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Effect of diacylglycerol addition on crystallization properties of pure triacylglycerols

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ABSTRACT

The objective of this study was to investigate the effects of blending triacylglycerols (TAGs) and diacylglycerols (DAGs) on the melting and crystallization properties in a fat system. To this end, differential scanning calorimetry (DSC), X-ray diffraction (XRD) and polarized light microscopy (PLM) methods were used. Different DAGs (diolein—OO, dipalmitin—PP and distearin—SS) were added at 5% to each TAG (triolein—OOO, tripalmitin—PPP and tristearin—SSS). DSC results showed that the addition of DAGs delayed the onset of crystallization of saturated TAGs (PPP and SSS). By contrast, the addition of DAGs to unsaturated TAG (OOO) accelerated the onset of crystallization, with the appearance of an extra crystallization peak upon the addition of SS and PP. PLM results revealed that the addition of OO affected the polymorphic transition of the TAGs studied findings were consistent with DSC melting curves and XRD results.

1. Introduction

Edible oils and fats are essential nutrients in the human diet, playing the important role of supplying essential fatty acids and energy. Fats are made up primarily of TAGs, representing approximately 98%, with the remainder of the fat comprising more polar lipids such as diacylglycerols (DAGs), monoacylglycerols (MAGs), free fatty acids (FFAs), phospholipids, glycolipids, sterols, and other minor components (Metin & Hartel, 2005).

The crystallization behavior of lipids has important implications for the industrial processing of food products whose physical characteristics are largely dependent on fat crystals. Such products include chocolates, margarines, spreads, confectionery and bakery fats, dairy products and general purpose shortenings (Sato, 2001). In the majority of foods, crystallization of triacylglycerols (TAG) is the most important, although crystallization of other lipids (i.e., monoacylglycerols, diacylglycerols, phospholipids, etc.) may also be important to product quality.

TAG molecules are inherently able to pack in different crystalline arrangements or polymorphs, whose melting temperatures differ significantly [19,20]. The polymorphic forms of fats are often simply classified into three categories, α, β', and β, in increasing order of stability. Thus, the α form is the least stable polymorph, having the lowest melting point and latent heat of fusion whereas the β form is the most stable, having the highest melting point and latent heat. Each polymorphic form has distinct short spacings (distances between parallel acyl groups in the TAG), used to distinguish the polymorphic forms based on their X-ray diffraction patterns.

Minor lipids include compounds of greater polarity and with amphiphilic structure, such as diacylglycerols (DAGs), monoacylglycerols (MAGs), free fatty acids, phospholipids and esters. These constituents have been considered molecular agents that affect crystallization. The presence of minor lipids can promote crystallization, whereas an inhibition effect is observed in some systems (Metin & Hartel, 2005; Sato, 2001; Smith, Bhaggan, Talbot, & van Malssen, 2011). According to Toro-Vazquez, Rangel-Vargas, Dibildox-Alvarado, and Charó-Alonso (2005), these compounds modulate the entire crystallization process from nucleation to post-crystallization events including polymorphism, driving force and solid fat content (SFC).

Diacylglycerols represent the minority class of lipids that are of most interest in studies of crystallization of lipids, since they occur at higher concentrations in practically all fats of vegetal or animal origin (Craven & Lencki, 2011a, 2011b). Therefore, with regard to the action of DAGs on the velocity of crystal nucleation and growth, the relevant technical literature shows that this glycerol class can exert a promoting or inhibitory effect on crystallization, conditioned mainly by the compatibility of its composition with that of the raw materials. According to Wright, Hartel, Narine, and Marangoni (2002), the ability of DAGs to act as modifiers of the crystalline behavior of TAGs is primarily related to the similarity in chemical composition between these glycerol

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classes. Studies reported to date suggest the parameters defining this degree of similarity are the isomerism or stereospecificity of the DAGs and the composition in fatty acids, with relation to chain size and saturation of the fatty acids.

In a review by Smith et al. (2011) on the effects of minor and additive lipids on the physical properties of lipid systems, the authors concluded several rules. For instance, when the acyl group of the minor lipid is similar to those present in the fat, a greater effect on crystallization was observed (Elisabettini, Desmedt, Gibon, & Durant, 1995; Garbolino, Bartoccini, & Floter, 2005; Smith & Povey, 1997). In addition, super-cooling reduced the effects of minor lipids (Cheong, Zhang, Xu, & Xu, 2009; Wright, Hartel, Narine, & Marangoni, 2000). The concentration of the minor lipid directly influenced the crystallization process of fat (Herrera & Marquez Rocha, 1996).

In relation to crystallization, DAG constituents have been studied in various fats and oils such as milk fat (Wright et al., 2002), palm olein TAGs (Siew & Ng, 1996), palm oil (Siew & Ng, 1999; Verstringe, Danthine, Blecker, Depypere, & Dewettinck, 2013), trilaurin (Smith & Povey, 1997) and lard blends with rapeseed oil (Cheong et al., 2009) and are widely reported as inhibitors of the crystallization process.

Studying the crystallization behavior and polymorphism of a pure lipid system is of great scientific importance as a means of gaining an understanding of the phenomena involved, serving as basic knowledge to help guide the addition or removal of these compounds in different raw materials. The purpose of the present study was therefore to characterize and compare the effects of the addition of 5% pure diacylglycerols (diolein——PP and distearin—SS) to pure triacylglycerols (triolein—OOO, tripalmitin—PPP and tristearin—SSS) using differential scanning calorimetry (DSC), polarized light microscopy and X-ray diffraction.

2. Material and methods

2.1. Material

2.1.1. Triacylglycerols

The samples were acquired from the company Sigma-Aldrich (United Kingdom).

Glyceryl trioleate > 99% (OOO)
Glyceryl tripalmitate > 99% (PPP)
Glyceryl tristearate ~99% (SSS)

2.1.2. Diacylglycerols

The samples were acquired from the company Nu-Chek Prep. Inc. (USA).

diolein > 99% (OO)
dipalmitin > 99% (PP)
1,3-distearin > 99% (SS)

2.2. Methods

2.2.1. X-ray diffraction

The polymorphic form of the fat crystals in the sample was determined according to the AOCS Cj 2-95 method (2004). Analyses were carried out on a Philips diffractometer (PW 1710), using Bragg–Brentano (θ:2θ) geometry with radiation of Cu-Kα ($\lambda = 1.54056$ Å, tension of 40 kV and 30 mA). Measures were attained with 0.02° in 2θ steps and an acquisition time of 2 s, using scans of 5–40° (2θ scale). The samples were melted in a microwave oven at approximately 80 °C and stabilized at 25 °C for 24 h. Analyses were carried out at 25 °C. Polymorphic form identification was performed based on the characteristic short spacings of the crystals. Form α presents a single diffraction line at 4.15 Å. Form β' is characterized by two strong diffraction lines at 3.8 Å and 4.2 Å, whereas form β is associated with a series of diffraction lines exhibiting a prominent line at 4.6 Å and lines of lesser intensity at 3.7 Å and 3.8 Å (Ribeiro, Basso, Grimaldi, Gioielli, & Gonçalves, 2009; Rousseau, Marangoni, & Jeffrey, 1998).

2.2.2. Differential scanning calorimetry (DSC)

The DSC curves were obtained by the differential scanning calorimetry (DSC) cell on a DSC 4000 Perkin Elmer (Perkin Elmer Corp., Norwalk, CT, USA) under a dynamic atmosphere of He (20 mL/min), a cooling rate of −10 °C/min, at temperatures ranging from 80 to −60 °C with an isothermal time of 10 min at 80 °C, using sealed aluminum capsules containing a sample mass of 5 to 10 mg. The melting curves were obtained from −60 to 80 °C (5 °C/min) with an isothermal time of 30 min at −60 °C. The temperature and heat of melting were calibrated with indium (initial temperature of 156.6 °C). Curves were processed by Pyris software and crystallization curves were analyzed for onset of crystallization (T_{onset} °C), peak crystallization temperatures (T_{peak} °C) and crystallization enthalpies (ΔH_c J/g) (Ribeiro et al., 2009).

2.2.3. Polarized light microscopy

The samples were heated to 70 °C in an oven and held at this temperature for 30 min to destroy the crystalline memory. One drop of melted fat was withdrawn using a capillary tube and then mounted on a slide with a similarly pre-heated coverslip. The prepared slide was placed on the temperature controller of the microscope. The sample was first subjected to 100 °C for 15 min to ensure total melting of the crystals. The sample was then cooled to 15 °C (rate of 10 °C/min) using a Linkam temperature controller, model EP-120 (Surrey, England). The crystallization images were captured every 2 s from 45 °C (PPP) and 55 °C (SSS) until complete crystallization of the sample. Subsequently, the samples were maintained at 15 °C for 40 min and melting then evaluated. The samples were heated to 100 °C (rate 5 °C/min). Melting images were obtained every 2 s from 35–40 °C (PPP) and 50–53 °C (SSS), until complete melting of the sample. The diameter of the crystals after complete crystallization was determined for each sample using Image-Pro Plus version 7.0 software (Media Cybernetics, USA). The images were used to determine the beginning and end of crystallization, induction time and crystallization time.

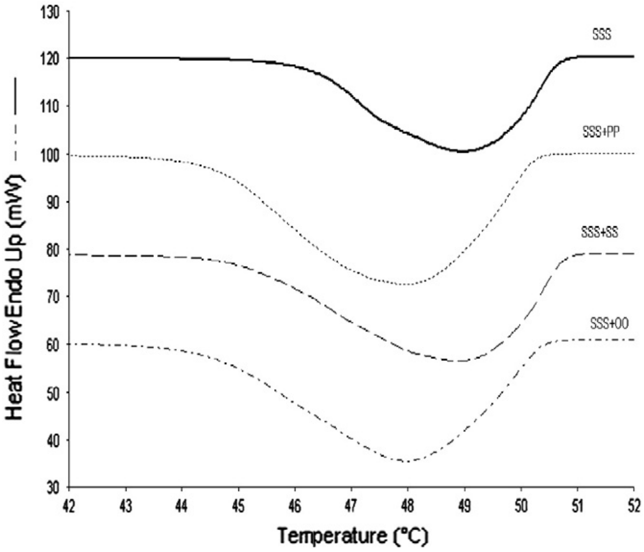

Fig. 1. Crystallization curves obtained by DSC of pure tristearin and with addition of 5% diacylglycerols.