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Modelling sugar, processing, and storage effects on palm oil crystallization and rheology

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ABSTRACT

While the physicochemical properties of bulk oils directly impact their quality and sensory attributes, this relationship is confounded by the presence of added non-fat ingredients such as sugar. Furthermore, the way in which a bulk oil responds to processing may not carry over when mixed with dispersed particles. The purpose of this study was to explore the effects of confectioner's sugar and cooling temperature on the solid fat content, polymorphism, morphology, viscoelastic properties, and textural properties of palm oil and mid-fraction over four weeks. Samples were cooled from 60 °C to endpoint temperatures of 15 °C, 20 °C, or 28 °C. Palm oil-specific models were generated along with confidence intervals to predict responses based on composition and cooling endpoint. The higher saturated and partial acylglycerol content of palm oil compared to the mid-fraction enhanced the extent of crystallization, storage modulus, and firmness. Cooling endpoint temperature also impacted solid fat content, viscoelasticity, and showed significant interactions with both palm oil type and confectioner's sugar. This endpoint parameter did not affect firmness, which is closely associated with quality at consumption. The models developed from this study offer insight and behavioural prediction for the confectionery industry where such materials are handled.

1. Introduction

Fat-based confections are composed of non-fat ingredients such as confectioner's sugar, milk solids, or cocoa powder dispersed throughout a continuous fat phase (Svanberg, Ahrné, Lorén, & Windhab, 2013). The physicochemical properties of these confections determine processing efficiency during unit operations such as extrusion and enrobing, product quality, and organoleptic attributes (Liu, Meng, Zhang, Shan, & Wang, 2010).

Palm oil (PO) and its fractions are regularly used in confectionery applications given their natural semi-solid consistency, low cost, and absence of *trans* fats (Aftab, Sherazi, Rubina, Razia, Ambrat, & Arfa, 2013). Achieving a zero *trans* fats label is particularly important to industry because of their association with cardiovascular disease and inflammation (Ascherio, Katan, Zock, Stampfer, & Willett, 1999). PO tends to crystallize slowly as a result of its high partial acylglycerol content although this mechanism is not fully understood (Siew & Ng, 1999).

The structure-functionality relationship of fats becomes more complex in the presence of non-fat ingredients where additional interactions and alterations in crystallization pathway occur. In confections, rheology is a product of the solid fat content (SFC), crystal morphology, and network development of the fat phase, the composition of the non-fat dispersion, and the resulting particle interactions between both phases (Tang & Marangoni, 2007). Manipulating these attributes permits significant changes in product properties. For example, with a narrower size distribution and larger volume fraction (φ) of sugar, there results a substantial increase in viscosity (De Graef, Depypere, Minnaert, & Dewettinck, 2011) and hardness of the confectionery sample (Afoakwa, Paterson, Fowler, & Ryan, 2008).

As the main ingredient in many fat-based confections, sugar imparts both sweetness and mouthfeel while occupying a φ up to 0.70 (Jamieson, 2008). The energy barrier for fat crystal nucleation is reduced in its presence as it behaves as a catalytic impurity (Metin & Hartel, 2005). The active sites on the surface of sugar

Abbreviations: PO, palm oil; PMF, palm mid-fraction; TAG, triacylglycerol; DAG, diacylglycerol; φ, volume fraction of non-fat ingredients; T_e, cooling endpoint temperature; t, storage time; SFC, solid fat content; $f_{\beta'}$, fraction of β' polymorph; G′, storage modulus; G″, loss modulus; F, firmness.

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crystals require fewer liquid-state acylglycerol molecules to assemble and form a nucleus of critical size (Hartel, 2001).

Fat crystallization may be further influenced by processing factors, e.g., cooling rate, shear speed, etc. (Kellens, Gibon, Hendrix, & De Greyt, 2007). For example, shear facilitates mass transfer where its speed is positively correlated with crystallization rate and the formation of higher-order polymorphs (De Graef, Dewettinck, Verbeken, & Foubert, 2006). Cooling endpoint temperature (T_e) is another important processing factor. Whereas α crystals have shown to form readily in PO and later undergo polymorphic transition at T_e values below 20 °C, β′ crystals form exclusively from the melt above 20 °C (Foubert, Dewettinck, Janssen, & Vanrolleghem, 2006; Litwinenko, Rojas, Gerschenson, & Marangoni, 2002). It is well recognized that understanding how processing impacts fat crystallization is necessary to optimize product quality (Afoakwa, Paterson, Fowler, & Vieira, 2008).

The purpose of this study was to explore the effects of φ of confectioner's sugar and T_e on the crystallization of commercial PO and a palm mid-fraction (PMF). Samples were characterized over four weeks of storage, which is analogous to the period that many palm-based products undergo prior to grocer distribution. Predictive palm oil-specific regression models were successfully generated for the output data in response to φ, T_e, and storage time (t).

2. Materials and methods

2.1. Sample preparation

Commercial PO and PMF (IOI Loders Croklaan, Channahon, IL, USA) were used to assess fat crystallization in bulk oil (φ = 0.00) and oil-sugar blends (φ = 0.37). The method for their compositional analysis is described in West and Rousseau (2016). To achieve similar melting properties as PO (25.1 ± 0.1 °C melting point) at 20 °C according to AOCS Official Method Cd 16b-93 (Firestone, 1998), PMF was blended with canola oil (Bunge North America, St. Louis, MS, USA) at 65 g/100 g (24.4 ± 0.1 °C melting point). The oil-sugar blends were prepared by creaming the oil with sieved (No. 18 Fisherbrand test sieve, Fisher Scientific, Nepean, ON, Canada) cane 6-x confectioner's sugar (Domino Foods Inc., Yonkers, NY, USA) in a stand mixer (Hobart Canada Inc., Toronto, ON, Canada) before processing. It contained 3 g/100 g starch, 0.5 g/100 g moisture, and consisted of particles averaging 30 μm in diameter.

In a scraped-surface jacketed kettle (Tenon Engineering Ltd., Leatherhead, UK) mated to a waterbath (VWR International 1157P, Mississauga, ON, Canada), samples were heated to 60 °C for 30 min under a constant shear of 100 rpm and then cooled at 1 °C·min^{-1} to a T_e of either 15 °C, 20 °C, or 28 °C. For a T_e of either 15 °C or 28 °C, a thin layer of sample was transferred to a baking sheet and either heated or cooled in an incubator set to either 0 °C or 40 °C, respectively, to 20 °C. Samples were either taken at t = 0 weeks, defined as < 15 min upon reaching 20 °C, or stored at 20 °C for weekly analysis (t = 1–4 weeks). All samples were made in triplicate.

2.2. Determination of solid fat content

Fat crystallization was monitored indirectly by measuring SFC via pulsed nuclear magnetic resonance (NMR) spectroscopy (Bruker Minispec mq20, Milton, ON, Canada) at 20 °C using AOCS Official Method Cd 16–81 (West & Rousseau, 2016), Samples were injected into glass NMR tubes (ID = 1 cm) to a height of 4 cm and stored until analysis. Six sub-replicate measurements were made for each NMR tube.

2.3. Differential scanning calorimetry

The enthalpy of melting for endotherms corresponding to β′ (T_{peak} = 35.4 ± 1.5 °C) and β polymorphs (T_{peak} = 42.8 ± 0.8 °C) were measured using a differential scanning calorimeter (Q2000 and Universal Analysis 2000 software, TA Instruments, New Castle, DE, USA). Samples were placed in aluminum pans for all runs. Nitrogen gas was used to prevent water condensation. After equilibrating the sample at 20 °C for 5 min, the temperature was increased to 90 °C at 5 °C·min^{-1}. The fraction of β′ polymorph ($f_{\beta'}$) was measured by:

$$f_{\beta\prime} = \frac{\Delta H_{\beta\prime}}{\Delta H_{\beta\prime} + \Delta H_{\beta}} \quad (1)$$

where $\Delta H_{\beta'}$ and ΔH_{β} are the enthalpies for β′ and β polymorphs, respectively. ΔHs were corrected to account for exclusively oil mass in the oil-sugar blends. A partial endotherm corresponding to the α polymorph (T_{peak} = 24.0 ± 0.9 °C) was detected but was cropped by the starting temperature of the thermogram and was therefore not included in quantification.

2.4. Confocal laser scanning microscopy

Confocal laser scanning microscopy (CLSM) (LSM510, Zeiss Inc., Toronto, ON, Canada) with 63 × oil objective and 10 × oculars and fluorol yellow stain was used to identify fat crystal morphology in the samples. A temperature of 20 °C was maintained using a Peltier-controlled temperature stage (PE120 with T95-PE controller, Linkam Scientific Instruments, Epsom, UK). Imaging software ZEN 2.3 (Zeiss Inc., Toronto, ON, Canada) was used to assess crystal morphology and size.

2.5. Oscillatory rheology

Viscoelasticity was measured with a controlled strain rheometer (AntonPaar Physica MCR 301, St. Laurent, QC, Canada). Storage (G′) and loss (G″) moduli were measured to determine the effects of φ and T_e on the crystal growth and network formation of stored samples (Omar, Let, Seng, & Rashid, 2005). This was achieved by performing frequency sweep tests at 0.01% strain [21 points of angular frequency (ω) were collected between 4 and 63 rad s^{-1}]. All rheological tests were performed at 20 °C with a gap size of 1.0 mm.

2.6. Texture analysis

Firmness (F) was measured using a TA.XT*Plus* Texture Analyzer with Texture Expert 1.22 software (Stable Micro Systems, Ltd., Surrey, UK) by filling 60 ml cups with sample. The height of a 45° steel cone with a 30 kg load cell was calibrated to 40 mm and approached the sample surface at 2 mm s^{-1}. Upon contact, the cone penetrated the sample at 1 mm s^{-1} over a distance of 15 mm where the absolute maximum positive force was interpreted as F.

2.7. Statistical analysis

A five-way analysis of variance from a mixed model using replicate, oil type (PO and PMF), φ (0.00 and 0.37), T_e (15 °C, 20 °C,