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X-ray diffraction and differential scanning calorimetry studies of $\beta' \rightarrow \beta$ transitions in fat mixtures

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Abstract

The polymorphism of five new fat mixtures was studied by differential scanning calorimetry and X-ray diffraction. The melting curves of blends were analysed by DSC and pulsed NMR. The short spacing determinations indicate that the $\beta' \rightarrow \beta$ transition was faster for mixtures II and V than for mixtures I, III and IV. The fatty acid composition was an important factor which influences polymorphic stability of the examined blends. The slightly higher content of palmitic acid in mixtures II and V had no impact on the rate of $\beta' \rightarrow \beta$ transitions under the experimental conditions. The *trans* fatty acids and stearic acid increased the stability of the β'–form and therefore mixtures I, III and IV appeared to be smooth and creamy.

Keywords: Fat mixtures; Phase transition; Crystallisation; DSC; XRD

1. Introduction

Triglycerides (TAG) are the main constituents of natural fats and vegetable oils. They appear in various crystal structures, because their long hydrocarbon chains can be packed into various crystal lattices, causing polymorphism. The different polymorphic forms, have different melting points. The three main polymorphs: α, β′ and β were named by Larsson (1966) in relation to the subcell structure: hexagonal, orthorhombic-perpendicular and triclinic-parallel for α, β′, and β, respectively. Out of these three, the α-form has the lowest stability and easily transforms to either β′ or β forms, depending on the thermal treatment.

The recrystallisation of the solid forms α and β′, is an irreversible and monotropic process, while the formation of the solid forms (α, β′, and β) from the melt is a reversible one. The crystallisation behaviour of TAG is a very important factor that determines such physical properties as consistency and plasticity of margarine and shortenings. The metastable β′-form is most functional in margarine and shortening, because of its optimal crystal morphology and fat crystal lattice which gives rise to the optimal rheological and textural properties. The most stable β-form tends to present large and plate-like crystals, causing rather deteriorated macroscopic features. However, certain crystallisation behaviour of TAG may lead to the growth of granular crystals (Miura & Konishi, 2001; Narine & Marangoni, 1999; Sato, 2001). This is a serious problem for margarine production, where the softness and good spreadability of the final products are essential properties. Therefore, the solidification and transformation into the β-form, and prevention of the granular crystal formation, appear to be important for the vegetable oil industry.

Among other methods, the thermal and structural properties of fats have been studied by a differential scanning calorimetry (DSC) and X-ray diffraction

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(XRD) (Aktaş & Kaya, 2001; Awad & Sato, 2002; Cebula & Smith, 1992; Cossement, Michaux, Lognay, Gibon, & Deroanne, 1990; Hongisto, Lehto, & Laine, 1996; Kellens, Meeussen, Gehrke, & Reynears, 1991a, Kellens, Meeussen, Gehrke, & Reynears, 1991b; Marikkar, Lai, Ghazali, & Che Man, 2002; Minato et al., 1996, 1997; Miura & Konishi, 2001; Narine & Marangoni, 1999; Sato, 1999; Sato, 2001, 1996; Ueno, Minato, Seto, Amemiya, & Sato, 1997; Sessa, 1996; Yap, deMan, & deMan, 1989; Zéberg-Mikkelsen & Stenby, 1999). DSC is widely used for investigation of the transitions crystal forms during melting processes of fats (Aktaş & Kaya, 2001; Cebula & Smith, 1992; Marikkar et al., 2002; Narine & Marangoni, 1999; Sessa, 1996; Zéberg-Mikkelsen & Stenby, 1999). However, DSC melting curves of fats are complex and they are not straight forward in interpretation. This is a consequence of the known fat polymorphism, which depends on the thermal history of the sample. Therefore, the DSC crystallisation curves, which are influenced only by the chemical composition of the sample, are more reproducible and simpler than the melting curves. Hence, in the present work we will focus on the crystallisation and melting curve analyses. X-ray diffraction, which is a phase-selective method, can be used for studies of the phase transition phenomena of TAG polymorphic forms. In addition, XRD studies, with high-flux X-ray beam, synchrotron radiation (SR), have enabled in situ observation of the fat solidification processes (Kellens et al., 1991a, 1991b; Minato et al., 1996, 1997; Sato, 1999; Sato, 2001; Ueno et al., 1997). Also, the kinetics of the polymorphic $\alpha \rightarrow \beta$ transformations of tripalmitin were studied applying two independent techniques: thermodiffractometry (TXRD) and microcalorimetry (MC) (Hongisto et al., 1996). The X-ray diffraction and DSC methods were applied in analyses of polymorphic forms, crystal growth and phase transitions of hydrogenated canola oils: (a) after addition of palm oil (Yap et al., 1989); (b) with high and low erucic acid contents (Cossement et al., 1990). Awad and Sato (2002) observed acceleration of the crystallisation process of palm kernel oil in an oil-in-water emulsion in the presence of hydrophobic emulsifier additives. Moreover, the discussed methods resulted in understanding the role of palm oil in margarine granular crystal formation (Miura & Konishi, 2001).

Therefore, XRD and DSC results of TAG studies can be applied for interpretation of the polymorphic transitions in the new fat mixtures, which may be used in production of margarines with low fat content. In the present paper, different crystal structures of TAG in the five blends will be described using DSC and XRD and results compared for the reliability of both methods. This study can be useful for fat technologists in production of margarines with the stable β′-form of TAG.

2. Materials and methods

2.1. Materials

Five fats mixtures: mixture I, mixture II, mixture III, mixture IV and mixture V, were kindly provided by the Margarine Plant, Kruszwica, Poland. The new fat mixtures were prepared by blending unhydrogenated, refined, bleached, and deodorized edible oils (rapeseed, soybean, palm and coconut) with hydrogenated oils and interesterified fats.

The mixtures were subjected to the plasticizing process described by Steffen and van der Wal (1957) and stored in the dark at 10 °C for three days.

2.2. Methods

2.2.1. Differential scanning calorimetry

Differential scanning calorimetry measurements were carried out on a SETERAM DSC 131 fitted with a liquid nitrogen cooling device. DSC heating and cooling curves were used for determination of possible crystalline phases and the polymorphic transformation of TAG in studied fat mixtures. The DSC apparatus was calibrated with indium (m.p.: 156.6 °C, $\Delta H_f = 28.47\ \mathrm{J\,g^{-1}}$). About 10 mg of each sample were sealed in an aluminium hermetic cell and the following temperature programmes were used to perform the melting and cooling measurements on each sample: initially, fat samples were heated at 10 $^{\circ}\mathrm{C\,min^{-1}}$ to 75 °C, followed by isothermal heating at 75 °C for 5 min to destroy any previous crystalline structure. Then mixtures were cooled from 75 to −40 °C at the rate 5 $^{\circ}\mathrm{C\,min^{-1}}$ to crystallise the material and subsequently reheated (after 30 min) to 75 at 10 $^{\circ}\mathrm{C\,min^{-1}}$ in order to determine the melting behaviour of studied fats. Finally, samples were again cooled to 20 at 5 $^{\circ}\mathrm{C\,min^{-1}}$. An empty, covered cell was used as a reference. All experiments were conducted with three replicates.

2.2.2. X-ray diffraction

X-ray diffraction was measured with a Philips X'PERT PRO diffractometer using Cu–Kα radiation ($\lambda = 1.54056$ Å, voltage 40 kV, current 30 mA) with a curved pyrdytic graphite crystal, fixed 1.0°, 1.0° and 0.1 mm divergence, anti-scatter and receiving slits, respectively. The 2θ-angle was calibrated with copper. The fat mixtures were isothermally crystallized at 22 °C for 60 min (Campbell, Goff, & Rousseau, 2002). Before XRD analysis, the fat samples were mounted on flat stainless steel plates with rectangular hole. The scanning was performed in 0.01° steps, using 6.0 s time in the range $2\theta = 10°–28°$ at ambient temperature.

2.2.3. Solid fat content

Solid fat content (SFC) was determined using a Bruker Minispec mq20 NMR spectrometer with a temperature – controlled sample chamber, according to the AOCS (1981). The applied procedure allowed determination of SFC at 10, 20, 30 and 35 °C in the studied fat mixtures. Instrument was automatically calibrated using three standards (supplied by Bruker) containing 0%, 31.3% and 74% solid. Before placing in NMR tubes, fat samples were melted at 75 °C for 15 min to erase crystal history. Then NMR tubes were filled with samples (3 cm^3), kept at 60 °C for 5 min, next chilled to 0 °C and left for 60 min. Prior to measurements the NMR tubes were placed in thermocirculated water baths at 10, 20, 30 and 35 °C for 30 min. NMR data collecting was set automatically by instrument software and SFC calculated.

2.2.4. Fatty acid composition

Fatty acid compositions of mixtures were determined using a Hewlett–Packard HP 5890 II PLUS gas chromatograph. BPX 70 (25 m × 0.22 mm, 0.25 μm film thickness) polar column coated with cyanopropyl and polysilphenylene-siloxane was applied. The temperature of the column was 160 °C, programmed to 190 °C. Injection and detector (FID) temperatures were both set at 240 °C. Helium, at flow-rate 1 cm^3/min, was used as a carrier gas.

3. Results and discussion

3.1. GC analysis of fatty acids

Results of GC analyses of five fat mixtures are listed in Table 1.

The absence of caprylic (C 8:0), caprynic (C 10:0) acids and the lower percentage of total saturated fatty acids (SAFA), but the highest percentage of monobasic unsaturated fatty acids (MUFA) and *trans* isomers (TI) in mixture I compared to the others mixtures were observed. TI and SAFA contents in mixtures III and IV were insignificantly higher than in II and V. Moreover, the palmitic (C 16:0) and linoleic (C 18:2) acid levels in mixtures I, III and IV were lower than in the mixtures II and V, whereas the stearic acid (C 18:0) content was the reverse. Studied fat mixtures showed a significant and comparable fraction of the polyunsaturated fatty acids (PUFA) (total$_{C:2 \text{ and } C:3}$ = 19.9%, 22.2%, 21.7%, 20.7% and 22%, respectively).

The factors which influenced polymorphic stability appeared to be TI and stearic acid (C 18:0) levels in the analysed fat mixtures. The higher content of TI in mixtures I, III and IV could increase stability of the β'-form. This can be caused by the steric effects of these isomers, which hinder the transformation to β form (D'Souza, deMan, & deMan, 1991). Moreover, higher percentages of stearic acid, in blends I, III and IV,

Table 1
GC analysis results of the new fat mixtures: fatty acid composition

Fatty acid (%)	Fat mixtures				
	Mixture I	Mixture II	Mixture III	Mixture IV	Mixture V
C 8:0	–	0.17	0.30	0.78	0.48
C 10:0	–	0.20	0.33	0.75	0.50
C 12:0	0.12	2.63	4.35	7.21	4.61
C 14:0	0.20	1.16	1.71	2.81	1.87
C 16:0	9.14	15.8	13.4	12.2	14.0
C 16:1	0.18	0.19	0.19	0.18	0.19
C 17:0	0.12	0.11	0.12	0.12	0.10
C 18:0	5.58	3.56	5.38	4.86	3.29
C 18:1 – total	61.9	51.3	50.0	47.8	50.4
C 18:1 – *trans* isomers	9.23	–	0.15	0.15	–
C 18:2 – total	13.7	15.6	15.2	14.5	15.4
C 18:2 – *trans* isomers	–	–	–	–	–
C 18:3 – total	6.22	6.61	6.53	6.25	6.59
C 18:3 – *trans* isomers	0.25	0.27	0.26	0.24	0.26
C 20:0	0.68	0.58	0.61	0.60	0.57
C 20:1	1.22	1.22	1.22	1.13	1.21
C 22:0	0.36	0.29	0.29	0.35	0.28
C 22:1	0.52	0.52	0.51	0.49	0.53
Total					
C:0	16.2	24.5	26.4	29.7	25.7
C:1	63.8	53.3	51.9	49.6	52.4
C:2 and C:3	19.9	22.2	21.7	20.7	22.0
trans isomers	9.48	0.27	0.41	0.39	0.26

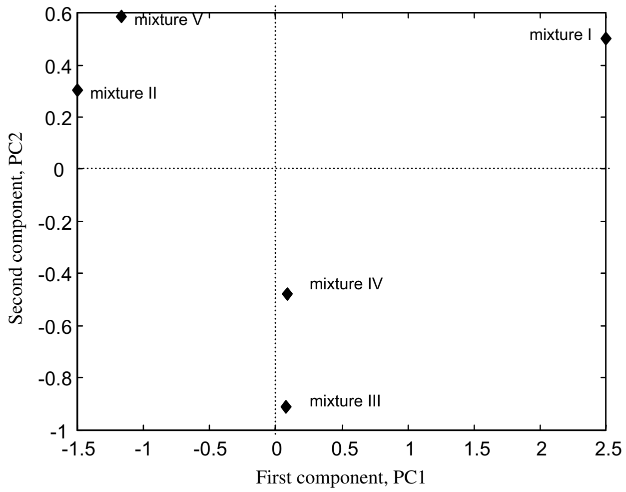

Fig. 1. The scores of the first two principal components for the new fat mixtures.

promoted the crystallisation of the stable β′ polymorph (Awad & Sato, 2002). Although, these mixtures contained slightly lower levels of palmitic acid, which naturally crystallises in the β′-form, they showed higher stability of the β′-form compared to the mixtures II and V. However, the latter blends can be transformed into the most stable β-form, because the contents of TI and stearic acid in those mixtures were approximately 1.5 times lower than in blends III and IV.

In order to elucidate the impact of the fatty acid composition on the polymorphic stability of the studied fat mixtures, the analytical data were subjected to principal component analysis (PCA). Before applying this method, the data set had to be autoscaled to equalize the variance of the different factors (Miller & Miller, 2000). In our case, there were three variables (PC1 = 2.4655, PC2 = 0.4368, and PC3 = 0.0977) and the sum of the variances for the data was 3. Thus, the first two principal components took into account 96.8% (PC1 = 82.2% and PC2 = 14.6%, respectively), of the total variation. The scores of the first two principal components, for five fat mixtures, are presented in Fig. 1. The analysis of the diagram revealed, that the studied mixtures fell into three distinct groups. Mixtures II and V were situated at the left and upper side of the plot, being well separated from the group of mixtures III and IV, whereas mixture I was evidently distinct. Moreover, there were strong positive correlations between the blends II and V and between blends III and IV (correlation coefficients = 1.000 and 0.957, respectively). This fact was readily apparent from the original data (Table 1).

3.2. Solid fat content

The differences in fatty acid and *trans* isomer contents in the fat mixtures were reflected in the SFC curves, obtained from NMR results and presented in Fig. 2.

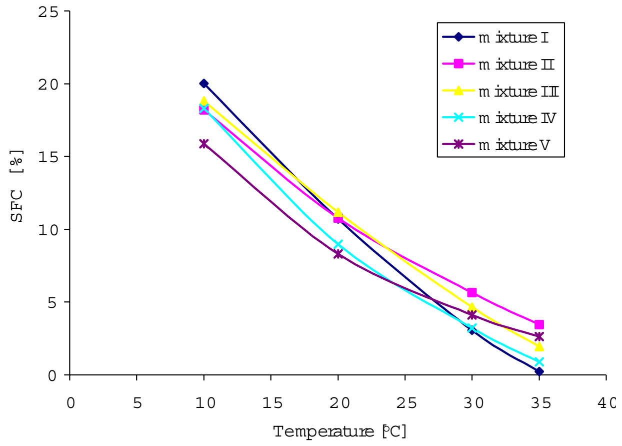

Fig. 2. Solid fat content–temperature profiles for the new fat mixtures calculated from NMR results.

SFC of new blends varied with temperature from 20% to 0.2% as depicted in Fig. 2. It is evident, that the SFC-temperature profile of mixture I is much steeper than the other samples. The SFC for mixture I is the highest, within the 10–20 °C range, but the lowest above 30 °C and this blend melts completely at 35 °C (99%). Mixtures II and V do not melt completely between 27 and 35 °C, because the SFC values at 35 °C were 3.46% and 2.64%, respectively. As reported (Moustafa, 1992), the presence of SFC at temperatures above 35 °C was recognizable as waxy residues and mixtures II and V can be qualified as poorly spreadable products.

Crystallisation rates of mixtures within 35 min, after being cooled from 75 °C (all crystals melted) to 10 °C, were also examined and results are presented in Fig. 3. Analysis of the crystallisation curves of blends indicates three distinguishable parts (Fig. 3).

After the rapid increase of SFC in the first two minutes, the slope of the curves become less steep (2–10 min). That may be caused by the crystallisation of a second fraction of TAG, or impingement of the crystal net-

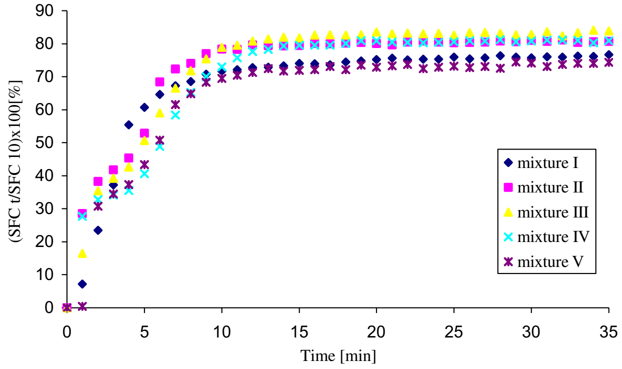

Fig. 3. Comparison of SFC values for the isothermal crystallisation (10 °C) of the analysed fat mixtures; SFC t is time course of SFC ($n = 2$) after cooling to 10 °C; SFC 10 is SFC at 10 °C.

work or polymorphic transitions. After 10 min, the final parts of the curves become stable, due to the slow crystallisation process of the lower melting TAG or polymorphic transitions to the more stable forms under experimental conditions. As depicted in Fig. 3, the increase of SFC values at 10 °C was found to be smaller in mixtures I and V, when compared to II, III and IV (after 35 min, ca. 76% and 74% for blends I and V, respectively). These results suggest that mixtures I and V consist of smaller amount of TAG species inside the oil droplets of blends, when they become solidified (Campbell et al., 2002; Miura, Yamamoto, & Konishi, 2002).

The blends I, III and IV melted faster than II and V between 27 and 35 °C. Because, the SFC for mixtures I, III and IV at 35 °C are less than 2%, they give a cool sensation in the mouth with simultaneous flavour release. However, mixtures II and V exhibited waxiness (SFC at 35 °C = 3.46% and 2.64%, respectively), and that is why the thickness in the mouth was noted.

3.3. DSC analysis of fat mixtures

The DSC thermograms of mixtures I–V are presented in Fig. 4.

The DSC cooling curves (Fig. 4. A, B, C, D, E from +75 to −40 °C) revealed two exothermic peaks with the onset temperatures ca. −40 and 20 °C, which can be assigned to a crystallisation process for the mixtures III, IV and V, begun at 20.26, 20.75 and 20.40 °C, respectively (Table 2). These exothermic crystallisation peaks can be caused by the presence of the β′ polymorph.

In the case of mixture I crystallisation, onset was lower (T_{onset} = 18.20 °C) while for mixture II, it reached 21.65 °C. The decrease of the maximum peak temperature for blend I can be related to the highest percentage of the unsaturated oleic acid in blend I (C 18:1 = 61.9%). However, the highest level of palmitic acid in mixture II accelerated the crystallisation of the β′ polymorph (Awad & Sato, 2002; Sato, 1999). An exothermic crystallisation peak at about −40 °C indicated that the main fractions in the analysed mixtures were TAG with unsaturated fatty acids, which crystallised at low temperatures. The latter peak can be connected with the occurrence of the least stable α form. When DSC heating thermograms of blends were taken directly after the rapid cooling, the formation of the α-form was evident ($T_{\text{peak}} \sim -40$ °C, Fig. 4. A′, B′, C′, D′, E′). Besides that, in DSC heating curves, both exothermic and endothermic peaks were observed. One can note three exotherms, which presumably result from the recrystallisation processes of α, β′ and β-forms. These were followed by three endotherms originating from the melting processes of α, β′ and β polymorphs, ranging between peak temperatures −19.58 and −20.79; 28.60 and 33.92 and 66.95 and 68.12 °C, respectively (Table 2). The latter can be rationalized as an α → β′ → β transformation process. A decrease of the endothermic peak temperatures for the β′ (T_c = 28.60 °C) and β (T_c = 66.95 °C) forms in the mixture I is also evident. This may be caused by the presence of a small amount of SAFA in this blend. Moreover, blends II and V had higher melting points of the β′ polymorph (33.92 and 33.18 °C, respectively), than other mixtures. The latter can be caused by the formation of a larger amount of high-temperature-melting crystals, due to polymorphic transitions β′ → β (Yap et al., 1989). Therefore, these fat mixtures were more susceptible to phase transitions than the mixtures I, III and IV.

It is noteworthy that DSC measurements do not allow accurate identification of the fatty acid fractions but rapid characterisation of the phase transitions of the fat mixtures is possible.

3.4. Calculation of β crystal contents in new fat mixtures

The β crystal contents of the fats were quantified, based on the relative density of the characteristic short spacings of β (4.6 Å) and β′ (4.2 Å), polymorphs, using a soft laser scanning densitometer (Yap et al., 1989). In the present paper, the percentages of β crystals in the analysed mixtures were calculated, based on the DSC results – enthalpy peaks of β′ and β polymorphs (Table 2). The percent β polymorph can be expressed by the following equation:

$$\%\beta = \frac{\Delta H_{\beta}}{\Delta H_{\beta} + \Delta H_{\beta'}} \cdot 100,$$

where ΔH is the peak area (enthalpy) corresponding the melting peaks of β′ and β polymorphs.

As depicted in Fig. 5, mixture V contained the highest (32.9%) amount of β polymorph, whereas mixture III had the lowest (25.8%). An insignificantly lower percentage of β crystal in blend II (31.9%) than in V was observed, as well. However, mixtures I and IV had comparable levels of β-forms (27.1% and 27.3%, respectively). The obtained results suggest that all new fat mixtures existed in the β-form but the β′ → β transitions were delayed in the case of mixtures I, III and IV. The crystal structures of these blends remained more in the β′ polymorph than did mixtures II and V under the experimental conditions.

3.5. X-ray diffraction analysis

Diffractograms of the fat mixtures are presented in Fig. 6.

The XRD short spacing diffractograms of all mixtures at ambient temperature showed lack of the diffraction peak at 4.15 Å ($2\theta = 21.39°$) from the α form (van Langevelde, van Malssen, Sonneveld, Peschar, & Schenk, 1999). On the contrary, analysed diffractograms showed

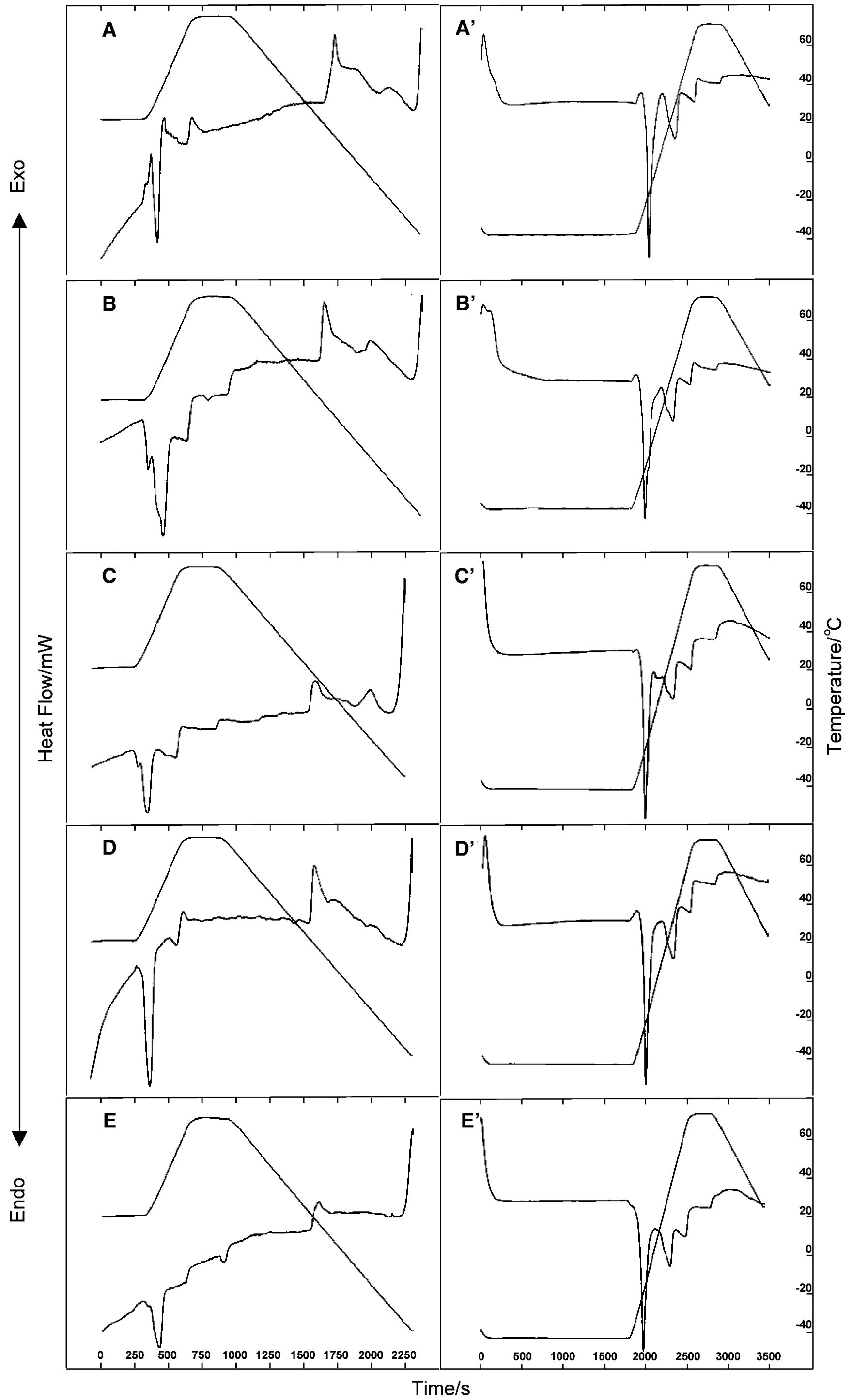

Fig. 4. DCS thermograms of mixtures: A, A', mixture I; B, B', mixture II; C, C', mixture III; D, D', mixture IV; E, E', mixture V.

two peaks of variable intensity at 4.20 Å ($2\theta = 21.13°$) and 3.80 Å ($2\theta = 23.38°$) (Lawler & Dimick, 2002; van Langevelde et al., 1999), both of which correspond to the occurrence of the β′ polymorph (Table 3).

Also, the strong lattice spacing at 4.6 Å ($2\theta = 19.27°$) was not observed in the case of mixtures I, III and IV (spectrum A, C, D). The latter indicates that the transformation into the stable β polymorph has not occurred at ambient temperature. Mixtures II and V contained the β-form (diffraction peaks at $2\theta = 19.28°$ and 18.97°), as depicted in diffractograms B and E. The XRD results listed in Table 3, and presented in Fig. 6, indicate that mixtures I, III and IV had only the β′ polymorphs, whereas blends II and V also included β-form at ambient temperature. Thus, it can be assumed that blends II and V were more susceptible to phase transi-

Table 2
DSC thermal data of the new fat mixtures[a]

Sample mixture	Sample weight (mg)	Crystallisation temperature (°C)			Crystallisation heat (J/g)	Melting temperature (°C)			Melting heat (J/g)
		Onset	Peak	Polymorph		Onset	Peak	Polymorph	
I	10.1	−37.08	−42.22	α	−15.43	−24.72	−19.58	α	26.38
		18.20	13.21	β′	−7.17	10.11	28.60	β′	12.23
						47.71	66.95	β	4.54
II	10.2	−35.55	−44.52	α	−16.49	−26.30	−20.43	α	31.57
		21.65	16.49	β′	−5.98	13.30	33.92	β′	10.03
						48.66	68.12	β	4.70
III	10.1	−32.77	−39.00	α	−16.86	−27.25	−20.79	α	28.38
		20.26	15.70	β′	−6.37	13.56	32.15	β′	10.96
						51.74	67.75	β	3.80
IV	10.0	−35.54	−41.11	α	−16.53	−26.25	−20.17	α	30.44
		20.75	16.83	β′	−6.65	13.90	32.98	β′	12.52
						47.91	67.02	β	4.69
V	10.2	−33.84	−40.61	α	−15.09	−27.38	−20.52	α	32.12
		20.40	16.83	β′	−4.52	13.05	33.18	β′	12.40
						47.13	67.65	β	6.07

[a] Each value in the table represents the mean of triplicate analyses.

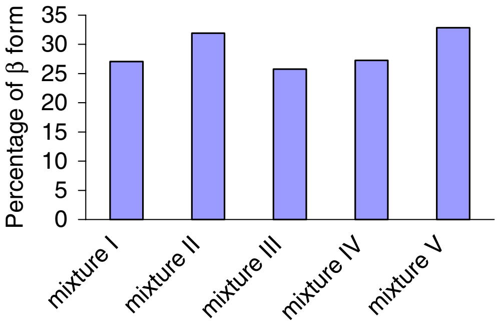

Fig. 5. Percentage of β polymorph in the new fat mixtures calculated from DSC results.

tion β′ → β than mixtures I, III and IV under the experimental conditions (temperature of XRD measurements and crystallisation conditions). Besides, the rate and extent of β′ → β transformation depends on the composition and configuration of the fatty acids (D'Souza et al., 1991). The lower percentage of stearic acid and trans isomers in mixtures II and V facilitates the transformation to β-form, as can be observed in the diffractograms of these mixtures. Moreover, the formation of β polymorph was attributed to the presence of a high concentration of trisaturated TAG (Busfield & Proschogo, 1990). Thus, it is likely that mixtures II and V contained larger amounts of high melting fully saturated TAG than mixtures I, III and IV.

4. Conclusion

It can be concluded that fatty acid composition, primarily trans isomers, stearic and palmitic acids, influence β′ → β transitions of the fat mixtures. Because fat mixtures I, III and IV had higher levels of trans isomers and stearic acid than had blends II and V, the latter showed higher stability of the β′-form, which is the most important factor in margarine production. The principal component analysis (PCA) allowed separation of studied fat mixtures into three groups: (a) mixtures II and V; (b) mixtures III and IV; (c) mixture I. Moreover, the blends I, III and IV have good mouth-melt characteristics; therefore they melt sharply at body temperature (SFC < 2% at 35 °C). In contrast, mixtures II and V exhibited waxiness (SFC > 2.5% at 35 °C) which reduced their organoleptic properties and spreadability.

On the other hand, the DSC melting and crystallisation curves provide useful information about the nature of the thermodynamic changes, which are associated with the phase transitions of the fat mixtures. The DSC results suggest that all new fats existed in β-form but the β′ → β transitions were delayed in the case of mixtures I, III and IV. However, the diffractograms indicate that blends I, III, IV had only the β′-form at ambient temperature, unlike blends II and V, which also included the most stable β polymorph. Probably, the differences in fatty acid composition of studied fats have impact on the rate of β′ → β transitions under the experimental conditions. Because new fat mixtures I, III and IV had better β′ polymorphic stability than blends II and V under the same conditions, the latter can be used in the manufacturing of margarines.

It is noteworthy, that correct processing, transporting conditions and treatments are very important and necessary for obtaining the highest quality of the final fat products.

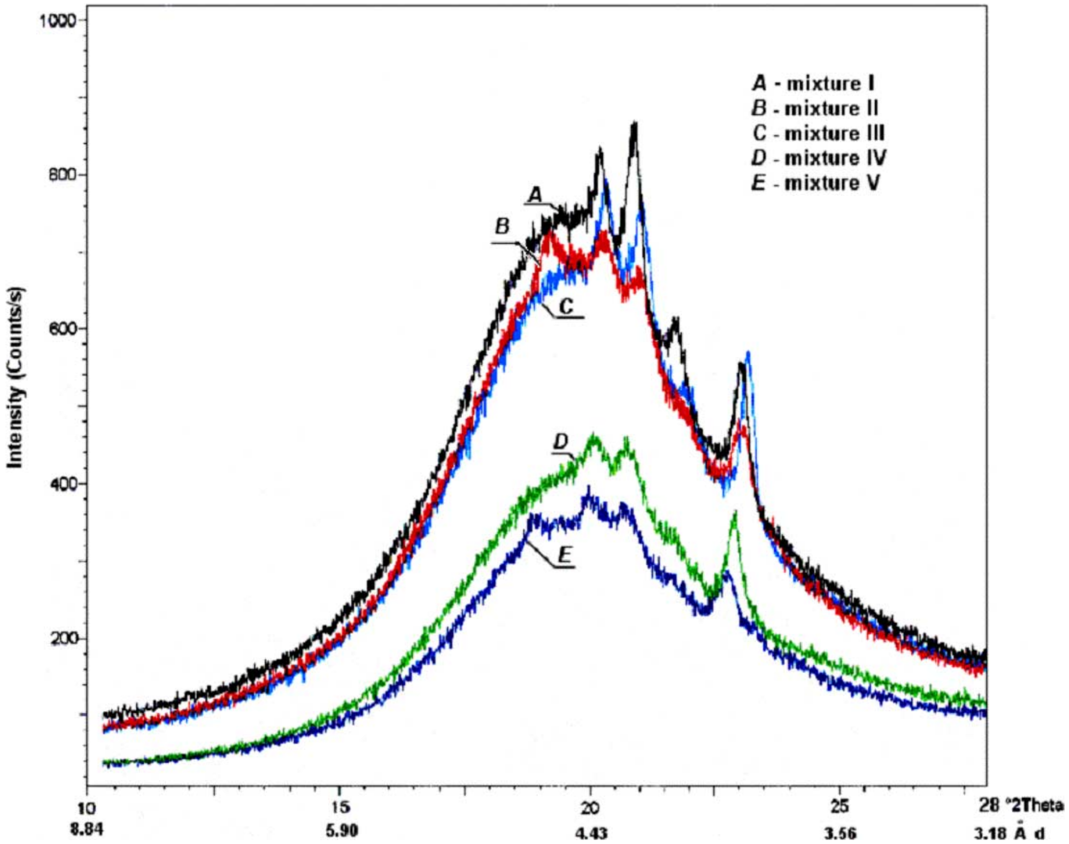

Fig. 6. Results of XRD analyses of the new fat mixtures.

Table 3
XRD short spacing of polymorphs of the new fat mixtures

Sample	*d*-spacing (Å)[a]	Angle (°2θ)	Polymorph
Mixture I	3.85 (w); 4.23 (s)	23.07; 20.96	β′
Mixture II	3.84 (m); 4.22 (vs) 4.60 (vs)	23.13; 21.05 19.28	β′ + β
Mixture III	3.83 (s); 4.20 (vs)	23.21; 21.11	β′
Mixture IV	3.88 (m); 4.27 (s)	22.93; 20.78	β′
Mixture V	3.90 (m); 4.28 (s) 4.67(m)	22.81; 20.72 18.97	β′ + β

[a] vs, very strong; s, strong; m, medium; w, weak.

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