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Effects of high intensity ultrasound and emulsifiers on crystallization behavior of coconut oil and palm olein

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ABSTRACT

The objective of this research is to evaluate the crystallization behavior of coconut oil (CO) and palm olein (PO) as affected by the addition of two monoacylglycerols (MAG) emulsifiers and by the use of high intensity ultrasound (HIU). MAG with high content of palmitic, oleic, and linoleic acid (EM1) and MAG with high content of stearic acid and no unsaturated fatty acids (EM2) were used. Results show that the addition of emulsifiers did not affect crystallization kinetics of CO and similar solid fat contents (1.32 ± 0.94) (SFC) and melting enthalpies (5.90 ± 4.56) were obtained. The addition of EM1, however, significantly delayed the crystallization of PO as evidenced by a significantly lower SFC and melting enthalpy. SFC for PO was 8.56 ± 0.913 while SFC for PO + EM1 was 3.63 ± 1.38. Sonication induced the crystallization of CO samples crystallized with and without EM1 and EM2 while only induced the crystallization of PO + EM1 as measured with SFC. The induction in crystallization by HIU was also evidenced by higher enthalpy with values up to a range of 8 J/g to 11 J/g. A decrease in elasticity from 3.17×10^6 to 2.52×10^5 was observed in CO crystallized with emulsifiers which could be reverted by the application of HIU. Contrarily, the addition of emulsifiers increased elasticity of PO from 3.35×10^2 to 4.83×10^4 and sonication did not affect these values significantly. Differences observed in elasticity values are attributed not only to the amount of solid material obtained but also to the type of microstructure of the crystalline network formed during crystallization.

1. Introduction

Emulsifiers, such as monoacylglycerols (MAG) have been used to change the crystallization properties of palm oil and dairy fat by food industry as shown by Basso et al. (2010) and Foubert, Dewettinck, Van De Walk, Dijkstra, and Quinn (2007). These studies showed that addition of MAG led to formation of greater number of seed crystals which are more stable to temperature fluctuations (Basso et al., 2010). Also, Verstringe, Danthine, Blecker, and Dewettinck (2004) reported that the addition of saturated MAG accelerates the crystallization of palm oil, enabling the use of palm olein in many industrial processes. The study of fat-emulsifier systems is of great interest since emulsifiers can be used as minor components in the production of edible fat products to provide desirable melting and crystallization properties (Marangoni & Wesdorp, 2013, Smith, Bhaggan, Talbot, & van Malssen, 2011). However, the role of emulsifiers as crystallization modifiers on natural and commercial fats is underexplored (Hasenhuettl, 2008). The main effects of these additives in the crystallization of fats occur during the stages of nucleation and growth of the crystalline material changing physical properties such as crystal size, solid fat content, and microstructure (Smith et al., 2011). Garti (1988) and other authors (Smith et al., 2011; Martini et al. Rincón-Cardona et al., 2015; Cerdeira et al., 2003, 2005, 2006; Martini et al., 2002, 2004; Puppo et al., 2002) have described that when emulsifiers have similar chemical composition to the fat, they can be incorporated in the crystalline lattice and delay crystal growth. If the chemical composition of the emulsifier is very different to that on the fat the emulsifier can induce crystallization. However, the issue of promoting or inhibiting crystallization, however, is still debatable.

High intensity ultrasound (HIU) has been used in the food industry as an efficient tool for large scale commercial applications, such as emulsification, homogenization, extraction, and viscosity alteration (Patist & Bates, 2008). In addition, previous research has shown that HIU can affect crystallization processes by affecting crystal nucleation, controlling the rate of crystal growth, promoting the formation of small and even-sized crystals, and preventing fouling of surfaces by the newly formed crystals (Kallies, Ulrich, & König, 1997; Luque de Castro & Priego-Capote, 2007; Virone, Kramer, van Rosmalen, Stoop, & Bakker, 2006). In particular, HIU has been used to change the crystallization behavior of several lipid systems. Studies have suggested that HIU affects primary or the secondary nucleation of lipids depending on different sonication parameters used such as processing time, duration, and acoustic pulse (Higaki, Ueno, Koyano & Sato, 2001; Ueno, Ristic, Higaki & Sato, 2003; Ueno, Sakata, Takeuchi & Sato, 2003; Patrick, Blindt &

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Janssen, 2014; Martini et al., 2005, Martini, Suzuki & Hartel, 2008; Suzuki, Lee, Padilla & Martini, 2010; Ye, Wagh & Martini, 2011; Chen, Zhang, Sun, Wang & Xu, 2013; Ye, Tan, Kim & Martini, 2014; Rincón-Cardona, Agudelo-Laverde, Herrera & Martini, 2015; Ye & Martini, 2015).

Previous studies have shown that HIU can be used in combination with a novel emulsifier to change the crystallization behavior of milk fat and broaden the range of physical properties achieved by this fat (Wagh, Walsh, & Martini, 2013). There is a need to explore the use of sonication with other emulsifier and fat systems to generate a wider range of physical properties in the fat and broaden their use in food products.

Previous research by our group showed that the addition of MAG in different proportions to coconut oil (CO) and palm olein (PO) not only affected the type of crystals formed but also the number of crystals formed which was due to either an induction or a delay in the crystallization. The type of emulsifier used and the chemical composition of the emulsifier mainly affected the crystallization behavior under static conditions of the final fat blend with the emulsifier produced. Based on our previous research the objective of this work was to study the effects of high intensity ultrasound (HIU) on the crystallization behavior of CO and PO with added MAG to change physical properties of these systems when crystallized with agitation.

2. Materials and methods

2.1. Materials

Palm olein (PO) was donated by Agropalma S/A (Pará, Brazil) and coconut oil (CO) was donated by Copra Alimentos Ltda. (Alagoas, Brazil). Emulsifiers were provided by Danisco Brasil Ltda (São Paulo, Brazil). PO and CO were stored at 0 °C prior to use. All other reagents and solvents were of analytical grade. Two emulsifiers were used in this study: EM1 — distilled monoglyceride (>90% MAGs) produced from edible vegetable oil; and EM2 — mono-and di-glyceride (>52% MAGs) produced from refined fully hydrogenated vegetable fats. Detailed chemical composition of coconut oil, palm olein, EM1 and EM2 are reported in Maruyama, Soares, D'Agostinho, Gioielli, and Silva (2014). Briefly, CO shows predominance of saturated fatty acids (83.3%), mainly lauric acid (42.6%), myristic acid (21.0%) and palmitic acid (12.2%). Unsaturated fatty acids not only are predominant in PO (57.1%), mainly oleic acid in 47.6%, but also have high amounts of palmitic acid (36.9%). EM1 consisted in approx. 60% of linoleic acid, 16% of oleic acid, and 23% of palmitic acid; while EM2 consisted of 89% of stearic acid and 10% of palmitic acid with <1% of unsaturated fatty acids.

2.2. Mixture preparation

Oils and emulsifiers were melted in the microwave (±70 °C) and mixed to obtain a 3% (wt/wt) of the two different commercial emulsifiers (MAG) in each oil. Therefore a total of 4 samples were analyzed: (a) coconut oil + 3% of EM1, (b) coconut oil + 3% of EM2, (c) palm olein + 3% of EM1, and (d) palm olein + 3% of EM2. CO and PO sample without the addition of emulsifier were used as control. Based on the previous study by Maruyama et al. (2014) a 3% concentration of emulsifier was used to obtain the greater effect in CO and PO.

2.3. Crystallization experiments

Samples were heated to 80 °C and kept at this temperature for 30 min to allow complete melting of the fat. The melted lipid samples were then placed in a thermostatized crystallization cell as described elsewhere (Martini et al., 2008) which was set at different crystallization temperatures (PO, PO + EM1 and PO + EM2: 19 °C; CO, CO + EM1 and CO + EM2: 21 °C). Different crystallization experiments were performed during this research to define the temperatures that were more appropriate for each sample and that would result in more relevant changes after HIU application. Samples were crystallized at a cooling rate of 5 °C/min with agitation using a magnetic stirrer (200 rpm) to increase the heat transfer between the sample and the external circulating water. After 15 min, sample reached the set temperature (T_c) and the agitation was stopped to avoid dissolution of bubbles generated during the sonication process. Crystallization time was recorded from the moment agitation was stopped (t = 0) and were kept at T_c for 90 min. For palm olein and the mixtures, HIU was applied to the sample when the first crystals were observed by the naked eye. In the case of coconut oil and mixtures sonication did not affect crystallization under these conditions (data not shown) and therefore HIU was applied 30 min after the first crystals were observed by the naked eye. Table 1 shows the time and conditions used in this experimental design. After 90 min at T_c physical properties were measured using the techniques described below. Samples crystallized without HIU application were used as control groups.

Table 1
Sonication conditions and nomenclature used to evaluate the effect of high intensity ultrasound (HIU) on the crystallization behavior and functional properties of samples.

	Stop agitation	Crystallization temperature (°C)	HIU application[a]
Palm olein (PO)	15 min	19 °C	5 min
PO + EM1			15 min
PO + EM2			0 min
Coconut oil (CO)	15 min	21 °C	30 min
CO + EM1			35 min
CO + EM2			45 min

[a] For palm olein and the mixtures, HIU was applied to the sample when the first crystals were observed by the naked eye. For coconut oil and mixtures, HIU was applied 30 min after the first crystals were observed by the naked eye.

2.4. HIU application

HIU was applied using a Misonix S-3000 sonicator (Misonix Inc., Farmingdale, N.Y., U.S.A.) operating at an acoustic frequency of 20 kHz for 10 s using 50 W of electrical power. A tip of 12.7 mm diameter and amplitude of vibration of 108 μm was used. A diagram of the experimental setup including the crystallization cell, thermocouple, agitation, and sonicator configuration can be found in Martini et al. (2008).

2.5. Polarized light microscopy measurements (PLM)

Crystal morphology was recorded during crystallization. A drop of lipid sample was taken from the crystallization cell at different times and placed between a slide and a cover-slide to evaluate crystals' microstructure during crystallization using a polarized light microscope (PLM, Olympus BX 41, Tokyo, Japan) with a digital camera attached.

2.6. Thermal behavior measurements

A differential scanning calorimeter (DSC, DSC Q20, TA Instrument, DE) was used to evaluate the melting behavior of the crystallized material. After the crystallization experiment, in which the sample was held at T_c for 90 min, 5–15 mg of material was placed in a hermetic aluminum pan for DSC use. The sample was heated to 60 °C at 5 °C/min to evaluate the melting behavior of crystallized material. Through this procedure, the onset (T_{on}) and peak temperature (T_p) and enthalpy (ΔH) of the melting process was determined.

2.7. Melting point

The melting point of samples was determined by AOCS official Method Cc 1-25 (2009).