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Hard fats as additives in palm oil and its relationships to crystallization process and polymorphism

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ABSTRACT

The application of palm oil in fat-based product can be inappropriate due to its low crystallization rates and formation of crystalline clusters in post-processing stages. The adjustment of these properties can be achieved with the addition of hard fats, which are low-cost industrial products resulting from the process of total catalytic hydrogenation of liquid oils. During the crystallization of palm oil, these components can act as preferential nuclei in a crystalline ordering process, and may induce or stabilize specific polymorphic habits. The present work evaluated the addition of hard fats from palm kernel (PKO), palm (PO), soybean (SO), cottonseed (CO) and crambe oils (CR), at concentrations of 1 g, 3 g, and 5 g/100 g of oil blend, on the crystallization behavior of palm oil. The study involves the crystallization kinetics, thermal behavior and polymorphism. The addition of hard fats provided a significant decrease of the induction time for nucleation in all blends, except with PKO. All blends showed a preference for crystallization in the polymorphic habit β', but blends with SO and CR, however, formed a miscellany of $\beta' + \beta$ crystals. Adding hard fats to palm oil increase its compatibility for uses in formulations of cocoa butter alternatives and fat-based products.

1. Introduction

Processed products such as margarines and shortenings, rich in palm oil may present slow crystallization rates and critical post-hardening effects due to its glyceride composition, especially high content of partial glycerides (Sue & Pantzaris, 2009). Monoacylglycerols are present at concentrations below 1 g/100 g, but diacylglycerols (DAGs) are found at levels of 5–8 g/100 g and may influence the crystallization history, delaying the crystallization rate of industrial palm oil (Bergel, 2001; Oliveira, Grimaldi, & Gonçalves, 2014; Smith, 2001). Furthermore, the triacylglycerol (TAG) profile of palm oil is very heterogeneous, with different possible combinations of saturated and unsaturated fatty acids with distinct carboxylic chain length, favoring the development of complex isothermal crystallization profiles with polymorphic diversifications. Therefore, palm oil undergoes different polymorphic events during crystallization and the transition from the α Form Crystal to the β' Crystal in palm oil is extremely slow compared to most other natural fats (Fredrick, Foubert, Sype, & Dewettinck, 2008). The polymorphism of lipid crystal and the crystallization processes affect the hardness, texture, rheology, and spreadability of lipid-based solid products (Sato, García, Calvet, Diarte, & Ueno, 2013).

External factors, as thermal variation, shear, and additives, applicable in crystallization processes also influence the functionality of vegetable oils and the organization of the TAGs. A small disturbance in these properties will change the kinetics of polymorphic transformations and hence can affect the

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List of abbreviations used: PKO, fully hydrogenated palm kernel oil; PO, fully hydrogenated palm oil; CO, fully hydrogenated cottonseed oil; SO, fully hydrogenated soybean oil; CR, fully hydrogenated crambe oil; TAG, triacylglycerol; SFC, solid fat content; DSC, differential scanning calorimetry; C12:0, La, lauric acid; C14:0, M, myristic acid; C16:0, P, palmitic acid; C18:0, S, stearic acid; C20:0, A, arachidic acid; C22:0, Be, behenic acid.

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crystallization and melting behavior of oils and fats. As an alternative to improve and/or modify these attributes, it is possible to use crystallization promoters, such as hard fats, additives obtained by total catalytic hydrogenation of liquid oils. Hard fats present homogeneous saturated TAG composition, high melting point (>40 °C) and can act as modifiers of the crystallization process. Furthermore, they can act as preferential nuclei in the crystal lattice ordering and induce specific polymorphic habits. Sato et al. (2013) reported that the relative rates and the extent of crystallization of α, β′ and β polymorphs are influenced by the rate of nucleation, which increases with the increase of supercooling and is governed by the activation free energy for nucleation, temperature, mass and heat transfer rates, and attachment/detachment rates of lipid molecules between cluster and liquid. Arishima and McBrayer (2002) added crystallization accelerators or seeding agents to compounds products formulated with palm kernel stearin and observed an acceleration in the crystallization of chocolates, stability to fat bloom formation with easy demolding of the compound. Verstringe, Dewettinck, Ueno, and Sato (2014) showed that morphology of the palm oil crystals were oriented by crystallized monopalmitin additives and the palmitic acid present in both lipids phases played decisive roles in a template effect. Hard fats from palm oil, cottonseed oil, soybean oil and crambe oil were used with success to modulate the crystallization kinetics and thermal behavior of cocoa butter (Ribeiro, Basso, Santos, et al., 2013).

This study uses DSC outputs, X-ray diffraction pattern and isothermal crystallization data in an attempt to understand the basic polymorphic transitions involved in the crystallization process of palm oil added with hard fat.

2. Materials and methods

2.1. Materials

Deodorized palm oil was supplied by Agropalma S/A (Brazil). Five different hard fats, provided by Cargill Agrícola S/A (Itumbiara, Brazil), were evaluated in this study: hard fat of palm kernel oil (PKO) (45.5 g/100 g C12:0, 15.8 g/100 g, C14:0, 9.2 g/100 g C16:0, 23.0 g/100 g C18:0); hard fat of palm oil (PO) (36.2 g/100 g C16:0, 61.2 g/100 g C18:0), hard fat of cottonseed oil (CO) (23.2 g/100 g C16:0, 73.9 g/100 g C18:0), hard fat of soybean oil (SO) (10.5 g/100 g C16:0, 87.3 g/100 g C18:0), and hard fat of crambe oil (CR) (2.8 g/100 g C16:0, 31.6 g/100 g C18:0, 56.3 g/100 g C22:0) where C12:0, C14:0, C16:0, C18:0 and C22:0 correspond to lauric, myristic, palmitic, stearic and behenic acids, respectively. The TAG composition of the hard fats are: PKO (21.5 g/100 g LaLaLa, 15.4 g/100 g LaLaM, 9.3 g/100 g LaLaP, 8.67 g/100 g LaMP, 6.2 g/100 g LaSM, 6.2 g/100 g LaSP, 6.2 g/100 g LaSS), PO (35.0 g/100 g PPS/PSP, 38.8 g/100 g PSS, 19.2 g/100 g SSS), CO (19.8 g/100 g PPS/PSP, 45.6 g/100 g PSS, 32.4 g/100 g SSS), SO (29.8 g/100 g PSS, 63.8 g/100 g SSS), and CR (28.6 g/100 g SBeBe, 18.1 g/100 g BeBeBe, 17.2 g/100 g SSBe, 9.9 g/100 g PSBe, 9.5 g/100 g SABe), where La, M, P, S, A and Be correspond to lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid and behenic acid, respectively (Ribeiro, Basso, & Kieckbusch, 2013).

2.2. Preparation of the blends

Initially, all raw materials were melted at 100 °C. Then, three different proportions of each hard fat were added to palm oil: 1 g/100 g, 3 g/100 g and 5 g/100 g of blend, totalizing fifteen different blends. After the addition, all blends were stirred for 10 min to ensure complete homogenization and then stored in a refrigerator at 10 °C until use.

2.3. Crystallization isotherm

The samples were melted at 100 °C for 15 min and kept in a high precision dry bath (TCON 2000, Duratech, Carmel, USA) at 70 °C for complete destruction of their crystalline history. The increase in solid fat content due to static crystallization was monitored by a Nuclear Magnetic Resonance spectrometer (RMN) Bruker pc120 Minispec (Silberstreifen, Rheinstetten, Germany), with the reading compartment stabilized at 25 °C. The data acquisition was automatic, with measurements taken every minute, during 90 min for the blends and 120 min for palm oil. The crystallization kinetics was parameterized by the induction time, τ_{SFC} – time relative to the onset of the formation of crystals – and by the maximum solid fat content, SFC_{max}. The constants of the Avrami model (Equation (1)), fitted to the data, were used to classify the nature of the crystal growth process and to quantify the crystallization kinetics:

$$\frac{SFC}{SFC_{máx.}} = 1 - e^{-B*t^{n}} \tag{1}$$

where, SFC corresponds to the solid fat content at a specific time, t, usually in minutes, SFC_{max} corresponds to the maximum value of SFC found during crystallization, n is the Avrami exponent (dimensionless) and indicates the mechanism of crystal growth, "B" is the Avrami constant (min^{-n}) and represents the crystallization rate constant (Marangoni, 2005). The determinations were performed in duplicate.

2.4. Thermal behavior by differential scanning calorimetry (DSC)

Thermal analyzes of the samples were performed by differential scanning calorimetry (DSC) according to American Oil Chemists' Society [AOCS] (2009) Cj 1-94 method. A TA Thermal Analyzer, model Q2000 V4.7A, coupled to a RCS90 Refrigerated Cooling System (TA Instruments, Waters LLC, New Castle, USA) was used. About 8–10 mg of the melted samples were weighed into aluminum pans, sealed and then thermally equilibrated. Another aluminum pan, empty and hermetically sealed, was used as a reference. The thermal analysis conditions were 5 min at a constant temperature of 80 °C followed by cooling down to −40 °C, at a rate of 10 °C/min and maintenance at this temperature for 30 min. The TA Universal Analysis V4.7A software was used to obtain the curves and the following parameters: onset of the temperature of crystallization (T_{oc}); peak temperature of crystallization (T_c); enthalpy of crystallization (ΔH_c); and offset temperature of crystallization (T_{of}). All the DSC analyses were carried out in triplicate.

2.5. X-ray diffraction

The polymorphic form of the fat crystals was determined by X-ray diffraction, according to the AOCS Cj 2-95 method (AOCS, 2009). Analyses were performed on a Philips PW 1710 diffractometer (PANalytical, Almelo, the Netherlands), using Bragg-Brentano geometry (θ:2θ) with radiation Cu kα ($\lambda = 1.54178$ Å, voltage 40 kV and current of 30 mA). The measurements were obtained with steps of 0.02° in 2θ and acquisition time of 2 s, with scans from 5 to 40° (range 2θ). Before determinations, the samples were melted in a microwave oven at about 100 °C and stabilized at 25 °C for 24 h in an incubator. The identification of the polymorphic forms was determined from the characteristic short spacings of each crystal. The relative amounts of the different types of crystals were estimated by the relative intensity of the short spacings (Schenck & Peschar, 2004).