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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, $\Delta H_f = 28.47$ 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 °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 °C min^{-1} to crystallise the material and subsequently reheated (after 30 min) to 75 at 10 °C min^{-1} in order to determine the melting behaviour of studied fats. Finally, samples were again cooled to 20 at 5 °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.