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Influence of monopalmitin on the isothermal crystallization mechanism of palm oil

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ABSTRACT

A multi-methodological approach (differential scanning calorimetry (DSC), X-ray diffraction (XRD) and polarized light microscopy (PLM)) was used to study the influence of monopalmitin (MP) on the isothermal crystallization process of palm oil (PO). MP was added in different concentrations up to 8% and the isothermal crystallization temperature was varied between 15 and 28 °C. From the DSC results, it was clear that the addition of MP leads to an earlier onset of crystallization along with the appearance of extra crystallization peaks. Combined with the results of the XRD measurements, a crystallization mechanism could be deduced. It was suggested that the high-melting MP initiated the crystallization process and induced a fractional crystallization of the PO triacylglycerols (TAGs), leading to a concentration of similar TAGs around MP cores. The PLM results indicated a coarser crystal structure through addition of MP to PO.

1. Introduction

Palm oil is a unique oil among all vegetable oils, which makes it the second most consumed oil in the world, after soybean oil (Tang & Pantzaris, 2009). The oil, obtained from the mesocarp of the fruits of the tropical tree *Elaeis guineensis*, is unique in having a balanced fatty acid composition with the level of saturated fatty acids being almost equal to that of the unsaturated fatty acids (Ebong, Owu, & Isong, 1999). Palm oil is characterized by a high diglyceride content, mainly palmitoyloleoyl glycerol (PO), dipalmitoyl glycerol (PP) and dioleoyl glycerol (OO), usually ranging between 4 and 7.5% (Goh & Timms, 1985; Jacobsberg & Ho, 1976). Palmitic acid (44–45%) and oleic acid (39–40%) are the major fatty acids present in palm oil (Siew, 2002). Because of the diversity in fatty acid chain length, palm oil is highly stable in the β′ polymorph. This yields relatively small crystals which give a smooth texture to e.g. margarines and shortenings (Sato, 1999; Siew, 2002). For these types of products, there is no need for hydrogenation of the palm oil as they are naturally semi-solid at room temperature (Siew, 2002). As such, it forms an ideal hard stock to be used in trans fat-free products (Berger, 2001). However, at the industrial level, palm oil also has some disadvantages such as a considerably slow crystallization rate, resulting in coarse crystals which cause graininess in margarines and shortenings (De Clercq, Danthine, Nguyen, Gibon, & Dewettinck, 2012). Moreover, palm oil has an unusually long α lifetime compared to other natural fats (Berger, 2001). The slow crystallization can be overcome by interesterification or by partial hydrogenation (Berger, 2001; De Clercq et al., 2012). Also, different emulsifiers including monoglycerides (Basso et al., 2010; Fredrick, Foubert, Van De Sype, & Dewettinck, 2008; Miura, Yamamoto, & Konishi, 2002; Miura, Yamamoto, & Sato, 2002), diglycerides (Calliauw, 2008; Saberi, Lai, & Toro-Vázquez, 2011; Siew & Ng, 1999, 2000), and sucrose esters/sorbitan esters (Garbolino, Bartoccini, & Floter, 2005) were added to affect the crystallization behavior of palm oil and its fractions.

The research that has been published on the influence of minor components and additives on the physical properties of fat systems has been reviewed by Smith, Bhaggan, Talbot, and van Malssen (2011). Minor components can be present naturally, such as the diglycerides present in palm oil, or added on purpose, such as emulsifiers. The latter are amphiphilic molecules with a hydrophobic and a hydrophilic part. Mono- and diglycerides, which contain an −OH functional group, are considered as the most important group of emulsifiers. Monoglycerides have a higher melting point compared to the fatty acid or the triglyceride out of which they are constructed (Droste, 1972). Like triglycerides, monoglycerides are polymorphic. Vereecken et al. (2009) investigated the polymorphic behavior of saturated and unsaturated monoglycerides. They concluded that three polymorphic forms, namely the sub-α, α and β polymorph, can be found for saturated monoglycerides with a chain length of less than 18 carbon atoms. A second sub-α polymorph could be found for saturated monoglycerides with a chain length of 18 carbon atoms or more. Only one polymorph, the most stable β polymorph, could be found for unsaturated monoglycerides.

Minor components can not only have different effects on fat crystallization, such as on the nucleation (promotion or inhibition), crystal growth, polymorphism and crystal morphology but also on the yield force, solid fat content (SFC), heat capacity, post-hardening phenomena, etc. (Smith et al., 2011). By combining the information

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gained out of the different studies, Smith et al. (2011) were able to derive some generic rules. When the acyl group of the minor component (in case one is present) is similar to the ones present in the fat, a stronger effect on the crystallization was observed (Elisabettini, Desmedt, Gibon, & Durant, 1995; Garbolino et al., 2005; Smith & Povey, 1997). It was also derived that increasing undercooling reduces the effect of a minor component (Cheong, Zhang, Xu, & Xu, 2009; Wright, Hartel, Narine, & Marangoni, 2000). Moreover, it was suggested that, to influence the crystallization process of the fat (mixture), a certain concentration is needed, depending on the mechanism involved (Herrera & Marquez Rocha, 1996). A summary of how emulsifiers might influence nucleation, crystal growth, and polymorphism was presented through a schematic overview (Smith et al., 2011).

As palmitic acid is the major fatty acid present in palm oil, it was decided to investigate the effect of monopalmitin (MP) on the palm oil crystallization behavior, because of its high degree of similarity with the crystallizing palm TAGs. In their review, Smith et al. (2011) criticize the fact that studied additives are mostly referred to by their trade name and are not adequately analyzed while the precise composition might vary, even from batch to batch. In this study, it was decided to work with pure MP (>99%). In this way, the composition was well known and observed effects could be completely attributed to the MP. The influence of pure MP on palm oil crystallization has been studied before (Miura, Yamamoto, & Konishi, 2002; Miura, Yamamoto, & Sato, 2002), as well as the influence of monoglycerides of fully hydrogenated PO (Basso et al., 2010; Fredrick et al., 2008), which contain a substantial amount of MP. Miura, Yamamoto, and Konishi (2002) and Miura, Yamamoto, and Sato (2002) only concluded that pure MP in a concentration of 1% did not affect the solid fat content when crystallization occurred at 5 °C. Moreover, all studied blends never had an emulsifier concentration higher than 2%. In this study, a more extended range of concentrations was investigated and different techniques have been used to elucidate the effect on different levels.

2. Materials and methods

2.1. Materials

Refined, bleached and deodorized palm oil (PO) was obtained from Loders Croklaan (Wormerveer, The Netherlands) and was used as received. Pure monopalmitin (>99%, MP) was obtained from Nu-Chek Prep (Elysian, USA).

2.2. Preparation of the palm oil–monopalmitin blends

Different concentrations of MP (1, 2, 4 and 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 15,063.0 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)

The 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. Three types of experiments were performed: non-isothermal crystallization experiments, isothermal crystallization experiments and stop-and-return experiments. For the non-isothermal experiments, the following time–temperature program was applied: holding at 80 °C (90 °C for pure MP) 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 80 °C (90 °C for pure MP). For the isothermal crystallization experiments, the procedure was adapted in that the sample was only cooled to the crystallization temperature (15, 18, 20, 25 or 28 °C) and was then held there for 120 min. For the stop-and-return experiments, the procedure was basically identical to the isothermal procedure except that the sample was heated at 20 °C/min to 80 °C after a certain isothermal period (Foubert, Fredrick, Vereecken, Sichien, & Dewettinck, 2008). The isothermal period prior to melting was varied in different experiments and was maximally 90 min. A heating rate of 20 °C/min is fast enough to prevent the occurrence of polymorphic transitions as much as possible but slow enough to prevent thermal lag (Fredrick et al., 2008). The DSC profiles were analyzed with the Universal Analysis software version 4.7A (TA Instruments, New Castle, USA).

2.5. Powder X-ray diffraction spectroscopy (XRD)

Polymorphic behavior of the 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 to the crystallization temperature and short-spacing runs (15–27° 2θ) were performed using a Vantec-1 detector (Bruker, Germany) every 2 min during the isothermal time (90 min).

2.6. Polarized light microscopy (PLM)

The 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