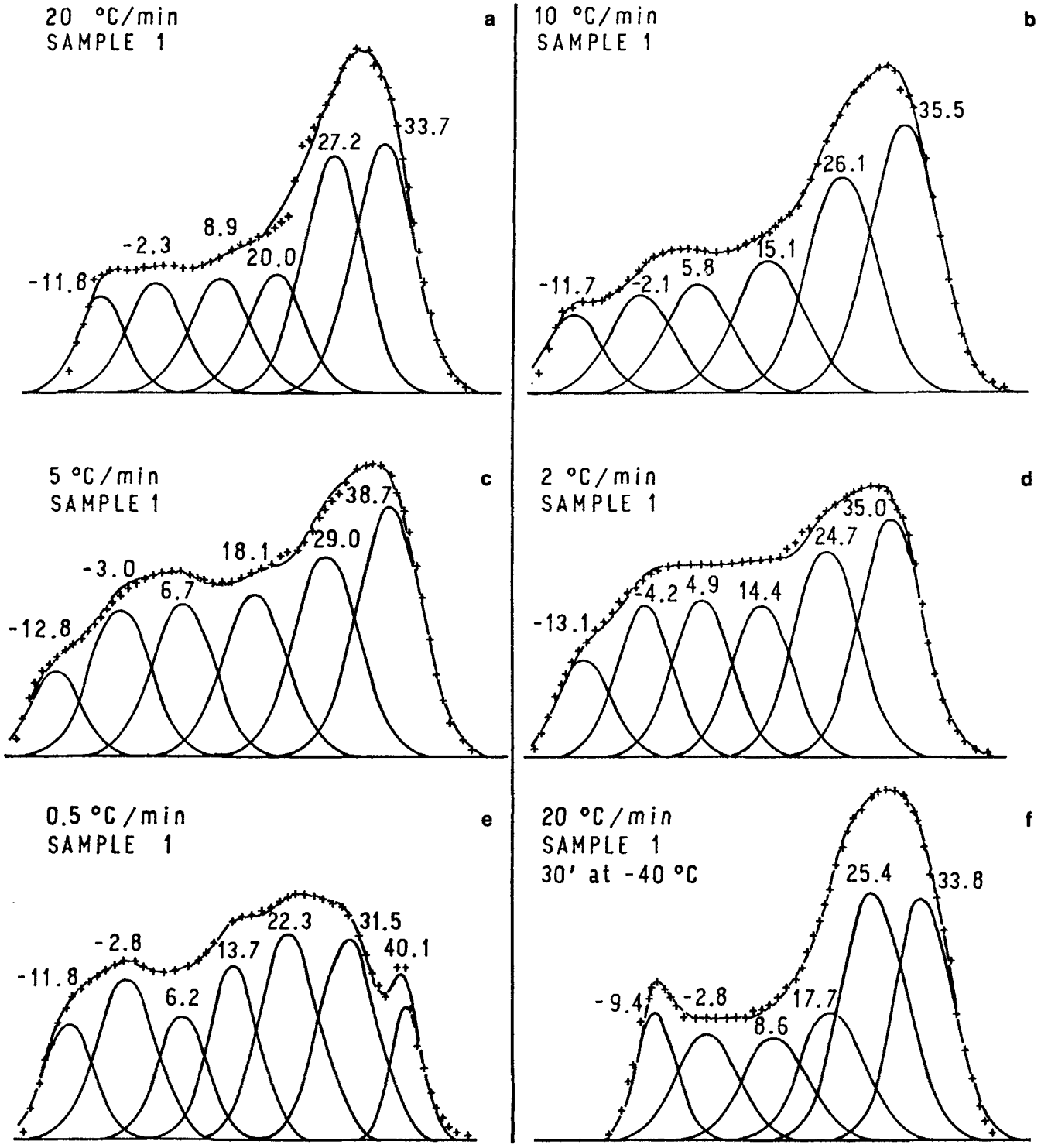

FIG. 4. Melting diagrams of Figure 3 samples after being kept for 2 min at −40°C (a, b, c, d and e) and sample 1 melting diagram crystallized at 20°C/min and kept isothermally 30 min at −40°C (f).

TABLE 2

Temperatures and Area Percents of Components Found When Sample 1 Was Crystallized at 20°C/min, 10°C/min, 5°C/min and 2°C/min

Cooling rate (°C)/min)	Temperature peaks, °C (area percent)					
20	7.9 (10.4)	−.6 (15.4)	−10.9 (38.6)	−22.3 (22.6)	−34.3 (12.9)	—[a] —
10	12.0 (12.1)	5.2 (37.7)	−2.4 (30.0)	−10.2 (13.2)	−18.6 (7.1)	— —
5	16.6 (9.8)	11.9 (31.6)	6.7 (25.0)	0.9 (17.4)	−5.1 (10.6)	−12.0 (5.5)
2	20.5 (56.2)	13.8 (24.6)	6.1 (12.5)	−3.1 (6.6)	— —	— —

[a]—, No component was found.

TABLE 3

Temperatures and Area Percents of Components Found When Sample 1 Crystallized as Provided in Table 2 Was Melted (β = 10°C/min)

Cooling rate (°C/min)	Temperature peaks, °C (area percent)						
20	−11.8 (6.3)	−2.3 (10.1)	8.9 (10.6)	20.0 (17.7)	27.2 (25.1)	33.7 (30.2)	—[a] —
10	−11.7 (6.8)	−2.1 (10.9)	5.8 (10.0)	15.1 (14.6)	26.1 (25.7)	35.5 (31.9)	— —
5	−12.8 (6.5)	−3.0 (13.7)	6.7 (15.4)	18.1 (17.2)	29.0 (21.0)	38.7 (26.2)	— —
2	−13.1 (8.4)	−4.2 (13.5)	4.9 (15.7)	14.4 (15.0)	24.7 (22.3)	35.0 (25.1)	— —
0.5	−11.8 (10.3)	−2.8 (16.3)	6.2 (11.1)	13.7 (14.6)	22.3 (20.8)	31.5 (19.9)	40.1 (7.0)

[a]—, No component was found.

at other rates. The area percents of components corresponding to samples crystallized at 20°C/min, 10°C/min, 5°C/min and 2°C/min are provided in Table 3. Total enthalpies calculated for the five melting diagrams were 77.2, 75.5, 82.8, 81.7 and 75.6 Joule/g for sample 1 crystallizing at 20°C/min, 10°C/min, 5°C/min, 2°C/min and 0.5°C/min, respectively. Crystallization enthalpies were similar at all cooling rates and all values were close to melting enthalpies. When sample 1 (which was crystallized at 20°C/min) was kept isothermally for 10, 20 and 30 min at −40°C, a total enthalpy of 88.3 Joule/g was found in all three cases (Fig. 4f). Ten minutes isothermal stage at −40°C was enough to crystallize triglycerides of the blend at all cooling rates. Little changes were found in component peak temperatures of samples kept at −40°C for 10, 20 and 30 min. Area percents of components found when sample 1 was crystallized at 20°C/min and kept isothermally 30 min at −40°C were 9.2%, 11.3%, 11.0%, 13.8%, 29.6% and 24.9%. Although small differences were found between percentages of components corresponding to sample 1 kept isothermally for 2 min at −40°C and for 30 min at −40°C, the profile was similar (Fig. 4a and 4f). Components of higher temperature peaks had the greater area percents. In all the diagrams of Figure 4 a great percentage of total solids was crystallized, but storage at −40°C improved crystallization, and although the temperature was so low, some triglyceride reaccommodation could be found. The percentages of crystals formed when samples were cooled down to −40°C were about 85% but only between 40% and 50% when cooled down to 0°C.

Figure 5 shows the results obtained when samples 2, 3 and 4 were crystallized at 2°C/min, 5°C/min, 10°C/min and 20°C/min and kept isothermally for 10 min at −40°C. Then, the samples cooled at the mentioned rates and one sample at 0.5°C/min were melted, and the results obtained are reported in Figure 6. Total enthalpies of all these samples are summarized in Table 4. For all these samples (Fig. 5), temperature peaks of components increased when cooling rate decreased. Not only did temperature peaks increase, but area percents of components with higher temperature peaks increased as well. The same results were obtained for sample 1. At slow cooling rates triglycerides had more time to interact. Equilibrium could

TABLE 4

Total Enthalpies of Samples 2, 3, and 4 (Joule/g)

Cooling rate	Sample	Crystallization	Melting: 2 min at −40°C	Melting: 10 min at −40°C
20°C/min	2	93.6	83.4	92.9
	3	76.2	68.5	76.2
	4	63.2	56.8	63.6
10°C/min	2	91.9	82.1	92.5
	3	76.1	69.3	76.0
	4	64.5	57.4	65.3
5°C/min	2	92.5	84.2	92.7
	3	76.8	67.2	76.4
	4	64.5	57.0	64.9
2°C/min	2	92.2	83.2	92.9
	3	75.9	68.5	76.2
	4	64.2	55.7	65.1
0.5°C/min	2	—	82.4	92.5
	3	—	66.9	76.4
	4	—	56.4	65.0

be established and crystals could be formed at higher temperature. As mentioned above, total enthalpies are similar at all cooling rates in all samples. Melting curves have the same tendency in these three samples. Components with higher temperature peaks were the most important ones in samples crystallized at 20°C/min. As cooling rate decreased, components of lower temperature peaks increased and smaller differences were found between amounts of components with higher and lower temperature peaks.

There are two important phenomena that are close to each other and that determine the behavior of natural fats: polymorphism and intersolubility (13). According to their chemical composition, samples with a greater amount of saturated fatty acid could be fitted with components of higher temperature peaks, and they had a higher total enthalpy. The way in which the profile was modified

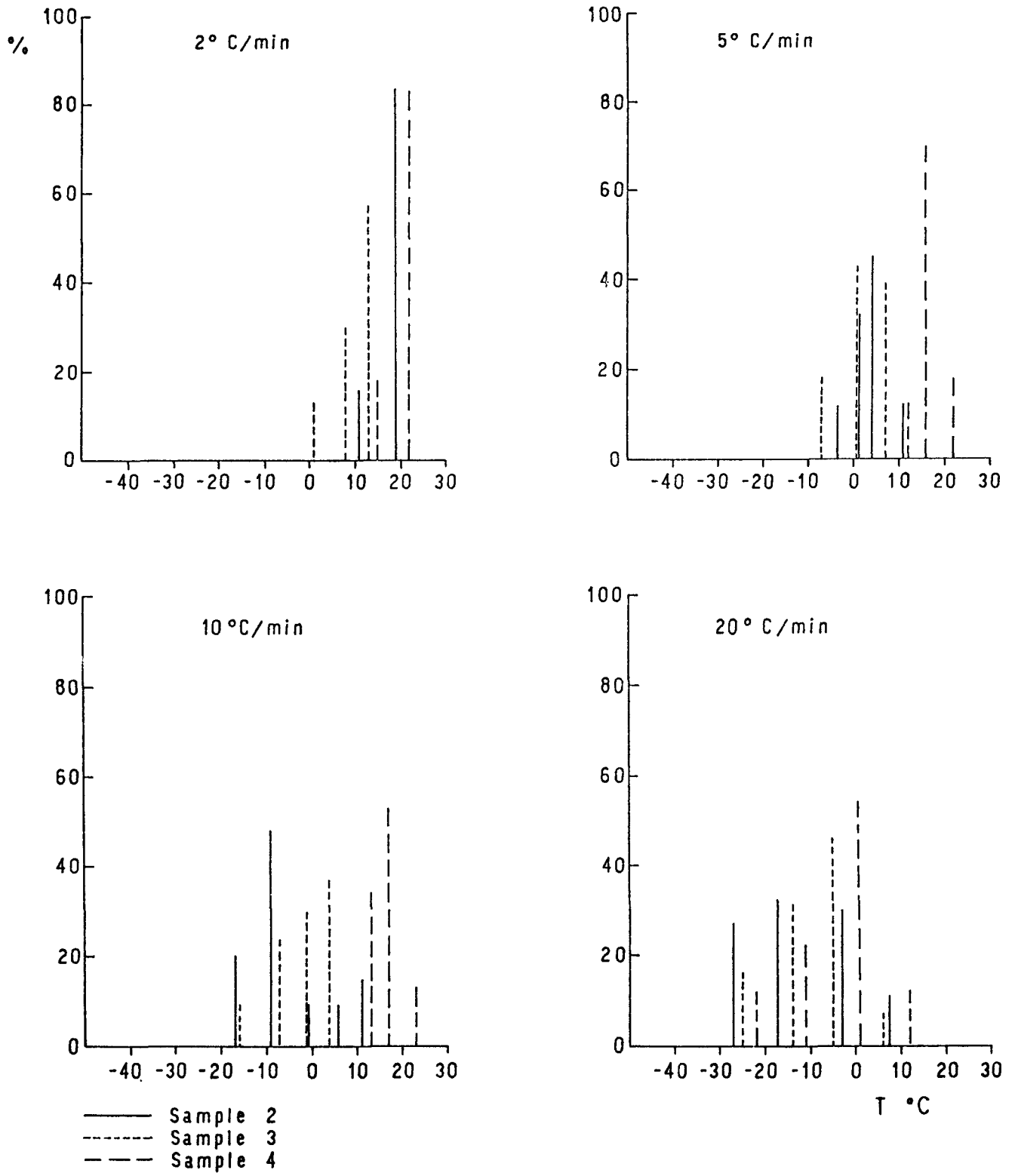

FIG. 5. Area percents and temperature peaks of components found when crystallization curves of samples 2, 3 and 4 were fitted by computer.

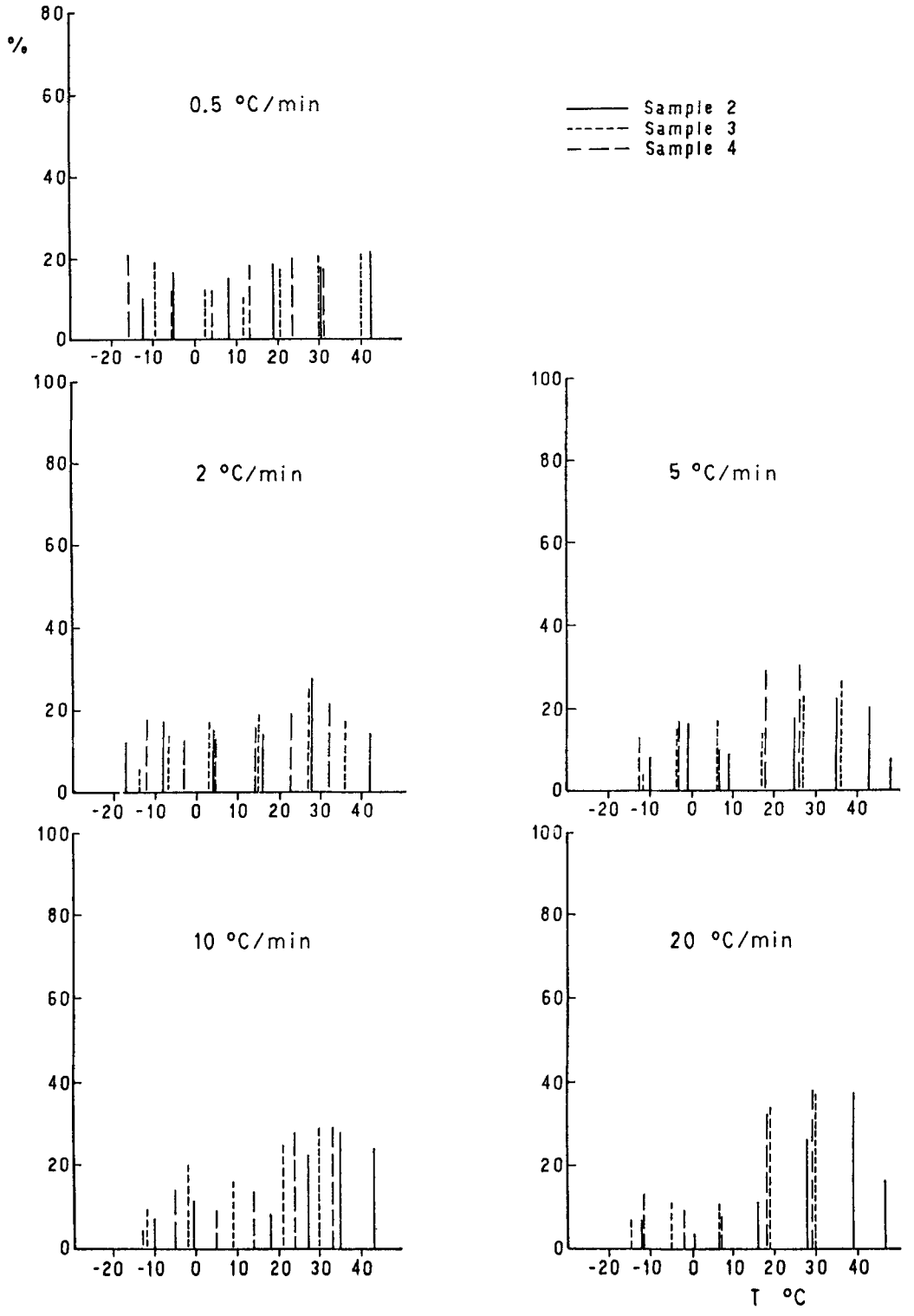

FIG. 6. Area percents and temperature peaks of components found when melting curves of Figure 5 samples were computer-fitted.

suggests that the differences found in melting curves could be due to the intersolubility of triglycerides. Samples crystallizing at slow cooling rate had more time to allow interactions between triglycerides: formation of solid solutions, eutectics or pseudocompounds. A triglyceride with a higher melting point could develop a solid solution with another triglyceride, which could have a lower melting point. Thus, for example, a 60°C melting-point triglyceride can melt at 40°C. In conclusion, the cooling rates used seemed to affect intersolubility more than polymorphism when sunflowerseed oil was crystallized.

REFERENCES

1. Garti, N., and K. Sato, *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti, and K. Sato, Marcel Dekker, Inc., New York, 1988, p. 227.
2. Sato, K., N. Yoshimoto and T. Arishima, *J. Disp. Sci. and Technol. 10*:363 (1989).
3. Sato, K., N. Yoshimoto and T. Arishima, *Ibid. 10*:392 (1989).
4. Wille, R.L., and E.S. Lutton, *J. Am. Oil Chem. Soc. 43*:491 (1966).
5. Chapman, G.M., E.E. Akehurst and W.B. Wright, *Ibid. 48*:824 (1971).
6. Deroanne, C., Contribution à l'étude de la cristallisation des glycérides. Application au fractionnement de l'huile de palme, Ph.D. Thesis, Gembloux, 1975.
7. Deroanne, C., Symposium Intern., *La Filtration dans le Raffinage et le Fractionnement des Corps Gras*, C.E.R.I.A. Bruxelles 28–29, Avril, Belgium, 1976.
8. Herrera, M.L., and M.C. Añón, *J. Am. Oil Chem. Soc. 68*:799 (1991).
9. Segura, J.A., M.L. Herrera and M.C. Añón, *Ibid. 67*:989 (1990).
10. Herrera, M.L., J.A. Segura and M.C. Añón, *Ibid. 68*:793 (1991).
11. Hoerr, C.W., *Ibid. 37*:539 (1960).
12. Rivarola, G., J.A. Segura, M.C. Añón and A. Calvelo, *Ibid. 64*:1537 (1987).
13. Gibon, V., P. Blanpain, F. Durant and Cl. Deroanne, *Belgian J. of Food Chem. and Biothechnol. 40*:119 (1985).

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