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In search of confectionary fat blends stable to heat: Hydrogenated palm kernel oil stearin with sorbitan monostearate

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ABSTRACT

The potential of sorbitan monostearate (SMS) addition to change the basic-crystal-structure of a confectionary fat blend (CFB) with the aim to enhance its heat resistance was investigated. The CFB used in this study was a blend of hydrogenated palm kernel oil stearin, lecithin, polyglycerol polyricinoleate (PGPR) and cocoa butter. Samples made with different proportions of SMS to CFB were prepared and the crystal structure, the melting behaviour, the crystal morphology and crystallization kinetics were studied. Heat resistance was evaluated using a temperature-variable rheological method. Powder X-ray diffraction (XRD) studies in the wide angle region (WAXS) revealed the presence of two crystalline polymorphs (α and β′) in all blends. While XRD studies in the small angle region (SAXS) revealed a shift in the CFB peak position upon addition of SMS. The presence of two polymorphic forms was confirmed by differential scanning calorimetry (DSC), while a third endotherm was evident when the amount of SMS present in the system was greater than 40%. Studies on the nucleation and crystallization kinetics showed that crystal nucleation and growth occurred in two stages: SMS appeared first followed by CFB. Iso-solid diagrams constructed from the melting profiles obtained from SFC-temperature measurements indicated monotectic solution behaviour between SMS and the CFB.

The microstructure, as observed under polarized light, changed from small crystals for the CFB to needles for mixtures with 10% SMS, to spherulites for mixtures with 50% SMS, to clusters for mixtures containing between 80 and 100% SMS. Cryo-TEM showed nanoplatelet formation for the CFB and nano-blobs for SMS. The storage modulus (G′) for mixtures containing 25% SMS decreased from $G' = 1.72\ 10^7 \pm 4.60\ 10^6$ Pa at 20 °C to $G' = 3.24\ 10^5 \pm 2.15\ 10^4$ Pa at 40 °C. Thus, SMS addition to confectionery fats can provide heat resistance to the CFB.

1. Introduction

Modified lauric fats obtained from fractionation and/or hydrogenation of palm kernel oil (PKO) are extensively used in the confectionery industry as cocoa butter (CB) substitutes (Calliauw et al., 2005; Lipp & Anklam, 1998; Young, 1983). As a substitute, the fat replaces 100% of the CB, however it is common to add CB (less than 4%) in order to provide a hint of the so desired "chocolate" aroma without inducing fat-incompatibility issues (Lonchampt & Hartel, 2004). If this limit is exceeded, fat softening becomes an issue due to the eutectic solution behaviour between cocoa butter and palm kernel oil which can lead to bloom formation (Laustsen, 1991; Seguine, 2001). This incompatibility is due to the significant differences in the fatty acid (FA) compositions and distributions between CB (Lipp & Anklam, 1998) and the substitutes (Calliauw et al., 2005; Young, 1983). Compound chocolates, like the ones made with lauric fats, have manufacturing advantages compared with cocoa butter, in that they do not require tempering (Timms, 1984), thus saving the manufacturing industry costly steps. Lauric fats are known to crystallize directly into the β′ crystal polymorph and to present a melting behaviour similar to that of cocoa butter (Garti & Widlak, 2012).

Stortz and Marangoni (2011) reviewed the many attempts that have been made to improve the thermal stability of chocolate by using different strategies. One promising approach among the many suggested, is the use of a secondary crystalline network of high melting point emulsifier (melting point between 50 °C and 90 °C) (Murdan, Gregoriadis, & Florence, 1999; Nalur & Napolitano, 2002). The idea behind this strategy is that this heat-resistant secondary network will prevent structural collapse of a lower-melting point fat. This is achieved by keeping the molten fat trapped within the network much in the same manner that a fat crystal network entraps the non-crystalline components. In this paper, we study the use of sorbitan monostearate (SMS), also known as Span 60, with a ~56 °C melting point, as the fat crystal structuring agent for the development of heat resistance in a hydrogenated PKO stearin mixture. SMS is a molecule made by esterifying sorbitol with a fatty acid. Sorbitan esters such as SMS and sorbitan tristearate (STS), along with their polysorbate derivates (Tweens), are some of the most commonly-used emulsifiers in foods (Lonchampt & Hartel, 2004). Murdan et al. (1999) showed that SMS was capable of gelling a number of organic solvents as well as vegetable oils and fatty acid esters at concentrations as low as 1% wt/wt. Pernetti and co-workers (Pernetti, van

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Malssen, Kalnin, & Floter, 2007; Pernetti, van Malssen, Floter, & Bot, 2007) investigated the structuring potential of lecithin and STS mixtures in sunflower oil. Those authors showed that STS by itself is unable to gel the oils. However, the addition of lecithin remarkably enhanced the oil structuring ability of STS. Lecithin is a traditional emulsifier used in chocolates that decreases the viscosity and yields stress of molten chocolate, allowing it to be moulded and formed (Garti & Aserin, 2012). It is also known that lecithin aids in the prevention of fat bloom (Lonchampt & Hartel, 2004). Polyglycerol polyricinoleate (PGPR) is a hydrophobic emulsifier, also commonly used in the chocolate industry because it makes chocolate flow easily (Garti & Aserin, 2012). Garti and Yano (2001) reported that even though PGPR and lecithin are known to bind primarily to sugar particles, they could also be incorporated into the fat phase. PGPR is known to exhibit synergy with lecithin in chocolates by improving the texture and by increasing the crystallization rate (Garti & Aserin, 2012; Schantz, Linke, & Rohm, 2003). The chocolate industry tends to use lecithin and PGPR together.

In this paper, we explore the effects of adding different amounts of SMS to a fat blend composed of hydrogenated PKO stearin, lecithin, PGPR and CB. We had studied the blends using small-angle oscillatory rheology to depict the heat resistance. We characterise the blends by performing measurements using powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), low resolution nuclear (proton) magnetic resonance (pNMR), turbidimetry, polarized light microscopy (PLM) and cryo-transmission electron microscopy (TEM).

2. Material and methods

2.1. Materials

The confectionery-fat-blend, referred to as CFB was prepared using 1.9% CB, 0.8% PGPR, 1.7% lecithin and 95.6% HPKO stearin. The CFB was mixed with different amounts of SMS to prepared mixtures with an SMS concentration of 0%, 5%, 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% (w/w). The two components were mixed while molten at 70 °C, and kept for 15 min at this temperature, to erase crystal memory, before cooling down.

2.2. Fatty acid analysis by gas chromatography

Fatty acid methyl ester (FAME) analysis was performed by Dr. Lyn Hillyer of the Department of Human Health and Nutritional Sciences at the University of Guelph on the hydrogenated PKO stearin. The gas chromatography protocol was adapted from several references (Christie, 1982, 1987; Touchstone, Chen, & Beaver, 1979). 10 μL of material was added to 4 mL of chloroform: methanol solution (2:1, v/v; Fisher Scientific). Samples were vortexed for 1 min, flushed with nitrogen gas (Boc gases, Guelph, ON) and incubated at 4 °C overnight. 24 h later, the samples were centrifuged at 1000 rpm for 10 min at 21 °C to separate phases. The lower chloroform layer was extracted and transferred to a fresh test tube and dried down with a gentle stream of nitrogen gas. The lipid was saponified in 0.5 M potassium hydroxide in methanol and heated for 1 h at 100 °C. Samples were then methylated by adding 2 mL hexane and 2 mL 14% BF_3-MeOH and heating for 1 h at 100 °C. After cooling, 2 mL of double distilled water was added and samples were centrifuged at 1000 rpm for 10 min. The top layer was removed and analysed by GC. FAME were quantified on an Agilent 7890A gas chromatograph equipped with an FID and separated on an Agilent J &W fused-silica capillary column (DB-FFAP; 15 m, 0.1 μm film thickness, 0.1 mm inside diameter; Agilent, Pal Alto, CA, USA). Samples were injected in split 1:200 mode. The injector and detector ports were set at 250 °C. FAME were eluted using a temperature programme set initially at 150 °C and held for 0.25 min, increased at 35 °C/min and held at 170 °C for 3 min, increased at 9 °C/min, and held at 225 °C for 0.5 min, increased at 80 °C/min and finally, held at 245 °C for 2.2 min to complete the run. Total run time was 12.88 min. The carrier gas was hydrogen, set to a 30 mL/min constant flow rate. The experiment was repeated three times. An average of two repetitions is presented.

2.3. Small angle oscillatory shear rheology

Rheology was used to establish the thermal stability of the samples by performing oscillatory shear experiments at temperatures of 20 °C, 30 °C, and 40 °C on specific concentrations of SMS (0, 15, 25, 50 and 100%). Measurements were performed using an AR-2000 controlled-stress rheometer (TA Instruments, Newcastle, Delaware, USA) equipped with a 20 mm diameter steel plate geometry. A Peltier element was used as the bottom plate. 60 grid sandpaper was attached to the geometry and to the Peltier plate to minimize slippage. Cylindrical, flat samples of 10 mm in radius and 3.2 mm in height were prepared for the different mixtures using three-part moulds (Dibildox-Alvarado, Rodrigues, Gioielli, Toro-Vazquez, & Marangoni, 2004; Peyronel & Campos, 2012). Samples were melted at 80 °C for 15 min in order to erase any crystal history before making the discs. Two cooling rates were used to make the samples. The two cases were obtained by (1) letting the molten sample crystallized at either room temperature (3 to 6 °C/min) and (2) by using a temperature controlled aluminium three-part mould (10 to 20 °C/min). The aluminium mould was kept at 5 °C using circulating water from a water-bath. In both cases the base of the mould was cover with parafilm before the intermediate plate was screwed in place in order to help dissipate heat. The de-moulded sample discs were stored at 10 °C until the rheological analysis was performed. The bottom Peltier was set to the desired temperature (20 °C, 30 °C or 40 °C) and the samples were allowed to equilibrate for 10 min before the measurement was carried out.

The storage moduli (G′) was determined from oscillatory stress sweeps (10 Pa to 2000 Pa) at a constant frequency of 1 Hz and a normal force of 4 N. The 1 Hz frequency was chosen after finding the LVR region for different frequencies when the strain was not allow to exceed 0.05%. The values reported are an average of five measurements.

2.4. Characterization using powder X-ray diffraction

The X-ray data for structural analysis were collected using a Multiflex 2 kW theta/theta (Rigaku, Japan) X-Ray diffractometer in Bragg–Brentano geometry using Cu $K\alpha_{1,2}$ radiation, operating at 40 kV and 44 mA, with primary and secondary Soller slits. The area of the sample in the beam was such that a divergence slit and related scattered slit of 1/2° were appropriate to cover the 2θ angle between 1 and 35°. A 0.3 mm receiving slit into the monocromator and a 0.8 mm one to the detector were used. The vertical Debye–Scherrer geometry, selected by a RiNT fixed curved-graphite monochromatic with a curvature radius of 225 mm was detected by a scintillation detector. The sample was static in a horizontal position as the goniometer rotates using two focusing circles: one for the X-ray source and one for the scintillator detector. The diffractometer was computer-controlled using the MultiFlex software (Rigaku, version 1.1.2). Diffraction patterns were analysed using MDI Jade Plus V9.01 (Materials Data, Incorporated: MDI). The 2-theta-calibration feature was used with Silver Behenate as the standard.

After CFB and SMS were mixed at the different desired percentages, the mixtures were crystallized at room temperature (~22 °C) and kept at this temperature for 1 h before storing them at 5 °C. X-ray scans were collected using a home-made cold stage that utilizes a Peltier plate in intimate contact with a copper support that perfectly fits the Rigaku glass sample holder (part number #901887) with an indent of 1.5 cm × 1.5 cm × 2 mm in depth. The sample surface exposed to the X-ray is flat and "flashed" with the sample holder glass height.

Three different experiments were performed:

I) For the 0%, 10%, 15%, 20%, 25%, 35%, 50%, 65, 85%, and 100% (w/w) of SMS in CFB, a full scan was carried out on days 1 (24 h after preparation), 28 and 77, which included both region of interest