

The Influence of Chemical Interesterification on the Physicochemical Properties of Complex Fat Systems.

3. Rheology and Fractality of the Crystal Network

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ABSTRACT: Chemically interesterified and noninteresterified lard–canola oil (LCO) and palm oil–soybean oil blends ranging from 100% hardstock to 50%:50% hardstock/vegetable oil (w/w) were evaluated for hardness index (HI) using cone penetrometry and viscoelastic properties, such as shear storage modulus G' , using controlled-stress rheometry. The HI and G' of palm oil decreased upon addition of soybean oil, and chemical interesterification did not affect the HI or G' of palm oil or palm oil–soybean oil blends. The HI and G' of lard decreased upon addition of canola oil, while chemical interesterification led to increases in both the HI and G' of lard and LCO blends. All these effects were nonsolid fat content-related, since solid fat content did not change substantially upon chemical interesterification. The microstructure of the fat crystal network in lard and palm oil was quantified rheologically using fractal analysis. Chemical interesterification did not affect the fractal dimension of the fat crystal networks in palm oil or lard (2.82 and 2.88, respectively). The rheological properties of the macroscopic systems were not affected by the spatial distribution of mass within their fat crystal networks. Moreover, our results suggest that the increases in G' observed in lard upon chemical interesterification are potentially due to changes in the properties of the particles which make up the network (crystal habit).

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The rheological characteristics of semisolid foods, including margarine and spreads, has been a topic of extensive study in recent years. However, advances in our understanding of the viscoelastic properties of plastic fats have been slow. Plastic fat rheological properties can be characterized using small or large deformation tests. Large deformation tests include cone penetrometry and uniaxial compression. Parameters such as the hardness index (HI) and yield stress can be derived from such measurements. Small deformation measurements are usually performed using dynamic oscillatory controlled stress or controlled strain rheometry. Parameters such as the shear

and/or compression storage and loss moduli can be derived from such measurements. Data from both types of rheological measurements can yield substantial information on the structure of the fat crystal network. Large deformation tests usually lead to irreversible structural breakdown of the fat crystal network, while small deformation tests do not lead to the destruction of structure (1).

Plastic fat functionality is affected by the polymorphic form of the crystallized triglycerides (2). However, it has been known for a long time that polymorphism is not the only factor affecting fat consistency (3). Many researchers have stated that the nature of the fat crystal network in plastic fats strongly influences the rheology of spreads (4–9). What exactly constitutes this fat crystal network still remains largely undefined. Interaction between fat crystals, and/or aggregates of fat crystals in a network, can range from tenuous van der Waals interactions to solid (sintered) bridges (10,11).

Until recently, the nature of flocculated network aggregates was best described by models aiming at geometric simplicity rather than at realism (12). Van den Tempel (13,14) was first to propose a model to describe fat crystal networks. He suggested that fat crystal networks consisted of linear chains of fat particles which were responsible for a linear dependence of the elastic constant with solid fat content (SFC). He also proposed that two types of bonds—primary (irreversible) and secondary (reversible)—were present within a fat crystal matrix.

Fractal geometric scaling relationships between volume fraction and elastic modulus have been used to characterize low SFC fat crystal networks (5,15), water-in-oil emulsions (12), protein gels (16,17), boehmite alumina aggregates (18), and high SFC butterfat–canola oil plastic fat systems (4). In this study, we have used small and large deformation rheological tests to characterize the structure of the fat crystal network in lard and palm oil using a fractal geometric approach.

EXPERIMENTAL PROCEDURES

Blend preparation. As described in Marangoni and Rousseau (19).

Chemical interesterification. As described in Marangoni and Rousseau (19).

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Cone penetrometry. Liquefied samples (30 min at 100°C) were placed in polypropylene containers (i.d. = 16 mm, height = 23 mm) and refrigerated for 24 h [palm oil–soybean oil blends (POSBO)] and 72 h [lard–canola oil blends (LCO)] at 5°C prior to analysis. Penetration depths in 0.1-mm increments were read following a 5 s contact time between the penetrating cone assembly and sample. Five replicates were performed for each sample and the averages and standard deviations reported.

A different cone was used for the analysis of each system as each fat had large differences in penetration depths. Cone characteristics are shown in Table 1. K_{palm} and K_{lard} are constants based on cone angle, established by Haighton (20). HI was calculated as:

$$\text{HI} = \frac{\text{mass of cone (g)}}{\text{depth of penetration (mm)}} \quad [1]$$

SFC. SFC was determined by pulsed nuclear magnetic resonance (NMR) using a Bruker PC/20 series NMR analyzer (Bruker, Milton, Ontario, Canada). Blends were melted above 60°C, poured into NMR tubes, and crystallized statically at 5°C for 24 h (POSBO system) or 72 h (LCO system) prior to measurement. Analyses were performed in triplicate.

Viscoelasticity. Dynamic oscillatory measurements were conducted using a Carri-Med CSL² 500, controlled stress rheometer (TA Instruments, New Castle, DE) using a 2 cm parallel plate geometry with a solvent trap. Sample slippage was minimized by attaching 50 grit sandpaper to both the upper flat fixture and Peltier base.

Liquefied samples were crystallized in a three-piece PVC mold assembly consisting of a top and bottom plate and a midplate (height = 3200 μm , diam. = 2 cm). The pieces of the mold were securely fastened with screws. Care was taken to avoid formation of air bubbles. Sample compression was minimized to prevent sample deformation, yet sufficient to achieve contact between the sample and constraining surfaces. The molds were incubated in a refrigerator for 24 h at 5°C. Triplicate analyses were performed for all samples.

The linear viscoelastic region (LVR) was determined at 1 Hz with a torque sweep of 0.64–150 Pa. The LVR range observed was approximately 5.0×10^{-5} to 1.0×10^{-3} rad, after which irreversible sample damage or slippage occurred. For sufficient instrument sensitivity, a minimal displacement of 1.5×10^{-4} radians was judged necessary.

A frequency sweep of 0.1 to 10 Hz at a displacement of 1.5×10^{-4} radians was performed at $5.0 \pm 0.1^\circ\text{C}$. To reduce heating from the surroundings, the fixture, solvent trap,

spacer, and all utensils used to handle the fat were cooled in ice water before use.

Dynamic oscillatory test parameters, G' and G'' at 1 Hz, were calculated using the software provided by the manufacturer. Average values of two replicate experiments and their standard deviations are reported.

Fractal analysis. As described in Marangoni and Rousseau (4) in the weak-link regime.

RESULTS AND DISCUSSION

SFC. The SFC of the POSBO and LCO blends were significantly affected by chemical interesterification (IE) and dilution with soybean and canola oil, respectively ($P < 0.0001$) (Fig. 1). Changes in SFC induced by chemical interesterification (IE) were relatively small (<4%), except for 100% palm oil. Upon IE, the SFC of palm oil decreased from 64.7 to 54.5%.

Cone penetrometry. The HI of a fat can be directly correlated to its yield stress. The HI of both POSBO and LCO blends gradually decreased as the proportion of canola oil in the mixture increased ($P < 0.0001$) (Fig. 2). The HI of the POSBO blends were largely unaffected by IE ($P > 0.05$), whereas for the LCO blends, the HI increased significantly ($P < 0.0001$) (Fig. 2). All HI are reported as a function of SFC; therefore, any changes in HI induced by IE are due to non-SFC related factors.

The crystal habit (polymorphism and morphology) of IE lard differed substantially from that of native lard (21). Differences in crystal habit and aggregation behavior could have led to an alteration in the structure of the fat crystal network in lard, resulting in altered rheological properties, such as HI. Examination of margarines by Stern and Cmolik (22) showed that rheological properties partially depended on the shape and amount of fat crystals. The observed changes in crystal habit of lard (21) could be responsible for the diverse effects observed in this study.

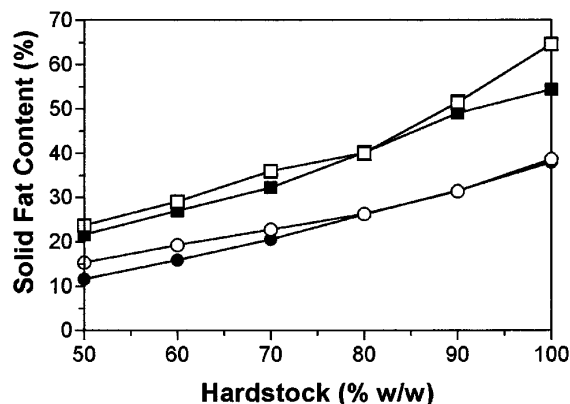


FIG. 1. Solid fat content (%) as a function of hardstock content for palm oil–soybean oil (POSBO) blends and lard–canola oil (LCO) blends after crystallization at 5°C for 24 and 72 h, respectively. POSBO noninteresterified (NIE) blends (□–□), POSBO interesterified (IE) blends (■–■), LCO NIE blends (○–○), LCO IE blends (●–●). Values represent means and standard deviations of three replicates, with one determination per replicate experiment.

TABLE 1
Penetrating Cone Assembly Characteristics Used for Hardness Index Determinations in Lard–Canola Oil Blends and Palm Oil–Soybean Oil Blends

Characteristic	Palm oil–soybean oil blends	Lard–canola oil blends
Cone weight (g)	45	57.7
Cone angle (°)	10	30
K factor	42970	9670

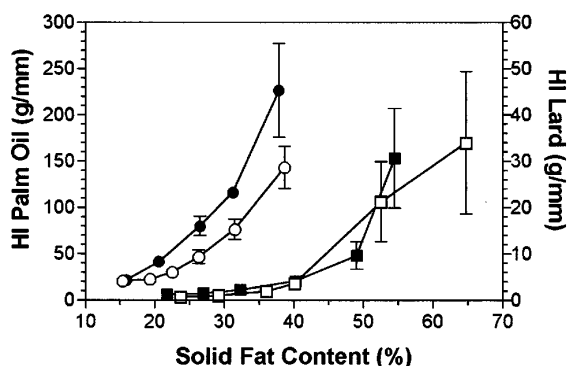


FIG. 2. Hardness index (HI) (g/mm) of POSBO and LCO blends as a function of solid fat content (%). POSBO NIE blends (□-□), POSBO IE blends (■-■), LCO NIE blends (○-○), LCO IE blends (●-●). Values represent means and standard deviations of five replicates, with one determination per replicate experiment. See Figure 1 for abbreviations.

Viscoelastic properties. Viscoelasticity studies provide valuable data which can be correlated to fat crystal network structure. Parameters derived from such studies include the storage (solid-like or elastic) (G') and loss (liquid-like or viscous) (G'') moduli (23). Small deformation measurements take place below a critical value of deformation (yield stress). In plastic fats, G' is about an order of magnitude higher than G'' (24,25).

The G' of all LCO blends increased as a result of IE at equivalent SFC ($P < 0.0001$), while the G' of the POSBO blends was not affected by IE ($P > 0.05$) (Fig. 3), mirroring the cone penetrometry results. As shown with butterfat (24), small and large deformation parameters are correlated.

Fractal analysis. The effects of crystal habit, such as polymorphic form and morphology, are considered key factors affecting rheological properties of plastic fats (7,26,27). As well, the actual structure of the three-dimensional network formed by fat crystals, and the interaction between solid and liquid triglycerides, are probably also key factors determining the rheological behavior of plastic fats. Several research groups (4,5,28) have previously proposed the application of fractal geometry principles to quantitatively describe the three-dimensional crystal network structure in fat systems. Using the same approach in this study, the effects of IE on the fractal dimension (D) of lard and palm oil fat crystal networks was studied. A power-law relationship between the elastic modulus and the SFC for noninteresterified (NIE) and IE blends (at 5°C) was established (Fig. 3):

$$G' = \gamma(SFC)^m \quad [2]$$

where m represents the slope used to derive the fractal dimension, while the constant γ can be related to properties of the particles which make up the network. The fractal dimension, D , can be derived for a strong-link or weak-link regime, where the latter generally applies to high-SFC systems, while the former generally applies to low-SFC systems (4). According to the relationship between the strain at the limit of lin-

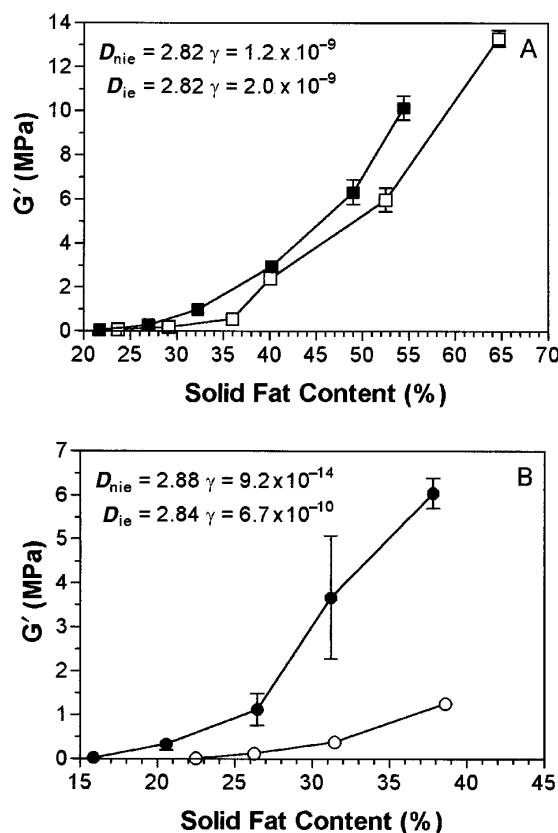


FIG. 3. Elastic shear modulus, G' (Pa), at a frequency 1 Hz, of (A) POSBO, and (B) LCO blends as a function of solid fat content (%) at 5°C. POSBO NIE blends (□-□), POSBO IE blends (■-■), LCO NIE blends (○-○), LCO IE blends (●-●). The fractal dimensions (D) are indicated in the figures, as well as the proportionality constant γ . Values represent means and standard deviations of two replicates, with two determinations per replicate experiment. See Figure 1 for abbreviations.

earity (γ_0) and the SFC, it is possible to define the regime— γ_0 increases for weak link regimes, while γ_0 decreases for strong-link regimes (18).

The fractal dimension of palm oil ($D = 2.82$) and lard ($D = 2.88$), derived for a weak-link regime, did not change upon IE ($P > 0.05$) (Fig. 3). However, the factor γ , which is related to properties of the particles making up the network (17), increased fourfold in the IE LCO system. The factor γ did not change significantly in the POSBO system (Fig. 3). These results suggest that the rheological properties of these fats were strongly influenced by the properties of the particles which made up the fat crystal network. IE may have caused changes in the properties of the particles, leading to macroscopic increases in the hardness of lard. Polarized light microscopy results showed a stark alteration in crystal size and shape following interesterification of lard. As well, large changes in the long spacings were observed (29). Examination of the PLM crystal morphology in the POSBO system showed little variation in the spherulitic structure. No drastic changes in polymorphic behavior were observed either (21).

These results suggest that the rheological properties of palm oil and lard are controlled by the properties of the parti-

cles which make up the network, which are influenced by crystal habit (morphology and polymorphism). In contrast, as shown in previous work (4), the rheological properties of butterfat are controlled by the spatial distribution of the fat particles in the network, and, to a lesser extent, by properties of the particles which make up the network (29).

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