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Influence of a commercial monoacylglycerol on the crystallization mechanism of palm oil as compared to its pure constituents

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ABSTRACT

The effect of a commercial monoacylglycerol (MAG), Myverol™ 18 04-PK (Myverol), on the non-isothermal crystallization mechanism of palm oil (PO) was investigated and compared to the effect of the two main constituents of Myverol, monopalmitin and monostearin. The MAGs were added to PO in concentrations up to 8% and the blends were studied using different techniques (differential scanning calorimetry (DSC), X-ray diffraction (XRD) and polarized light microscopy (PLM)). The DSC crystallization profiles revealed an earlier onset of crystallization along with extra crystallization peaks when MAGs were added to PO. Combined with X-ray results, it could be concluded that the crystallization process of the blends is initiated by the MAGs crystallizing in the α form and then transforming to sub-α. The effect on the non-isothermal crystallization of the PO TAGs is confined to an earlier onset of crystallization, probably through a template effect, and an effect on the crystal structure coarseness.

1. Introduction

Polar lipids and other emulsifiers have traditionally been used in several food applications. Monoacylglycerols and diacylglycerols are considered as the most important group, as they represent about 70% of total food emulsifier production (Moonen & Bas, 2004). Major areas of application are bakery, margarines, ice cream and chewing gums. About 60% of all monoacylglycerols (MAGs) are used in bakery (Moonen & Bas, 2004). Distilled commercial MAGs are produced from the reaction of a natural fat or oil with glycerol, yielding a mixture of monoacylglycerols, diacylglycerols and triacylglycerols and a small fraction of unreacted glycerol. Subsequently, a molecular distillation process yields a distillate containing typically 95% MAGs, 3–4% diacylglycerols (DAGs), 0.5–4% free glycerol and 0.5–1% free fatty acids (Krog & Sparso, 2004). The fatty acid composition reflects the chain length distribution of the fat from which it is made (Stauffer, 2005). Myverol, the commercial MAG used in this study, is made from hydrogenated palm oil. Palmitic acid (44–45%) and oleic acid (39–40%) are the major fatty acids present in palm oil (Siew, 2002; Sumathi, Chai, & Mohamed, 2008). Consequently, the main constituents of Myverol are monopalmitin and monostearin.

Among other functions, MAGs can be used to control fat crystallization in fat-based products. For this study, palm oil was chosen as bulk fat as it is the second most consumed oil in the world, after soybean oil (Tang & Pantzaris, 2009). Palm oil has a balanced fatty acid composition with an almost equal level of saturated and unsaturated fatty acids (Ebong, Owu, & Isong, 1999). It is highly stable in the β′ polymorph, yielding relatively small crystals which give a smooth texture to e.g. margarines and shortenings (Sato, 1999; Siew, 2002). However, it has a slow crystallization rate and an unusually long α lifetime compared to other natural fats (Berger, 2001; De Clercq, Danthine, Nguyen, Gibon, & Dewettinck, 2012). To overcome these problems, different approaches are possible. One possibility is the addition of an emulsifier, as investigated for MAGs (Basso et al., 2010; Fredrick, Foubert, Van De Sype, & Dewettinck, 2008; Miura, Yamamoto, & Konishi, 2002; Miura, Yamamoto, & Sato, 2002; Verstringe, Danthine, Blecker, Depypere, & Dewettinck, 2013), DAGs (Calliauw, 2008; Saberi, Lai, & Toro-Vázquez, 2011; Siew & Ng, 1999, 2000), sucrose esters/sorbitan esters (Garbolino, Bartoccini, & Floter, 2005) and polyglycerol behenic acid esters (Sakamoto et al., 2003).

In a previous study, the effect of pure monopalmitin on the crystallization process of palm oil was investigated (Verstringe et al., 2013). However, pure monopalmitin (>99%) is too expensive to be used in everyday applications. Therefore, this study focuses on the effect of a commercial MAG, Myverol, which is an inexpensive source of MAGs. Using different techniques, the effect of Myverol on the crystallization process of palm oil was investigated. In order to study how the effects of a commercial MAG differ from the effects of pure MAGs, the two main components of Myverol, monopalmitin and monostearin, were added separately to PO. The crystallization process of the PO/monopalmitin

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and the PO/monostearin blends was then compared to the crystallization process of the PO/Myverol blend.

2. Experimental section

2.1. Materials

Refined, bleached and deodorized palm oil (PO) was obtained from Loders Croklaan (Wormerveer, The Netherlands) and was used as received. Myverol™ 18 04-PK (referred to as Myverol throughout the paper) was obtained from Kerry Group (Ireland). This commercial emulsifier contained 60.17 ± 0.22% palmitic acid and 37.29 ± 0.50% stearic acid as determined by gas chromatography. According to the supplier, Myverol contained a minimum of 95% MAGs. Pure monopalmitin (>99%, MP) and pure monostearin (>99%, MS) were obtained from Nu-Chek Prep (Elysian, USA).

2.2. Preparation of the palm oil — monoacylglycerol blends

An imitated Myverol sample was prepared by mixing MP and MS in the same ratio as they are present in Myverol, i.e. 62% MP and 38% MS. Different concentrations of Myverol (1, 2, 4 and 8% w/w), imitated Myverol (8% w/w) and MP and MS (8% w/w) were dispersed in the melted PO and stirred with a magnetic stirrer at 80 °C until a homogeneous sample was obtained. When the blend was visibly free of dispersed material, it was further mixed for at least 2 h. The blends were stored at −24 °C until analysis.

2.3. TAG composition

Separation of the TAG species was performed on a Thermo Finnigan Surveyor HPLC system with four solvent lines, degasser, autosampler and Chromquest software (Thermo Electron Corporation, Brussels, Belgium), which was coupled with an Alltech ELSD 2000ES evaporative laser light scattering detector (Grace Alltech, Lokeren, Belgium). The column was a 15063.0 mm Alltima HP C18 HL with 3 mm particle diameter (Grace Alltech). A precolumn with a silica packing was used. A dichloromethane/acetonitrile gradient was applied. The analysis was executed in duplicate and the sample injections were performed in duplicate. Table 1 gives the TAG composition of the used palm oil. The amount of DAGs (% area) concluded from the HPLC results was 4.2%.

Table 1
TAG composition of the used palm oil.[a]

TAG	% of the total TAG content
PLL	1.30 ± 0.02
LOO	1.09 ± 0.02
PLO	10.98 ± 0.03
PLP	10.45 ± 0.06
OOO	3.12 ± 0.01
POO	25.78 ± 0.05
POP	34.11 ± 0.06
PPP + SOO	7.38 ± 0.02
POS	4.83 ± 0.01

[a] P: palmitic acid, L: linoleic acid, O: oleic acid, S: stearic acid.

2.4. Differential scanning calorimetry (DSC)

DSC experiments were performed with a Q1000 DSC with a refrigerated cooling system and an autosampler system (TA Instruments, New Castle, USA). The DSC was calibrated with indium (TA Instruments, New Castle, USA), azobenzene (Sigma-Aldrich, Bornem, Belgium) and undecane (Acros organics, Geel, Belgium) prior to analysis. Nitrogen was used to purge the system. Samples were sealed in hermetic pans and an empty pan was used as a reference. Non-isothermal crystallization and melting profiles of the MAGs were recorded using the following time-temperature program: holding at 90 °C for 10 min to ensure complete melting and to erase the crystal memory, cooling at −10 °C/min to −40 °C, holding at −40 °C for 10 min and heating at 10 °C/min to 90°. The non-isothermal crystallization profiles of the PO/MAG blends were recorded by holding the samples at 80 °C for 10 min and cooling at a rate of −10 °C/min. The DSC profiles were analyzed with the Universal Analysis software version 4.7A (TA Instruments, New Castle, USA). Measurements were done in triplicate. Crystallization onset temperatures were determined by the intersection of the baseline with the absolute highest tangent of the crystallization curve. One-way ANOVA was performed on the measurements using SPSS Statistics 20 to detect statistically significant differences ($p < 0.05$). To identify the differences, Tukey's test was used in the case of equal variances while Dunnett's T3 test was used when the variances were not equal.

2.5. Powder X-ray diffraction spectroscopy (XRD)

Polymorphic behavior of PO and the PO/MAG blends was investigated by XRD using a Bruker D8-Advance Diffractometer (Bruker, Germany) (λ Cu = 1.54178 Å, 40 kV, 30 mA) equipped with an Anton Paar temperature control system composed of a TTK450 low-temperature chamber connected to a water bath (Julabo) and heating device (TCU 110 Temperature Control Unit) (Anton Paar, Graz, Austria). Just as for the DSC measurements, the samples were first heated to 80 °C and held at that temperature for 10 min to ensure complete melting and to erase the crystal memory. After that, the samples were cooled at −10 °C/min and short-spacing runs (15–27° 2θ) were recorded every 30 s using a Vantec-1 detector (Bruker, Germany).

2.6. Polarized light microscopy (PLM)

Samples were viewed between crossed polarizers in a Leitz Diaplan light microscope (Leitz, Wetzlar, Germany) mounted with a Linkam hot stage (Linkam, Tadworth, UK). A droplet of liquid oil was applied on a preheated carrier glass and covered with a preheated cover glass. The sample was then held at 80 °C for a sufficient time to ensure complete melting and an erased crystal memory. Next, the sample was cooled at −10 °C/min to 20 °C and images were taken using an Olympus color view camera (Olympus, Aartselaar, Belgium).

3. Results and discussion

3.1. Crystallization behavior of Myverol and its pure constituents

Before investigating the behavior of the MAGs in blends with palm oil, it is useful to obtain insight into the crystallization behavior of the pure MAG substances. Indeed, similar to triacylglycerols (TAGs), MAGs crystallize and melt at certain temperatures and form different polymorphs depending on the temperature (Vereecken et al., 2009). The crystallization and melting profile of Myverol and its main constituents, MP and MS, are shown in Fig. 1. In all three cases, the melting profile is similar to the profile during cooling. The crystallization behavior of MP was already described (Verstringe et al., 2013). In this previous study, it was concluded that MP first crystallized into an α polymorphic form which transformed into a sub-α polymorph upon further cooling. This transformation occurs via the solid state and is reversible, as can be seen in the melting profile. Sub-α forms do not have a melting point. However, the enthalpy change associated with the transition can be measured by DSC and yields a 'melting point' (i.e. the peak temperature) (Hagemann, 1988; Krog, 2001). Similar to MP and in accordance with the study of Vereecken et al. (2009), MS firstly crystallized into an α polymorph, followed by a transformation to sub-α upon further cooling. In contrast to MP, a second sub-α polymorph could be detected (Fig. 1). This is observed for MAGs with a chain length