

The cooling rate effect on the microstructure and rheological properties of blends of cocoa butter with vegetable oils

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Received 16 March 2006; accepted 30 July 2006

Abstract

The elasticity (G') and yield stress (σ^*) of blends of cocoa butter (CB) in vegetable oils (i.e., 30% CB/canola and 30% CB/soybean oil) crystallized at temperatures (T_{Cr}) between 9.5 °C and 13.5 °C and two cooling rates (1 °C/min and 5 °C/min) were determined, evaluating their relationship with parameters associated with the formation and structural organization of the crystal network [i.e., solid fat content (SFC), Avrami index, crystallization rate, fractal dimension (D)]. The results showed that T_{Cr} and cooling rate had a different effect for each blend on the three-dimensional organization of the crystal network, and on the proportion and size of β' and β crystals. Thus, under low supercooling conditions at both cooling rates, the crystallized CB/canola oil blend was formed by a mixture of small β' and large β crystals that provided high G' and σ^* at low SFC (i.e., 20.5–20.9%) and D (i.e., 1.66–1.72) values. The CB/soybean oil blend achieved similar G' and σ^* independent of cooling rate only at high supercooling. In this case, the crystal network was formed mainly by small β' crystals with SFC (i.e., 25.4–26.3%) and D (i.e., 2.86–2.79) values higher ($P < 0.05$) than in the CB/canola oil blend at low supercooling. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Cooling rate; Cocoa Butter; Rheometry; Fractals; Microstructure

1. Introduction

Vegetable oils and vegetable oil blends are multicomponent systems containing different families of triacylglycerides (TAGS). In these systems the molecular relationships occurring among TAGS families determine the thermodynamic conditions (i.e., supercooling and supersaturation) that drive the formation of a solid in a liquid phase and the phase behavior of the solid phase. The resulting three-dimensional TAGS crystal network and the phase behavior of TAGS are major factors determining the physical and functional properties (i.e., rheology, liquid phase entrapment, mouthfeel, appearance, and spreadability) in prod-

ucts such as margarine, butter, confectionary coatings, and fillings (Campos, Narine, & Marangoni, 2002; Pérez-Martínez et al., 2005; Takeuchi, Ueno, Flöeter, & Sato, 2002). Additionally, crystallization conditions such as cooling rate, and thermal history (i.e., crystallization temperature and tempering process) have significant effects on the kinetics and physical properties of the crystallized systems.

Cocoa butter (CB) is also a mixture of different TAGS. Nevertheless, CB observes a great extent of homogeneity in both TAGS conformation and composition with more than 75% of TAGS with oleic acid in the sn-2 position and saturated fatty acids in the sn-1 and sn-3 positions. Consequently, its polymorphism is complex observing at least six polymorphic forms (van Malsen, van Langevelde, Peschar, & Schenk, 1999; Wille & Lutton, 1966). CB is used as the main lipid phase in chocolate, and

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in confectionary products blended with hydrogenated soybean oil, palm oil fractions, palm kernel, and coconut oil. Crystallization of CB provides to these products unique characteristics of texture and flavor release. Nevertheless, these vegetable oils have *trans* fatty acids and/or high proportion of saturated fatty acids, both with recognized negative health implications because their impact on the ratio of high density to low density lipoproteins. Limited research has been done to study the crystallization process of CB in blends with native unsaturated vegetable oils.

Several authors have investigated the effect of cooling rate on crystallization of multicomponent TAGS systems (Campos et al., 2002; deMan, 1964; Herrera & Hartel, 2000a, 2000b, 2000c). In the present investigation we studied the cooling rate effect on the rheology and microstructure in binary model systems, where different extent of molecular compatibility existed between the major TAGS of the crystallizing phase (i.e., CB) and major TAGS of the solvent phase (i.e., canola or soybean oil). Major TAGS in soybean oil have a higher degree of unsaturation (i.e., LLL, LLO and LLP) than the major TAGS present in canola oil (i.e., OOO and LOO). This ought to result in different extent of molecular compatibility between TAGS of vegetable oils and the symmetrical saturated–unsaturated–saturated (SUS) TAGS and saturated TAGS from CB. Blending between vegetable oils provides flexibility to achieve particular functional properties in crystallized systems. However, the complex interactions that occur among TAGS as a function of the crystallization conditions must be first understood to achieve particular physical and functional properties through blending. Within this framework our objective was to study the relationships between the rheological properties of CB crystallized in blends with canola or soybean oil at two cooling rates (1 °C/min and 5 °C/min) with parameters associated with the development and structural organization of the crystal network such as the Avrami index, the crystallization rate constant, the fractal dimension, and the solid fat content.

2. Materials and methods

2.1. Preparation of cocoa butter/vegetable oil blends

The 30% (wt/vol) blend of CB in canola or soybean oil was prepared with CB previously vacuum filtered through Whatman paper No. 5. The CB was melted (80 °C for 20 min) and the corresponding proportion weighted in a 100 mL volumetric flask. The volume was completed with the vegetable oil (25 °C) and the blend stored (4 °C) under nitrogen in the dark. For some dynamic calorimetric analysis blends of CB in the vegetable oil were prepared at ratios between 0% and 100% CB (% wt/vol). The TAGS profiles for CB and the vegetable oils were determined by HPLC as reported by Pérez-Martínez et al. (2005).

2.2. Calorimetry analysis

Dynamic calorimetric analyses were done in a Perkin Elmer DSC-7 (Norwalk, CT, USA) equipment calibrated as previously indicated (Toro-Vazquez, Dibildox-Alvarado, Charó-Alonso, Herrera-Coronado, & Gómez-Aldapa, 2002). Briefly, 0.12 mg samples of the blends (i.e., 0–100% CB/vegetable oil) were sealed in aluminum pans held at 80 °C for 20 min and then cooled down (10 °C/min) from 80 °C to –50 °C. After 1 min at –50 °C the melting thermogram was obtained at a heating rate of 5.0 °C/min.

For differential scanning calorimetry (DSC) analysis under isothermal conditions the blends of 30% CB in the vegetable oils were first held for 20 min at 80 °C. The sample pans were then cooled at 1 °C/min or 5 °C/min until attaining a particular crystallization temperature (T_{Cr}). After completion of the crystallization exotherm (i.e., heat capacity returned to the baseline) the system was left for additional 30 min and then the melting thermogram was determined by heating (5 °C/min). Two independent determinations were done at each T_{Cr} and cooling rate. The corresponding T_{Cr} 's used in the isothermal crystallization studies were 9.5 °C, 10.5 °C, 11.5 °C, and 13.0 °C for the 30% CB/canola oil and 10 °C, 11 °C, 12 °C, and 13.5 °C for the 30% CB/soybean oil. The T_{Cr} 's investigated were between the onset of crystallization in the corresponding dynamic crystallization thermogram and 3.5 °C above this temperature. The use of isothermal T_{Cr} 's above this temperature interval produced a significant increase in the induction time of crystallization and broadened the exotherm making difficult to determine the beginning and end of crystallization.

2.3. Solid fat content and determination of the Avrami index and crystallization rate constant

Samples (4 mL) of the blends were heated (80 °C for 20 min) in NMR tubes (10 mm × 20 cm) and then cooled in a programmable temperature bath (Julabo Labortechnik GMBH, Selbach, Germany) set to provide linear cooling rates of 1 °C/min (± 0.1 °C/min) (Model F25) or 5 °C/min (Model F25 connected to a Presto system). The SFC (%) of the CB blends was determined as a function of time at a particular T_{Cr} and cooling rate by pulsed NMR with a Minispec Bruker model mq20 equipped with a jacketed measuring probe connected to a circulating water bath set to the corresponding T_{Cr} . The SFC readings as a function of isothermal crystallization time (SFC_t) were recorded by the equipment software until 30 min after achieving a sustained plateau in the measurements. These values were considered the maximum or equilibrium SFC (SFC_{eq}). Using as crystallization model the Avrami equation (1), the SFC values were used to calculate the fractional crystallization, F , as a function of isothermal crystallization time, t , as $F = \text{SFC}_t / \text{SFC}_{eq}$. The Avrami index (n) and the crystallization rate constant (z) were

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