Mechanical Basis of Shortening Functionality

by

Braulio A. Macias Rodriguez

A Thesis
Presented to
The University of Guelph

In partial fulfillment of requirements
for the degree of
Doctor of Philosophy
in
Food Science

Guelph, Ontario, Canada

©Braulio A. Macias Rodriguez, May, 2017
This thesis is an investigation on the functionality of bakery fat shortenings, with major emphasis on the mechanical function of those designed for lamination. Laminating or roll-in shortenings are fats used in the manufacture of layered doughs. Their main role is to separate sheets of dough to allow the formation of a multilayered structure responsible for pastry quality (“puff” and “flakiness”). To achieve this, laminating shortenings must “survive” processing deformations. To date, there is limited understanding on the factors underlying the functionality of these materials. There is also a major shortcoming with their utilization; their typically high content of trans and saturated (inconclusive evidence) fatty acids, implicated in cardiovascular health. These provide strong motivation to understand the structure-function relationships in laminating shortenings. Here, we differentiated physico-chemical and rheological properties of laminating shortenings, from those of shortenings designed for all-purpose, cake and icing applications. We found that laminating shortenings had contents of trisaturated and unsaturated TAGs higher than other shortenings, although their overall “hard” fat content were comparable. Physical properties, believed to be crucial to designate the laminating functionality such as polymorphism, solid fat content and melting, were comparable. Laminating shortenings hosted a range of rheological properties; some common to other fats and some unique to their mechanical functionality. While elastic material properties were comparable to those of other shortenings, their viscous properties were strikingly different. Stress responses to large amplitude oscillatory shear (LAOS) revealed that the laminating shortenings behave as viscoelastic ductile solids, in that they convert the vast majority of the released strain energy into viscous dissipative energy, associated with plastic flow. Structural investigations indicated that laminating shortenings featured smaller and smooth crystal nanoplatelets, three hierarchy levels, and crystal aggregates with layer-like arrangements. It is suggested that the hierarchy and microstructure spatial distribution play a pivotal role on
high-energy dissipation (rather than on energy storage) which confers superior load-bearing ability in laminating shortenings. This research provides a good ground for advancing our understanding on the macro functionality of laminating shortenings and guide the selection and design of healthier alternative lipid structuring materials based on the displayed rheological behavior.
DEDICATION

To the loving memory of my mother who fought till the end of her days and who continues to light up my everyday
ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my advisor Prof. Alejandro Marangoni for his enthusiasm, support and guidance, and providing me the freedom to choose my own research path without any objection. This latter aspect allowed me to think more independently and more critically as a scientist. I would like to thank the members of my PhD committee and PhD defense: Dr. Doug Goff, Dr. Shai Barbut, Dr. David Pink, Dr. Don Mercer, Dr. Peter Fischer, for their time devotion to this research work. I appreciate the very candid critical insights of Dr. David Pink, his scientific skepticism and his many interesting and thoughtful chats on structure-probing techniques, futurism, highly advanced civilizations (scha'thani), among other exciting topics. I would like to thank Dr. Fernanda Peyronel whose devotion to science and fine experience, have been equally important in my development as a scientist. I acknowledge the contribution of Dr. Ewoldt whose superb insights and visual supports helped me to enrich the quality of this work and become a better researcher.

I would like to thank my parents: Aura and Antonio, whose unconditional love and care, and hard work, have provided a constant source of motivation, strength and inspiration in the pursuit of this degree and every of my endeavors. I am also immensely grateful to my parents for instilling the value of resilience in me, and encouraging me to stick to my values even when things become difficult and challenging. I thank my siblings: Xavier, Elizabeth and Vanessa, for all the treasured memories growing up which have provided much needed mental breaks during the writing-up process. Special thanks to Mercedes, Victor and Anita, and many other relatives for their constant support. To Chloë, for patiently listening and questioning my ideas, for being there when I needed her, and for every colorful adventure.

To my numerous lab mates, colleagues and friends, and to many others, unmentioned here but not forgotten—I thank you.
LIST OF TABLES

3.1 TAG composition as determined by HPLC ................................................................. 57
3.2 FA composition as determined by GC ................................................................. 59
3.3 Thermal and rheological properties .................................................................................. 67
3.1 Bulk composition, functionality as specified by manufacturer, and volume fraction of shortenings ................................................................. 78
3.2 Elastic modulus determined from strain sweeps at $\omega=6.28$ rads$^{-1}$ and $\gamma_0=5\times10^{-4}$. Yield strain and stress defined at $G'/G'_0=0.95$. Group means sharing superscripts were not significantly different (p>0.05). Yield stress measured with smooth surfaces are shown to illustrate the effect of slippage and premature yielding ................................................................. 86
4.3 Inverse slope ($k$) obtained from fitting the relative intensity of the third harmonic $I_3/I_1$ from LAOS experiments to Eq. 2. Power law exponent ($n$) derived from log-log plots of $G'$ vs. $t$ like those displayed in Fig 4.8. Relative rebuilding ($G'/G'_0$) after 20 s of flow cessation in thixotropy tests. Group means sharing superscripts were not significantly different (p>0.05) .... 96
5.1 Fat functionality and bulk composition for each material class, linear elastic moduli and maximum stress at rupture or fracture at $\omega=3.6$ rads$^{-1}$ and $\gamma_0=0.01\%$ ......................................................... 106
5.2 Selected parameters obtained from Unified Fit and Guinier-Porod models and length scales probed in each structure level of the Unified Fit model. Standard error means for $P$ and $S$ parameters were equal or below 0.1 ................................................................. 130
5.1 Functionality and bulk composition for each material class, linear elastic moduli at $\omega=3.6$ rads$^{-1}$ and $\gamma_0=0.01\%$ ................................................................. 141
6.2 Selected parameters obtained from Unified Fit and Guinier-Porod models and length scales probed in each structure level of the Unified Fit model. Standard error means for $P$ and $S$ parameters were equal or below 0.1 ................................................................. 154
7.1 Functionality, bulk composition and elastic moduli at $\gamma_0=0.005\%$ and $\omega=6.28$ rads$^{-1}$. Adapted from [3] ................................................................. 165
7.2 Creep and recovery parameters obtained from fitting data to a 4-element Burgers model. From left to right: creep or recovery section (C/R), instantaneous compliance ($J_0$), retarded compliance ($J_1$), retardation time ($\Lambda$) and maximum compliance ($J_{max}$) ................................................................. 173
LIST OF FIGURES

2.1 The hierarchical structure of fat materials. (a) TEM micrograph of epitaxial stacking of crystal lamellae form a nanoplatelet (side view). Schematic representation of an individual crystal lamellae illustrating side-to-side packing of pairs of TAGs, each TAG is in a tuning fork conformation. (b) Top view of crystal nanoplatelets. (c) Nanoplatelets continue to aggregate into meso-scale and micro-scale structure that are somewhat different depending on composition and processing. (d) Polarized-light micrograph of the fat microstructure (birefrigent) embedded in liquid oil (dark) ................................................................. 5

2.2 (a) Creep and recovery curve of laminating and all-purpose shortenings. Dotted gray lines indicate viscoelastic parameters and time intervals used by the Burgers model (b) ..................... 13

2.3 (a) Elastic $G'$ and viscous $G''$ moduli as a function of stress as procured from a strain amplitude sweep ($\gamma_0$=0.01-100%, $\omega$= 3.6 rads$^{-1}$). (b) Stress versus strain plots of laminating and all-purpose shortenings. Inset denotes ideal ductile and brittle solid behavior .................... 19

2.4 (a) Stress (full black lines) and strain (dotted gray lines) waveforms versus time. Raw Lissajous-Bowditch plots of (b) stress versus strain (elastic representation) and (c) stress versus shear rate (viscous representation). The gray lines correspond to transients. Whereas the solid black lines represent the steady state data. (d) frequency-domain Fourier spectra. The data on the top row were collected in the SAOS regime, whereas the data on the down row were obtained in the LAOS regime ($\gamma_0$=10 %), for a laminating shortening at T=16 °C...... 21

2.5 Definitions of material measures as proposed by (Ewoldt et al., 2008), for reporting viscoelastic moduli: (a),(b) elastic moduli and dynamic viscosities, respectively, for a model linear viscoelastic response at \{$\omega = 3.59$ rad s$^{-1}$, $\gamma_0$= 0.01\}; (c),(d) elastic moduli and dynamic viscosities, respectively, for a nonlinear viscoelastic response at \{$\omega = 3.59$ rads$^{-1}$, $\gamma_0$= 1.34\%\}. The first harmonic moduli are shown for comparison. In the linear regime [(a),(b)] all measures are equivalent to the linear viscoelastic moduli. A nonlinear material response [(c),(d)] will result in different values for each material measure. All the shown data were measured for an all-purpose shortening at T=16 °C................................................................. 26

2.6 (a) Wall slip on a smooth surface and elimination of wall slip on a sandpapered surface, respectively, for a water-in-oil emulsion (Nivea Lotion) tested using parallel plates of diameter D= 40 mm at multiple gaps $h$= 450-1050 µm. Adapted from Ewoldt et., (2015). (b) Wall slip on a custom sandblasted surface and absence of wall slip on a filter-paper surface, respectively, in a cake shortening using parallel plates of diameter $D$= 20 mm at a fixed gap $h$= 1300 µm ........................................................................................................ 29

2.7 Macroscopic appearance of laminating and all-purpose shortenings. (a) laminating and (b) all-purpose shortening, during capillary flow. (a) and (b) share the same scale bar. (c) “entangled” threads of laminating shortening collected at the exit of capillary rheometer. (d) laminating and (e) all-purpose shortenings, after compression. (d) and (e) share the same scale bar ........................................................................................................ 32

2.8 a) Third-order harmonic of laminating and all-purpose shortenings as obtained from LAOS experiments at $\omega = 3.6$ rads$^{-1}$. b) Shear and elongational viscosity as determined from entrance pressure and pressure drops measured by capillary rheometer .................................................................. 33
2.9 Normalized elastic (a, c) and viscous (b, d) Lissajous-Bowditch curves collapsed in a Pipkin space at the corresponding input parameters of frequency and strain-amplitude. Continuous shapes correspond to the total stress, whereas lines contained inside the figures represent the decomposed elastic and viscous stress, respectively. The maximum stress $\tau_{\text{max}}$ in each test is shown above each limit cycle. (a,b) laminating and (c,d) all-purpose shortenings

2.10 Nonlinear a) elastic and b) viscous measures for laminating and all-purpose shortenings as calculated from LAOS data at $\omega = 3.6$ rads$^{-1}$. (b) Measures are parametrized by the linear dynamic viscosity $\eta_{\text{LVE}}$ at $\gamma_0 = 0.01\%$, inset shows absolute values.

2.11 Microscopic-to-nanoscopic structure of laminating and all-purpose shortenings as assessed by SEM and USAXS. SEM images (a,b) share the same magnification bar. Dotted lines in the USAXS plots (c) serve as ‘guide to the eyes’.

3.1 X-ray Wide Angle X-ray Spectra. From bottom to top: sample 1 to sample 9

3.2 DSC melting endotherms. From bottom to top: sample 1 to sample 9

3.3 SFC curves as a function of temperature. a: roll-in shortenings. b: other shortenings

3.4 True strain true stress curves. a: non hydrogenated canola oil, modified palm and palm kernel oils roll-in (2) b: non hydrogenated palm oil and modified palm oil all-purpose (5) c: soybean oil interesterified cake (6) d: palm oil icing (8)

4.1 Impact of normal force on the elastic modulus $G'$ and yield stress $\tau_y$ of roll-in (R2) and all-purpose shortening (S1) post loading. $G'$ was obtained at fixed frequency $\omega = 6.28$ rads$^{-1}$ and strain $\gamma_0 = 5 \times 10^{-4}$. Linear viscoelastic stress limits defined at $G'/G_0 = 0.95$

4.2 Frequency sweep of selected shortenings at fixed strain $\gamma_0 = 5 \times 10^{-4}$. R1: roll-in, S1: all-purpose shortenings

4.3 Strain sweep conducted at fixed frequency $\omega = 6.28$ rads$^{-1}$. R1: roll-in and S1: all-purpose shortenings. Linear viscoelastic strain limits defined at $G'/G' = 0.95$

4.4 Lissajous-Bowditch curves after 20 oscillatory cycles for a roll-in shortening (R1) at fixed frequency $\omega = 6.28$ rads$^{-1}$ with a) $\gamma_0$ ($\times 10^2$)= 0.03, 0.06, 0.09, 0.14; b) $\gamma_0$ ($\times 10^2$)= 0.22, 0.36, 0.57, 0.92; c) $\gamma_0$ ($\times 10^2$)= 1.46, 2.34, 3.74, 5.99; d) $\gamma_0$ ($\times 10^2$)= 9.56; 15.3; 24.5. Arrows indicate the direction of the oscillation

4.5 Lissajous-Bowditch curves after 20 oscillatory cycles for an all-purpose shortening (S1) at fixed frequency $\omega = 6.28$ rads$^{-1}$ with a) $\gamma_0$ ($\times 10^2$)= 0.03, 0.06, 0.09, 0.14; b) $\gamma_0$ ($\times 10^2$)= 0.22, 0.36, 0.57, 0.92; c) $\gamma_0$ ($\times 10^2$)= 1.46, 2.34, 3.74, 5.99; d) $\gamma_0$ ($\times 10^2$)= 9.56; 15.3; 24.5. Arrows indicate the direction of the oscillation

4.6 a) Relative intensity of the third harmonic ($I_{3\gamma_1}$) as a function of shear strain amplitude at $\omega = 6.28$ rads$^{-1}$. R1: roll-in shortening; S1: all-purpose shortening. Data was fitted to Eq. 2. Inset is a continuation of the main plot showing higher strain values. b) Relative intensity of the fifth harmonic ($I_{5\gamma_1}$) as a function of shear strain amplitude at $\omega = 6.28$ rads$^{-1}$. R1: roll-in shortening; S1: all-purpose shortening

4.7 Energy dissipated per oscillatory strain cycle calculated from the area of the Lissajous-Bowditch curves using Eq (3.3), for selected shortenings. R1: roll-in and S1: all-purpose shortenings
4.8 Recovery of the elastic modulus $G'$ after cessation of steady shear. a) R1-R5: roll-in shortenings, b) S1-S4: all-purpose, cake and icing shortenings

5.1 Evidence of ductile (D1) versus brittle (B1) deformation of representative fats during compression. a) views from below a transparent bottom plate for specimens with $h_0=2$ mm, b) side views for specimens with $h_0=10$ mm. A ductile fat (D1) plastically deforms, whereas a brittle fat (B1) fails showing cracks and a cleavage line at $\Delta h/h_0=-0.10$. At higher deformations, ductile (D1) also show cracks that onset at the periphery of the test piece possibly triggered by shear stresses.

5.2 Compressive engineering stress ($\sigma_e = F/A_0$) as a function of compressive engineering strain ($\epsilon_e = \Delta h/h_0$) for a representative ductile (D1) and brittle (B1) fat. The dimensions of the specimens were 20mm×10mm (DIA×height). A thin layer of mineral oil was applied to the parallel plate geometries to diminish frictional force at the edges.

5.3 First-harmonic viscoelastic moduli and stress as functions of increasing gap $h=1.3-2$ mm. Stress perspective of strain amplitude sweeps for a) ductile fat D1 and b) brittle fat B1. c) First harmonic stress amplitude $\tau_1$ as a function of apparent strain amplitude $\gamma_0$ for both fats.

5.4 Scaled third order elastic $\epsilon_3/\epsilon_1$ and viscous $\nu_3/\nu_1$ Chebyshev coefficients as a function of strain input $\gamma_0$ at $\omega = 3.6$ rads$^{-1}$ for ductile D1 and brittle B1 fats in LAOS.

5.5 Steady state Lissajous-Bowditch curves for a ductile fat D1, shown for a selected range of strains and frequencies. a) and b) Normalized 2D projections arranged in a Pipkin space according to the input parameter $\{\omega, \gamma_0\}$, that generated each response curve. The maximum stress is shown above each curve. a) Individual plots of normalized stress (black solid lines) and elastic stress (green dashed line) vs. strain. b) Individual plots of normalized stress (black solid lines) and viscous stress (green dashed line) vs. strain rate.

5.6 Steady state Lissajous-Bowditch curves for a brittle fat B1, shown for a selected range of strains and frequencies. a) and b) Normalized 2D projections arranged in a Pipkin space according to the input parameter $\{\omega, \gamma_0\}$, that generated each response curve. The maximum stress is shown above each curve. a) Individual plots of normalized stress (black solid lines) and elastic stress (blue dashed line) vs. strain. b) Individual plots of normalized stress (black solid lines) and viscous stress (blue dashed line) vs. strain rate.

5.7 Dynamic viscosities at a fixed frequency $\omega = 3.6$ rads$^{-1}$ as a function of strain amplitude input $\gamma_0$: a) minimum strain-rate, b) large strain-rate and c) average strain-rate viscosities. Insets show viscosity metrics normalized by $\eta_{LVE}$ at $\gamma_0=0.01\%$. d) Lissajous-Bowditch curve (viscous perspective) showing normalized shear-rate $\dot{\gamma}_0$ versus stress $\tau$ normalized by $\tau_{LVE}$ at $\gamma_0=0.01\%$, for a selected data point $\gamma_0=1.47\%$ ($\dot{\gamma}_0 = 0.05$ s$^{-1}$), displaying graphical representation of local (instantaneous) and global (average) LAOS viscosity measures.

5.8 Absolute scattering intensity $I(q)$ as a function of the scattering vector $q$. Slope values included in the plot serve as guides for the actual values obtained by the Unified Fit model and summarized in Table 5.2.
5.9 Cryo-scanning electron images of ductile (D1, D2) and brittle (B1, B2) fats: a) D1, b) D2, c) B1, d) B2; e) D1 after deformation \( \gamma_0=50\% \) and f) B1 after deformation \( \gamma_0=50\% \). All images share the same magnification bar= 30\( \mu \)m.

6.1 Average storage \( G'_1 \) and loss moduli \( G''_1 \) as a function of strain amplitude at \( \omega= 3.6 \text{ rads}^{-1} \) for a laminating shortening (R1) and a cake shortening (S1). ................................................................. 131

6.2 (a,b) elastic and (c,d) viscous Lissajous-Bowditch plots for selected amplitudes for a laminating shortening (R1) and a cake shortening (S1). ................................................................. 148

6.3 (a) elastic stress and (b) viscous stress extracted from Lissajous-Bowditch plots for selected amplitudes for a laminating shortening (R1) and a cake shortening (S1). ................................................................. 149

6.4 Scaled third-order elastic \( e_3/e_1 \) and viscous \( v_3/v_1 \) Chebyshev coefficients as a function of strain amplitude \( \gamma_0 \) for a laminating shortening (R1) and a cake shortening (S1). ................................................................. 150

6.5 Local elastic (a) minimum-strain modulus \( G'_M \) and (b) maximum-strain modulus \( G'_L \), both normalized by the linear elastic moduli for laminating shortenings (R1, R2, R3) and a cake shortening (S1). Insets show absolute values of the same elastic measures. ................................................................. 151

6.6 Local dynamic (a) minimum-strain-rate viscosity \( \eta'_M \), (b) maximum-strain-rate viscosity \( \eta'_L \), both normalized by the linear dynamic viscosity for laminating shortenings (R1, R2, R3) and a cake shortening (S1). Insets show absolute values of the same viscous measures. ................................................................. 152

6.7 Absolute scattering intensity \( I(q) \) as a function of the scattering vector \( q \). Slope values included in the plot serve as guides for the actual values obtained by the Unified Fit model and summarized in Table 6.2. ................................................................. 153

6.8 Cryo-scanning electron images of laminating fats: (a, d) R1, (b) R2, and a cake shortening (c, e) S1. Images a, b, c share the same magnification bar= 30\( \mu \)m. Images d, e share the same magnification bar= 100\( \mu \)m. ................................................................. 154

7.1 SEM micrograph of R laminating shortenings and S all-purpose and cake shortenings after deoiling the crystal network. R1 and S2 are included also at lower magnification to visualize the spatial distribution of the crystal aggregates. ................................................................. 156

7.2 Frequency sweep of selected shortenings at fixed stress \( \bar{\tau}_i= 100 \text{ Pa} \). Shortenings: S1 All-purpose, R1 Roll-in. ................................................................. 157

7.3 Typical creep and recovery of a linear viscoelastic material under a constant stress and a schematic diagram of the Burgers model, which consists of Maxwell and Kelvin elements in series. ................................................................. 158

7.4 Linear viscoelastic creep and recovery curves for (a) laminating: R and (b) all-purpose and cake shortenings: S. Stress steps of \( \bar{\tau}_0= 200 \text{ Pa} \) were applied for all samples except for S2 and S3 that were subjected to \( \bar{\tau}_0= 80 \text{ Pa} \) and \( \bar{\tau}_0= 50 \text{ Pa} \) respectively. The data are ignored for times \( t \leq 100 \text{ ms} \) due to high-frequency creep ringing. ................................................................. 159

7.5 Shear (a) Steady shear viscosity and (b) fractional recovery at various shear stresses. Laminating show lower fractional recover than all-purpose and cake shortening. ................................................................. 160

7.6 Macrographs of (a) laminating shortening R5, (b) all-purpose shortening S1 collected at the die exit and (c) laminating shortening R5 collected on a weighing pan. Laminating shortening sustain large shear deformation, remain continuous and produces a thin extrudate.
compared to all-purpose shortening. Apparent shear viscosity $\eta_a$ as a function of apparent strain-rate $\dot{\gamma}_a$ .................................................................

A.8

8.2 Lissajous curves of stress versus strain–elastic projection, and shear rate–viscous projection recorded at $\omega = 3.6$ rads$^{-1}$ and $\gamma_0=0.01$-10% for laminating and all-purpose shortenings. Insets of all-purpose shortening illustrate ellipsoidal elastic and viscous response within the linear viscoelastic region ($\gamma_0\simeq0.01$-05%). Arrows highlight the observed qualitative differences.............

A.1 Modified parallel plate geometries used for oscillatory shear experiments. Filter paper (Whatman grade 5) was glued to the upper and lower plates.........................................................

A.2 Filter performance for $\gamma_0=6\%$ at $\omega=5.9$ rads$^{-1}$ for a) ductile (D1) and brittle fat (B1). The nonlinearities are described by harmonic contributions lower than $n=7$ ($e_0/e_1$, $\nu_0/\nu_1$<0.05). Secondary local minimums at high strains in the stress response are a consequence of data processing.................................................................

A.3 Side view for ductile (D2) and brittle (B2) with $h_0=10$ mm under compression. A ductile fat plastically deforms, whereas a brittle fat breaks or "crumbles" at $\Delta h/h_0=-0.10$. .........................

A.4 First-harmonic moduli as a function of apparent strain amplitude $\gamma_0$ at $\omega = 3.6$ rads$^{-1}$ for ductile (D1) and brittle fats (B1). .................................................................

A.5 First harmonic stress amplitude $\tau_1$ as a function of apparent strain amplitude $\gamma_0$ at $\omega = 3.6$ rads$^{-1}$ for ductile D2 and brittle B2 fats. .................................................................

A.6 Un-normalized steady state Lissajous-Bowditch curves for a ductile (D1) fat at $\omega = 3.6$ rads$^{-1}$. (a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\dot{\gamma}$ (viscous perspective). ........................................

A.7 Un-normalized steady state Lissajous-Bowditch curves for a ductile (D2) fat at $\omega = 3.6$ rads$^{-1}$. (a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\dot{\gamma}$ (viscous perspective). ........................................

A.8 Un-normalized steady state Lissajous-Bowditch curves for a brittle (B1) fat at $\omega = 3.6$ rads$^{-1}$. (a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\dot{\gamma}$ (viscous perspective). ........................................
A.9 Un-normalized steady state Lissajous-Bowditch curves for a brittle (B2) fat at $\omega = 3.6 \text{ rads}^{-1}$. 
(a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\gamma$ (viscous perspective).

A.10 Un-normalized 3D Lissajous-Bowditch curves obtained at $\gamma=2.34\%$ and $\omega = 3.6 \text{ rads}^{-1}$ for (a) ductile (D1) and (b) brittle (B1) fats.

A.11 Normalized difference between local elastic measures: minimum strain ($G_M'$) and large strain modulus ($G_L'$) as a function of strain input $\gamma_0$ at $\omega = 3.6 \text{ rads}^{-1}$ for ductile (D1, D2) and brittle fats (B1, B2). (b) Lissajous-Bowditch curve (elastic perspective) showing strain $\gamma_0$ versus stress $\tau$ for a selected data point $\gamma_0 = 1.47\%$, displaying graphical representation of local (instantaneous) and global (average) LAOS elastic measures.

A.12 Cryo-scanning electron images of ductile (D1, D2) and brittle (B1, B2) fats: a) D1, b) D2, c) B1, d) B2. All images share the same magnification bar= 60$\mu$m.
**LIST OF ACRONYMS AND SYMBOLS**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>fatty acid</td>
</tr>
<tr>
<td>TAG</td>
<td>triacylglycerol</td>
</tr>
<tr>
<td>DLCA</td>
<td>diffusion limited cluster aggregation</td>
</tr>
<tr>
<td>RLCA</td>
<td>reaction limited cluster aggregation</td>
</tr>
<tr>
<td>SFC</td>
<td>solid fat content</td>
</tr>
<tr>
<td>Φ, φ</td>
<td>volume fraction SFC/100</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>SAXS</td>
<td>small angle x-ray scattering</td>
</tr>
<tr>
<td>WAXS</td>
<td>wide angle x-ray scattering</td>
</tr>
<tr>
<td>USAXS</td>
<td>ultra small angle x-ray scattering</td>
</tr>
<tr>
<td>CNP</td>
<td>crystalline nanoplatelet</td>
</tr>
<tr>
<td>D</td>
<td>fractal dimension</td>
</tr>
<tr>
<td>SAOS</td>
<td>small amplitude oscillatory shear</td>
</tr>
<tr>
<td>LAOS</td>
<td>large amplitude oscillatory shear</td>
</tr>
<tr>
<td>G’</td>
<td>elastic modulus</td>
</tr>
<tr>
<td>G”</td>
<td>viscous modulus</td>
</tr>
<tr>
<td>τ</td>
<td>shear stress</td>
</tr>
<tr>
<td>γ</td>
<td>shear strain</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

**ABSTRACT**.................................................................................................................. ii  
**DEDICATION**................................................................................................................ iv  
**ACKNOWLEDGEMENTS**................................................................................................. v  
**LIST OF TABLES**.......................................................................................................... vi  
**LIST OF FIGURES**......................................................................................................... vii  
**LIST OF ACRONYMS AND SYMBOLS**......................................................................... xii  
**CHAPTER 1: INTRODUCTION**....................................................................................... 1  
  1.1 Organization of this dissertation ............................................................................. 3  
**CHAPTER 2: LINEAR AND NONLINEAR RHEOLOGICAL BEHAVIOR OF FAT CRYSTAL NETWORKS**.................................................................................................................. 4  
  2.1 Abstract .................................................................................................................... 4  
  2.2 Introduction ............................................................................................................. 4  
  2.3 Physical length scales of fats .................................................................................. 8  
    2.3.1 Molecular structure and polymorphism ......................................................... 8  
    2.3.2 Nanoscopic-to-mesoscopic structure ............................................................. 9  
    2.3.3 Mesoscopic structure .................................................................................... 10  
  2.4 Rheological properties of fats .............................................................................. 11  
    2.4.1 Linear viscoelasticity ..................................................................................... 11  
    2.4.2 Linear viscoelasticity and microscopic modelling approaches .................... 13  
    2.4.3 Nonlinear viscoelasticity .............................................................................. 15  
    2.4.4 Large amplitude oscillatory shear fundamentals ......................................... 20  
    2.4.5 Experimental difficulties in shear rheology ................................................... 27  
  2.5 Structure and mechanical function of fats: a case study ........................................ 30  
  2.6 Conclusions and perspectives ............................................................................... 38  
  2.7 References ............................................................................................................ 39  
**CHAPTER 3: PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION OF ROLL-IN SHORTENINGS**........................................................................................................... 49  
  3.1 Abstract .................................................................................................................... 49  
  3.2 Introduction ............................................................................................................. 50  
  3.3 Materials and Methods ........................................................................................... 52
3.3.1 Triacylglycerol composition ................................................................. 53
3.3.2 Fatty acid composition ................................................................. 53
3.3.3 Polymorphism ............................................................................... 53
3.3.4 Thermal behavior ......................................................................... 54
3.3.5 Solid fat content (SFC) ................................................................. 54
3.3.6 Large deformation rheology ........................................................... 54
3.3.7 Statistical Analysis ...................................................................... 55
3.4 Results and Discussion ..................................................................... 56
3.4.1 TAG composition ........................................................................ 56
3.4.2 FA composition ........................................................................... 58
3.4.3 Polymorphism .............................................................................. 59
3.4.4 Thermal behavior ......................................................................... 61
3.4.5 Solid fat content .......................................................................... 63
3.4.6 Large deformation rheology ........................................................... 64
3.5 Conclusions ...................................................................................... 68
3.6 Acknowledgements .......................................................................... 69
3.7 Conflict of interest ........................................................................... 69
3.8 References .......................................................................................... 69

CHAPTER 4: RHEOLOGICAL CHARACTERIZATION OF LIPID SHORTENINGS .. 74

4.1 Abstract ............................................................................................. 74
4.2 Introduction ......................................................................................... 75
4.3 Materials and Methods ..................................................................... 77
  4.3.1 Sample preparation ...................................................................... 77
  4.3.2 Sample loading ........................................................................... 79
  4.3.4 Linear rheology: small amplitude oscillatory rheology (SAOS) ... 79
  4.3.5 Nonlinear rheology: large amplitude (LAOS) oscillatory rheology .. 80
  4.3.6 Statistics .................................................................................... 81
4.4 Results and discussion ...................................................................... 81
  4.4.1 Sample loading ........................................................................... 81
  4.4.2 Linear viscoelasticity .................................................................. 83
  4.4.3 Nonlinear viscoelasticity ............................................................. 86
4.4.5 Energy dissipation ................................................................. 93
4.4.6 Thixotropic behavior .......................................................... 95
4.5 Conclusions ............................................................................ 97
4.6 Acknowledgements ................................................................ 98
4.7 Compliance with ethical standards ......................................... 98
4.8 References .............................................................................. 98

CHAPTER 5: NONLINEAR VISCOELASTICITY OF FAT CRYSTAL NETWORKS ..103
5.1 Abstract ................................................................................. 103
5.2 Introduction ............................................................................ 103
5.3 Experimental .......................................................................... 106
  5.3.1 Sample preparation ............................................................ 106
  5.3.2 Rheometry .......................................................................... 107
  5.3.3 LAOS analysis .................................................................... 108
  5.3.4 Scanning electron microscopy ............................................. 111
  5.3.5 Ultra Small Angle X-Ray Scattering (USAXS) ..................... 112
5.4 Results and discussion............................................................ 115
  5.4.1 Effect of sample thickness on rheological material functions ..... 117
  5.4.2 Linear to nonlinear viscoelasticity ....................................... 117
  5.4.3 Chebyshev coefficients and Lissajous-Bowditch curves ........... 121
  5.4.4 Nonlinear viscoelastic metrics ............................................. 125
  5.4.5 Structural characterization ................................................ 129
5.5 Conclusions ............................................................................ 133
5.6 Acknowledgements ................................................................ 134
5.7 References .............................................................................. 134

CHAPTER 6: THE ROLE OF NONLINEAR VISCOELASTICITY ON THE FUNCTIONALITY OF LAMINATING SHORTENINGS ........................................ 138
6.1 Abstract ................................................................................. 138
6.2 Introduction ............................................................................ 139
6.3 Experimental .......................................................................... 140
  6.3.1 Materials ........................................................................... 140
  6.3.2 Sample preparation ............................................................ 141
6.3.3 Measurements and Analysis .......................................................... 142
6.4 Results and discussion ................................................................. 147
  6.4.1 Linear viscoelasticity ............................................................... 147
  6.4.2 Nonlinear viscoelasticity ......................................................... 148
  6.4.3 USAXS .............................................................................. 153
  6.4.5 SEM .............................................................................. 156
6.5 Conclusions .................................................................................. 157
6.6 Acknowledgements ..................................................................... 157
6.7 References ................................................................................... 158

CHAPTER 7: BAKERY SHORTENINGS: STRUCTURE-MECHANICAL FUNCTION RELATIONS ......................................................... 161
  7.1 Abstract .................................................................................... 161
  7.2 Introduction ............................................................................... 161
  7.3 Materials and Methods ............................................................. 164
    7.3.1 Materials ............................................................................. 164
    7.3.2 Sample preparation ............................................................ 165
    7.3.3 Measurements .................................................................. 166
  7.4 Results and discussion .............................................................. 168
    7.4.1 Microstructure ................................................................. 168
    7.4.2 Shear rheometry ............................................................... 169
    7.4.3 Capillary rheology ........................................................... 175
  7.5 Conclusions ............................................................................... 176
  7.6 References ............................................................................... 177

CHAPTER 8: UNDERSTANDING THE FUNCTIONALITY OF LIPID-BASED MATERIALS UNDER LARGE-AMPLITUDE NONLINEAR DEFORMATIONS ...... 180
  8.1 Abstract .................................................................................... 180
  8.2 Introduction ............................................................................... 180
  8.3 Small amplitude (SAOS) versus Large Amplitude (LAOS) oscillatory shear ................................................. 181
  8.4 LAOS fundamentals and rheological measures .......................... 183
  8.5 A case study: rationalizing the functionality of laminating shortenings .................................................. 184
  8.6 Conclusions ............................................................................... 187
8.7 Acknowledgements ........................................................................................................ 187
8.8 References ..................................................................................................................... 187

CHAPTER 9: CONCLUSIONS AND FUTURE WORK ............................................................... 189

APPENDIX 1: SUPPLEMENTARY MATERIAL (CHAPTER 5) ........................................... 189
CHAPTER 1: INTRODUCTION

In the design of any material, a desired performance is identified which is then linked to a particular property or set of properties. Selection of existing materials or creation of novel materials (i.e. organogels) that meet the desired criteria is then possible. Such process is not uncommon to edible fats whose functionalities (i.e. “meltability”, “spreadability”) are related to their physical and rheological properties, which are supervenient on their structure. In this thesis, we establish the first step towards rational design of edible fats intended for laminating purposes, that is we link performance to specific physico-chemical (i.e. crystal polymorphism, melting) or rheological (i.e. elastic modulus) properties.

Laminating performance or functionality (as referred to throughout this thesis) can be loosely described as “the ability of a fat to gradually change from firm to spreadable and remain continuous during extrusion, rolling and sheeting of layered doughs”. We investigate the laminating functionality motivated by scientific and practical reasons. We seek to gain a fundamental understanding of the factors defining the unusual functionality of laminating fats, to allow the reformulation of these products. A laminating fat is a truly remarkable material that resists macroscopic fracture and forms micron-width during the manufacture of croissants, Danish, among other layered pastries. This functionality confers adequate lamination, which is necessary to prevent fusion of the multilayered dough structure, and is strongly related to quality of pastries (good “puff” and flaky texture). In these products, laminating fats are one of the major ingredients (at least 30% w/w). One major shortcoming with the use of laminating fats is their typically high content in “hardstock” fats: saturates and trans fatty acids (as high as 54% w/w altogether). International regulations and nutritional guidelines have banned the use of trans fats and also advised on the reduction of saturated fats, due to their implications on cardiovascular health.

In general, the physical and rheological properties of fats are a result of the complex hierarchical structure, which exhibits multiple length scales ranging from the molecular to the microscopic. During crystallization, high-melting TAG molecules pack longitudinally typically in double or triple chain lengths, and laterally, in a specific subcell unit arrangement or polymorphism (α, β, β’), to form the crystal lamellae (Sato, 2001). Crystal lamellae stack to give rise to platelet-like structures with various surface morphologies, commonly referred as to crystal nanoplatelets.
(CNPs). The CNPs, considered the basic building blocks, self-assemble into sub-micron and micron-size fractal clusters or aggregates mainly via diffusion diffusion-limited cluster aggregation (DLCA) and reaction limited cluster aggregation (RLCA) (Peyronel et al., 2014b) to ultimately form a volume-filling network similar to that of flocculated colloidal gels (DeMan and Beers 1987; Narine and Marangoni 1999d).

To date, there is a wealth of knowledge on the structure and functionality of edible fats (Marangoni et al., 2012). Major milestones in this area include the understanding of linear viscoelasticity of fats and its relation to microstructure, and the recent characterization of nano-to-meso scales structures (Acevedo et al., 2011; Peyronel et al., 2014b). Despite these advances, there has been scarce work on the nonlinear viscoelasticity of fats, which is a major focus on this thesis. Essentially all processing and application uses such as extrusion, rolling and spreading of laminating shortenings involve nonlinear viscoelastic responses triggered by large deformations. It has been suggested that a fat without adequate rheology finds little to no use as bulk structural material for laminating applications (Renzetti et al., 2015).

In the past, some of the main techniques that have been used to characterize the rheology of fats include cone penetrometry (The official American Oil Chemists’ Society method AOCS Cc 16-60) and compression methods. Despite their utility of these methods, these methods are plagued with several limitations, i.e. cone penetrometry provides only textural viscoelastic attributes rather than fundamental material properties. Therefore, there is an obvious need to adapt novel rheological techniques that provide true criteria relatable to the mechanical functionality of fats. Lately, there has been growing scientific interest in large amplitude oscillatory shear (LAOS) rheology, which has been successfully applied to colloids, polymers, among other material classes. In these systems, LAOS rheology has shed insights into nonlinear viscoelastic behavior, structure and functionality, aspects that were otherwise undistinguishable by other traditional rheological methods. The LAOS technique presents several advantages over conventional methods (i.e. steady shear), some of which include: (i) gradually lead up to yield, (ii) simultaneous decomposition of energy storage and loss mechanisms, and (iii) better signal-to-noise ratio. In this thesis, we adopt this technique to gain insights into the nonlinear viscoelasticity of laminating fats.
Hypothesis and Objectives

My hypothesis for this thesis is that the mechanical functionality of shortenings is characterized by their nonlinear rheological behavior.

To test this hypothesis, the following objectives will be met:

1. to determine whether physico-chemical properties of fats (i.e. composition, solid fat content), commonly used to assess functionality, vary among shortening type
2. to assess whether viscoelastic texture attributes, apparent material properties or traditional viscoelastic properties such as Young modulus, yield stress and yield strain relate to laminating functionality
3. to determine whether nonlinear viscoelastic properties dictate functionality
4. to characterize the structural levels of shortenings from molecular to microscopic scales
5. to correlate the observed rheological behavior with structure

1.1 Organization of this dissertation

This dissertation is organized according to traditional methods and new methods (large amplitude oscillatory shear) used for the study of the physico-chemical properties and rheological behavior of fats. Chapter 3 summarizes molecular composition, crystalline solid fat, thermal behavior and typical large deformation properties. Chapter 4 describes linear viscoelastic (i.e. linear moduli) and conventional nonlinear viscoelastic (i.e. yield stress) oscillatory shear material properties. Chapter 5 and Chapter 6 further elaborate on nonlinear viscoelastic material properties and their relation to structure. Chapter 7 deals with linear and nonlinear viscoelastic properties from step shear and capillary rheology experiments. Chapter 8 provides a technical note on the use of large amplitude oscillatory shear as a tool to understand functionality of lipid-based materials.
CHAPTER 2: LINEAR AND NONLINEAR RHEOLOGICAL BEHAVIOR OF FAT CRYSTAL NETWORKS

Braulio A. Macias-Rodriguez\textsuperscript{a} and Alejandro G. Marangoni\textsuperscript{*a}

Critical Reviews in Food Science and Nutrition DOI:10.1080/10408398.2017.1325835

\textsuperscript{a}Department of Food Science, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. \textit{E-mail:} amarango@uoguelph.ca

2.1 Abstract

Fats are ubiquitous in biological membranes, foods and many other commercial products. In these, they play essential roles in biological, nutritional and physical functions. In this review, we focus on physical mechanical functions. The rheology of fats arises from the crystal network, which displays hierarchical structural levels from the molecular to the mesoscopic. Under linear deformations, the crystal network behaves as a viscoelastic solid with elasticity dictated by particle concentration and microstructural features as represented in fractal rheomechanical models. Under nonlinear deformations, the crystal network yields, showing a variety of nonlinear phenomena, i.e. softening, stiffening, thixotropy. These features largely contribute to functionality or performance as essentially all processing and end-uses of fatty materials involve large nonlinear deformations. Early work on rheology of fats gave hints of their nonlinear mechanical behavior, although in many cases the measured properties were empirical. In contrast, recent efforts from our group measured fundamental rheological functions using large amplitude oscillatory shear rheology. We demonstrate the ability of this technique to discern among the bulk functionality of bakery fats (all-purpose and lamination shortenings) based on well-defined rheological signatures that also relate to the fat structure. This technique has the potential to provide similar insights on other fatty systems and novel ideas for reformulation and design of alternative lipid-structuring materials.

\textbf{Keywords:} fat, linear and nonlinear rheology, texture, structure, \textit{trans} and saturated fatty acids

2.2 Introduction

Fats are ubiquitous in nature, foods and in many commercial applications. In our body, they serve as supply and reservoir of energy (9 kcal g\textsuperscript{-1}) and contribute to cellular structuring,
compartmentalization, biomolecular synthesis, among other vital biological roles (Kulkarni, 2012; Marangoni et al., 2012). In foods (i.e. chocolate, butter) and other commercial products (i.e. cosmetic creams), they provide nutritional value, texture control, mouthfeel and other physical characteristics (i.e. oil binding), which play pivotal roles in consumer acceptability (Marangoni et al., 2012). From a nutritional standpoint, consumption of mono or polyunsaturated fatty acids (FA) are preferred over saturated and trans FAs as monounsaturated FAs are linked with reduced risk of cardiovascular disease, while the latter with higher propensity for developing cardiovascular diseases (R. P. Mensink et al., 2003; Mozaffarian et al., 2006; Uauy et al., 2009). From a mechanical perspective, texture is inherently linked to rheological properties that result from the hierarchical structure of fats (Marangoni and Narine 2002).

**Figure 1.1** The hierarchical structure of fat materials. (a) TEM micrograph of epitaxial stacking of crystal lamellae form a nanoplatelet (side view). Schematic representation of an individual crystal lamellae illustrating side-to-side packing of pairs of TAGs, each TAG is in a tuning fork conformation. (b) Top view of crystal nanoplatelets. (c) Nanoplatelets continue to aggregate into meso-scale and micro-scale structure that are somewhat different depending on composition and processing. (d) Polarized-light micrograph of the fat microstructure (birefringent) embedded in liquid oil (dark).
The complex hierarchical structures of fats, ranging in length from the molecular to the microscopic scale, are responsible for their mechanical properties (Fig. 2.1). At the molecular level, high-melting TAGs pack longitudinally typically in double or triple chain lengths, and laterally, following a specific subcell unit arrangement or polymorphism (α, β, β’), to form the crystal lamellae (Fig. 2.1a) (Sato, 2001). At the nanoscale level, epitaxial stacking of 7-10 crystal lamellae give rise to plate-like structures with various surface morphologies, which are defined as the basic building blocks (Fig. 2.1b) (Acevedo and Marangoni 2010; Acevedo et al. 2011). At the submicron and microscopic level, crystalline nanoplatelets (CNPs) self-assemble into larger fractal cluster or aggregates via DLA/RLA or DLCA/RLCA (Peyronel et al., 2014b) to ultimately form a volume-filling network similar to that of flocculated colloidal gels (Fig. 2.1c) (DeMan and Beers 1987; Narine and Marangoni 1999d). The manner in which CNPs are organized into higher-order structures can vary considerably, which in turn opens the possibility for various microstructures (i.e. spherulitic-like, needle-like, etc) embedded in a liquid oil phase (Heertje 1993; Juriaanse and Heertje 1988). These structures confer viscoelastic solid behavior ($G' > G''$) at small deformations, and their diversity reflects the adaption of fats to its mechanical function (Heertje 1993; van den Tempel 1961; Narine and Marangoni 1999d; Narine and Marangoni 1999b).

The rheological properties of fats as related to the crystal network have been a major field of study (Scott Blair 1938; Davis 1937; Blair 1954; Haighton 1959; DeMan and Beers 1987; Narine and Marangoni 1999e; Thareja 2013). Significant advances have been made in this area, enabling us to partly understand linear viscoelasticity in terms of fat microstructure (Narine and Marangoni 1999a; Narine and Marangoni 1999b; Narine and Marangoni 1999d). Of major interest, are the endeavors of Narine and Marangoni (1999b), who extended the microscopic fractal model, originally proposed for colloidal gels, to explain the elasticity of the crystal network (Narine and Marangoni 1999a; Narine and Marangoni 1999b; Narine and Marangoni 1999d; Coussot 2007). The fundamental basis of developed and modified fractal models is the assumption that fats self-assemble into fractal flocs or aggregates. According to this, the elastic modulus $G'$ of the system scales in a power-law fashion with particle volume fraction $G' \sim \phi^n$, where $n$ is related to the compactness of the individual clusters or mass fractal dimension ($D$) (Marangoni and Rousseau 1996; Narine and Marangoni 1999a; Narine and Marangoni 1999d). Depending on $\phi$, $G'$ is
dictated by the elasticity of the microstructural interlinks (weak-link regime \( \phi > 0.1 \)) or that of the flocs (strong-link regime \( \phi < 0.1 \)) (Narine and Marangoni 1999b; Narine and Marangoni 1999e). Despite these efforts, relating the microstructure to mechanical properties is still largely unresolved due to complexity imposed by the various structural levels. Moreover, the structure of the network “ages” over time (i.e. crystal sintering occurs) which in turn affects its mechanical properties, making the task of establishing structure-mechanical function relations a very challenging one (Scott Blair 1954).

While there has been considerable scientific interest on linear rheology at small deformations, there has been limited focus on nonlinear rheology of fats at large deformations. The study of nonlinear rheology is of outstanding fundamental and practical interest given that the morphology of the microstructure, determined by its preceding structural levels, have strong influence on the nonlinear response (Heertje, 1993). Most notably, nonlinear rheology occurs in essentially all industrial processing and end-uses of fatty materials, i.e. extrusion of shortening, spreading of butter and rubbing of a cosmetic cream. Therefore, linear rheology appears insufficient to understand the rheological function of fats. It has been recently demonstrated that multicomponent fats (shortenings) with similar linear viscoelastic properties show different nonlinear viscoelastic properties and hence diverse performance (Macias-Rodriguez and Marangoni 2016b). Likewise, it has been tacitly revealed in the literature that fats show intriguing nonlinear phenomenon including yielding, strain hardening and stress softening, thixotropic behavior, which merit special attention (Haighton 1965; Scott Blair 1938; Sone 1961; Gonzalez-Gutierrez and Scanlon 2013).

Previous works on the nonlinear rheology of fats have largely measured textural attributes by empirical methods (i.e. cone penetrometry). Conversely, nonlinear rheological characterization of colloidal gels and polymeric materials has focused on fundamental techniques including large amplitude oscillatory rheology (LAOS), which has proven extremely fruitful (Hyun et al., 2011; Petekidis, 2014). We favor the latter approach as it enables to define true material properties relating to the structure. In addition, it allows probing an ample range of deformations and timescales capturing the yielding transition of fats. This approach, powerful as it may be, needs to be used with caution to minimize potential artifacts hindering data analysis or masking small rheological differences between samples.
This review aims at providing an overview of the rheological properties of fats at both small and large deformations. To this end, we briefly review the hierarchical levels of organization, which range in scale from nano to micrometers and in turn determine the mechanical properties of fats. We then review linear viscoelastic properties, microscopic models relating linear viscoelasticity to the microscopic network, and place special emphasis on nonlinear viscoelastic properties as investigated by LAOS applied to fat crystal networks. Moreover, we discuss the implementation of LAOS protocol pointing out instrumental challenges associated with this technique and in general with shear rheology. Finally, we provide a study case where LAOS successfully elucidated the mechanical functionality of two contrasting types of fats: all-purpose designed to function under many bakery applications and roll-in shortening intended for lamination applications.

2.3 Physical length scales of fats

2.3.1 Molecular structure and polymorphism

Triacylglycerols molecules, made of three FA moieties esterified to a glycerol backbone, are the base constituents of fats and oil. The characteristics of the FA moieties: chain length (4-22 carbons), degree of unsaturation, isomerism, regiospecificity, determine physical properties (i.e. molecular packing, solid-to-liquid mass fractions or SFC) and pose important nutritional significance (Marangoni et al., 2012). For instance, long-linear (trans) saturated fatty acid chains pack more efficiently than short-kinked (cis) unsaturated FAs, have higher melting points and contribute to solid-like functionality (or greater SFC) (Ghotra et al., 2002). In terms of nutritional benefits, polyunsaturated fatty acids are preferred over saturated fatty acids as the primer is correlated with improved cardiovascular health, whereas trans fatty acids are overall not recommended as they are associated with increased risk of cardiovascular diseases (Ronald P Mensink et al., 2003; Mozaffarian et al., 2006; Uauy et al., 2009).

During nucleation, TAGs stack side-by-side in pairs following either a “chair” or “tuning fork” configuration to give rise to crystal unit cell. The unit cell is the primary unit from which the crystal lamellae is built by three-dimensional translations (Acevedo et al. 2011). The unit cell is highly asymmetric with a very long c-axis (relative to the small a and b short axes) whose longitude is equivalent to the thickness of the crystal lamellae as determined by long spacings in the small-angle x-ray diffraction spectra (Acevedo and Marangoni 2010; Acevedo et al. 2011).
The thickness of the crystal lamellae depends on TAG packing ("back-to-back" or "seat-to-seat") which typically form double or triple chain length structures (Marangoni et al., 2012; Sato, 2001).

During crystallization, high-melting TAGs pack into a preferred polymorphic form which is defined on the basis of the subcell unit describing the lateral packing of the zigzag hydrocarbon chains (−CH₂−) (Marangoni et al., 2012). Three major polymorphic states with their respective subcell packing are distinguished: α (hexagonal), β’ (orthorhombic), β (triclinic) (Sato and Ueno 2011). Each polymorphic form, available from the melt, evolve towards the most stable polymorphic state (β) via melt-mediated or solid-mediated monotropic phase transformations (Himawan et al. 2006). Each polymorphic form displays unique short-spacings in the Wide-angle X-ray diffraction spectra (Marangoni et al., 2012). For in-depth information on fat polymorphism, the readers are referred to the excellent reviews of Sato (Sato 2001; Sato and Ueno 2011).

2.3.2 Nanoscopic-to-mesoscopic structure

Early work on fat structure imaging led to long-standing assertions that micron-sized crystal aggregates were the smallest structural length scale in fats (Acevedo et al., 2011). However, further explorations on sub-mesoscale structures conclusively identified highly anisotropic crystal nanoplateles (CNPs) or crystal domains as the primary crystal units (Acevedo and Marangoni 2010; Acevedo et al. 2011). Crystalline nanoplatelets result from the epitaxial packing of typically 7-10 TAG lamellae as confirmed by TEM and SAXS experiments (Acevedo and Marangoni 2010). A large number of studies have confirmed the presence of CNPs in a wide range of binary or multicomponent lipid systems including tristearin in triolein, cocoa butter, milk fat (Marangoni and Pink 2014).

Formation and aggregation of CNPs into clusters forming the crystal network (or microstructure), is driven by Van der Waals attractions. Pioneering works based on Monte Carlo computer simulations and ultra-small-angle x-ray scattering (USAXS), have shed much-needed light in the field of fat aggregation (Peyronel et al., 2014b). These reports have elucidated the process of CNP aggregation into intermediate physical structures in the “nano-to-micro world” and the features (size, morphology) of such aggregates in binary and multicomponent TAG systems. To illustrate, for a simple binary system of tristearin (SSS) in triolein (OOO), it was
reported that CNPs, characterized by a smooth surface, stacked into 1-dimensional TAGwoods (Peyronel et al., 2013). Subsequently, TAGwoods self-assembled into fractal clusters initially via diffusion limited cluster-cluster aggregation (DLCA, $D=1.7-1.8$), and then via reaction-limited cluster-cluster aggregation (RLCA, $D=2.0-2.1$) as steady-state relaxation is reached (Peyronel et al., 2013; Pink et al., 2013). For multicomponent systems (i.e. SSS in cottonseed oil, SSS in shea butter, SSS in partially hydrogenated canola oil) aggregation appeared far more complex as a gamut of self-assembled structures became possible (Peyronel et al., 2014c; Quinn et al., 2014). Liquid-liquid or solid-liquid nano-phase separation induced smooth, diffuse or rough coatings on CNPs. Smooth or diffuse surfaces favored the formation of TAGwoods that either grew into larger DLCA/RLCA structures and then clusters uniformly distributed in space, or end-to-end connected TAGwoods (Peyronel et al., 2014c; Quinn et al., 2014). Rough surfaces hindered the formation of TAGwoods, promoted a mixture of CNPs and TAGwoods or side-to-side connected TAGwoods (Peyronel et al., 2014c; Quinn et al., 2014). In both cases, the connected TAGwood strings gave rise to a diffuse surface. For a comprehensive description on characterization and aggregation of CNPs, the readers are referred to (Acevedo et al., 2011; Peyronel et al., 2014b).

### 2.3.3 Mesoscopic structure

Crystal aggregates form the volume-filling space network so-called the microstructure (DeMan and Beers 1987; Marangoni et al. 2012; Juriaanse and Heertje 1988; Heertje 1993; van den Tempel 1961). This level of structure is the closest to the macroscopic world and hence it has tremendous bearings on rheological properties of bulk fats (DeMan and Beers 1987; Heertje 1993; Narine and Marangoni 1999d; Tang and Marangoni 2007). It is considered the first structural level to be stressed or strained during deformation (Heertje 1993; Narine and Marangoni 1999d). The microstructure encompasses crystal aggregates differing in size (0.1 μm-140 μm) and morphology, held by a wide spectrum of bonds of variable degree strength or reversibility (DeMan and Beers 1987; Narine and Marangoni 1999e; Shama and Sherman 1970). Some of these morphologies include broad spherulites with radially-arranged needles, closely-bound spherulites with randomly-orientated crystals, closely-bound spherical clusters and open randomly-arranged bundles (Juriaanse and Heertje 1988; Heertje 1993). Such variety in crystal morphology offers equal variety in the mechanics of deformation, i.e. the fat crystal network displays viscoelasticity, yielding, thixotropy, e.g. shear softens and subsequently restructures, local strain stiffening (van den Tempel 1961; Narine and Marangoni 1999b; Haighton 1965;
2.4 Rheological properties of fats

Rheology is primarily concerned with describing flow or deformation of matter when subjected to stress or strains deformations. Early studies on fat rheology or fat-structured materials (i.e. cheese) were undertaken as early as 1930 by the founding father of food rheology Scott Blair, and Davis (Scott Blair 1938; Davis 1937; Scott Blair 1954). These authors were the first to quantify the elastic and viscous properties of fat crystal networks, and attempted to relate fundamental linear viscoelastic measures to texture attributes (i.e. firmness, spreadability). At small or linear reversible deformations, fats behave as viscoelastic solids materials, whereas above critical or nonlinear irreversible deformations they show viscoelastoplastic behavior (Marangoni et al. 2012; Gonzalez-Gutierrez and Scanlon 2013). Linear viscoelasticity as related to the microstructural network has been vastly researched, while nonlinear viscoelasticity have been less investigated. This is unfortunate since all processing and applications of fatty materials involve nonlinear deformations, i.e. lamination of shortenings, rubbing of a cosmetic cream, that trigger nonlinear stress responses. Such responses relate intimately to performance and consumer perception and therefore merit special attention. In this section, we briefly summarize the salient points on linear viscoelasticity of fats as related to microstructure via micromechanical models. Most importantly, we cover past work on nonlinear viscoelasticity of fats and our most recent research efforts on this area. Moreover, we give caveats for collecting shear rheology data, and investigate the rheology of complex fats: laminating versus all-purpose shortenings. These fat systems serve as paradigms for ductile rupture and brittle failure, respectively, and their rheological behavior is ascribed to their differing structural organization.

2.4.1 Linear viscoelasticity

Most of the published literature on the rheology of fats describes linear viscoelastic properties measured by small strain amplitude oscillatory shear rheology (SAOS) (van den Tempel 1961; Marangoni and Narine 2002; Narine and Marangoni 1999c; Narine and Marangoni 1999b; Rohm and Weidinger 1993; Thareja et al. 2013). During SAOS, strain inputs in the order of $\gamma_0 = 0.01\%$ within the linear viscoelastic region (LVR) are applied, which are typical of materials having short-range van der Waals attractions (van den Tempel 1961). Unlike polymer chains, fat crystal
networks possess irreversible bonds and hence cannot be substantially strained without losing memory of their original configuration (van den Tempel 1961). Given the narrow linear envelope, rheological techniques must minimize disturbance of the underlying network. This can be achieved for example by using normal-force loading protocol for pre-crystallized fats or geometries that facilitate in-situ characterization (Macias-Rodriguez and Marangoni 2016b; Thareja et al. 2011). Under the SAOS regime, strain and stress maintain their linear proportional and the crystal network act as a viscoelastic solid \((G' > G'')\) that exhibit high storage modulus \((G' \approx 10^5 - 10^6 \text{ Pa})\) with low-frequency dependence \((G'' \approx 10^5 - 10^6 \text{ Pa})\) (van den Tempel 1961; Narine and Marangoni 1999b; Macias-Rodriguez and Marangoni 2016b; Rohm and Weidinger 1993; Thareja et al. 2013). For a sinusoidal strain excitation \(\gamma(t) = \gamma_0 \sin(\omega t)\), a sinusoidal stress response is obtained and expressed as:

\[
\tau(t) = \gamma_0 G'(\omega) \sin(\omega t) + \gamma_0 G''(\omega) \cos(\omega t) \quad \text{Eq. (1)}
\]

In which \(G'\), the in-phase elastic or stored energy represents the real component, and \(G''\), the out-of-phase viscous or dissipated energy represents the imaginary component of the complex modulus \(G^*\) at a given frequency \((\omega)\) (Ferry, 1980; Macosko, 1994; Tschoegl, 1989). In the LVR, the stress \(\tau(t)\) response is sinusoidal and shares the same harmonic with \(\gamma_0\), shifted only by a phase angle. Material response is represented by the first or fundamental harmonic of a Fourier series. Another rheometric technique to probe linear viscoelasticity is shear creep and recovery test (Fig. 2.2a). This technique consists in loading and unloading step stresses for longer time scales to probe the associated relaxation phenomena (Macosko, 1994; van den Tempel, 1961). Linear viscoelasticity can be captured by a standard four-parameter Burgers model, which comprises a Maxwell model (spring and dashpot in series) coupled to a Kelvin-Voigt model (spring and dashpot in parallel) (Steffe, 1996) (Fig. 2.2b). In the Burgers model, the compliance function \(J(t) = \gamma(t)/\tau_0\) during the creep (a) and recovery (b) is described by the following equations:

\[
J(t) = \frac{t_c}{\mu_0} + \frac{1}{G_0} + \frac{1}{G_1} \left[1 - \exp\left(-\frac{t_c}{\lambda_1}\right)\right] \quad \text{Creep Eq. (2)}
\]

\[
J(t) = \frac{t_c}{\mu_0} + \frac{1}{G_1} \left[1 - \exp\left(-\frac{t_c}{\lambda_1}\right)\right] \exp\left(-\frac{t_r-t_c}{\lambda_1}\right) \quad ; \quad t_r > t_c \quad \text{Recovery Eq. (3)}
\]
Where $t_c$ and $t_r$ are the creep and recovery times, respectively, $G_0$ and $\mu_0$ are the elastic modulus and viscosity of the Maxwell element, $G_1$ and $\mu_1$ are similar parameters in the Kelvin-Voigt element and $\lambda_1 = \frac{\mu_1}{G_1}$ is the characteristic retardation time. Note that $G_0$ and $G_1$ are equivalent to instantaneous $J_0$ and retarded compliances $J_1$ as $J = 1/G$ in the LVR. Although incrementing the number of Kelvin-Voigt elements is necessary for describing a complex spectrum of retardation times, this increases the phenomenology of the model (Blair and Burnett 1959). From a practical standpoint, the elastic shear modulus correlates well with textures attributes such as fat hardness and consistency (Narine and Marangoni 1999b).

![Figure 1.2](image)

**Figure 1.2** (a) Creep and recovery curve of laminating and all-purpose shortenings. Dotted gray lines indicate viscoelastic parameters and time intervals used by the Burgers model (b)

### 2.4.2 Linear viscoelasticity and microscopic modelling approaches

The microstructure is critical in determining the mechanics of deformation of fats (DeMan and Beers 1987; Thareja 2013; Marangoni et al. 2012). Many rheo-physical models have been put forward ranging from the very reductionist linear chain model (van den Tempel, 1979) to the more comprehensive fractal model (Narine and Marangoni 1999b), to link the microstructure to the linear viscoelastic properties of the network (Tempel 1979; Vreeker et al. 1992; Heng et al.
The fractal model exploits the framework of fractal theory to describe the fat network as a collection of self-similar flocs or clusters that result from particle aggregation (Vreeker et al. 1992; Marangoni and Rousseau 1996; Narine and Marangoni 1999a). Above the critical volume fraction ($\phi_{c} \approx 0.05-0.10$), flocs grow enough as to overlap and give rise to the elastic-like character of the network. The elasticity of system scales as a function of volume fraction ($\phi$) or solid fat content (SFC/100) in two distinct regimes. These regimes include the strong-link regime and the weak-link regime (Marangoni and Rousseau 1996; Narine and Marangoni 1999a). The strong-link regime occurs at lower particle concentration ($\phi<0.1$) where each individual cluster grows large, and the elasticity of the flocs rather than that of the links, dictates the elastic modulus of the system ($G'$):

$$G' \sim \phi^{[(d+x)/(d-D)]} \text{ Eq. (4)}$$

Where $d$ is the Euclidean dimension of the embedding space (usually 3), $D$ is the fractal dimension, which describes spatial distribution, “compactation” and morphology of the network, $x$ is the backbone fractal dimension (≈1-1.3). It is also noteworthy that the fractal dimension provides information on the aggregation mechanism of the network, e.g. $D=1.75$ for DLCA and $D=2.1$ for RLCA (Narine and Marangoni 1999e). The weak-link regime occurs at higher particle concentration ($\phi>0.1$), characteristic of most model systems and commercial fats. Here, small clusters behave as rigid or strong springs and the links among clusters or microstructures govern the elasticity of the system:

$$G' \sim \phi^{1/(d-D)} \text{ Eq. (5)}$$

An additional pre-exponential factor $\lambda = \frac{A}{\pi a d_0^2}$ may be introduced to the weak-link relationship to discern among crystal networks showing similar $D$ and $\phi$ but different $G'$ (i.e. cocoa butter and salatrim) (Narine and Marangoni 1999d). In the pre-exponential term, $A$ corresponds to the Hamaker’s constant, $a$ to the dimension of the primary crystal unit and $d_0$ to the intercluster distance (Narine and Marangoni 1999b). The weak-link fractal model may be used to estimate the Young modulus ($E=\sigma/\epsilon$) (Marangoni, 2000). Furthermore, the elasticity of some fat systems may show no power-law dependence due to stress localization in a small fraction of the network connections which serve as “weakest bonds” (Tang and Marangoni 2007). For this case, a
modified fractal model accounts for separate effects of the network microstructure, stress distribution and interconnectivity as follows:

\[ G' \sim \phi_e^{1/(d-D)} \]  
Eq. (6)

Where the effective volume fraction of solids responsible for stress-bearing is \( \phi_e = 1 - e^{-k\phi_b} \) and \( k \) and \( b \) are constants. For complete reviews of the network mesoscopic models, the readers are referred to Narine and Marangoni (1999d), and Tang and Marangoni (2006).

2.4.3 Nonlinear viscoelasticity

Under increasing deformations, interlink bonds start to break, triggering yielding of the crystal network which switches gradually from solid-like to liquid-like behavior (Marangoni and Rogers 2003). Yielding as related to strain and stress, is dependent on solid volume fraction, particle size, fractal dimension of the network, among other parameters (Marangoni and Rogers 2003). Despite of much debate about the existence of a “true” yield stress, the yield stress remains a valuable parameter in the rheological characterization of fats and other pasty materials (Coussot, 2007). As yielding takes place, fats display rich nonlinear viscoelastic responses (i.e., network softening and structural reversibility) which shall be investigated in depth, as these features pose enormous relevance in the usability of fats (Blair 1954; Thareja 2013; Sone 1961; Macias-Rodriguez and Marangoni 2016b). A survey of the literature reveals that most of the published work on nonlinear viscoelasticity involves more empirical methods that measure texture attributes than fewer fundamental methods that characterize true material properties. In what follows, we describe both types of approaches and place special emphasis on large amplitude oscillatory shear (LAOS) rheology as a novel and emerging technique to measure nonlinear viscoelasticity of fat crystal networks.

2.4.3.1 Empirical methods

Major empirical methods include indentation or penetration tests that assess viscoelastic texture attributes such as hardness or firmness, “yield” value and spreadability of butter, margarine, shortenings and other fatty products (Blair 1954; Haighton 1959; DeMan and Beers 1987). Falling rods or balls measured hardness of butter and margarine as correlated to their temperature and melting (Scott Blair, 1954). Penetration with standard cones includes the official method of
the American Oil Chemists’ Society (AOCS Cc 16-60) to evaluate fat texture, which deserves special attention (Haighton, 1965). This method employs constant load or constant speed cone geometries with variable or no truncation, to penetrate a fat sample. Depending on the specifics of the test, several empirical relationships have been developed to calculate textural attributes. For example, hardness index $HI = W/p$ and “yield value” $C = KW/p^n$, where $W$ is the cone weight, $p$ is the penetration depth, $K$ is a cone constant dependent on angle, and $n$ is an arbitrary material constant equal to 1.6 for margarine, butter and shortenings (Haighton 1959; deMan et al. 1989; deMan, et al. 1991; Shen, et al. 1991; Hayakawa and deMan 1982). The intended use of shortenings and margarines can be differentiated based on these parameters, although that is not always necessarily the case (Haighton 1959; Macias-Rodriguez and Marangoni 2016a).

Despite the economy and simplicity of this method, several considerations should be borne in prior to using the cone penetrometer. For instance, whether hardness is measured remains debatable, considering the definition of ‘hardness’ as “the resistance of the surface of a body to penetration”. In the same manner, the concept of “yield value” is ill-defined and possibly, it is far from the true yield stress by several orders of magnitudes, considering the intuitively larger shear deformations associated specially with “pointy” or small-angle cones (Atkins and Tabor 1965).

Our reservations to this method are justified by previous correlations of cone penetrometer parameters with spreadability of butter and margarine, a property involving extensive shear deformations and structural breakdown (Haighton 1959; Haighton 1965; Shama and Sherman 1970).

Some other methods to determine hardness and spreadability include the Mohr and Wellm’s cone- and sphere- yield tests, Trouton measure of sagging of a beam fastened at its ends, uniaxial compression and imitative tests (Texture Profile Analysis: TPA) (Scott Blair, 1954; Szczesniak, 2002). Previous studies have shown that the hardness obtained from compression does not necessarily correlate with that from cone penetrometry. Finally, one of the most subjective methods is the so-called “thumb” test that relies on the capability in discriminating textural properties such as firmness, recovery and plasticity of fats by purely tactile sensitivity (Cavillot et al., 2009; Garcia-Macias et al., 2012, 2011; Pajin et al., 2011).

2.4.3.2 Fundamental methods

Much of the fundamental work in fat rheology involves capillary flow, creep and recovery tests, uniaxial compression, steady-shear tests, oscillating viscometry and parallel-plate plastometry,
steady-shear tests. Capillary tests measure steady shear viscosities and closely resemble manufacturing processes of soft solids, i.e. pipe flow, paste-ram or cold extrusion (Castro et al., 2010; Macosko, 1994). A capillary rheometer uses gravity, compressed gas or driving tools such as a piston ram to exert pressure and force the material through a barrel and die with diameters $D_0$ and $D$, respectively (Macosko, 1994). During this operation, pressure drops are recorded, and used along with the flow rate of the tube to determine steady shear viscosities. Previous reports showed that thin fat layers and hardened peanut oil flowing through capillaries display either simple or anomalous nonlinear behavior (Scott Blair, 1954). True fluids hold linear relationship between shear stress $PR/2L$ and shear rate $4V/\pi R^3$ at the wall when flowing through a capillary with radius $R$ and length $L$ under pressure $P$. It was found that the most hardened peanut oil mixtures behave as Bingham plastic fluids, obeying the Buckingham-Reiner expression, 

$$V = \frac{\mu R^4}{8L} \left( P - \frac{4}{3} p + \frac{p^4}{3P^3} \right),$$

where $\mu$ corresponds to the linear slope of the curve and $p$ to the yield value below which there is a plug flow (Scott Blair, 1954).

Creep and recovery tests for standardized times, stress loads or deformation loads showed that butter and margarine has elastic recoverable and plastic non-recoverable components from which elastic moduli and viscosity were determined. Successive experiments with increased stresses suggested a type of stress softening (fall in viscosity) in butter, whereas experiments with increased strains pointed out to a type of strain-hardening (rise in viscosity) in butter and 25% glycercyl tristearate in oil (Blair 1954; van den Tempel 1958). Experiments on the effects of work-softening, loading creep phase and temperature revealed that butter recovered more of its instantaneous elasticity and less of its Newtonian viscosity during aging compared to margarine. This was apparently due to higher shear sensitivity of margarine given a larger proportion of irreversible bonds originally present in the network (Shama and Sherman 1970). Increased stress and loading time decreased more the instantaneous elasticity than the retarded elasticity and viscosity, whereas increased temperature strongly diminished all viscoelastic parameters (deMan et al. 1985). Uniaxial compression tests revealed similar strain-hardening at rising true strains $\varepsilon = 4\%$, followed by strain-softening and ideal plastic response at larger deformations (Gonzalez-Gutierrez and Scanlon 2013).

Steady shear experiments demonstrated that margarines failed to follow the so-called Cox-Merz “rule” that implicates correspondence between steady state viscosity $\eta$ and complex viscosity $\eta^*$
(Bistany and Kokini 1983). However, evidence of slip, edge fracture, transients and thixotropic effects affecting the reproducibility of the test and the steady state data were not ascertained in this report. Oscillating viscometry and parallel plate plastometry indicated thixotropic behavior of butter and margarine as measured by the decrease of viscosity, elasticity and yield value after kneading and their subsequent recovery after prolonged setting time. Rupture and recovery were attributed to crystal melting and recrystallization of the network (Sone, 1961).

Although some of the abovementioned methods, both empirical and fundamental, provide useful information on the nonlinear viscoelasticity of fats, they have many inherent limitations. For example, uniaxial compression allows only calculation of apparent elastic modulus and viscosity. Moreover, the elastic modulus cannot be precisely determined below 2% as is the case for most fat systems, while the viscosity is subject to large errors after yielding (Kloek et al. 2005; Gonzalez-Gutierrez and Scanlon 2013). Shear creep or stress relaxation impose sudden and large displacements providing inhomogeneous and uncontrolled flow. Steady shear gives an indication of shear-sensitivity, formability or shaping of fat during processing, nevertheless; fats may not fully relax to a steady state and may slip at the shear-rates imposed by these tests. Likewise, empirical test such as cone penetrometry, useful for drawing correlations at best, suffer from lacking a sound theoretical foundation and do not measure clearly defined physical properties. Therefore, there is an obvious need to adapt novel rheological techniques that provide true criteria relatable to the macroscopic functionality of fats during nonlinear deformations.

To address this gap, recent work in our laboratory has explored the use of large amplitude oscillatory shear (LAOS). Lately, there has been growing scientific interest on LAOS which has proven extremely useful, to understand mechanical functionality of a variety of polymeric, colloidal and biological materials, indistinguishable by SAOS (Ewoldt et al., 2007; Hyun et al., 2011; Petekidis, 2014). Fig. 2.3 provides a striking example of the shortcomings of the traditional SAOS test, and motivation for adapting the LAOS protocol. While the viscoelastic moduli $G'_1$ and $G''_1$ remain unremarkable in the LVR, these material functions depart drastically outside the LVR, e.g. $G'_1$ and $G''_1$ shows a steady decrease for laminating shortening, whereas $G'_1$ and $G''_1$ display abrupt drop and backward bending for all-purpose shortening, evoking strong softening and catastrophic failure for the latter.
Figure 1.3 (a) Elastic $G'$ and viscous $G''$ moduli as a function of stress as procured from a strain amplitude sweep ($\gamma_0=0.01-100\%$, $\omega=3.6$ rads$^{-1}$). (b) Stress versus strain plots of laminating and all-purpose shortenings. Inset denotes ideal ductile and brittle solid behavior.

These features are also captured in the strain-stress plots, e.g. the local slope, reflecting the stress increase per increment of applied strain, appears steeper for an all-purpose than for a laminating shortening. Likewise, an all-purpose shortening shows a strong peak overshoot ensued by marked decay of stress, whereas a laminating shortening exhibits a stress plateau. Similar behavior has been previously reported in compression and imitative large deformation tests where a fat is deemed plastic if the required stresses at low amplitudes and large amplitudes are comparable, and a fat is regarded work-softened if the required stress at low amplitudes is higher.
than that of at large amplitudes (de Bruijne and Bot, 1999; Heertje, 1993). Currently, a protocol for easily characterizing fat materials with this type of behavior lacks.

Large amplitude oscillatory shear rheology offers many advantages over traditional methods including simultaneous viscoelastic characterization in both deformation and timescale domains, controlled flow, ample operational window, superior sensitivity and several frameworks for data interpretation (Hyun et al., 2011). LAOS enables varying two parameters independently: the amplitude of the deformation $\gamma_0$ and frequency $\omega$ of deformation, rendering a two-dimensional regime map-space known as the Pipkin space (Pipkin, 1972). The Pipkin space relates viscoelastic responses as a function of loading amplitudes, shear rates and timescales of relaxation (Pipkin, 1972). It also seamlessly connects nonlinear viscoelastic measures $G'(\omega, \gamma_0)$ and $G''(\omega, \gamma_0)$ with linear viscoelastic moduli $G'(\omega)$ and $G''(\omega)$, and with the steady flow viscosity $\eta(\dot{\gamma})$ (Dealy and Wissbrun 1999; Ewoldt and Bharadwaj 2013). LAOS generates relatively controlled flow allowing for probing weakly-bonded and stiff materials such as high-volume fraction fats that fracture, slip, and migrate out of the gap during steady shear (Hyun et al., 2011). It provides a wider deformation window due to improved resolution as deformation inputs are extended to medium and high amplitudes. Hence, LAOS is able to discriminate among structural architectures, which are insensitive to SAOS (Hyun et al., 2011). This is particularly advantageous for fats due to their restricted linear envelope. Substantial improvement on the signal-to-noise ratio, two to three orders of magnitude higher than former work on polymer rheology ($S/N \approx 10^2$), has been achieved due to improvements in state-of-the-art hardware and software (i.e. more sensitive torque transducers, oversampling techniques, accessible computational power and special FT algorithms) (Hyun et al., 2011). Likewise, a wide variety of frameworks have been proposed to quantify the nonlinear viscoelastic response including Lissajous-Bowditch curves, Fourier Transform (FT), stress-Chebyshev decomposition method, power-function expansions, time-dependent moduli, among others (Wilhelm 2002; Ewoldt et al. 2008; Rogers et al. 2011; Rogers 2012).

2.4.4 Large amplitude oscillatory shear fundamentals

At large amplitudes (LAOS), complex and nonlinear shear stress responses arise in many viscoelastic materials including fats. For a strain input test, the stress material response is considered nonlinear when either of the viscoelastic moduli are variant to changes in $\gamma_0$, e.g.
$G'(\omega, \gamma_0)$ or $G''(\omega, \gamma_0)$ or when the response is no longer sinusoidal. As a result, $G'$ and $G''$ lose their mathematical and physical underpinnings in this region (Hyun et al. 2011; Ewoldt et al. 2008).

### 2.4.4.1 Nonlinear stress waveforms

![Figure 1.4](image)

**Figure 1.4** (a) Stress (full black lines) and strain (dotted gray lines) waveforms versus time. Raw Lissajous-Bowditch plots of (b) stress versus strain (elastic representation) and (c) stress versus shear rate (viscous representation). The gray lines correspond to transients. Whereas the solid black lines represent the steady state data. (d) frequency-domain Fourier spectra. The data on the top row were collected in the SAOS regime ($\gamma_0$), whereas the data on the down row were obtained in the LAOS regime ($\gamma_0=10\%$), for a laminating shortening at T=16 °C.

Nonlinear sinusoidal waveforms represent the most simple way to qualitative detect and interpret nonlinear data. They may be presented in the form of time-domain signals $\tau(t)$ or in two-coordinate axes figures referred as to Lissajous-Bowditch curves. Lissajous-Bowditch curves are orbital trajectories of $\gamma_0$ on the abscissa and $\tau(t)$ on the ordinate (elastic representation) or $\dot{\gamma}_0$ on the abscissa and $\tau(t)$ on the ordinate (viscous representation).

As an illustration, Fig. 2.4 shows the stress response in the time domain and elastic and viscous perspectives of the Lissajous-Bowditch curves within the LVR and outside the LVR for a commercial shortening. In the LVR region ($\gamma_0= 0.01\%$), the shape of the stress remains as a perfect sinusoid, whereas the Lissajous-Bowditch plots appear as ellipsoids where the tangent
slope corresponds to \( G' \) and the area enclosed by the ellipsoid represents \( G'' \). Outside the LVR, the stress signal becomes distorted leading to non-ellipsoidal rectangular Lissajous-Bowditch curves that enclose larger areas (Ewoldt et al., 2008; Hyun et al., 2011). With the aid of the Lissajous-Bowditch curves, typical features, i.e. global strain softening of the network, and additional features obscured by the average viscoelastic moduli, i.e. local strain stiffening, are revealed. Global or average elastic softening, is manifested as the intercycle clockwise rotation in slope of the stress-strain curve at strain minima \( \gamma_0=0 \) (where strain rate \( \dot{\gamma} \) is at maxima) toward the strain-axis. Local strain stiffening is clearly visible as the intracycle upturn of the shear stress at strain maxima \( \gamma_0=\text{max} \) (where \( \dot{\gamma}=0 \)). Stress overshoots, akin to those generated during steady shear flow, indicate substantial disruption of the microstructure. The reversibility of the stress overshoot within the period of oscillation evokes microstructure “healing” or thixotropy (Renou et al. 2010; Kim et al. 2014; Ewoldt and McKinley 2009) as previously reported for margarines and commercial shortenings (Sone 1961; Macias-Rodriguez and Marangoni 2016b).

2.4.4.2 Fourier transform (FT) rheology

Although Lissajous-Bowditch curves provide a physical picture of nonlinear viscoelastic responses, they do not provide any quantitative parameter describe such responses. Fourier transform (FT) rheology constitutes the foremost method for quantifying nonlinear responses (Wilhelm 2002). In FT rheology, the time-varying stress signal is expressed in a frequency-domain Fourier space encoding components that are in-phase and out-of-phase with the strain input (Dealy and Wissbrun 1999; Giacomin and Dealy 1993). For a sinusoidal strain input \( \gamma(t)=\gamma_0 \sin(\omega t) \), the Fourier series of the stress response is represented as follows:

\[
\tau(t) = \gamma_0 \sum_{n=1}^{\infty} \left[ G_n'(\omega, \gamma_0) \sin(n \omega t) + G_n''(\omega, \gamma_0) \cos(n \omega t) \right] \quad \text{Eq. (7)}
\]

Where \( n \) captures higher-order harmonics in the expansion which equals an integer number of the excitation or fundamental frequency in the nonlinear regime and reduces to \( n=1 \) in the linear region (Fig. 2.4 \( \gamma_0=0.01 \% \)), with its corresponding real and imaginary coefficients represented by the generalized storage and loss modulus \( G_n' \) and \( G_n'' \) \((n=1, 2, 3\ldots)\), respectively (Wilhelm, 2002). Higher-order harmonics are ideally odd due to non-negativity of the stored energy although even harmonics may appear in the signal and may be associated with nonperiodic or transient responses (Christensen 1982; Ewoldt and Bharadwaj 2013). To quantify the nonlinear
viscoelastic response, normalized intensities of the leading-order 3rd harmonic ($I_{3/1}$) or total Harmonic Distortion are typically used in combination with first-harmonic moduli as reported by the rheometer ($G_1', G_1''$). The use of the first-harmonic moduli is arbitrary although it provides some meaningful information (Hyun et al. 2011; Ewoldt et al. 2008). Depending on the strain-dependence of $G_1'$ and $G_1''$, nonlinear response of complex materials is classified into four groups: type I, strain thinning ($G_1'$ and $G_1''$ decreasing); type II, strain hardening ($G_1'$ and $G_1''$ increasing); type III, weak strain overshoot ($G_1'$ decreasing, $G_1''$ increasing followed by decreasing); type IV, strong strain overshoot ($G_1'$ and $G_1''$ increasing followed by decreasing) (Hyun et al., 2002). It has been observed that fats yield without and with weak or strong local maxima, that is fats show type I, type III and type IV behavior depending on their formulation and processing regimes (Macias-Rodriguez and Marangoni 2016b).

2.4.4.3 Chebyshev decomposition method

Although FT-rheology spectra offers a simple and mathematically-robust method for characterizing material nonlinearities, higher harmonics do not lend any physical insight. In the last decade, there has been significant progress in the development of mathematically- and physically- sound frameworks for analyzing LAOS responses such as the Chebyshev stress-decomposition method and the time-dependent moduli to measure a sequence of physical processes, being the former one of the most generalized methods (Ewoldt et al. 2008; Rogers 2012). In the following theoretical description of the Chebyshev stress-decomposition method for LAO-Strain protocol, we refer to the pioneering works of Cho et al. (2005) and Ewoldt et al. (2008). The Chebyshev stress-decomposition extends the so-called geometrical interpretation method originally introduced by Cho et al. (2005). The Chebyshev stress-decomposition overcomes two major shortcomings of this work. First, it provides a unique description of the decomposed stress signal by mutually-orthogonal first-order Chebyshev polynomials. Second, it defines unequivocal material parameters for quantifying nonlinear viscoelasticity, which reduce to the conventional linear viscoelastic moduli in the LVR (Ewoldt et al. 2008). In brief, the total stress response is expressed as the sum of the elastic $\tau'(x)$, where $x = \gamma / \gamma_0 = \sin \omega t$ and viscous stresses $\tau''(y)$, where $y = \dot{\gamma} / \dot{\gamma}_0$, based on the idea that $\tau'$ and $\tau''$ are odd functions of $x$ and $y$, respectively. Unlike the closed loops observed in the Lissajous-Bowditch projections, the decomposition of the total stress renders single-valued functions of strain and strain-rate, respectively, and relates to the Fourier series as follows:
\[
τ' \equiv \frac{τ(γ, \dot{γ}) - τ(-γ, \dot{γ})}{2} = γ₀ \sum_{n \text{ odd}} G'ₙ(ω, γ₀) \sin n \omega t \quad \text{Eq. (8)}
\]

\[
τ'' \equiv \frac{τ(γ, \dot{γ}) - τ(-γ, -\dot{γ})}{2} = γ₀ \sum_{n \text{ odd}} G''ₙ(ω, γ₀) \cos n \omega t \quad \text{Eq. (9)}
\]

The elastic and viscous stress components can then be described unambiguously by orthogonally-integrable Chebyshev polynomials of the first kind over the finite domain [-1, +1] as:

\[
τ'(x) = γ₀ \sum_{n \text{ odd}} eₙ(ω, γ₀)Tₙ(x) \quad \text{Eq. (10)}
\]

\[
τ'(y) = γ₀ \sum_{n \text{ odd}} vₙ(ω, γ₀)Tₙ(y) \quad \text{Eq. (11)}
\]

Where \(Tₙ(x)\) and \(Tₙ(y)\) correspond to \(n\)th-order of the Chebyshev basis functions, \(γ₀\) and \(\dot{γ}_₀\) represent the maximum in-cycle strain and shear rate, and \(eₙ(ω, γ₀)\) and \(vₙ(ω, γ₀)\) refer to the elastic and viscous Chebyshev coefficients of order \(n\). The generic form of the Chebyshev polynomials of the first kind is given by \(T_{n+1}(x) = 2xTₙ(x) - T_{n-1}(x)\). The Chebyshev coefficients are directly related to the higher order Fourier coefficients in the time-domain as:

\[e^n = G'_n(-1)^{(n-1)/2}\] and \[v^n = G''_n/ω = η''_n\], respectively. The \(n\) order is odd as even Fourier coefficients are neglected since they lack a clear physical foundation as stated earlier. Just as the third-order Fourier harmonic, the third-order Chebyshev basis function hints the onset of nonlinearity in addition to assign physical meaning to the nonlinear stress signal. Material functions \(G'_1\) and \(G''_1\) denote average stress responses equivalent to first-order Chebyshev coefficients as \(e₁ → G'_1\) and \(v₁ → η''_1 = G''_1/ω\) in the LVR given that effective higher-order contributions tend to zero. When higher-order Chebyshev coefficients become significant, the elastic and viscous stresses set along the strain and strain-rate axis respectively, changing gradually to non-straight lines (i.e., bend upward or downward). Based on the sign of the leading higher-order harmonic, the local stress response is interpreted as intracycle strain stiffening \((e₃>0)\) or strain softening \((e₃<0)\) and intracycle strain-rate thickening \((v₃>0)\) or strain-rate thinning \((v₃<0)\), respectively. It is noteworthy that \(G'_1\) and \(G''_1\) dominate by far the nonlinear response, and that the combination of these average measures with local measures provide the best information to infer on microstructural features of materials. Ewoldt and Bharadwaj (2013), recently demonstrated that the sign of the leading-order Chebyshev coefficients reveals the input function, e.g. strain or rates-of-strain, that drives the average elastic and viscous responses. For
fat crystal networks, negative- global elasticity and global viscosity \((e_1<0, v_1<0)\) coupled with positive intracycle elasticity \((e_3>0)\) and negative intracycle viscosity \((v_3<0)\), indicate that average- elastic softening and viscous thinning are driven by large instantaneous strain rates, respectively.

To capture local elastic- and viscous- effects at minimum- and large- instantaneous strains or rates-of-deformation, the following meaningful nonlinear metrics have been proposed by Ewoldt et al. (2008):

\[
G_M' \equiv \frac{dx}{d\gamma} = \sum_{n:odd} nG'_n = e_1 - 3e_3 + \cdots, \text{ Eq. (12)}
\]

\[
G_L' \equiv \frac{\tau}{\gamma} = \sum_{n:odd} G'_n (-1)^{(n-1)/2} = e_1 + e_3 + \cdots, \text{ Eq. (13)}
\]

\[
\eta_M' \equiv \frac{dx}{d\dot{\gamma}} = \frac{1}{\omega} \sum_{n:odd} nG''_n (-1)^{(n-1)/2} = v_1 - 3e_3 + \cdots, \text{ Eq. (14)}
\]

\[
\eta_L' \equiv \frac{\tau}{\dot{\gamma}} = \frac{1}{\omega} \sum_{n:odd} G''_n = v_1 + v_3 + \cdots, \text{ Eq. (15)}
\]

Where \(G_M'\) is the minimum-strain or tangent modulus at \(\gamma_0=0\) and and \(G_L'\) is the large-strain or secant modulus at \(\gamma_0=\gamma_{\text{max}}\). Likewise, \(\eta_M'\) is the minimum-rate viscosity and \(\eta_L'\) is the large-rate viscosity. These deliberately-chosen material functions reduce to \(G_1'\) and \(G_1''\) \((\eta'=G_1''/\omega)\) in the linear regime. A graphical depiction of these measures in the elastic and viscous Lissajous-Bowditch projections is shown in Fig. 2.5. Alternatively, relative differences between elasticity and viscosity at large- strain or shear-rates and at minimum strains or shear-rates are captured by adimensional strain stiffening \(S \equiv \frac{G_L'-G_M'}{G_L'}\) and shear thickening \(T \equiv \frac{\eta_L'-\eta_M'}{\eta_L'}\) ratios. For simple linear viscoelastic responses, \(S, T=0\). For nonlinear responses, \(S, T>0\) indicates intracycle- strain stiffening and shear-thickening and \(S, T<0\) corresponds to intracycle- strain softening and shear-thinning. Moreover, nonlinear rheological material functions have been described for a LAOSTress protocol (Dimitriou et al., 2013).
Figure 1.5 Definitions of material measures as proposed by (Ewoldt et al., 2008), for reporting viscoelastic moduli: (a),(b) elastic moduli and dynamic viscosities, respectively, for a model linear viscoelastic response at \( \{ \omega = 3.59 \text{ rad s}^{-1}, \gamma_0 = 0.01 \} \); (c),(d) elastic moduli and dynamic viscosities, respectively, for a nonlinear viscoelastic response at \( \{ \omega = 3.59 \text{ rad s}^{-1}, \gamma_0 = 1.34\% \} \). The first harmonic moduli are shown for comparison. In the linear regime [(a),(b)] all measures are equivalent to the linear viscoelastic moduli. A nonlinear material response [(c),(d)] will result in different values for each material measure. All the shown data were measured for an all-purpose shortening at T=16 °C.

2.4.4.4 LAOS Data collection

Several experimental considerations shall be borne in mind when performing LAOS experiments including the data collection method, the type of experiment, e.g. strain control versus stress-control tests, and potential challenges arising during shear experiments. LAOS requires the collection of raw oscillatory waveforms which is typically achieved by two ways. The first
involves collecting strain stress signals using standard capabilities included in commercial rheometers software (i.e., *TA Orchestrator* software, *Raw data LAOS* waveform) (Ewoldt et al. 2008; Läuger and Stettin 2010). The second consists in installing additional hardware that allows collection and conversion of analog voltage outputs of torque and motor displacements into digital signals using an analog-to-digital converter (ADC) card (Wilhelm, 2002). Although the latter approach confers superior sensitivity, we favor the former as it provides adequate sampling rates, signal-to-noise ratios, and does not require extra instrumental setup as highlighted by Ewoldt et al. (2008).

The selection between strain- and stress- controlled protocols is influenced by three main factors (Ewoldt, 2013). First, the rheometer design constrains performance and sensitivity under stress or strain control mode. Second, the processing application supports the type of test. Third, the framework used for data reduction, analysis, and the application of structure-rheology models to the data (when applicable) determine the type of test. Considering these factors, we opted to use LAOStrain experiments for investigating the rheological behavior of fats in lamination-like conditions. Slight increments in the stress input (LAOStress) would lead to substantial jumps in strain deformation, given the shear-sensitivity of the fat microstructure (Läuger and Stettin 2010). During rolling, fat is also subject to drag flows depending on the speed (or frequency) of the rotating cylinders, deformations which can be mimicked using LAOStrain. Therefore, LAOStrain seems suitable for characterizing material functions. The use of LAOStrain experiments make it also possible to analyze our data by the well-developed Chebyshev stress decomposition method (Ewoldt et al. 2008).

2.4.5 Experimental difficulties in shear rheology

Rheological experiments can be plagued by several artifacts that obscure differences on mechanical behavior of materials or inform false mechanical behavior at worst. Therefore, it is necessary to offer a basic overview of technical difficulties encountered in shear rheology and provide diagnosis and remedies to some of these “bad symptoms”. It is our purpose to raise awareness among practitioners of these issues, so they consider them when conducting rheology of fatty materials. For a comprehensive description on these and other experimental challenges, the reader is referred to the excellent treatise of Ewoldt et al. (2015), from which this section is built upon. Experimental issues include but are not limited to: instrumental inertial, slip at
boundaries, gap setting and gap underfilling, edge fracture and other intrinsic nonlinearities attributed to the measuring geometry or instrument (Ewoldt et al. 2015).

Rheometric inertia occurs due to unsteady motion at the moving boundary where both load and displacements are simultaneously measured, which is the case for most rheometers. Instrument leads to measured torque ($T$) signal associated not only with material deformation but also with instrument acceleration during unsteady motion. This effect may be neglected as long as $T_{\text{material}} > T_{\text{inertia}}$ (typically the case of most fat systems), but in any case may be diagnosed by checking the raw phase ($0^\circ < \delta < 90^\circ$) at high frequencies, or identifying damping oscillations within short-time creep responses from which the viscoelastic moduli can be calculated (Ewoldt et al. 2015). Slip is a prevalent artifact largely overlooked in the rheological characterization of fat-based materials. It is plausible that the self-lubricated nature of fats prevent them from sticking firmly to the contacting boundaries. Key symptoms of slip include gap-dependence of apparent stress and shear-rate, reduced flow stress, and if present strongly, it can be visually observed as “free” motion of the contacting surfaces or migration of the sample outside the measuring gap (Ewoldt et al. 2015; Zhong and Wang 2003). Fig. 2.6 depicts the effect of slip in the rheology of a water-in-oil emulsion (Nivea Lotion) and a cake shortening during steady shear and LAOS tests, respectively. For the first case (Fig. 2.6a), the data that superposes for all gaps for roughened plates confirms the absence of slip, while the data that shifts to higher apparent strain rates for increasing gaps for smooth plates lends evidence of slip (Ewoldt et al. 2015). For the second case (Fig. 2.6b), the data that display an increase followed by a decrease of intracycle strain-stiffening, as measured by $(G'_{\text{L}}-G'_{\text{M}})/G'_{\text{L}}$, indicate absence of slip, whereas the data that show inconsistent strain-stiffening behavior signals to wall slip. Some of the approaches to check for and minimize slip include collect data at different gaps, modifying measuring geometries, assessing sample adhesion to different contacting boundaries such as sandpaper (the most typical), crosshatched plates, filter paper (like in our example), grooves or “cleats” (Ewoldt et al. 2015; Macosko 1994; Castro et al. 2010).
Figure 1.6 (a) Wall slip on a smooth surface and elimination of wall slip on a sandpapered surface, respectively, for a water-in-oil emulsion (Nivea Lotion) tested using parallel plates of diameter $D = 40$ mm at multiple gaps $h = 450$–1050 µm. Adapted from Ewoldt et al., (2015). (b) Wall slip on a custom sandblasted surface and absence of wall slip on a filter-paper surface, respectively, in a cake shortening using parallel plates of diameter $D = 20$ mm at a fixed gap $h = 1300$ µm.

Errors due to gap setting, edge fracture, gap under-filling are equally important during shear rheological characterization. For smaller gaps, apparent viscosity may decrease due to gap offset between the calibrated gap (smaller) and the true gap. For larger gaps, the offset condition may be mitigated if smaller radius plates are used although this comes to the expense of lower-torque boundary. For larger gap, there is also higher probability of edge failure (i.e. migration outside gap, edge fracture) and heterogeneous deformation (i.e. plastic deformation) especially for viscoelastic materials and pasty materials such as fats during nonlinear tests. Edge fracture is particularly relevant to stiff fats (i.e. cocoa butter) and can be detected by visually monitoring the edge of the sample and noticing the reduction of the apparent stress due to decrease of effective contact area or gap dependence of the data (Zhong and Wang 2003). Overall, edge effects seriously limit the shear rate (or strain) window. Regarding gap setting, it is recommended that $D/h$ (Diameter/gap height) be in the range of 10-50 (Macosko, 1994). Sample overfilling or underfilling greatly affect the measured torque as dependent on radial contact $T\sim(1/R^3)$ of the samples with the plate boundaries (Macosko, 1994). Underfilling due to contraction may arise during formation of the volume-filling network of fats, or sol-to-gel transition of organogels. It can be evidenced as the development of a large negative normal force and leads to erroneous estimation of network elasticity $G'$. Viable ways to eliminate this issue include applying zero normal force control during crystallization or using internal gap adjustment procedures to

Finally, geometry configurations, intrinsic system nonlinearities and transients affect the reproducibility of rheometric data. Certain geometries such as parallel plate significantly weakens the relative intensity of the higher harmonic components or simply introduces qualitative artifacts (Ewoldt et al. 2010; Giacomin et al. 2015). These effects are attributed to the non-affine deformation field inherent to plate-plate geometry as typically only the sample located at the periphery experiences the highest shear-rate amplitude (Macosko, 1994). Likewise, instrumental features such as active deformation control loops and temperature control units (e.g., Peltier and convection-based) can introduce additional nonlinearities (i.e. higher $I_{3/1}$) (Merger and Wilhelm 2014). Finally, non-equilibrium transients effects hinder the application of the LAOS protocol. Some solutions to these issues involve comparing the results obtained from homogenous (e.g., cone-plate) and heterogeneous (e.g., plate-plate) kinematics side-by-side, awaiting sufficient time for thermal equilibration and for decay of transients. For the latter, the moduli can be monitored as a function of time or number of oscillatory cycles. Overlapping and symmetry of the Lissajous-Bowditch curves provide good indication of absence of preferential flow and attainment of steady state (Li et al. 2009).

2.5 Structure and mechanical function of fats: a case study

Here we present a case study where rheometric techniques (especially LAOS) are exploited to discriminate between two classes of rheologically complex fats: roll-in and all-purpose shortenings, and establish function-structure relationships in these materials. The approach used herein is applicable to many other classes of lipid-based materials where functionality and rheology are inherently related.

A roll-in or laminating shortening is a highly functional tough material (strong and ductile) used in the manufacture of croissants, Danish and puff pastry and other such laminates. Roll-in shortening stand out from any other fat since they can be extruded, squeezed and shaped into micron-width films without breaking or losing their deformation. During manufacture of pastries, roll-in shortenings are exposed to strong shear and extensional flows involving rates of deformation of 1-100 s$^{-1}$ and pressures of up to 50kPa (Steffe, 1996). The use of roll-in shortenings in laminated baked goods render crucial processing characteristics such as uniform
sheeting and lamination, optimal bubble formation and lift that result in good sensory attributes such as flakiness and good mouthfeel (Ooms et al., 2015). On the other hand, an all-purpose shortening is used for multiple bakery applications primarily cake and icing and might be even used for the manufacture of laminates. However, it is a fact that an all-purpose shortening does not perform as good as a laminating shortening (Fine et al., 2006). The functionality of a laminating shortening has been explained for a longtime using physicochemical arguments. “Optimal” physicochemical properties have been outlined for this product: $\phi=0.25-0.20$ at $20-30^\circ$C, $T_{\text{melting}}>40^\circ$C, $\beta'$ polymorphism and high “yield value” as determined by cone penetrometry (Ooms et al., 2015). Nevertheless, we have conclusively demonstrated that laminating shortening can share physicochemical properties with other bakery fats shortenings (Macias-Rodriguez and Marangoni 2016a). We have shown that rather the rheology of these materials related to structure, play an essential role in functionality. A further motivation for studying laminating shortenings stems not only from their unique rheological function but also from the fact that these materials are rich in “hard fat” content (30% by weight of combined trans and saturated fatty acids).

To mimic elongational and shear flows during rolling, oscillatory shear experiments sweeping from small (SAOS) to large (LAOS) amplitudes at $\omega=0.1-5.9$ rads$^{-1}$, and capillary rheology were conducted. At a fixed frequency $\omega=3.6$ rads$^{-1}$, similar linear viscoelasticity and strikingly different nonlinear viscoelasticity were observed as earlier mentioned, e.g. laminating shortening behaves as a ductile viscoelastic solid, whereas all-purpose shortening act as a brittle viscoelastic solid. This behavior is in line with the macroscopic appearance of the samples during capillary rheology and compression test. During extrusion, a laminating shortening has the ability to be drawn into continuous fine “threads” (Fig. 2.7a, c), ~1mm of diameter, without fracturing, whereas an all-purpose shortening forms into thicker, less uniform filaments that break easily and support less elongation (Fig. 2.7b). During compression, e.g. the surface of a laminating shortening (Fig. 2.7d) is free of cracks (or at least cracks are invisible within the length scale of observation), while the surface of all-purpose shortening (Fig. 2.7e) is full of cracks.
Figure 1.7 Macroscopic appearance of laminating and all-purpose shortenings. (a) laminating and (b) all-purpose shortening, during capillary flow. (a) and (b) share the same scale bar. (c) “entangled” threads of laminating shortening collected at the exit of capillary rheometer. (d) laminating and (e) all-purpose shortenings, after compression. (d) and (e) share the same scale bar.

To investigate the yielding process and pinpoint differences in material functionality, we interrogate the LAOS response by using a number of analysis techniques including FT rheology, Lissajous-Bowditch curves and Chebyshev-stress decomposition. All shortenings show similar quantitative and qualitative behavior depending on their functionality (Macias-Rodriguez et al., 2017). FT coefficients and material functions determined from stress-decomposition via Chebyshev analysis are reported at a fixed frequency $\omega = 3.6 \text{ rads}^{-1}$ (Fig. 2.9). Regarding Fourier coefficients, the leading-order harmonic $I_{3/1}$ (Fig. 9) rises above $\sim 5\%$ at $\gamma_0 \geq 0.05$, which signals the boundary between linear and nonlinear region and coincides with the mild distortion of the Lissajous waveforms in both samples (Fig. 2.8a). Subsequently, $I_{3/1}$ increases exponentially as a function of strain input and stabilizes to a plateau at $\gamma_0 \approx 10\%$. It is observed that the peak intensity of $I_{3/1}$ is roughly twice higher for an all-purpose shortening than for a roll-in shortening, revealing that a roll-in shortening undergoes a more delayed transition toward the non-linear regime (Fig 2.9) (Macias-Rodriguez and Marangoni 2016b).
Figure 1.8 a) Third-order harmonic of laminating and all-purpose shortenings as obtained from LAOS experiments at $\omega = 3.6$ rads$^{-1}$. b) Shear and elongational viscosity as determined from entrance pressure and pressure drops measured by capillary rheometer.

Elastic and viscous Lissajous-Bowditch curves are depicted in the two-dimensional $\{\omega, \gamma_0\}$ Pipkin (Pipkin, 1972) regime maps (Fig. 2.9). Throughout the frequency range, at $\gamma_0 < 0.09\%$ (not shown), linear viscoelastic responses dictate the stress signal as correlated with ellipsoidal Lissajous-Bowditch curves and linear decomposed elastic and viscous stresses (dotted lines). At $\gamma_0 \geq 0.09\%$, nonlinear viscoelasticity initiate, indicated by nonelliptical curves caused by periodic variations in the total stress. As the strain amplitude keeps increasing, roll-in and all-purpose shortenings display rich nonlinear response in which the elastic Lissajous-Bowditch curves shows stress upturns indicating local strain stiffening for $\gamma_0 \geq 0.57\%$. This is concomitant with the appearance of stress bends at $\dot{\gamma}_{\text{max}}$ invoking viscous shear thinning. The nonlinearity is sufficiently large as to induce self-intersection and formation of secondary loops $\{\omega=3.6, 6$ rads$^{-1}$, $\gamma_0 \geq 6\%\}$, physically related to a material that accumulates new deformations slower than it unloads instantaneous elastic stresses (Ewoldt et al. 2008), and showing strong overshoots such
as an all-purpose shortening (Fig. 2.3). At sufficiently high strains ($\gamma_0 \geq 6\%$), Lissajous-Bowditch curves become increasingly rectangular and larger indicating marked plastic response as more evident in a roll-in shortening. Based on the Lissajous-Bowditch curves, it can be inferred that a laminating shortening presents less degree of softening and thinning than an all-purpose shortening, nevertheless; we shall determine nonlinear metrics that support these observations.
Figure 1.9 Normalized elastic (a, c) and viscous (b, d) Lissajous-Bowditch curves collapsed in a Pipkin space at the corresponding input parameters of frequency and strain-amplitude. Continuous shapes correspond to the total stress, whereas lines contained inside the figures represent the decomposed elastic and viscous stress, respectively. The maximum stress $\tau_{\text{max}}$ in each test is shown above each limit cycle. (a,b) laminating and (c,d) all-purpose shortenings.
Figure 1.10 Nonlinear a) elastic and b) viscous measures for laminating and all-purpose shortenings as calculated from LAOS data at $\omega = 3.6 \text{ rads}^{-1}$. (b) Measures are parametrized by the linear dynamic viscosity $\eta_{LVE}'$ at $\gamma_0 = 0.01\%$, inset shows absolute values.

Intracycles elastic and viscous material functions are shown in (Fig. 2.10). We observe marginal differences in the ratio between large- ($G_M'$) and small- ($G_L'$) strain elastic moduli (Fig. 2.10a) given that fats do not display high elasticity. In contrast, $\eta_M'$ and $\eta_L'$ differ considerably as a function of $\gamma_0$, i.e., the normalized minimum- and maximum- shear rate viscosities of a roll-in shortening were over two times higher than those of an all-purpose shortenings. Therefore, it is concluded that a roll-in shortening experiences substantially more viscous dissipation than an all-purpose shortening, characteristics that are key hallmarks of ductile (roll-in) and brittle (all-purpose) behavior of solids (Macias-Rodriguez et al. 2017). The results of oscillatory rheometry agree with those of shear creep and capillary rheology which also show that laminating shortening behave as a highly viscous pastes. It was found that at stress steps $\tau_0 = 200 \text{ Pa}$, a laminating shortening had a steady shear viscosity approximately one log order higher than that
of an all-purpose shortening (laminating $\eta_0 = 1 \times 10^9$ Pa.s, all-purpose $\eta_0 = 2 \times 10^8$ Pa.s). As stated previously, it was also observed that a laminating shortening remained more viscous and continuous when being extruded (Fig. 2.8b) ($\eta, \eta_E = 10^2$-$10^3$ Pa.s at 10-100 s$^{-1}$), whereas an all-purpose shortening ruptured and flowed more easily through the capillary die so that the value of the pressure drop substantially decreased and was not measurable with the used instrumental setup.

![Figure 1.11](image)

**Figure 1.11** Microscopic-to-nanoscopic structure of laminating and all-purpose shortenings as assessed by SEM and USAXS. SEM images (a,b) share the same magnification bar. Dotted lines in the USAXS plots (c) serve as ‘guide to the eyes’.

To rationalize the observed nonlinear mechanical response and establish function-structure relationships, we investigate both the underlying nanostructure as well as the microstructure (20 nm to 6 \(\mu\)m) using USAXS and SEM techniques. USAXS data informs of the mechanisms involved in particle/cluster aggregation and structural features of the network, i.e. size, morphology, mass distribution, and of the fundamental scatterers, i.e. crystal nanoplatelets (Peyronel et al., 2014c; Pink et al., 2015). Using the Unified Fit model, three and two power laws
(structural levels or hierarchies) are identified for laminating and all-purpose shortenings, respectively (Fig. 2.10). The high-q power law slope $P_1$ (level 1) indicates CNPs with either smooth ($P=4$) or rough surfaces ($P<4$) irrespective of shortening functionality (Peyronel et al. 2014). Remarkably, ‘particle’ or CNP sizes ($R_{gl}$) of laminating shortening are up to eleven folds smaller than those all-purpose shortening. The intermediate-power law slope $P_2$ (level 2) for laminating shortening, indicates self-assembly of CNPs into fractal clusters due to competition between their condensation and diffusion ($P_2>2.1$) or DLCA mechanisms ($P_2\approx1.8$). The low-q power law $P_3$ (level 3) suggests the presence of micrometer-scaled crystal clusters with fractally diffuse interfaces ($P_3>4$). Using the Guinier-Porod model, it was found that CNPS aggregated into mesoscopic-scale “supra-platelets” ($S=2$) or structures intermediate between rods and platelets (1<$S<2$) (Macias-Rodriguez et al. 2017). SEM micrographs revealed homogenous and elongated microstructures composed of “multilayers” made of well-defined crystal aggregates (~4 μm length) for laminating shortening, whereas heterogeneous networks of distorted sheet-like crystal aggregates (~4 μm length) for all-purpose shortening. Based on our rheo-structural investigation, we suggest that a laminating shortening dissipates more effectively shear loads since energy is allocated among three hierarchies in contrast to an all-purpose shortening where energy is exchanged solely between two hierarchies. In addition, the microstructure of a laminating shortening relieves better local stresses by inelastic deformation due to control sliding motion of the elongated crystal layers in which the liquid oil serves as a lubricant. These explanations seem plausible, as similar findings have been reported for biological and biological-like materials with similar constituents and volume fractions (Sen and Buehler 2011; Ritchie 2011). Furthermore, it is noted that several compositions meet the unique rheological “fingerprint” describing laminating functionality, suggesting that in designing for performance the exact bulk composition does not matter (Macias-Rodriguez et al. 2017).

2.6 Conclusions and perspectives

Fat viscoelasticity is imparted by the structure of the anisotropic crystal network. Significant progress has been made on structural characterization of fats, being the findings of USAXS the most recent advance. As supported by the literature, the development of the solid like network encompasses the formation of hierarchical levels affected by non-trivial thermodynamics and kinetics of crystallization. These concurring factors make the task of drawing meaningful
correlations among structure, physicochemical properties and mechanical functionality of complex fats, a very difficult one. Functionality or macroscopic performance as related to linear viscoelasticity has been extensively studied; however nonlinear viscoelasticity of fats has been scarcely investigated or at least not in a systematic fashion. At large deformations, beyond a critical strain or stress, fats yield irreversibly and display rich nonlinear behavior (i.e., softening, stiffening, thixotropy) that deserve special attention given that all processing and end-uses are nonlinear flows. At a fundamental level, it is desirable to elucidate the nonlinear rheology of fats by computer simulations and rheo-scattering probes. Moreover, it is essential to understand nonlinear rheological properties in terms of mechanical contributions of each of the multiple hierarchical levels or at least relate specific mechanical functions to structure as highlighted in this review (refer to case study section). At an applied level, it is possible to define macroscopic performance in terms of unique rheological “fingerprints” to answer pragmatic questions such as “what rheological functions and magnitudes are desirable for a good laminating shortening?”. Such analysis is highly beneficial not only for quality control purposes, but also for reformulation of fats (no-trans and low-saturates) or design of alternative lipid-structuring materials (organogels) where nonlinear viscoelasticity can serve as a screening tool for targeting functionality.

2.7 References


Colloid Interface Sci. 16: 384–390.


CHAPTER 3: PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION
OF ROLL-IN SHORTENINGS

Braulio Macias-Rodriguez¹, Alejandro G. Marangoni¹


¹Department of Food Science, Ontario Agricultural College, University of Guelph, Guelph ON N1G 2W1, Canada

3.1 Abstract

The composition and physical properties of roll-in shortenings, commonly rich in trans and saturated fatty acids, were investigated and compared to other specialty fats, to provide insights into the physico-chemical origins of their functionality. Triacylglycerols and fatty acid composition, polymorphic and melting behavior, solid fat content and large deformation rheological properties were determined. Roll-in shortenings contained higher amounts of trisaturated and unsaturated triacylglycerols (12-27%; 47-62%) than other shortenings (9-11%; 6-44%). However, all exhibited high levels of saturates and trans fatty acids and similar crystal characteristics:β’ or mixed β’ and β, irrespective of their end use. Roll-in shortenings had comparable melting peaks (42-62 °C) but sharper melting endotherms with higher enthalpies (38.6-43.3 J/g) than other bakery fats (18.7-25.4 J/g). This was in accordance with their well-defined short spacings, indicative of smaller crystallites with more-ordered packing. Solid fat profiles of roll-in shortenings were akin to all purpose and cake interesterified shortenings, but not to all-purpose and icing shortenings which displayed substantial melting as temperature rises. Differences in large deformation rheology (yield stress: σ*, apparent Young modulus: E_app, yield value: C) were marginal and inconsistent with their solid fat content. Roll-in shortenings exhibited E_app, σ and C in the order of 1-2 × 10⁶Pa, 4-7 × 10⁴Pa and 7-29 ×10⁴ Pa, respectively. Particularly, the σ* and C, previously established as major parameters to specify the functionality of roll-in shortenings, were not significantly different (p>0.05). Overall, roll-in shortening differed from other samples in regard to molecular makeup but not greatly in their physical parameters, suggesting that triacylglycerol composition have important implications on their functionality.
Keywords: roll-in, shortening, trans, saturated, functionality.

3.2 Introduction

The consumption of trans (TFA) and saturated (SFA) fatty acids, and their negative health implications have been focus of intense debate over decades. Numerous experimental and epidemiological studies suggest that the consumption of TFA, and SFA over polyunsaturated fatty acids increase the risk of cardiovascular diseases by affecting low-density (“bad”) and high-density (“good”) lipoproteins levels [1, 2]. Based on these findings, food organizations worldwide have implemented strict measures such as regulatory limits, mandatory TFA labelling and dietary recommendations to minimize the intake of “bad fats” [3]. For example, Denmark and Canada have restricted the use of industrial TFA to 2-5% of a product’s fat content, while, US has removed the GRAS (generally recognized as safe) status of TFA.

Similarly, this has provided impetus to the development of products low in TFA following two major directions: interesterification of tropical oils (i.e., interesterified palm) and blending of oil with high-melting fractions (fully hydrogenated and fractionated fats). Nevertheless, these approaches have particular drawbacks from the standpoint of nutrition, functionality and processing as they result in products high in SFA, hard and waxy consistency, and low yield efficiency [4, 5]. Therefore, the reformulation of specialty bakery fats such as roll-in shortenings pose the greatest challenge [6, 7].

Roll-in or laminating shortenings are highly structured fats used in the preparation of puff and Danish pastries [8]. Roll-in shortenings possess a firm but plastic consistency that enables them to behave as solids and viscous liquids at low and high deformations without breaking during layering and folding operations [9]. Such remarkable property is fundamental for the optimal lamination and puffing of the thin fat-dough layers (more than 700) into a flaky structure upon baking [10].

Like in any edible fat, the functionality of roll-in shortenings, tailored by their chemical composition and processing conditions, is intimately linked to their physical parameters including solid fat content, melting and mechanical strength of the crystal network. Their formulation is high in partially hydrogenated and saturated fats (up to 54% w/w altogether)
The customary solid fat content (SFC) of roll-in shortenings is 40-10% solid fat in a thermal range of 10-33.3 °C which provide a considerably wider melting range and higher melting point than other bakery fats [11]. Their mechanical properties involve enhanced resistance to structural breakdown and adequate hardness and plasticity [12, 13]. With regards to composition, roll-in shortenings are rich in partially hydrogenated and saturated fats (up to 54% altogether) [14]. Furthermore, their crystallization process involves a high degree of cooling and extensive shearing to maximize crystal nucleation and limit crystal growth by dissipation of heat of crystallization and polymorphic transformation, and breakage of crystal aggregates [13].

The physical properties of edible fats result from the solid state structure formed upon crystallization. Upon cooling, triacylglycerols (TAG) crystallize from the melt and adopt a preferred polymorphic form. There are three major types of polymorphs classified according to their subcell structure: α (hexagonal), β’ (orthorhombic) and β (triclinic) in increasing order of melting and kinetic stability. In roll-in shortenings, β’ polymorphism is traditionally the most preferred as it is associated with small, dense needle-like crystals and a smooth and plastic consistency. Following the formation of the subcell, TAG self-assemble into lamellae and pack epitaxially into nanoplatelets deemed the fundamental crystal unit. Crystal growth and aggregation continue to form crystal clusters that finally group into a continuous three-dimensional network regarded as the microstructure, in which the oil fraction is trapped [15, 16]. The microstructure or mesoscale comprises crystallites of various morphology (spherulites, needle-like, etc) and size (1-140 μm), which are held by strong or irreversible bonds and weak or reversible bonds ensuing from crystal growth and van de Waals interactions respectively [17]. Fats crystallized under dynamic conditions such as roll-in shortenings display a higher ratio of primary-to-secondary bonds leading to higher yield stress [17].

To develop healthier roll-in shortenings and substitutive systems, it is necessary to link their physical properties to the structural levels formed upon processing. Previous works have primarily focused on the reformulation of roll-in shortenings with low content of TFA and SAFA, investigation of processing parameters and optimization of the crystallization and fat-dough lamination processes. Garcia-Macias et al. [18, 19] formulated palm and stearic-based roll-in shortenings with similar SFC to commercial samples but poor functionality. This is not
surprising as it has been reported that SFC is not a definitive factor of fat macroscopic behavior [20]. Acevedo and Marangoni [21] developed a zero-trans roll-in shortenings based on soybean oil, its hydrogenated counterpart and emulsifiers (i.e., glycerol monopalmititate). Interestingly, the produced samples had comparable functionality to commercial products, given by their similar physical attributes such as SFC and yield stress but different polymorphism. Lefebure et al.; Ronholt et al. (2013) demonstrated that processing parameters such as flow rate, rotational speed and thermal regimes influence the SFC, hardness and ability of puff pastry fat to resist work softening [13, 22]. Spitzbarth (2013) improved the plastic behavior of puff pastry fats by enhancing heat transfer during crystallization [23]. Furthermore, Besseris (2015); Renzetti et al. (2016) found that the fat consistency and number of laminations are the primary determinants of controlling puff pastry overall quality [24, 25].

Despite these research efforts, there remains a need for understanding the physico-chemical origins offunctionality of roll-in shortenings. The fact that these products are richer in hard-stock fat, and more plastic than any other bakery fat, makes them a relevant fat system to study in light of the reduction of SFA and TFA. The present work involved a characterization of the solid-state structure, physical and rheological parameters of roll-in shortenings and their comparison with bakery shortenings differing in their intended use and composition. The systems studied herein represent the common basestock used for bakery shortenings, and more specifically for roll-in shortenings containing TFA and SAFA procured mainly from soybean and palm oils, and their hydrogenated or modified fractions. The “top-down” approach of this work seeks to gain insight of the contribution of characteristic length scales and/or physical properties to the functionality of roll-in shortenings.

3.3 Materials and Methods

A total of nine shortenings with a wide variety of molecular compositions and functionalities were used for this study. Eight of the shortenings were obtained from local retailers and one roll-in shortening (9) was manufactured in house in line with Acevedo and Marangoni [21]. The composition and intended used of the shortening per manufacturer were as follows: 1: hydrogenated soybean oil and cottonseed oil puff-pastry; 2: non-hydrogenated canola oil, modified palm and palm kernel oils roll-in, 3: hydrogenated vegetable oil and modified palm oil
roll-in, 4: palm oil, modified palm oil and soybean oil puff-pastry, 5: non hydrogenated palm oil and modified palm oil all-purpose, 6: soybean oil interesterified cake, 7: soybean oil interesterified all-purpose, 8: palm oil icing 9: fully hydrogenated soybean oil, soybean oil and glycerol monopalmitate roll-in. To preserve the crystal memory and original properties of the shortenings, they were kept at 5 °C and no further manipulated prior to any measurement. Caress

3.3.1 Triacylglycerol composition
TAG composition was determined using a high-performance liquid chromatography system (HPLC, model 110; Agilent Tech, Palo Alto, CA) equipped with a quaternary pump, autosampler, Hewlett-Packard Chem Station software (Version A.10). TAGs were detected using a refractive index detector. Prior to measurements, samples were dissolved in a 37.5:62.5 (v/v) solution of chloroform and acetone-acetonitrile (60:40 v/v). 10 μL of each sample was injected into a Econosil colum (C18, 250×4.6 mm) in isocratic mode at a flow rate of 1.0 mL/min. The mobile phase was acetone-acetonitrile (60:40 v/v). TAGs species were identified via comparison with internal standards (Sigma Aldrich, Oakville, ON, Canada), and quantified by integration of the relative peak area.

3.3.2 Fatty acid composition
Samples were converted initially to fatty acid methyl esters (FAME) following the protocol outlined by Christie [26]. FAME analysis was conducted by an Agilent 6890 series GC (Agilent Technologies, Inc., Wilmington, DE, USA). The G1C was equipped with a CP-Sil 88 capillary column (100 m×0.25mm×0.20 μm), flame ionization detector (FID), split/splitless injection port and autosampler (7,683 series). Hydrogen was used as the carrier gas at a flow rate of 1 mL/min and operational conditions were established as those described by Kramer et al. [27]. Samples were dissolved in hexane containing 1-2 μg/μL of total FAME and 1μL volume was injected. FA composition was determined via comparison with internal standards and quantified by integration of the relative peak area.

3.3.3 Polymorphism
Approximately 1 gr of each sample was placed onto a holder and equilibrated to room temperature (20 °C) prior to polymorphism characterization by powder X-ray diffraction (XRD) (Rigaku, Tokio, Japan). The copper lamp was operated at 40 kV and 44 mA with the use of the
following slits: divergence (0.57 mm), scatter (0.57 mm) and receiving (0.3 mm). Polymorphic forms were identified from the wide angle region (WAXS, 2θ: 12-35°, scanning rate: 0.5°/min) as described by Larsson [28], using the MDI’s Jade 6.5 software (Rigaku, Japan). When two polymorphic forms coexisted, a 4th order polynomial background was applied to the WAXS spectra and then fitted to a Voigt function (Gaussian+Lorentzian symmetrical). The polymorph present in the greatest proportion was qualitatively determined by a comparison of the peak heights.

3.3.4 Thermal behavior
Thermal behavior was determined using a Mettler Toledo differential scanning calorimeter (DSC) (Mettler Toledo, Mississauga, ON, Canada). 9-10 mg of each sample was placed into aluminum crucibles. The samples were subjected to the following thermal sequence: isothermal holding at 10 °C for 15 min and heating from 10 °C to 80 °C at 5 °C/min. The peak temperature (T_m), and enthalpy of melting (ΔH_m) were calculated by extrapolation and integration of the area under the curve using a tangential baseline in the STARe software (Mettler Toledo).

3.3.5 Solid fat content (SFC)
Solid fat content (SFC) were measured by low resolution pulsed magnetic resonance (pNMR) using a Bruker Minispec PC-20 Series NMR analyzer and its corresponding software (Bruker Optics Ltd., Milton, ON, Canada). Each sample was brought to the measurement temperature and then equilibrated in a water bath for 30 min prior to SFC determination.

3.3.6 Large deformation rheology
Rheological tests were conducted at 14-16 °C (T_set) as this temperature range results in optimal plasticity, proper lamination and prevents oiling off or rupturing during lamination of the dough [29]. Under processing conditions, nonlinear material response typically arise from large deformation. In this regard, uniaxial compression and cone penetrometer tests have proven useful to probe the range of usability of plastic fats. For uniaxial compression, each shortening was prepared in 2 × 2 cm (height × diameter) cylindrical cylinders using a metal plunger and a thin, taut metal wire. These dimensions were selected as ratios of height to diameter higher than 1.5 or too low may result in friction and buckling effects during measurements [30]. A thin layer of mineral oil was also applied to both compression platens to minimize frictional effects.
Samples were equilibrated to $T_{\text{set}}$ for 3-4 h and then compressed 70% between two parallel plates at a test speed of 1mms$^{-1}$ using a TA.XT2 texture analyzer (Stable Micro Systems, Scarsdale, NY, USA) with a 30 kg load cell. Force-deformation curves were converted into stress-strain curves. The true stress ($\sigma$) and true strain ($\varepsilon_h$) associated with the deformation cycle were calculated as follows:

$$\varepsilon_h = \int_{h_0}^{h} \frac{1}{h} dh = \ln \frac{h}{h_0}$$

$$\sigma = \frac{F}{A}$$

where $h_0$ is the initial height of the specimen, $h$ the actual height after deformation, $F$ the force measured during compression and $A$ the cross-sectional of the specimen. Subsequently, the apparent Young modulus ($E_{\text{app}}=\sigma/\varepsilon$) was determined in the linear region at the onset of deformation ($\leq 5\%$ of $\varepsilon_h$), and the peak stress ($\sigma_y$) prior to fracture or plastic deformation [31]. Additionally, semi-empirical yield values (C) were determined in accordance with the official AOCS method (AOCS method CC 16-60) and obtained using the following relation:

$$C = K W / p^{1.6}$$

Where $K$ is 19000 for a 15° cone, $W$ is the weight of the cone (42.5 g) and $p$ is the penetration depth in 0.1 mm after 5 s [13].

### 3.3.7. Statistical Analysis

All data manipulation, curve fitting and statistical analysis were performed using GraphPad Prism 5.0 (GraphPad Software, San Diego, CA, USA). Reported values corresponded to group means with their respective standard error mean. An univariate analysis of variance (ANOVA) followed by a post hoc Tukey test ($p<0.05$) were conducted for mean group comparison of the melting peaks and rheological parameters.
3.4 Results and Discussion

3.4.1 TAG composition

As mentioned earlier, the functional properties of shortenings are commonly rationalized according to their TAG composition. The type of TAGs, determined by their FA makeup and stereospecific arrangement on the molecules[32, 33]. In this manner, trisaturated (S₃) TAGs provide structure, disaturated-monounsaturated (S₂U) TAGs confer both structure and lubricity, and mono-unsaturated (U₂S) provide lubricity and nutritional properties [32].

As shown in Table 3.1, the TAG composition reflected a vast range of molecular species. Samples 1 and 3 had a fairly similar composition with prepondering TAG species such as OLeLe, OOLE, POLe, OO, POO, SOO and PSS totaling 80% related to their basestock source and processing history (partially hydrogenation). Likewise, samples 5 and 8, and 6 and 7 had affine molecular ensemble attributed to their basestock formulation. The former were rich in TAGs (POLe, PLeP, POO, POP, PPP and POS) commonly found in palm oil or its modified fractions, and the latter in those encountered in interesterified soybean oil blends (i.e., LeLeLe, OLeLe, PLeLe, POLe, POO, POP, SOO, SOS and SSS) which exhibit randomized TAGs species [6]. While sample 2 had a broader TAG spectrum containing medium-chain species such as LLL and MLP, sample 5 had considerably higher levels of PSS and SSS found in soybean oil-fully hydrogenated soybean oil blends. Overall, roll-in shortenings contained slightly or considerably higher percentages of S₃ TAGs, and lower amount of S₂U TAGs with exception to sample 4. These TAGs species endow them with improved structure and lubricity characteristics compared to other shortenings. In the same manner, roll-in shortenings had lower U₂S but higher U₃ TAGs with exception to roll-in 1 and 4, which altogether contribute to adequate lubricity and nutritional profile. The incorporation of higher percentages of U₃ TAGs in roll-in shortenings (except from sample 4) is in accordance with their improved oil binding capacity reported in the literature [21].
Table 3.1 TAG composition as determined by HPLC

<table>
<thead>
<tr>
<th>TAG (%)</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>MAGs+DAGs</td>
<td>0.6</td>
<td>1.7</td>
<td>4.14</td>
<td>6.1</td>
<td>1.7</td>
<td>3.2</td>
<td>6.0</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>LLL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>LnLnLe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>LeLeLn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>LnLnLn</td>
<td>0.9</td>
<td>2.9</td>
<td>0.6</td>
<td>1.7</td>
<td>3.0</td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LeLeLe</td>
<td>3.3</td>
<td>3.0</td>
<td>3.9</td>
<td>7.8</td>
<td>6.0</td>
<td>17.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LnLeO</td>
<td>0.6</td>
<td>0.7</td>
<td>1.7</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLeLn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>OOLn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>LnLeO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>MMM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>OLeLe</td>
<td>5.46</td>
<td>13.7</td>
<td>3.1</td>
<td>0.4</td>
<td>8.0</td>
<td>5.8</td>
<td>0.5</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>PLeLe</td>
<td>3.52</td>
<td>1.3</td>
<td>3.3</td>
<td>3.1</td>
<td>9.5</td>
<td>8.6</td>
<td>2.22</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>MLeP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>OOLe</td>
<td>11.08</td>
<td>19.9</td>
<td>13.8</td>
<td>3.9</td>
<td>1.8</td>
<td>18.6</td>
<td>1.8</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>POLe</td>
<td>7.04</td>
<td>3.1</td>
<td>6.8</td>
<td>6.8</td>
<td>9.7</td>
<td>19.7</td>
<td>9.1</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>PLeP</td>
<td>1.4</td>
<td>1.7</td>
<td>7.2</td>
<td>10.2</td>
<td>2.2</td>
<td>2.7</td>
<td>9.5</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>OOO</td>
<td>25.4</td>
<td>16.9</td>
<td>24.8</td>
<td>14.9</td>
<td>4.1</td>
<td>10.4</td>
<td>4.1</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>POO</td>
<td>17.1</td>
<td>4.4</td>
<td>14.8</td>
<td>4.9</td>
<td>23.2</td>
<td>11.2</td>
<td>11.2</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>POP</td>
<td></td>
<td>6.2</td>
<td>23.1</td>
<td>28.2</td>
<td>8.6</td>
<td>27.1</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPP</td>
<td>0.6</td>
<td>9.6</td>
<td>5.0</td>
<td>13.7</td>
<td>5.6</td>
<td>7.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOO</td>
<td>8.3</td>
<td>1.1</td>
<td>4.4</td>
<td>1.5</td>
<td>2.4</td>
<td>9.9</td>
<td>12.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>POS</td>
<td>32</td>
<td>0.8</td>
<td>2.3</td>
<td>3.5</td>
<td>5.0</td>
<td>3.5</td>
<td>3.2</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>PPS</td>
<td>2.6</td>
<td>1.6</td>
<td>6.9</td>
<td>2.4</td>
<td>1.0</td>
<td>1.5</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOS</td>
<td>1.4</td>
<td></td>
<td>3.1</td>
<td>4.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSS</td>
<td>5.3</td>
<td>4.5</td>
<td>3.8</td>
<td>3.9</td>
<td>8.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSS</td>
<td>4.0</td>
<td>6.1</td>
<td>4.3</td>
<td>17.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

L: lauric acid; Le:linoleic acid; Ln:linolenic acid; O: oleic acid; P: palmitic acid, M: myristic acid; S: stearic acid
3.4.2 FA composition

Generally speaking, the characteristics of roll-in shortenings is attained by an adequate blend of soft and hard components which represents a compromise between functionality (structure, oil-binding) and a good mouthfeel. To achieve this goal, a molecular TAG composition rich in SFA and TFA appears to be a requisite. Table 3.2 summarizes the FA composition determined for all commercial shortenings. Overall, samples (~41-60% w/w) had high levels of SFA and TFA with vastly different FA composition irrespective of their application. Shortenings 1 and 3 had comparable SFA composition derived mainly from palmitic (16:0) and stearic (18:0) acids contained in soybean, cottonseed and palm oils. In addition, TFA procured from partial hydrogenation and, comprised mainly elaidic (18:1 t9) and linoelaidic acid (18:2 t9, 12). The TFA content greatly exceeded the accepted levels (0-5% w/w) stipulated by regulatory agencies such as the Food and Drug Administration and Health Canada. In contrast, samples 2 and 4 contained higher levels of even-numbered SFA (12:0-16:0) commonly found in palm and palm kernel oils, accompanied by traces of stearic acid and negligible levels of TFA. In samples 5, the predominant FA was 16:0 found in palm oils with minor presence of 18:0 and myristic (12:0) acids. Samples 6, 7 and 9 had intermediate and high levels of 16:0 and 18:0 respectively, found in soybean oil. Not surprisingly, in all shortenings, oleic (18:1) and linoleic (18:2) FAs contributed to the main unsaturated fraction due to their enhanced oxidative stability.
3.4.3 Polymorphism

Three major polymorphic forms are noted in fats: α, β’ and β” listed in increasing order of melting point, packing density, thermodynamic stability, and traditionally associated with different mesoscale structures [35]. From these, the β’ is commonly preferred in roll-in shortenings attributed to its tiny needle-like and dense crystal network that impart optimal rheological properties, baking performance and good mouthfeel. However, it has been demonstrated that β can also adopt diverse microstructural morphologies (i.e., clustered, featherlike), providing comparable functionality for pastry lamination [21, 36, 37].

The predominance of a specific polymorphic form over others is mainly influenced by thermodynamic stability, TAG diversity and FA chain-length, phase transitions, among other factors [38, 39]. As discussed previously, the β’ is fairly stable, functionally desirable and therefore it is common to blend a β’-tending basestock (5-20%) with oil to attain its crystal characteristics in shortenings [40]. Depending on their composition, fats are grouped into β’ or β tendency, a behavior primarily alluded to the content of palmitic acid, its ratio to stearic acid and its distribution along the glycerol molecule which determine the occurrence of monoacid (i.e., PPP) or mixed acid (PSP) which yield β and β’ polymorphs respectively [32, 38]. However, the

Table 3.2 FA composition as determined by GC

<table>
<thead>
<tr>
<th>FA (%)</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
<th>Sample 6</th>
<th>Sample 7</th>
<th>Sample 8</th>
<th>Sample 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:0</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:0</td>
<td>2.5</td>
<td>1.3</td>
<td>1.1</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:0</td>
<td>13.1</td>
<td>30.0</td>
<td>20.1</td>
<td>47.9</td>
<td>45.1</td>
<td>11.4</td>
<td>12.4</td>
<td>45</td>
<td>11.4</td>
</tr>
<tr>
<td>18:0</td>
<td>16.8</td>
<td>3.4</td>
<td>13.1</td>
<td>3.9</td>
<td>4.8</td>
<td>31.2</td>
<td>33.6</td>
<td>5.1</td>
<td>26.6</td>
</tr>
<tr>
<td>18:1 (e9)</td>
<td>44.1</td>
<td>40.4</td>
<td>34.9</td>
<td>29.8</td>
<td>39.2</td>
<td>17.5</td>
<td>16.5</td>
<td>39.0</td>
<td>21.3</td>
</tr>
<tr>
<td>18:1 (t9)</td>
<td>8.6</td>
<td></td>
<td>13.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:2 (t9, 12)</td>
<td>3.0</td>
<td></td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:2 (e9, 12)</td>
<td>13.4</td>
<td>12.5</td>
<td>14.4</td>
<td>12.7</td>
<td>9.9</td>
<td>35.1</td>
<td>33.9</td>
<td>8.9</td>
<td>36.4</td>
</tr>
<tr>
<td>18:3 (3)</td>
<td>1.0</td>
<td>6.2</td>
<td>0.8</td>
<td>1.5</td>
<td></td>
<td>4.8</td>
<td>3.6</td>
<td></td>
<td>5.03</td>
</tr>
<tr>
<td>SFA+TFA</td>
<td>41.5</td>
<td>40.9</td>
<td>49.9</td>
<td>51.8</td>
<td>51</td>
<td>42.6</td>
<td>46</td>
<td>51.2</td>
<td></td>
</tr>
</tbody>
</table>
more diverse the TAG structure of the highest melting fractions, the slower the transition
towards the most stable polymorphic state ($\beta$) is, due to restricted mobility in the crystal lattice.
Apart from formulation, polymorphic phase transformations can be accelerated under
appropriate processing conditions.

Figure 3.1 shows the WAXS spectra and the associated polymorphic behavior identified
according the short-spacing early established by Larsson [28]. Sample 1 and 8 exhibited $\beta'$
polymorphism due to their complex mixture of TAGs (i.e., POP, POO, PSS) arising from partly
hydrogenated blends, and palm oil which delay the conversion into $\beta$. Sample 2 showed greater
preponderance of $\beta$ and $\beta'$, related to canola oil and palm stearin containing POP and PPP ($\beta$
formers), along with palm oil ($\beta'$ former) [41]. The presence of mixed crystals in shortenings and
margarine comprising blends of canola with palm oil and soybean oil has been previously
reported by several researchers [42, 43]. Sample 3 displayed higher prevalence of $\beta'$ promoted
by PSS and PPS (the latter produced from POP upon hydrogenation) [38]. Likewise, sample 4
showed similar polymorphism although PPP and POP were its main solid components. In spite
of being formulated entirely with soybean oil, samples 5 and 6 presented both $\beta'$ and $\beta$ due to
steric hindrance promoted by randomized TAG species, unlike sample 9 which exhibited only $\beta$
due to its rich content of SSS [44]. In addition to formulation, crystallization conditions may
favor the achievement of specific polymorphic forms. On an industrial scale, roll-in shortenings
experience substantial supersaturation attained by a high degree of cooling and mechanical
working. Such events, enhance the removal of heat of crystallization and transformation inducing
a stepwise transition through increasingly stable phases ($\beta' \rightarrow \beta' + \beta \rightarrow \beta$) in accordance with the
Ostwald rule [45]. By contrast, under statistic crystallization (low supercooling), the most stable
$\beta$ form generally prevails. Overall, roll-in shortenings demonstrated stronger XRD reflections
suggesting more ordered crystal packing. However, a quantitative determination and comparison
of the amount of $\beta'$ and $\beta$ crystals among shortenings was not possible due to technical
limitations. As all samples shared similar polymorphic forms, it can be implied that
polymorphism is not a definitive factor of the macroscopic functionality of roll-in shortenings,
which finds good agreement with previous studies. To illustrate, Garcia-Macias (2011; 2012)
developed puff pastry butter rich in stearic and palmitic acids TAGs with a wide array of crystal
polymorphism. [18,19].
3.4.4 Thermal behavior

An important aspect of the physical properties of shortenings is their melting and crystallization behavior which is influenced by crystal habit, number and size. Since the aim of this study was to explore differences among samples inherent to their manufacturing process, we focused only on their melting step prior to which the crystalline solid-state structure had remained unaffected. Typically, a wide melting range is highly desirable in roll-in shortenings as it provides adequate functionality and good mouthfeel in the finished baked product [8]. As seen in Figure 3.2, all shortenings (except sample 9) presented two major melting events at lower and higher temperature ranges respectively. For the determination of bulk thermal characteristics (Table 3.3), we focused on the melting event occurring at higher temperature as this had well-defined onset and offset points for integration, and are more relevant to the temperature of application of roll-in shortenings (10-33 °C). Palm-based (samples 5 and 8) and interesterified soybean-based...
shortenings (samples 6 and 7) displayed identical shallow melting profiles ascribed to their close TAG profile. All-purpose shortening displayed a peak melting point ($T_m$) shifted to higher temperature compared to the icing which might be related to the incidence of the most stable $\beta$ form. Likewise, the thermograms and $T_m$ of interesterified samples were quite similar due to their composition and existence of mixed crystals.

**Figure 3.2** DSC melting endotherms. From bottom to top: sample 1 to sample 9.

While these arguments seem plausible for some samples, similarities in the melting profile with slight differences in $T_m$ of roll-in shortenings may be also ascribed to their processing history. At the low temperatures, samples 1-4 exhibited shallow and wide endotherms extending approximately from 10 to 30 °C. At higher temperatures, their endotherms were broad but sharper with peak maxima of 48-52 °C and melting enthalpies of 39-43 J/g. This observed behavior is consistent with the SFC curves that indicated slight and more substantial melting of crystalline solids in low (10-20 °C) and high (40-50 °C) melting regions respectively. Melting
peaks of partially hydrogenated samples (1 and 3) shifted towards higher °T given their increased content of stearic and trans FA. Closer examination of the melting diagram of sample 4, showed that it has a shoulder at 35-45 °C attributed to higher contribution of palm midfraction or palm stearin to compensate for the absence of trans FAs. Sample 2 had the lowest peak Tm due to the incorporation of TAGs with medium chain FAs. Samples 5 and 8 exhibited more defined lower-melting endotherm at 10-23 °C, and broad and less sharp endotherms with peak maxima of 42-44 °C and melting enthalpies of 19 and 25 J/g characteristic of palm oil [46]. Again, these trends are in accordance with the SFC curves which show substantial melting of solid fat between 10-20 °C. Likewise, samples 6 and 7 showed broad and shallow lower-melting endotherms at 10-20 °C, and at 50-53 °C with enthalpies of 24-26 J/g. Conversely, sample 9 had the highest melting peak associated with their high SSS content. Overall, roll-in shortenings exhibited significantly higher melting enthalpies (p<0.05) although Tm remained comparable (p>0.05), except for sample 9. Moreover, their sharper melting endotherms suggest highly ordered and smaller crystals, in agreement with their X-ray diffraction spectra (Figure 3.1). Such behavior has been ascribed to the high degree of cooling and mechanical working that they are exposed to during crystallization [14, 47].

### 3.4.5 Solid fat content

The solid fat content (SFC) is one of the main parameters used to predict the structuring potential of a shortening blend [48]. Figure 3.3 (a, b) illustrates the SFC vs. temperature curves for each shortening. Overall, all samples experienced appreciable melting of solids at 0-10 °C with exception to roll-in shortening 9, and substantial melting at 30-60 °C. It was noticed from these results that SFC profiles followed similar patterns to the ones recorded from DSC melting thermograms.

The development of plasticity in shortenings requires a concentration of solids of 10-25% [8]. Roll-in shortenings contain 40-10% solid fat in a thermal range of 10-33.3 °C that provides a wide window of functionality [12]. In accordance with this criteria, roll-in shortenings 1-4 exhibited flat slopes and fell into this SFC range related to their broader compositional spectrum and extensive cooling and shearing during processing [49]. In contrast, roll-in shortening 9 had considerable higher solids above 30 °C due to fully hydrogenated soybean oil. These values are
in good agreement with those reported by other researchers [18, 19, 21, 50]. Surprisingly, interesterified shortenings (6 and 7) displayed quite similar SFC profiles although with lower crystalline solids resulting from the randomization process that TAGs undergo during interesterification [51]. In contrast, all-purpose and icing shortenings (5 and 8) exhibited steeper slopes due to proportional melting of palm oil as temperature increases, indicative of a narrow range of functionality [47].

![SFC curves as a function of temperature](image)

**Figure 3.3** SFC curves as a function of temperature. a: roll-in shortenings. b: other shortenings.

### 3.4.6 Large deformation rheology

The rheological properties of shortenings are a consequence of their microstructure, comprising a three-dimensional space-filling network formed by fat crystals, clusters or aggregates in which liquid oil is trapped. As a result, shortenings exhibit a viscoelastic behavior and yield value [46]. Fats subject to high supersaturation regimes such as roll-in shortenings crystallize into compact
and isometric aggregates with little sintering, manifested by lower viscoelastic moduli (\(G^*\)) and fairly high yield stress (\(\sigma^*\)) compared to fats crystallized under static conditions [46].

Figure 3.4 depicts true stress (\(\sigma\)) and true strain (\(\varepsilon_h\)) plots for a qualitative comparison of the mechanical response of selected shortenings. In all samples, a fairly small apparent linear elastic region (~0.05-1%) accompanied by a larger nonlinear region was observed, which concurs with previous works [30]. Likewise, two other regions including stress overshoot and plastic flow were distinguished. These phenomena have been associated with localized deformation or shear banding inducing strain hardening, and stress unloading from the low strain adjacent zones promoting softening of the fat crystal network [52]. However, considerable differences are observed among the shortenings. For example, the linear elastic region extended up to about 1% for roll-in and all-purpose shortenings. Nevertheless, the latter exhibited a more pronounced stress overshoot followed by marked softening, indicating prompt shear localization, and unloading of the strain field. At \(\varepsilon_h > 0.3\), a stress build-up ensued as deformation progressively increased until it reached its peak value at \(\varepsilon_h = 1.2\). Such behavior appeared to occur faster for roll-in shortenings, which might be attributed to continuous development and propagation of shear bands [52]. Large deformation properties of fat crystal networks such as yield stress (\(\sigma^*\)) stress, apparent Young modulus (\(E_{app}\)), and yield values (C) provide valuable information related to the hardness, spreadibility and overall functionality of shortenings.
Figure 3.4 True strain true stress curves. a: non hydrogenated canola oil, modified palm and palm kernel oils roll-in (2) b: non hydrogenated palm oil and modified palm oil all-purpose (5) c: soybean oil interesterified cake (6) d: palm oil icing (8).

Table 3.3 summarizes the $E_{app}$, $\sigma^*$ and C determined by uniaxial compression and cone penetrometry. On the whole, no quantitative trends on the mechanical behavior of shortenings were observed. Shortening 2 exhibit comparable $E_{app}$ ($p>0.05$) to samples 4 and 9 but higher than samples 1 and 3 ($p<0.05$) despite of having similar SFC. Shortenings 3, 6, 7 and 8 had not significantly different $E_{app}$, but lower $E_{app}$ than samples 1 and 9, which was unrelated to their SFC. Similarly, sample was harder than expected (high $E_{app}$) considering its low percentage of solids. These findings are consistent with previous studies indicating that correlations between SFC and the strength of the fat crystal network of multicomponent mixtures are not straightforward due to complex crystallization behavior and crystal-crystal interactions [48]. Likewise, the $\sigma^*$ remained unremarkable suggesting similar transitions from viscoelastic to viscous behavior for all shortenings.
### Table 3.3 Thermal and rheological properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Enthalpy (J/g)</th>
<th>Young modulus $(E_{app}) \times 10^6$ Pa</th>
<th>Yield value (C) $\times 10^4$ Pa</th>
<th>Yield stress $(\sigma^*) \times 10^4$ Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.6±0.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.2±0.4&lt;sup&gt;a,d,c&lt;/sup&gt;</td>
<td>7.0 ±0.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.7±0.1&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>41.0±1.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.8±0.1&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>6.6±0.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.3±0.2&lt;sup&gt;b,c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>41.6±0.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.0±0.1&lt;sup&gt;a,d&lt;/sup&gt;</td>
<td>8.0±0.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.5±0.2&lt;sup&gt;a,c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>43.3±0.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.2±0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>28.7±0.4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.5±0.4&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>18.7±0.6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.3±0.0&lt;sup&gt;a,c&lt;/sup&gt;</td>
<td>14.4±0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.7±0.2&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>25.7±1.2&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>1.1±0.1&lt;sup&gt;a,d,e&lt;/sup&gt;</td>
<td>4.7±0.1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.7±0.1&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>24.1±1.0&lt;sup&gt;b,d&lt;/sup&gt;</td>
<td>0.8±0.1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>6.7±0.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.2±0.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>8</td>
<td>25.4±1.0&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>1.0±0.1&lt;sup&gt;a,d&lt;/sup&gt;</td>
<td>11.8±0.3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.5±0.2&lt;sup&gt;b,c&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>60.0±1.76&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.7±0.1&lt;sup&gt;c,e&lt;/sup&gt;</td>
<td>11.2±0.3&lt;sup&gt;e&lt;/sup&gt;</td>
<td>4.3±0.2&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Samples sharing the same superscripts were not significantly different (p>0.05)

According to Haighton [13], C varies depending on the intended use of a shortening. Values of 800-1000 g/cm<sup>2</sup> (7.8-9.8×10<sup>4</sup> Pa) corresponds to satisfactorily plastic and spreadable shortenings, and values of 1000-1500 g/cm<sup>2</sup> (9.8-14.7×10<sup>4</sup> Pa) or above correspond to extremely hard shortenings. More specifically, functionality ranges of 800-1600 g/cm<sup>2</sup> (7.8-15.7×10<sup>4</sup> Pa) for roll-in shortenings, and 200-900 g/cm<sup>2</sup> (2.0-8.8×10<sup>4</sup> Pa) for normal-to-hard bakery fats, are proposed. It can be seen from Table 3.3, that roll-in shortenings fell roughly within the lower limit of this predefined criteria with exception to sample 4 which exhibit the largest C. Sample 1-3 had comparable C (p>0.05) which agrees with their close SFC, while sample 4 and 9 displayed significantly higher C (p<0.05). Such behavior may be related to distinctive mesoscale structures and the addition of high melting fully hydrogenated fats and stearin that increase yielding of the fat network. Remarkably, sample 7 had comparable C to roll-in shortenings 1-3, and higher C than sample 6, which correlates, well with its SFC.

These results confirm that the rheological properties of roll-in shortenings cannot be related to aspecific composition, polymorphism, thermal behavior or SFC. From these observations, it also follows that shortenings may display variable $E_{app}$, $\sigma^*$ and C regardless of their end use. The most striking case was that of sample 4 that despite of being extremely firm (high $E_{app}$, $\sigma^*$ and C), it is considered plastic and suitable for roll-in applications.
3.5 Conclusions

In this study, roll-in shortenings were evaluated and compared with shortenings for various intended use, in terms of their composition, polymorphic crystal characteristics, melting profile, SFC and rheological behavior. Traditionally, the functionality of roll-in shortenings has been associated with high levels of saturated TAGs, SFA and TFA, β’ polymorphic form, high melting points, wide melting range of solids which altogether contribute to a relatively firm and plastic crystal network. According to our TAG and FA determination, roll-in shortenings contained higher percentage of S₃ along with higher U₃ (except sample 4). Total SFA and/or trans FAs were comparable to those of all-purpose, cake and icing shortenings, and varied on type according to their basestock composition. During the manufacture of roll-in shortenings great care is exercised to develop them in the most desirable and appropriate β’ crystal habit. Nevertheless, β’ and/or the most stable β polymorph, were identified in their WAXS spectra. In the same way, the other shortenings shared identical polymorphic behavior irrespective of their end use. Melting endotherms of roll-in shortenings were wider but sharper than any other shortening and correlated well with their more defined WAXS spectra. These findings may be ascribed to their broad composition, substantial supersaturation during crystallization and the presence of smaller and more-ordered crystalline structures. However, their melting peak maxima remained similar to those of other shortenings. Roll-in shortenings also displayed flatter SFC curves than all-purpose and icing shortenings, indicating a wider melting range, but surprisingly followed a similar trend to cake and pie shortenings. Large deformation rheological properties such as $E_{app}$, $\sigma^*$ and $C$ did not differ significantly among shortenings, did not correlate with their polymorphism or SFC, and hence revealed no differences on the mechanical strength or yielding behavior of the fat crystal network. With molecular composition being the most prominent difference, there are many different formulations that can achieve roll-in performance. However, the fact that the abovementioned physico or mechanical parameters remained unremarkable, calls for a more robust framework that guide developers in designing for roll-in functionality. Future studies on the rheological behavior of roll-in shortenings at small and large deformation along with further characterization of their solid-state structure may lend insight on their functionality.
3.6 Acknowledgements

We thank Saeed Mirzaee Ghazani for his assistance on the HPLC analysis and Cristina Fernandez-Avila for her assistance on the GC technique.

3.7 Conflict of interest

The authors declare that they have no conflict of interest.

3.8 References


50. DeMan L and DeMan JM (1994) Functionality of palm oil, palm oil products and palm kernel oil in margarine and shortening. PORIM.
CHAPTER 4: RHEOLOGICAL CHARACTERIZATION OF LIPID SHORTENINGS

Braulio Macias-Rodriguez, Alejandro G. Marangoni*


Department of Food Science, Ontario Agricultural College, University of Guelph, Guelph ON N1G 2W1, Canada

*Email: amarango@uoguelph.ca, Phone: 519.824.4120

4.1 Abstract

The rheological properties of shortenings with similar physico-chemical characteristics but diverse functionality were investigated under small and large oscillatory shear. Particular attention was drawn to the mechanical behavior of roll-in shortenings, characterized for resisting work softening and forming continuous fat thin films during dough lamination and sheeting. All shortenings displayed low-frequency ω dependence, reminiscent of viscoelastic solids where the storage modulus is higher than the loss modulus, and displayed comparable linear envelope, encompassing relatively small shear strains, such as those encountered in other fat systems. Linear elastic moduli and yield stress, previously used to designate roll-in functionality, remained unremarkable. In contrast, nonlinear viscoelastic behavior of roll-in shortenings differed considerably from all-purpose commercial shortenings. Lissajous-Bowditch curves suggested less local intracycle strain stiffening and less average intercycle strain softening for roll-in shortenings than other shortenings. Likewise, their Fourier spectra indicated a gradual evolution of the third harmonic into the nonlinear regime characterized by higher slopes. Third and fifth harmonics grew monotonically, and the third overtone leveled off and showed no stress decays unlike other samples, suggesting marked ability of roll-in shortenings to withstand deformation at high stresses. Conversely, the dissipative energy scaled in a similar fashion for all shortenings. Moreover, roll-in shortenings displayed enhanced thixotropic behavior supported by lower power law indexes and prompt structural rebuilding after shear cessation. Overall, these rheological signatures facilitated the differentiation among the utilization of shortenings and correlated well with the functionality of roll-in shortenings.

Keywords: roll-in, shortenings, thixotropy, oscillatory, rheology
4.2 Introduction

At the most general level, shortenings are structured as high volume fraction ($\Phi$) triacylglycerol crystal network with liquid oil embedded within. This network is responsible for their viscoelastic behavior. Shortenings have been widely studied due to their industrial uses as structuring, lubricating, foaming and emulsifying agents (Ghotra et al. 2002). The macroscopic physical properties of shortenings depend on their rheological behavior imparted via specific formulations and processing schemes which alter the kinetics of crystallization and give rise to a rich gamut of crystal microstructures including spherulitic, feather-like, grain-like and needle-like shapes (Heertje 1993). Therefore, the determination of the rheological properties of shortenings is of vital importance in designing functionality as well as for guiding reformulation and process optimization efforts.

Like any other edible fat, the rheological properties of shortenings arise from their complex solid-state structure involving a hierarchy of multiple physical length scales and their interactions (Marangoni et al. 2012). Upon cooling, high-melting triacylglycerols (TAGs) crystallize from their melt into a preferred polymorphic state. Polymorphism is related to the cross-sectional packing of the aliphatic ($\ce{CH2}$) fatty acid chains, and interpreted in terms of subcell units as: $\alpha$ (hexagonal), $\beta'$ (orthorhombic), $\beta$ (triclinic) (Sato and Ueno 2011). Then, TAGs self-assemble into lamellae and pack epitaxially into crystal domains or nanoplatelets, deemed the primary crystal unit (Acevedo and Marangoni, 2010a,b). Subsequently, nanoplatelets aggregate into crystal clusters via diffusion-limited-cluster and reaction-limited cluster aggregation (Peyronel et al. 2014a; Peyronel et al. 2014b; Quinn et al. 2014; Pink et al. 2015). The described levels of structure give rise to a polycrystalline continuous 3D network regarded as the microstructure, in which the oil fraction is trapped (Marangoni et al. 2012).

Owing to the influence of the microscopic structure on the macroscopic rheology, many endeavors have sought to link these structural length scales. Among these works, the micromechanical model proposed by our group (Narine and Marangoni 1999a; c; Marangoni, 2000; Marangoni and Rogers, 2003), describing the mechanical properties of bulk fats based on fractal theory remains the most relevant. According to the fractal model, fats are visualized as a 3D self-similar network formed by the collection of inter-connected microstructural elements of a characteristic size. Moreover, at a relatively high volume fraction, fat systems (i.e., cocoa
butter, lard) exist in a weak link regime where the elastic of the inter-microstructural links prevails over that of the microstructures (Narine and Marangoni 1999b). Using these arguments, it was proposed that the elastic modulus ($G'$) of fat networks exhibits a power-law scaling behavior on the $\Phi$, related to the mass fractal dimension ($D$). Marangoni and Rogers (2003) further extended the fractal model to predict the yield stress, an important macroscopic parameter correlated to the performance of shortenings. Subsequently Kloek et al. (2005) provided further evidence that the apparent Young’s modulus, yield stress and deformation, and the Bingham extensional viscosity of model shortenings scaled with $\Phi$ in a power-law fashion with values similar to those deducted from fractal aggregation experiments.

Conversely, other studies have described the rheological properties of fats in terms of their $\Phi$ and processing conditions. deMan et al. (1991) noted that the breaking force or degree of brittleness of shortenings displayed not exact proportionality with $\Phi$. Likewise, Narine and Humphrey (2004) found that increasing $\Phi$ did not consistently increase the hardness of canola-based shortenings. Perez-Martinez et al. (2012); Ronholt et al. (2014); showed that high supersaturation achieved by cooling and shearing rates confer shortenings less solid-like character, decreased the brittleness and increased resistance to structural breakdown. Similarly, Herrera and Hartel (2000) demonstrated that $G'$ of milk fat blends was higher for samples crystallized at slower cooling rates and was unrelated to $\Phi$.

Despite these contributions, relating the mechanical properties of fats to both their physico-chemical parameters (i.e., triacylglycerol composition, $\Phi$, melting behavior) and processing simultaneously has proven an elusive task. Therefore, limited attention has focused on the mechanical properties of multicomponent systems crystallized in industrial-like conditions due to the intricacies associated in replicating such experiments in a controlled way (Marangoni et al. 2012). To date, only a few studies have been published on the characterization of commercial shortenings albeit yielding ill-defined rheological parameters (Haighton 1959; deMan 1991). Due to their ease of use and ubiquitous nature, empirical instruments such as cone penetrometry are still widely used as the best and most reliable source of rheological information to designate the functionality of shortenings, besides their $\Phi$. Consequently, the current literature lacks the use of scientifically rigorous rheological techniques for characterization of commercial fats and specifying their functionality.
The purpose of this work is to provide a framework that allows the quantification of the rheological properties of commercial shortenings in order to categorize functionality according to these. To this end, we probe the linear and nonlinear rheological viscoelastic response of shortenings in addition to their thixotropic behavior in shear oscillatory mode. We focus on providing a rheological fingerprint of roll-in shortenings, containing above 30% of trans and/or saturated fatty acids, motivated by the health-driven trend towards reducing the intake of these unhealthy fats worldwide (Mozaffarian et al. 2009; Astrup et al. 2011). From a rheological perspective, roll-in shortenings used in the manufacture of puff pastry, are truly intriguing materials due to their complex deformation phenomena. During rolling and sheeting roll-in shortenings remain highly elastic and form continuous micron-size thin films despite of being exposed to strong shear and extensional flows (Marangoni et al. 2012). It is widely believed that the mechanical properties of roll-in shortenings, particularly the yield stress, should fall within some range to match the rheology of the dough, and allow their utilization (Haighton 1959; Renzetti et al. 2016). Despite the heterogeneous molecular ensemble and intended use of the shortenings studied herein, all behave as viscoelastic solids and share similar rheological features in the linear regime. However, roll-in shortenings stand apart from the rest of specialty shortenings for displaying less intracycle strain stiffening and less intercycle strain softening in the nonlinear regime and improved thixotropic behavior. Here we argue that these simple yet fundamental rheological signatures satisfactorily relate to their unique functionality irrespective of their chemical composition and Φ.

4.3 Materials and Methods

Materials

4.3.1 Sample preparation
The majority of the samples were commercially acquired, as industrial crystallization high gradients of temperature, viscosity and shearing rate prevail, and therefore are extremely to replicate in a lab scale. A total of nine shortenings were selected to reflect a vast range of molecular compositions and functionalities. Shortenings were obtained from local retailers, except one roll-in shortening which was manufactured in-house according to the protocols outlined by Acevedo and Marangoni(2011). The composition and intended used specified per
manufacturer and $\Phi$ estimated at 16-18 °C by pulsed nuclear magnetic resonance (Bruker Minispec PC-20 Series, Bruker Optics Ltd., Milton, ON, Canada) are summarized in Table 4.1.

**Table 4.1** Bulk composition, functionality as specified by manufacturer, and volume fraction of shortenings

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>$\Phi^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Puff-pastry hydrogenated soybean oil and cottonseed oil</td>
<td>0.25</td>
</tr>
<tr>
<td>R2</td>
<td>Roll-in non-hydrogenated canola oil, modified palm and palm kernel oils</td>
<td>0.25</td>
</tr>
<tr>
<td>R3</td>
<td>Roll-in hydrogenated vegetable oil and modified palm oil</td>
<td>0.25</td>
</tr>
<tr>
<td>R4</td>
<td>Puff-pastry palm oil, modified palm oil and soybean oil</td>
<td>0.30</td>
</tr>
<tr>
<td>R5</td>
<td>Roll-in fully hydrogenated soybean oil, soybean oil and glycerol monopalmitate</td>
<td>0.31</td>
</tr>
<tr>
<td>S1</td>
<td>All-purpose non hydrogenated palm oil and modified palm oil</td>
<td>0.16</td>
</tr>
<tr>
<td>S2</td>
<td>All-purpose soybean oil interesterified</td>
<td>0.21</td>
</tr>
<tr>
<td>S3</td>
<td>Cake soybean oil interesterified</td>
<td>0.25</td>
</tr>
<tr>
<td>S4</td>
<td>Icing palm oil</td>
<td>0.31</td>
</tr>
</tbody>
</table>

$^a$Volume fraction $\Phi$ was measured at 16 °C for all shortenings except for R4 which was determined at 18 °C.

Moreover, fatty acid, molecular triacylglycerol composition and other physico-chemical properties such as melting behavior, crystal polymorphism, have been reported elsewhere (Macias-Rodriguez and Marangoni 2015). To preserve the crystal memory and integrity of shortenings, samples were stored at 5 °C and no manipulated until further measurements.

**Methods**

The rheological properties of roll-in shortenings should complement those of the dough at room and retarder (cooling) temperatures in commercial-scale applications. Based on manufacturer’s recommendations, conditioning shortenings at 16 °C results in optimal plasticity, proper lamination and prevents oiling-off or dough rupturing during lamination, except for R4 which performs better at ambient conditions (18-20 °C). Prior to rheological characterization, samples were carefully prepared in the form of cylinders of 20×1.5 mm (diameter×thickness) and stored...
at 16 °C and 18 °C (only R4) for approximately 24 h to allow for reformation of fractured bonds or local damaged induced by cutting. Cutting was performed using a wire lubricated with mineral oil to minimize frictional effects and the formation of cracks that may serve as stress concentrators.

4.3.2 Sample loading
Soft solids are highly susceptible to deformation flows, which impose changes on microstructure and hence on mechanical properties. Therefore, developing a protocol for loading is necessary to confer a reproducible initial state and prevent the formation of new mesoscale structures within the fat crystal network, known to have a relatively small linear region (in the order of $10^{-3}$ strain) (Heertje 1993). The loading protocol consisted in applying an increasing normal force control (NFC: 1-10 N), allowing the sample to relax the axial force to a constant value over a zero strain relaxation test for 15 min. Consequently, $G'$ and the yield stress ($\tau_y$) associated with the yield strain ($\gamma_y$) were determined with the linear viscoelastic region (LVR) as later described.

4.3.4 Linear rheology: small amplitude oscillatory rheology (SAOS)
Dynamic oscillatory measurements were conducted using a Physica MCR 302 (Anton Paar, Graz, Austria) rheometer equipped with true strain control. Plate-plate geometry (20 mm) with gaps set by a NFC of $3\pm0.5$ N was used for all measurements. To minimize the effect of slippage, sand-blasted fixtures were used along with a NFC (0.5±0.5 N) during measurements to ensure continuous contact of the plates and avoid outward migration of the sample. Temperature was set using Peltier controls located in the lower and hood of the rheometer. Amplitude sweeps were performed at the lower (0.1 rad s$^{-1}$) and upper frequency ($\omega$) limits (100 rad s$^{-1}$). Frequency sweeps were then conducted using a deformation of $\gamma_0 = 5\times10^{-5}$ to probe the linear viscoelastic region (LVR). Subsequently, amplitude sweeps with a deformation ($\gamma_0$) range of $5\times10^{-6}$-1 were performed imposing a constant $\omega = 6.28$ rad s$^{-1}$. The newest Physica software and firmware (RheoCompass) which outputs the values of $G'$ and $G''$ and allows the acquisition of time-dependent raw data, was used for analysis. For SAOS analysis, $G'$, $G''$ were determined at $\gamma_0 = 5\times10^{-5}$ and fixed frequency of $\omega = 6.28$ rad s$^{-1}$ within the LVR region. The $\gamma_y$ and $\tau_y$ were determined at the point where $G'$ dropped by 5% of its initial value.
4.3.5 Nonlinear rheology: large amplitude (LAOS) oscillatory rheology

Typically at large amplitudes (LAOS), complex nonlinear shear stress responses arise in many viscoelastic materials. Such nonlinearities occur above a critical strain and manifest either when $G'$ or $G''$ are not a function of $\gamma_0$, or the $\tau(t)$ response is no longer sinusoidal, and hence it possesses higher harmonic contributions (Wilhelm 2002). When these conditions are met, $G'$ and $G''$ are no longer well defined and lack a physical interpretation. In the analysis of the nonlinear regime, we used two of the most commonly utilized methods to fingerprint the nonlinear response of our samples at similar $\omega = 6.28$ rad s$^{-1}$. The first method consisted in plotting the periodic strain-stress data obtained at steady state, in the form of so-called Lissajous-Bowditch curves. Each curve is a parametric plot of $\gamma_0$ on the abscissa and $\tau(t)$ on the ordinate. In the LVR region, viscoelastic plots appear as ellipse which gradually become distorted taking different shapes as $\gamma_0$ increases. The second method involved using a Fourier transform (FT) rheology to decompose the time-domain stress response into a frequency dependent spectrum. For a sinusoidal strain input $\gamma(t) = \gamma_0 \sin(\omega t)$, the total stress response can be completely expressed in a Fourier series of the following form:

$$\tau(t) = \gamma_0 \sum_{n=1}^{\infty} \left[ G'_n(\omega, \gamma_0) \sin(n\omega t) + G''_n(\omega, \gamma_0) \cos(n\omega t) \right]$$  \hspace{1cm} (1)

Where $n$ equals an integer number of the fundamental harmonic ($n=1$ in the LVR region) within its corresponding generalized $G'_n$ and $G''_n$. The higher-order harmonic contributions may be ideally odd due to the non-negativity of stored energy as stated by Christensen (1982). However, the occurrence of even harmonics is also possible although their physical underlying reasons are not fully understood. Some current explanations include slippage, edge fracture, time-dependent memory effects, among others (Hyun et al. 2003; Li et al. 2009). Under our experimental setup, the presence of even harmonics was negligible (in the order of $I_2=0.5-1 \times 10^{-3}$).

To quantify the nonlinear response of our samples, the raw strain-stress data was collected at a sampling rate of 513 s$^{-1}$. A minimum of 20 oscillatory cycles to allow most of the transient oscillations to die out. Several quasi-steady state waveforms (typically 3-5), were input to a fast FT rheology to provide greater accuracy and increased signal to noise ($S/N$) ratio (Wilhelm et al. 1999; Ewoldt et al. 2008). The normalized intensity of higher harmonics [$I(n\omega_1)/I(\omega_1)$] was used to generate a power spectrum for each sample. FT analysis was constrained to amplitudes of
\( \gamma_0 = 0.15 \), to minimize the occurrence of edge fracture and shear banding, which become especially important for high shear strain amplitudes (Li et al. 2009).

Thixotropy is a rheological phenomenon commonly encountered in gel-like systems and is responsible of the abovementioned time-varying transients observed in the LAOS response. Thixotropic behavior was evaluated by tracking the dynamic moduli in a three-interval oscillatory test (6.28 rad s\(^{-1}\)). The test involved applying an initial \( \gamma_0 = 5 \times 10^{-5} \) for a period of 2 min (within the LVR), then applying a \( \gamma_0 = 0.1 \) (outside the LVR) for 2 min and finally applying the initial \( \gamma_0 \) again for a rebuilding period of 3 min. The \( \gamma_0 \) used was sufficiently low to not interfere with the recovery kinetics of the samples.

4.3.6 Statistics

All data manipulation, curve fitting and statistical analysis were performed using GraphPad Prism 5.0 (GraphPad Software, San Diego, CA, USA). Reported values corresponded to group means with their respective standard error mean (SEM). An univariate analysis of variance (ANOVA) followed by a post hoc Tukey test (\( p < 0.05 \)) were conducted for mean group comparisons.

4.4 Results and discussion

4.4.1 Sample loading

Minimizing the effect of sample handling and shear history on the inherent viscoelastic properties of soft solids such as shortenings is desirable for consistent and reproducible rheological characterization. Strain sweeps revealed large differences on the values of the \( G' \) and \( \tau_y \) depending on the applied normal force \( (F_n) \), asserting again the importance of adequate sample loading (Fig. 4.1). The initial rise of the elastic modulus upon increasing the normal force applied upon sample loading, between 1 and 3 N, is due to the fact that as the normal force increases the samples progressively become fully in contact with the plate and plate geometry. This also reveals the absence of slippage as \( G' \) is indeed independent of the gap distance. Above 5N, \( G' \) rises possibly associated with strain-induced compaction of the fat crystal network, as it was visually observed that the samples buckled at their boundaries. Compaction may induce slight rearrangement or reorientation of the present mesoscale structure, conferring a more solid-like character. The alteration of the microstructure has been well documented by Heertje et al.
(1988) who demonstrated that axial compression breaks the links of the fat crystal network but not its microstructural elements. Additionally, Fukada et al. (1961) showed that the elasticity, viscosity and yield value of margarine and butter remarkably decrease during mechanical stress but recover gradually after specific setting times. With regards to the yield stress, it was also found that between 1 and 3 N, it rises almost linearly as the sample become in total contact with the geometry. Between 3 and 5 N, the yield stress did not show significant change due to absence of slippage or premature yielding at the plate interface.

![Figure 4.1](image)

**Figure 4.1** Impact of normal force on the elastic modulus $G'$ and yield stress $\tau_y$ of roll-in (R2) and all-purpose shortening (S1) post loading. $G'$ was obtained at fixed frequency $\omega=6.28$ rads$^{-1}$ and strain $\gamma_0=5\times10^{-4}$. Linear viscoelastic stress limits defined at $G'/G_0=0.95$.

Subsequently, the yield stress remains nearly constant for R1 and decreases for S1 respectively. We attribute this yield stress dependence on normal force effects (artifacts) due to microstructure alteration, which does not disturb the crystal network of R1 but affects adversely the linear viscoelastic envelope of brittle samples such as S1. Furthermore, it was also noted that the “flow” point located at the crossover point of the elastic and viscous moduli ($G'=G''$), shifts to higher values (data not shown) for R1 when increasing the applied normal force. These observations suggest that subtle variations in loading disturb the original microstructures, and hence can lead to erroneous estimation of material properties ($G'$, $\gamma_y$, $\tau_y$). From these results, we found a normal force control of 3N to be the most suitable for sample loading. It is worth noticing that roll-in shortenings (R1) withstood higher normal forces without appreciable decrease of their yield stress possibly due to their greater plastic deformation. This finding is in
agreement with Ronholt et al. (2014) who indicated that puff pastry shortenings possess improved ability to resist structural breakdown during working.

**4.4.2 Linear viscoelasticity**

Linear material properties were determined by small amplitude oscillatory rheology (SAOS) with the aim of investigating potential differences attributed to macroscopic functionality. The frequency dependencies of the elastic and viscous contributions were studied in the region of 0.1-100 rad/s, within the LVR ($\gamma = 5 \times 10^{-3}$). Fig 4.2, show log-log frequency sweeps of selected samples: R1 roll-in and S1 all-purpose shortenings. In general, it was observed that the viscoelastic moduli were weak functions of frequency for all samples, which is a typical behavior for viscoelastic solids. This was expected, as the mechanical properties of fat crystal networks are dominated by their solid-like particles and their interactions (Van de Tempel 1961).

Based on the frequency sweeps, we established the frequency regime where the stress response is linear and hence $G'$, $G''$ remain nearly constant. We set $\omega = 6.28$ rads$^{-1}$ and sweep from small to large strain amplitudes to determine linear material functions. Fig. 4.3 shows strain sweeps of two selected samples (all shortenings display similar behavior). Data illustrate that $G'$ and $G''$ maintained a plateau at low strains within the LVR region. Beyond $\gamma_y$, $G'$ begins to decline and $G''$ increases slightly and then decreases, marking the onset of nonlinearity. Interpreting in terms of stress, this corresponds to: linear strain-stress proportionally (LVR region), critical or yield stress, stress overshoot and stress softening accompanied by viscoplastic flow (Walstra et al. 2001). In addition, the slight rise of $G''$ before monotonically dropping refers to a non-linear complex response attributed to “type III” materials (Hyun et al. 2002). The $G'$ was determined at $\gamma_0=0.05 \times 10^{-2}$, where it is independent of $\gamma_0$. In addition, the extent of the linear regime was determined by $\gamma_o$ and its associated $\tau_o$, defined as the value at which $G'$ drops by 5% from its initial plateau. The comparison of these parameters constitutes a practical way to discern among the rheological performance of the investigated samples and probe their microstructure. As alluded to earlier, high-volume-fraction fats ($\Phi>0.1$) such as shortenings exist in the weak-link regime and hence their elasticity is governed by the inter-microstructural links carrying most of the stress (Heertje 1993; Rousseau and Marangoni 1996; Narine and Marangoni 1999a, c; Marangoni, 2000; Marangoni and Rogers, 2003; Awad et al. 2004). In the weak-link regime, $G'$ exhibits a power-law dependence on $\Phi$ and increases as the average size of the microstructural
elements, described by the fractal dimension, decreases (Narine and Marangoni 1999a, c). $G'$ also correlates quite well with macroscopic sensory impressions such as hardness and spreadibility (Narine and Marangoni 1999c).

**Figure 4.2** Frequency sweep of selected shortenings at fixed strain $\gamma_0 = 5 \times 10^4$. R1: roll-in, S1: all-purpose shortenings

On the other hand, $\gamma_y$ refers to the distance from pulling crystal flocs apart from their equilibrium state relative to their size while $\tau_y$ relates to the product of $\gamma_y$ and the Young modulus. From these microscopic considerations, it is conceivable that shortenings will differ on their mechanical properties resulting from their potentially dissimilar microstructure, and their physico-chemical properties manipulated via formulation and processing. However, typical viscoelastic parameters summarized in Table 4.2, showed no particular trends among the samples. $G'$, $\gamma_y$ and $\tau_y$ were in the order of 0.8-3.8 MPa, 0.8-2.5 $\times$ 10$^4$, 46.4-593.9 Pa (sandblasted) and 47-315 Pa (smooth) respectively.
Figure 4.3 Strain sweep conducted at fixed frequency $\omega = 6.28$ rads$^{-1}$. R1: roll-in and S1: all-purpose shortenings. Linear viscoelastic strain limits defined at $G'/G'_0 = 0.95$.

In the absence of roughened surfaces and normal force adjustment, premature yielding initiates at the geometry interface and samples are slightly ejected from the gap. The use of sandblasted surfaces in combination with normal axial force overcomes these issues as defers yielding to higher values. Despite of having similar $\Phi$ (Table 4.1), $G'$ of roll-in shortenings R1-R3 differed from those of all-purpose and cake shortenings S2, S3. Likewise, roll-ins R2 and R5 had $G'$ comparable to the icing shortening S4 although only the last two share the same $\Phi$. In contrast, roll-in R2 and all-purpose S1 shortenings had similar elasticity albeit their vast difference in $\Phi$. Furthermore, the “stiffest” shortening was roll-in R4 which coincidently was one of the shortenings with the highest $\Phi$. These contrasting findings are not surprising as it has been widely disproved that $\Phi$ is not the sole predictor of $G'$ in multicomponent systems where complex crystallization behavior and crystal-crystal interactions occur (Ghotra et al. 2012). Other factors potentially affecting $G'$ include the molecular ensemble, thermal behavior and the crystal arrangement of the subcell unit or polymorphism. However, previous studies suggest that none of these play a major role on the mechanical properties of roll-in shortenings (Acevedo and Marangoni 2014; Macias-Rodriguez and Marangoni 2015).

Other rheological properties of major relevance such as $\gamma_y$ and $\tau_y$ may affect the processability and formability of roll-in shortenings into thin films during extrusion and sheeting of the fat-dough layers. As illustrated, $\gamma_y$ was comparable for all-purpose shortening S1 and roll-in shortenings but R2 presented $\gamma_y$ analogous to all-purpose, cake and icing shortenings (S2-S4).
The onset of non-linearity of roll-in shortenings given by $\gamma_3$ is comparable in magnitude than those of other shortenings. Moreover, these results underscore the importance of applying a sufficiently low strain to ensure linear response and find agreement with the literature (Kloek et al. 2005). Regarding $\tau_y$, we found that roll-in shortenings are very versatile as their $\tau_y$ fall within ample spectra similar to those of all-purpose and icing shortenings. These results defy those presented by Haighton (1959) who reported a well-defined range of yield value for roll-in shortenings using cone penetrometry. However, the semi-empirical nature of this method makes it difficult to conceive a clear physical interpretation of the parameters being measured and therefore hard to compare with our data. One may assume that roll-in shortenings will be significantly stiffer (higher $G'$ and $\tau_y$) than other bakery shortenings, as they are tailored for more mechanically demanding processes. However, our results revealed no peculiarities on linear material functions ($G'$, $\gamma$, $\tau$).

Table 4.2 Elastic modulus determined from strain sweeps at $\omega=6.28$ rads$^{-1}$ and $\gamma_0=5\times10^{-4}$. Yield strain and stress defined at $G'/G''_\theta=0.95$. Group means sharing superscripts were not significantly different ($p>0.05$). Yield stress measured with smooth surfaces are shown to illustrate the effect of slippage and premature yielding.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G'$ ($\times10^6$ Pa)</th>
<th>$\gamma_3$ ($\times10^{-3}$)</th>
<th>$\tau_y$ (Pa) sandblasted</th>
<th>$\tau_y$ (Pa) smooth</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1.3±0.1$^{b,c}$</td>
<td>2.3±0.2$^a$</td>
<td>287.8±11.3$^{a,c}$</td>
<td>56.3±5.7</td>
</tr>
<tr>
<td>R2</td>
<td>2.6±0.1$^b$</td>
<td>1.0±0.1$^b$</td>
<td>257.9±4.5$^a$</td>
<td>137.5±8.5</td>
</tr>
<tr>
<td>R3</td>
<td>1.6±0.1$^{b,d}$</td>
<td>2.0±0.0$^a$</td>
<td>310±13.6$^{a,c}$</td>
<td>79.3±28.7</td>
</tr>
<tr>
<td>R4</td>
<td>3.8±0.1$^c$</td>
<td>1.0±0.5$^b$</td>
<td>438.4±37.5$^{c,b}$</td>
<td>230.0±38.0</td>
</tr>
<tr>
<td>R5</td>
<td>2.2±0.1$^{b,d}$</td>
<td>2.4±0.1$^a$</td>
<td>547.9±41.3$^{b,d}$</td>
<td>242.0±5.5</td>
</tr>
<tr>
<td>S1</td>
<td>2.7±0.3$^b$</td>
<td>2.5±0.4$^a$</td>
<td>593.9±42.1$^d$</td>
<td>315±100</td>
</tr>
<tr>
<td>S2</td>
<td>0.8±0.1$^{a,c}$</td>
<td>0.8±0.1$^b$</td>
<td>70.9±17.9$^e$</td>
<td>53.5±8.5</td>
</tr>
<tr>
<td>S3</td>
<td>0.6±0.2$^e$</td>
<td>0.9±0.1$^b$</td>
<td>46.4±4.4$^e$</td>
<td>47.0±4.0</td>
</tr>
<tr>
<td>S4</td>
<td>2.5±0.2$^b$</td>
<td>1.1±0.1$^b$</td>
<td>271.0±35.9$^a$</td>
<td>212.5±26.5</td>
</tr>
</tbody>
</table>

4.4.3 Nonlinear viscoelasticity
Beyond the LVR region, $G'$ and $G''$ lose their theoretical and physical underpinning and therefore cannot fully describe LAOS rheological behavior (Wilhelm 2002). It was observed that as shortenings depart from linearity, $G'$ decreases monotonically while $G''$ shows a more complex behavior including an initial increase and subsequent monotonic decrease. These rheological features are characteristic of type III materials, which exhibit weak strain overshoots according to Hyun et al. (2002). Several interpretations have been put forward to explain this
behavior such as initial resistance to deformation of weakly associated polymers up to certain
strain beyond which the polymer structure is distorted and the chains aligned in the flow
direction. In filled elastomers, the $G''$ maxima has been referred to as to the “Payne effect” and
linked to bond breaking between load-bearing elements, release of trapped entanglements, and
particle jamming-unjamming processes (Allegra et al. 2008). In our samples, the “Payne effect”
seems more prominent for all-purpose shortenings (S1) than roll-in shortenings (R1), particularly
at higher frequencies (data not shown), though the exact reason for this is unknown. However, it
is conceivable that the extensive shearing that roll-in shortenings undergo during processing,
induce preferred crystallographic orientation, which contributes to prompt alignment in the
direction of the flow field. The possibility of higher structural ordering is qualitatively supported
by our previous wide-angle X-ray scattering analysis which displayed sharper Bragg’s peaks for
roll-in shortenings (Macias-Rodriguez and Marangoni, 2015). Further evidence is provided by
several accounts in the literature demonstrating that shear accelerates polymorphic transitions
and orients fat crystallites at the molecular and mesoscale levels respectively (Mazzanti et al.
2011; Maleky et al. 2011).

Several methods have been proposed to analyze the LAOS rheological response of complex
fluids including the so-called Lissajous-Bowditch curves and FT-rheology (Hyun et al. 2011). In
this work, Lissajous-Bowditch curves, parametric plots of strain and stress response, were used
to qualitatively fingerprint the liner-to-nonlinear transition of fat crystal networks. In addition,
FT analysis was adopted to quantify the time-periodic nonlinear stress response due to its
convenience and sensitivity (Wilhelm et al. 1999). Fig 4.4 and Fig 4.5 display Lissajous-
Bowditch curves (last quasistationary state cycle) for two reference samples: roll-in shortening
R1 and all-purpose shortening S1 respectively. Likewise, Fig. 4.6 shows the relative intensity of
higher harmonics ($In\omega_l$) as a function of strain amplitude for the same samples. For FT analysis,
3-5 quasisteady cycles were typically used.
Figure 4.4 Lissajous-Bowditch curves after 20 oscillatory cycles for a roll-in shortening (R1) at fixed frequency $\omega = 6.28$ rads$^{-1}$ with a) $\gamma_0 \times 10^{-2} = 0.03, 0.06, 0.09, 0.14$; b) $\gamma_0 \times 10^{-2} = 0.22, 0.36, 0.57, 0.92$; c) $\gamma_0 \times 10^{-2} = 1.46, 2.34, 3.74, 5.99$; d) $\gamma_0 \times 10^{-2} = 9.56, 15.3, 24.5$. Arrows indicate the direction of the oscillation.

Regarding the Lissajous-Bowditch curves, at $\gamma_0$ of $\approx 0.05 \times 10^{-2}$ and below, all shortenings exhibit a linear response manifested by nearly-elliptical waveforms, except from R3 which was slightly skewed. Within this region, the viscoelastic moduli are independent of the imposed strain amplitude. The critical strain value corresponds approximately to $\gamma_y$ determined for all samples. Beyond $\gamma_y$, a transition from simple ellipses to complex shapes signals the departure from linearity. Distinctive features appear, which persist qualitatively throughout the course of the strain sweep include strain softening, strain hardening and the occurrence of a linear region followed by stress overshoots. Strain softening is visually observed as the decrease of the slope of the stress-strain curve at $\gamma = 0$ (where strain rate $\dot{\gamma}$ is at a local maximum) toward the strain-axis, while strain hardening is indicated by the upturn of the shear stress at large strains (where $\dot{\gamma} = 0$). Interestingly, the maximum of the strain stiffening roughly coincides with strains where $G''$ exhibits a maximum before its subsequent decrease. A closer inspection of roll-in
shortenings suggests less degree of local strain stiffening, supported by milder stress upturns. Likewise, the intracycle evolution of the slope of the stress-strain curve at $\gamma=0$ (i.e., in R1) with increasing strains, indicates less extent of strain softening for roll-in shortenings manifested by less clockwise rotation toward the strain axis and higher average stress.

![Graphs showing stress-strain curves](image)

**Figure 4.5** Lissajous-Bowditch curves after 20 oscillatory cycles for an all-purpose shortening (S1) at fixed frequency $\omega=6.28$ rads$^{-1}$ with a) $\gamma_0 \times 10^{-2} = 0.03, 0.06, 0.09, 0.14$; b) $\gamma_0 \times 10^{-2} = 0.22, 0.36, 0.57, 0.92$; c) $\gamma_0 \times 10^{-2} = 1.46, 2.34, 3.74, 5.99$; d) $\gamma_0 \times 10^{-2} = 9.56, 15.3, 24.5$. Arrows indicate the direction of the oscillation.

We interpret this behavior as reduced shear sensitivity and improved restructuring ability within the oscillatory cycle, as described later. The linear region corresponds to a linear elastic deformation of the fat network and extends to higher strain amplitudes whereupon the stress upturn fades $\gamma_0 \approx 0.36 \times 10^{-2}$ and the stress overshoot begins to appear on the upper-left quadrant of the curves within the vicinity of the “flow” point ($G'=G''$). As $\gamma_0$ increases, the magnitude of the peak increases as well as the enclosed area of the curves, indicating progressively yielding
and dissipative response. Moreover, the Lissajous-Bowditch curve becomes more box-shaped or circular-shaped (only for S2, not shown) and secondary broad peaks followed by stress local minimums appear, after the first one. These secondary peaks (more visible in S1) seem not be a measuring artifact and have been previously observed in other colloidal systems (Renou et al. 2010; Poulos et al. 2013; Kim et al. 2014). Moreover, after the flowing portion of the curves (post stress overshoot where instantaneous shear rate is at maxima), it was more evident for some samples that the stress increased again indicating network reforming or thixotropy as instantaneous shear rate decreases. This proceeds until the end of the half-cycle (at positive strain maxima) and begins again in the other spatial direction. Furthermore, the occurrence of reversible stress overshoots during flow reversal suggest that the oscillatory deformation timescales are longer than the thixotropic restructuring timescales (Ewoldt and McKinley 2010). From this qualitative analysis, it becomes evident that the conventional linear dynamic moduli ($G'$ and $G''$) cannot fully fingerprint the rich and complex non-linear response of shortenings.

In the context of microstructural changes conducive to yielding, the shape of Lissajous curves during shear deformation has been attributed to different nonlinear mechanical events (i.e., bond rupturing, cage breaking). As so far no further data on yielding of fat crystal networks is available in the literature, we draw analogies with previous works on solid-like colloidal systems. As the structure of fat crystal networks share similarities with flocculated colloids, the work of Kim et al. (2014) on yielding of heterogeneous concentrated colloidal gels seems the most relevant. Nevertheless, a fundamental difference lies on that the elastic network studied by Kim et al. (2014) comprises a bicontinuous structure of droplet-lean (entrapping mainly solvent) and droplet-rich domains (containing fractal cluster microstructure) at large scales (2100 nm) and a fractal microstructure consisting of droplet clusters at moderate (21-420 nm) length scales. In contrast, edible fats are comprised of a three-dimensional continuous network embedded in oil and made of fractal microstructures linked together at large length scales (1-5 μm), and crystal aggregates formed by diverse aggregates of nanoplatelets at moderate-to-low scales (500-2000 nm) (Peyronel et al. 2014b).

Kim et al. (2014) investigated the time-dependence response of the stress at a fixed strain and provided a comprehensive picture of a multi-yielding process reflected in the Lissajous-Bowditch waveforms. The nearly linear region of the curves was associated with mild
To quantify the differences observed in the Lissajous-Bowditch curves and further the nonlinear properties of shortenings, we report the normalized intensity of the odd harmonics up to $I_{3/1}$ as higher overtones did not contribute greatly to stress response (i.e., $I_{7/1} \leq 5\%$) (Fig. 4.6). The maximum intensity of $I_{3/1}$ is comparable for all shortenings but not the curve evolution. It was observed that at $\gamma_0 = 0.05-0.09$, $I_{3/1}$ slightly rises, which matches the mild distortion of the Lissajous waveforms. As $\gamma_0$ increases, $I_{3/1}$ grows monotonically and then saturates reaching a plateau at $\gamma_0 = 0.01-0.02$ which roughly coincides with the “flow” point ($G' = G''$). While this plateau maintains relatively constant for roll-in shortenings, the intensity of S1 and S3 sharply decays above $\gamma_0 = 0.01-0.02$, being S3 the most notable case. Moreover, S2 exhibit double-arc shaped behavior with local minimum occurring at $\gamma_0 = 0.01-0.02$, while S4 monotonically rises as a function of strain. Furthermore, the growth of higher overtones ($I_{3/1}$) displays the same monotonous increase for roll-in shortenings. In contrast, the intensity of higher harmonics of other shortenings exhibit sharp maximum at the “flow” point followed by marked decrease or double-arc behavior.
Figure 4.6 a) Relative intensity of the third harmonic ($I_{3/1}$) as a function of shear strain amplitude at $\omega = 6.28 \text{rads}^{-1}$. R1: roll-in shortening; S1: all-purpose shortening. Data was fitted to Eq. 2. Inset is a continuation of the main plot showing higher strain values. b) Relative intensity of the fifth harmonic ($I_{5/1}$) as a function of shear strain amplitude at $\omega = 6.28 \text{ rads}^{-1}$. R1: roll-in shortening; S1: all-purpose shortening.

We draw our attention back to the leading-order harmonic ($I_{3/1}$), commonly used in other colloidal systems to monitor the departure from the LVR (Renou et al. 2010; Kim et al. 2011; Poulos et al. 2013). The observed trends on $I_{3/1}$ can be associated with a basic yielding picture such that provided for the Lissajous-Bowditch curves. As LAOS is imposed, initial hindrance of the fractal microstructures and potential breaking of their links induces mild-to-strong nonlinear deformation of the fat network ($I_{3/1}$ increases). As $\gamma_0$ increases, further disturbance of crystal clusters or aggregates (i.e., TAGwoods) results in sharp nonlinear deformation ($I_{3/1}$ at maxima). At sufficiently high strains ($\gamma_0 > 0.01-0.02$), crystal clusters begin to breakup and/or become aligned by the shear flow as stress decays ($I_{3/1}$ keeps increasing or drops). The prevalence of a double-arch shape in $I_{3/1}$ in some samples might be attributed to two separate yielding processes.
as observed in some concentrated colloidal gel or shear instabilities (Wilhelm 1999; Rogers et al. 2014). To describe the evolution of $I_{3/1}$, we used a descriptive function proposed by Wilhelm et al. (2000):

$$I_{3/1} = A[1 - \exp(-(\gamma_0 - \gamma_L)/k)], \gamma_0 > \gamma_L$$ (2)

The parameter $A$ reflects the maximum possible contribution of $I_{3/1}$ at an idealized infinite shear amplitude $\gamma_0$. The parameter $\gamma_L$ describes the maximum shear amplitude within the linear region. Finally, the parameter $k$ describes the change in intensity (or inverse slope) as a function of shear amplitude, and has shown to be heavily dependent on polymer chain topology. We found that Eq. (2) described well the experimental data although no clear crossover between the linear and nonlinear regime was detected but rather a constant increase in intensity. For samples, where $I_{3/1}$ displays a maxima and subsequently decreases, we selected cut-off strain values where the $I_{3/1}$ levels off (typically $\gamma_0 \approx 0.06$). From the fitting, we solely report the parameter $k$ as the predicted $A$ and $\gamma_L$ parameters roughly coincide with the maximum intensity found experimentally, and $\gamma_0$ was previously estimated from the curves of $G'$ and $G''$ curves. Although it has been shown that FT is a more sensitive indicator of the onset of non-linear behavior, the fact that $\gamma_L$ and $\gamma_y$ are similar in magnitude may be related to the lower $S:N$ ratio (2000:1) for the spectra in the strain range of $\gamma \approx 2\times10^{-4}-9\times10^{-4}$ due to noise during measurements. At higher strains $S:N$ ratios in the order of 50000:1 were typically obtained. Overall, it was observed that the inverse slope of roll-in shortenings was characterized by higher values ($k=0.58-1.26 \times10^{-2}$) than those of other shortenings ($k=0.27-0.40 \times10^{-2}$), indicating a more gradual transition into the nonlinear regime. In addition, the plateau behavior of $I_{3/1}$ of roll-in shortenings correlates with the increase performance of roll-in shortenings for withstanding high stress without collapsing during fat-dough sheeting operations.

### 4.4.5 Energy dissipation

To investigate potential differences on the dissipated energy ($E_d$) during LAOS yielding, we compute the $E_d$, represented by the area enclosed by the Lissajous-Bowditch curves. The $E_d$ of an oscillatory cycle is given by (Ganeriwala and Rotz 1987):

$$E_d$$
\[ Ed = \gamma_0^2 \omega \int_0^{2\pi/\omega} \sum_{n=1}^{N \_{nodd}} \left[ G'_n \sin(n\omega t) + G''_n \cos(n\omega t) \right] \cos(\omega t) \, dt \]  
(3.1)

Due to the orthogonal properties of the trigonometric basis functions, Eq. (3.2) reduces to:

\[ Ed = \gamma_0^2 \omega G''_1 \int_0^{2\pi/\omega} \cos^2(\omega t) \, dt \]  
(3.2)

\[ Ed = \gamma_0^2 \pi G''_1 \]  
(3.3)

**Figure 4.7** Energy dissipated per oscillatory strain cycle calculated from the area of the Lissajous-Bowditch curves using Eq (3.3), for selected shortenings. R1: roll-in and S1: all-purpose shortenings.

From Eq (3.4), it is clear that \( E_d \) depends only on \( G''_1 \) as reported by the rheometer in both the linear and nonlinear regime. In contrast, elastic energy is stored in a more complex manner as demonstrated by FT analysis. Fig. 4.7 shows \( E_d \) as a function of \( \gamma_0 \) given for two representative samples (R1 and S1) displaying contrasting nonlinear behavior as illustrated by their respective Lissajous-Bowditch curves and FT spectra. Overall, both shortenings displayed similar \( E_d \) behavior encompassing three different scaling regions. In the first region (at low \( \gamma_0 \)), \( E_d \) scales nearly as a quadratic function of \( \gamma_0 (E_d \propto \gamma_0^2) \) in accordance with the linear regime (Tschoegl 1989; van der Vaart 2013). The reason why an exact power of 2 is not observed is related to the mild increase of \( G'' \) at low \( \gamma_0 \) (Fig. 4.7). In the second region (at medium \( \gamma_0 \)), \( E_d \) raises to a larger power ascribed to material yielding and the concomitant rise of \( G'' \). Finally, in the third region, \( E_d \) increases linearly (\( E_d \propto \gamma_0 \)) attributed to the decrease of \( G'' (G'' \propto \gamma_0^{-1}) \).
4.4.6 Thixotropic behavior

On a microscopic context, thixotropy of fats can be seen as a time-dependent reversible process involving two potential processes. The first deals with the breakdown of linkages among fractal microstructures forming the space-filling network and possibly its separation into flocs during strong shear. The second comprises the subsequent rebuild of the network initiated by weak crystal bonds undisrupted by shear stress, during rest (Fukada et al. 1961). The primer reduces structural strength and viscosity while the latter results in their recovery (Mewis and Wagner 2009). A robust approach to measure the degree of thixotropy of solid pasty materials in a non-destructive fashion is by following the evolution of the elastic modulus ($G'$) during rest after preshearing (Coussot et al. 2006).

![Figure 4.8](image)

**Figure 4.8** Recovery of the elastic modulus $G'$ after cessation of steady shear. a) R1-R5: roll-in shortenings; b) S1-S4: all-purpose, cake and icing shortenings.

To quantify thixotropy precisely, we imposed sufficiently small oscillations ($\gamma_0=5\times10^{-5}$) to probe the LVR region and not interfere with the kinetics of recovery at “rest”. Fig. 4.8 illustrates the thixotropic behavior of R1 and S1 in which the application of $\gamma_0=0.1$ in the second period resulted in 2 and 3 log order reduction in $G'$ for R1 and S1 respectively. This finding suggests that roll-in shortenings are less shear sensitive than other bakery shortenings. After shearing, the
moduli evolve with time following a power law relationship \((G' \sim t^n)\) in accordance with the literature (Mewis and Wagner 2009). According to the power law scaling with \(n<1\), the changing rate \(dG'/dt\), indicating rebuilding of the crystal network, decreases monotonically with time. The rest time after cessation of shear was constrained to 3 min although no equilibrium state \(G'\) was reached, as we are concerned with short timescales relevant to the lamination process.

Table 4.3 Inverse slope \((k)\) obtained from fitting the relative intensity of the third harmonic \(I_3/1\) from LAOS experiments to Eq. 2. Power law exponent \((n)\) derived from log-log plots of \(G'\) vs. \(t\) like those displayed in Fig 4.8. Relative rebuilding \((G'/G'_0)\) after 20 s of flow cessation in thixotropy tests. Group means sharing superscripts were not significantly different \((p>0.05)\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(k (-) \times 10^{-2})</th>
<th>(n (-))</th>
<th>(G'/G'_0 (-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1.26±0.06(^a)</td>
<td>0.10±0.02(^a)</td>
<td>0.64±0.03(^a)</td>
</tr>
<tr>
<td>R2</td>
<td>0.58±0.04(^b,c)</td>
<td>0.12±0.01(^a,c)</td>
<td>0.56±0.01(^b,c)</td>
</tr>
<tr>
<td>R3</td>
<td>0.72±0.07(^b)</td>
<td>0.08±0.01(^a)</td>
<td>0.65±0.01(^a)</td>
</tr>
<tr>
<td>R4</td>
<td>0.72±0.05(^b)</td>
<td>0.08±0.02(^a)</td>
<td>0.70±0.05(^a)</td>
</tr>
<tr>
<td>R5</td>
<td>0.87±0.08(^b)</td>
<td>0.09±0.01(^a)</td>
<td>0.71±0.02(^a)</td>
</tr>
<tr>
<td>S1</td>
<td>0.40±0.02(^c)</td>
<td>0.31±0.03(^b)</td>
<td>0.34±0.00(^b)</td>
</tr>
<tr>
<td>S2</td>
<td>0.39±0.06(^c)</td>
<td>0.24±0.03(^b,c)</td>
<td>0.42±0.03(^b,d)</td>
</tr>
<tr>
<td>S3</td>
<td>0.27±0.07(^c)</td>
<td>0.29±0.04(^b)</td>
<td>0.34±0.00(^b)</td>
</tr>
<tr>
<td>S4</td>
<td>0.36±0.03(^c)</td>
<td>0.16±0.01(^a,c,d)</td>
<td>0.52±0.02(^c,d)</td>
</tr>
</tbody>
</table>

Table 4.3 summarizes the relative thixotropic time and percentage of regeneration within the first \(t=20\) s of rest. Generally, lower power law exponents of \(n=0.08-0.12\) characterized the kinetics of the thixotropic recovery of roll-in shortenings independent of their composition and \(\Phi\). In addition, roll-in shortenings reversed the most \((G'/G'_0)\) the strain softening imposed by shear forces, with values ranging from 0.56 to 0.71 after ceasing flow. In contrast, other commercial shortenings regenerated to less extent their original structure \((G'/G'_0=0.34-0.42)\) except icing S2 \((G'/G'_0=0.52)\). As alluded to earlier, our experimental results can be interpreted as follows: during shearing, fractal microstructures making up the fat crystal network are detached from their links and possibly fragmented into smaller flocs. After cessation of shear, microscopic rearrangements take place, reinforcing the pre-existing structural network, which translate into the monotonic increase of \(G'\). Similar findings have been reported for butter, attributing thixotropic softening and recovery to the disintegration and reformation of the network, indicated by changes on the degree of crystallization (Fukada et al. 1961). In an industrial setup, roll-in shortenings are extruded and continuously layered onto the dough. As observed, a great extent of
recovery takes place instantaneously at rest, suggesting that increased thixotropy plays a relevant role on the functionality of roll-in shortenings where process times of lamination are of the order of a few seconds at most (Chakrabarti-Bell et al. 2010). Commercially, a certain degree of strain softening or “flowing” for proper sheeting of the fat onto the dough as well as a fast recovery for preventing oiling-off or fusion of the dough-fat layers may be highly desirable features.

4.5 Conclusions

In this paper, we have investigated many aspects of the rheological behavior of shortenings as inherently related to their performance and functionality. Special emphasis has been laid on the mechanical properties of roll-in shortenings due to their intriguing nonlinear phenomena. Prior to any measurement, a protocol was devised that allowed for accurate characterization of material functions and circumvented problems commonly encountered in soft solids such as structural breakdown and slippage. Generally, the linear rheological parameters of shortenings are assumed to be functions of physico-chemical properties including molecular composition and $\Phi$. However, this is clearly not the case as demonstrated by their similar linear viscoelastic properties irrespective of these parameters. All shortenings exhibited weak-frequency dependency and comparable $G'$ ranging from $0.6-4.5 \times 10^6$ Pa, reminiscent of viscoelastic solids ($G' > G''$). Likewise, $\gamma_y$ (0.8-2.5$\times 10^{-4}$) and $\tau_y$ (46.4-593.9 Pa) remained unremarkable defying the prima facie assumption that specific ranges in these material properties leads to improved roll-in functionality. Nevertheless, roll-in shortenings displayed prominent differences in nonlinear viscoelastic behavior reflected in the contours of the Lissajous-Bowditch curves and their FT spectra. In the Lissajous figures, less local intracycle strain hardening and average intercycle strain softening were observed qualitatively. In the FT spectra, the intensity of $I_{3/1}$ of roll-in shortenings denotes a more-gradual transition into the nonlinear regime, reaching a smooth plateau without stress decays unlike other samples. Conversely, the energy dissipated during oscillation shows similar power law regimes for all samples. Remarkably, all roll-in shortenings presented enhanced thixotropy manifested by lower power law exponents ($n= 0.08-0.12$), indicative of prompt structural rebuilding ($G'/G'0 = 0.56-0.71$) after cessation of shear. Based on the foregoing observations, we can infer that roll-in shortenings possess a distinctive multiscale network encompassing fragile and robust structural elements. The former confer their small linear envelope, while the latter the ability to withstand substantial shear deformations
without rupturing and rapidly reforming at rest periods. Such rheological signatures may be essential to the roll-in process, which demands some degree of shear softening for adequate lamination coupled with the need for retaining continuous, unbroken fat thin films. Finally, we note that albeit Lissajous-Bowditch curves and FT spectra lend insight into the nonlinear behavior of roll-in shortenings, they have major shortcomings such as lack of a clear physical interpretation for the patterns observed. In the future, we seek to define more accurate LAOS viscoelastic functions and establish structure-rheology relationships for roll-in shortenings.

4.6 Acknowledgements

The authors thank Randy Ewoldt of the University of Illinois, Urbana-Champaign for providing the Matlab FT algorithm and for his always-stimulating conversations on rheology.

4.7 Compliance with ethical standards

The authors declare no conflict of interest

4.8 References


CHAPTER 5: NONLINEAR VISCOELASTICITY OF FAT CRYSTAL NETWORKS

Braulio A. Macias-Rodriguez\textsuperscript{a}, Randy H. Ewoldt\textsuperscript{b} and Alejandro G. Marangoni*\textsuperscript{a}

Under revision: Soft Matter

\textsuperscript{a}Department of Food Science, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. Email: amarango@uoguelph.ca

\textsuperscript{b}Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, 6801, USA

5.1 Abstract

The rheology of fat crystal networks under linear shear deformations has been extensively studied due to its role in material functionality and sensory perceptions. In contrast, there has been limited focus on their viscoelastic response under large shear deformations imposed during processing (e.g. extrusion and rolling) and product use (e.g. spreading). We probed the nonlinear viscoelastic behavior of fats displaying mechanics akin to ductile and brittle solids using large amplitude oscillatory shear (LAOS). Using the FT-Chebyshev stress decomposition method, and local measures of nonlinear viscoelasticity, we obtained rheological “fingerprints” relevant to bulk material properties. We found that ductile fats dissipate more viscous energy than brittle fats and show increased plastic deformation. Structural characterization revealed the presence of three hierarchy levels and layered microstructures in ductile fats in contrast to only two hierarchies and random microstructures in brittle fats. We suggest that these structural features account for increased viscous dissipation, which contributes to the ductile-like macroscopic behavior.

Keywords: fat, ductile, brittle, rheology, nonlinear.

5.2 Introduction

Fats are an example of polycrystalline pasty materials composed by an interacting continuous network at particle concentrations above the critical volume fraction ($\phi \approx 0.05$-$0.10$), and a liquid phase contained within.(Marangoni et al., 2012) The essential role of fats in foods (i.e., lubrication, texture), and the consumer health-driven trend towards low-saturates and no-\textit{trans}
foods due to the association of “bad fats” with cardiovascular diseases,(Marangoni et al., 2012; Uauy et al., 2009; Vartiainen et al., 2010) have led to increased interest in these systems. From a mechanical perspective, fats resemble flocculated colloidal gels with the magnitude of the elastic modulus depending on the microscopic crystal network and its structural heterogeneity.(Narine and Marangoni, 1999b; van den Tempel, 1961) This structural organization allows fats to sustain stress or deformation up to a certain limit, beyond which they yield and irreversibly deform displaying some intriguing nonlinear rheological phenomena. Some of these rheological features include yielding, work softening, shear thinning, intracycle strain stiffening and thixotropy.(Haighton, 1965; B. Macias-Rodríguez and Marangoni, 2016a; Scott Blair, 1954; Sone, 1961; Thareja, 2013)

The rheological properties of fats are a consequence of the remarkably complex hierarchical organization, showcasing structural building blocks spanning from the molecular to the micro world, and their physical interactions.(Marangoni et al., 2012; Narine and Marangoni, 1999a) Nano-scaled crystal units arise from the epitaxial stacking of crystal lamellae which in turn results from translational displacements of the unit cell.(Acevedo et al., 2011) The unit cell is made up by TAGs molecules stacked longitudinally and side-by-side, adopting a specific subcell unit arrangement or polymorphic state ($\alpha$, $\beta'$, $\beta$). Nanoplatelets further self-assemble into large fractal clusters or aggregates via diffusion-limited-cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA) to form a space-filling micro-scaled gel-like network.(Narine and Marangoni, 1999b; Peyronel et al., 2014b) The microstructure is held together by van der Waals forces or short-range attractive interactions and presents a variety of morphologies (e.g., spherulitic, needle-like, grain-like) which offers equal variety in the mechanics of deformation.(Heertje, 1993)

A number of research studies have sought to establish rheology-structure relationships infat crystal networks.(Marangoni and Rogers, 2003; Narine and Marangoni, 1999a, 1999b; van den Tempel, 1961) Particularly, there has been significant progress on understanding fat linear viscoelasticity, due to its role in macroscopic mechanical functionality. By functionality or performance, we refer to the range of textural viscoelastic attributes that make fats suited for specific applications, i.e. a roll-in fat must be firm and spreadable to enable extrusion, sheeting and folding of layered doughs”. Fat linear viscoelasticity concepts have been developed based on
fractal theories originally proposed for colloidal gels. Like colloidal gels, the elastic modulus of fats (correlated to their firmness) scales in a power-law fashion with particle volume fraction $G' \sim \phi^n$, where $n$ is related to the compactness of the individual clusters or mass fractal dimension ($D$). (Narine and Marangoni, 1999b, 1999c) At higher particle concentrations $\phi > 0.1$, as observed for most complex fats, fats exist in a weak-link regime where the elasticity of the network is given by the interfloc links rather than the fractal flocs. (Narine and Marangoni, 1999b, 1999c) Given the complexities imposed by the multiple physical length scales of fats, developing rigorous relationships between their interparticle forces, structure and rheology remains a challenging problem.

While there has been much focus on fats’ mechanical response in the linear regime, there has been limited attention on their nonlinear regime—that is, at large deformations. (B. Macias-Rodriguez and Marangoni, 2016a) During application processes and final product use, fats are subjected to substantial deformations well beyond their onset of nonlinear behavior ($\gamma_c = 0.03\%$, $\tau_c = 50-500$ Pa). (B. Macias-Rodriguez and Marangoni, 2016a) For instance, extrusion and rolling, processes akin to cold working of metals (forging), induce plastic deformation to shape bulk fat into micron-sized thin films by imposing nonlinear rates of deformation in the order of $1-100$ s$^{-1}$ and pressures of up to 50 kPa. (Marangoni et al., 2012) In a broader context, yielding and nonlinear behavior of a variety of colloidal gels has been studied in much detail using large-amplitude oscillatory shear (LAOS) rheology. For example, the yielding process under LAOS has been attributed to fatigue-induced fluidization in attractive carbon black gels (Gibaud et al., 2016), breakdown from large to gradually smaller structural length scales far above the primary particle size in concentrated colloidal gels (Kim et al., 2014), and microstructural anisotropy in thermoreversible nanoparticle gels. (Min Kim et al., 2014)

Although these contributions have provided valuable insights, LAOS analysis have not been applied to fat crystal networks, which constitute materials, possibly more complex and heterogeneous in terms of structure (i.e. fats self-assemble in multiple physical lengthscales to form the polycrystalline microscopic network) than any model colloidal gel previously studied under LAOS. While step input tests (e.g. creep compliance, stress relaxation, start-up of steady shear) could also be used, we use LAOS because, in contrast to step-input tests, oscillations (i) gradually lead up to yield, (ii) can decompose energy storage and loss mechanisms, and (iii) have
a better signal-to-noise ratio for comparing between materials (since oscillations lock-in on each frequency probed). All three features are important for distinguishing the yielding behavior of the materials studied here. Various frameworks have been proposed to analyze the nonlinear LAOS response such as FT-Chebyshev stress decomposition and the sequence of physical processes (SPP), the latter of which was recently applied to describe the broadened yielding of a heterogeneous colloidal gel. Despite the utility of this approach for time-resolved data analysis, we refrain from using time-dependent dynamic moduli $R'$ and $R''$ as these measures are inherently high dimensional and paradoxical in the limit of small linear deformations (Rogers, 2012) Instead, we favor the FT-Chebyshev stress decomposition method as it provides “clean” and meaningful low-dimensional metrics that successfully simplify the complex nonlinear rheological phenomena of the fats investigated here. (Hyun et al., 2011)

In particular, we contrast two material classes of fats that share nonlinear mechanical responses similar to solid materials, from which we draw analogies. We determine clear elastic and viscous rheological fingerprints in the LAOS regime corresponding to ductile versus brittle failure in fat crystal networks, which correlate with their observed macroscopic behavior and hierarchical structure.

5.3 Experimental

5.3.1 Sample preparation

Bulk composition and linear elastic moduli of the samples used in this study are described in Table 5.1.

**Table 5.1** Fat functionality and bulk composition for each material class, linear elastic moduli and maximum stress at rupture or fracture at $\omega \approx 3.6$ rad{s$^{-1}$} and $\gamma_0=0.01\%$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>$G'_{LVE}(\times 10^6)$</th>
<th>$\tau_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>Roll-in non-hydrogenated canola oil, modified palm and palm kernel oils</td>
<td>2.1±0.2</td>
<td>3964.8±102.1</td>
</tr>
<tr>
<td>D2</td>
<td>Roll-in fully hydrogenated soybean oil, soybean oil and glycerol monopalmitate (in-house)</td>
<td>2.1±0.3</td>
<td>4464.4+117.9</td>
</tr>
<tr>
<td>B1</td>
<td>All-purpose non hydrogenated palm oil and modified palm oil</td>
<td>4.7±0.8</td>
<td>4874.7±61.1</td>
</tr>
<tr>
<td>B2</td>
<td>All-purpose soybean oil interesterified</td>
<td>1.8±0.1</td>
<td>3071.9±151.6</td>
</tr>
</tbody>
</table>
For a detailed description on the molecular composition and other physico-chemical properties of the samples studied herein, refer to (B. Macias-Rodriguez and Marangoni, 2016b). All samples had intermediate volume fraction ($\phi_{16^\circ C}\approx0.2-0.3$) (B. Macias-Rodriguez and Marangoni, 2016a) and were of commercial origin as their physico-chemical properties cannot be easily replicated in a bench scale, and hence represent “real” materials. The only exception was sample D2 which was formulated and crystallized in house as described elsewhere (Acevedo and Marangoni, 2013) Although exact material processing conditions of D1, B1 and B2 are unknown, it can be inferred that that brittleness is imparted via static crystallization where crystal growth is promoted over nucleation, while ductility or “plasticity” is obtained from dynamic crystallization, high degree of cooling and mechanical working, where crystal nucleation is favored and crystal growth is delayed (Acevedo and Marangoni, 2013) Prior to rheological characterization, samples were carefully prepared in the form of cylinders of 30mm diameter using a hollow steel cylinder and stored at 16 °C overnight to allow for reformation of fractured bonds or local damage induced by cutting and to remove residual stresses. Cutting was performed using a wire lubricated with mineral oil to minimize flaw or crack formation that may act as points of stress concentration leading to premature failure.

5.3.2 Rheometry

Samples were carefully transferred onto the lower plate of a rotational rheometer (MCR 302, Anton Paar) and loaded within a parallel plate geometry using 3±0.5 N axial force to avoid the formation of new microstructures and ensure reproducible results (Macias-Rodriguez and Marangoni, 2016a). It has been shown, that overloading modifies the rheology, i.e. it reduces the critical strain and critical stress and causes a right-shift of the “flow” point $G’=G’’$, and the microstructure of fat crystal networks. After loading, samples were allowed to relax the axial force to a constant value over a zero strain relaxation test for at least 15 min, being equilibrated at 16 °C. This temperature was chosen to resemble thermal conditioning during rolling and layering of fats (B. Macias-Rodriguez and Marangoni, 2016a) Temperature was controlled using Peltier units located in the lower plate and the hood of the rheometer. All experiments were performed with parallel plate geometries. Compression tests were performed with parallel plates (DIA= 50 mm) lubricated with a thin layer of mineral oil to reduce friction at the boundaries. Shear oscillatory tests were performed with parallel plates (DIA= 20 mm) modified with filter
paper (Whatman grade 5, GE Healthcare Life Sciences) attached to the top and bottom plates (See modified geometry in appendix 1 Fig. A.1) to improve sample adhesion to contacting boundaries and minimize wall slip during measurements. Parallel plate geometries were selected despite its heterogeneous shear rate field, as it allows for loading of preformed samples.

Small amplitude and large amplitude oscillatory shear experiments (SAOS, LAOS) were performed in strain-controlled mode on the combined-motor-transducer rheometer. Tests involved strain sweeps from the linear region until post-yielding of the material ($\gamma_0=0.01-100\%$) in a frequency space ($\omega=0.1-5.9$ rad s$^{-1}$) representative of the rolling process (Chakrabarti-Bell et al., 2010). Strains $\gamma_0$ and stresses $\tau$ represent bulk apparent responses after failure or when deviations occur due to shear instabilities ($\gamma_0\approx2\%$). However, overall stress is true as measured with loads and displacements at the boundary. Strain amplitude $\gamma_0$ represents apparent strain (e.g. deviates from true strain when there is shear-banding or slip).

5.3.3 LAOS analysis

Beyond the linear viscoelastic region, at large input amplitudes, complex nonlinear phenomena manifest in the oscillatory stress response as nonsinusoidal waves with higher-order harmonic contributions. If represented via Lissajous-Bowditch (L-B) curves, parametric plots of stress versus strain or strain rate, nonlinearity causes deviation from an elliptical shape of the response. Consequently, the conventional interpretation of the elastic and viscous moduli in the theory of linear viscoelasticity is no longer applicable. Several methods have been developed to interpret nonlinear contributions including Fourier transform (FT) rheology and stress decomposition method described via Chebyshev polynomials (Hyun et al., 2011) In FT rheology, the stress signal is expressed as a Fourier series encoding the amplitude $I_n$ and the phase $\phi_n$ of higher harmonics at each order $n$. In this framework, the extent of nonlinearity can be quantified with a simplified metric of the normalized intensity of the third harmonic $I_3/I_1$ (higher harmonics are also present, but the third-harmonic is dominant at leading order). Although useful, this single approach loses the ability to decompose energy storage and loss concepts, and therefore offers limited insights into the physics of nonlinear viscoelasticity. Several resolutions to this have been proposed, (Hyun et al., 2011) including the stress decomposition method proposed by (Cho et al., 2005) and extended by (Ewoldt et al., 2008), and local measures of elastic and viscous behavior. (Ewoldt et al., 2008; Rogers, 2012)
In the stress decomposition framework, the total stress is represented as a superposition of the so-called elastic $\tau'$ and viscous stresses $\tau''$ using symmetry arguments (The symmetry arguments are mathematically well-defined, so long as shear-symmetry is maintained. We note that in extreme cases, such as discontinuous constitutive equations with yield, the decomposed stresses may mix elastic and viscous effects at very large amplitudes) (Cho et al., 2005). The elastic and viscous stresses are then unambiguously described by a set of orthogonal Chebyshev polynomials of the first kind, as proposed by (Ewoldt et al., 2008)

\[
\tau'(x)=\gamma_0 \sum_{n\text{ odd}} e_n(\omega, \gamma_0) T_n(x),
\]
\[
\tau''(y)=\dot{\gamma}_0 \sum_{n\text{ odd}} v_n(\omega, \gamma_0) T_n(y),
\]

Where $T_n(x)$ and $T_n(y)$ corresponds to $n$th-order of the Chebyshev basis functions, $x=\chi(t)/\gamma_0$ and $y=\gamma(t)/\dot{\gamma}_0$, with $\gamma_0$ and $\dot{\gamma}_0$ being the maximum in-cycle strain and shear rate, and $e_n(\omega, \gamma_0)$ and $v_n(\omega, \gamma_0)$ refer to the elastic and viscous Chebyshev coefficients of order $n$. The Chebyshev coefficients are directly related to the higher order Fourier coefficients in the time-domain as:

\[
e_n = G'_n(-1)^{(n-1)/2}
\]
\[
v^n = G''_n/\omega = \eta''_n,
\]

respectively. Note that even-harmonic ($n = \text{even}$) Fourier and Chebyshev coefficients are neglected as they are associated with broken shear symmetry, e.g. with responses that have not yet reached the time-periodic state. (It is worth noting that even harmonics are not related to wall slip in general (Ewoldt et al., 2010). They are commonly mistaken as such in the literature, but the only slip-related even harmonics are those associated with broken shear symmetry, such as “dynamic” wall slip that inhibits steady state). Just as the third-order Fourier harmonic, the third-order Chebyshev basis function signals depart from linearity and additionally provide physical meaning to the stress response. It is important to emphasize that linear material functions $G'$ and $G''$ (equivalent to $G'_1$ and $G''_1$), represent average stress responses equivalent to first-order Chebyshev coefficients $e_1$ and $v_1$. Instead, third and higher-order Chebyshev coefficients capture uniquely local responses in the distorted stress signal (i.e., bent, twisted L-B curves). Specifically, the signs of the leading-order elastic and viscous Chebyshev coefficients $e_3$ and $v_3$, reveal the underlying cause driving average changes in the elastic and viscous intercycle stress response. For example, for $G'_1$ decreasing, and $e_3>0$, large instantaneous strain-rates are responsible for the average elastic softening. In the same way,
for $G_1''$ decreasing and $v_3<0$, large instantaneous strain-rates also drive average viscous thinning. For a full description on how to interpret the leading order Chebyshev LAOS strain nonlinearities, refer to Ewoldt and Bharadwaj (2013), who updated the physical interpretation of nonlinear measures provided by Ewoldt et al. (2008).

Separate from the stress-decomposition, we will find great value in using the local measures of nonlinear viscoelasticity proposed by (Ewoldt et al., 2008) for LAOS, which can be interpreted geometrically from L-B curves. Metrics of elastic energy storage and viscous energy dissipation can be determined from characteristic points during the oscillation (at extreme values of strain and strain-rate) as

$$G_M' = \frac{d\tau}{d\gamma} \bigg|_{\gamma=0} = \sum_{n:\text{odd}} nG_n' = e_1 - 3e_3 + \ldots,$$

$$G_L' = \frac{\tau}{\gamma} \bigg|_{\gamma=\pm \gamma_0} = \sum_{n:\text{odd}} G_n'(-1)^{(n-1)/2} = e_1 + e_3 + \ldots,$$

$$\eta_M' = \frac{d\tau}{d\gamma} \bigg|_{\gamma=0} = \frac{1}{\omega} \sum_{n:\text{odd}} nG_n''(-1)^{(n-1)/2} = v_1 - 3v_3 + \ldots,$$

$$\eta_L' = \frac{\tau}{\gamma} \bigg|_{\gamma=\pm \gamma_0} = \frac{1}{\omega} \sum_{n:\text{odd}} G_n' = v_1 + v_3 + \ldots,$$

where $G_M'$ is the minimum-strain or tangent modulus at $\gamma_0=0$ and $G_L'$ is the large-strain or secant modulus at $\gamma_0=\gamma_{\text{max}}$. Likewise, $\eta_M'$ is the minimum-rate viscosity and $\eta_L'$ is the large-rate viscosity. These deliberately-chosen material functions reduce to $G_1'$ and $G_1''$ $(\eta_1'' = G'' / \omega)$ in the linear regime.

For LAOS analysis, raw strain-stress data were collected at a sampling rate of 512 points per oscillatory cycle. Due to the thixotropic nature of our samples, a minimum of 20 oscillatory cycles were applied to reach a quasi-steady stress response. Typically, 3-5 waveforms at each coordinate pair $\{ \omega, \gamma_0 \}$ were input to a custom written MATLAB code (Ewoldt et al., 2009) The software processes the signal with a discrete Fourier transform, calculates relevant measures of
nonlinear viscoelasticity, and smooths and reconstructs the stress signal by allowing only odd, integer-harmonic components, up to a cutoff such that $I_n/I_1 \geq 0.05$ to avoid noise. Filter performance for selected deformations have been included in supplementary material (Appendix 1 Fig. A.2). Overall, the multiple waveform collection and post processing provides greater accuracy, increased signal to noise (S/N) ratio and removes random noise obscuring any real material response (Ewoldt et al., 2009). To further minimize the effect of shear artifacts (instabilities, slip, edge fracture) on the LAOS data, we constrained our LAOS analysis to $\gamma_0 \leq 10\%$ as experimental error increased at larger strains and severe slip was even visually observed at $\gamma_0 \approx 30\%$ and beyond.

5.3.4 Scanning electron microscopy

Fats were imaged before and after being subjected to oscillatory shear deformations. Prior to sampling, sheared fats were subjected to 25 oscillatory cycles ($\gamma_0 = 50\%$) and then carefully removed from the rheometer plate with the parallel disk in the zero strain position. Fat pieces (for both unsheared and sheared samples) were then carefully removed with a spatula at intermediate locations between the edge and the center of the samples for unsheared and sheared samples. To visualize the microstructural features of the fat crystal network is necessary to remove the liquid oil using solvents, which have shown to retain the structural integrity of the solid crystalline network to great extent (Chawla et al., 1990; Heertje, 1993). This was achieved by suspending thin sample pieces in a ratio of 1:25 fat-solvent. Ductile fats (D1 and D2) were suspended in a 8:2 (v:v) isobutyl alcohol-hexane mixture to enhance removal of the more-confined oil phase, while brittle fats (B1 and B2) were suspended uniquely in isobutyl alcohol (Chawla et al., 1990). Shortenings were statically deoiled at 20 °C (roll-in fat) and 14 °C (brittle fats) for 48 h, filtered (Whatman No 5) to remove solvent and liquid oil, and finally allowed to stand on filter paper overnight to vaporize any remaining solvent Minor structural changes include smoothing of the edges of crystal aggregates due to partial dissolving of triacylglycerols in the solvent during deoiling (Heertje, 1993). Cryo-SEM was used to image the microstructure of the samples. The samples were then attached to the copper sample holder using the Tissue-Tek embedding medium. The sample holder was immersed in a liquid nitrogen slush (-207 °C) using an Emitech K1250x Cryo-preparation unit (Ashford Kent, UK), freeze-fractured to expose the underlying microstructure and sputter-coated for 2m with gold using a 20 mA deposition
current, 7nm min\(^{-1}\) deposition rate. The sample holder was transferred to the SEM stage (Hitachi S-570, Tokyo, Japan) with accelerating voltage of the electron beam of 10 kV. Images were captured digitally using the Quartz PCI imaging package (Quartz Imaging Corp., Vancouver, Canada).

**5.3.5 Ultra Small Angle X-Ray Scattering (USAXS)**

Samples were prepared in the form of “disks” with approximate dimensions of 20mm×1mm (diameter×thickness) and were not subjected to oscillatory shear. Samples were then mounted into Grace-Bio-Labs (Oregon, USA) circular silicon isolators, and the isolator sides were sealed with microscope covers to contain the sample.

The one-dimensional (1-D)-collimated mode (Long et al., 1991) using the Bonse Hart Instrument (Ilavsky et al., 2012; Ilavsky and Jemian, 2009) at Argonne Photon Source (APS, Argonne National Laboratory) sector 9 was used for the X-ray scattering experiments. This instrument makes use of two sets of crystals pairs: the collimating set and the analyzer set. The USAXS geometry utilizes multiple crystal reflections to provide ultra-high resolution only in the vertical direction. By rotating the analyzer crystal pair using small steps, the scattered intensity at various angles can be measured with an extremely high angular precision or resolution. A complete operational description of the instrument can be found elsewhere. (Ilavsky et al., 2013)

Data collected was numerically desmeared (Lake, 1967) to recover the differential scattering cross section. Instrument control and data acquisition were performed using the Spec software for diffraction experiments. Each data point is one measurement for either 0.5, 1, or 2 seconds, as one goes from lower to higher \( q \) (\( A^{-1} \)). Indra, and IgorPro-based software were used for data reduction, removal of multiple scattering and to determine the absolute intensity. The Irena (Ilavsky and Jemian, 2009) IgorPro-based software was used for data interpretation using the Unified fit (Beaucage, 1996, 1995) and the Guinier-Porod model. (Hammouda, 2010) Both models, implemented in the Irena software, employ a non-linear regression analysis to find the best fitting parameters. Two repetitions for each sample were analyzed and the average of the fitting-parameters given by Unified Fit and Guinier-Porod models were reported.
5.3.5.1 Data Collection and Data Analysis
The one-dimensional (1-D)-collimated mode(Long et al., 1991) using the Bonse Hart Instrument(Ilavsky et al., 2012; Ilavsky and Jemian, 2009) at Argone Photon Source (APS, Argonne National Laboratory) sector 9 was used for the X-ray scattering experiments. This instrument makes use of two sets of crystals pairs: the collimating set and the analyzer set. The USAXS geometry utilizes multiple crystal reflections to provide ultra-high resolution only in the vertical direction. By rotating the analyzer crystal pair using small steps, the scattered intensity at various angles can be measured with an extremely high angular precision or resolution. A complete operational description of the instrument can be found elsewhere (Ilavsky et al., 2013). The collected data were numerically desmeared(Lake, 1967) to recover the differential scattering cross section. Instrument control and data acquisition were performed using the Spec software for diffraction experiments. Each data point is one measurement for either 0.5, 1, or 2 seconds, as one goes from lower to higher q (Å⁻¹). Indra, and IgorPro-based software were used for data reduction, removal of multiple scattering and to determine the absolute intensity. The Irena(Ilavsky and Jemian, 2009) IgorPro-based software was used for data interpretation using the Unified fit(Beaucage, 1996, 1995) and the Guinier-Porod model.(Hammouda, 2010) Both models, implemented in the Irena software, employ a non-linear regression analysis to find the best fitting parameters. Two repetitions for each sample were analyzed and the average of the fitting-parameters given by Unified Fit and Guinier-Porod models were reported.

5.3.5.2 USAXS Data Analysis
During USAXS the scattering intensity is measured as a function of the scattering vector q, defined as \( q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \) where \( \theta \) is the scattering angle and \( \lambda \) the wavelength of the incident X-ray. An estimation of the length scale (L) of the material probed can be obtained from the relation \( L = \frac{2\pi}{q} \). It is relevant to note that the Bonse-Hart system permits the collection of a sufficient number of data points in only a few minutes to cover the range \( \sim 100 \text{ nm} < L < 10-30 \mu\text{m} \). The scattering patterns were analyzed to find \( I(q) \) vs. q regions that either follow Guinier scattering or Porod-power law scattering.

Equation 5 shows the Unified Fit(Beaucage, 1996, 1995) model expression.
Where $P$ is the Porod exponent that yields information on the structure of the aggregate and $R_g$ is the radius of gyration. The exponential term $\exp(-\frac{q^2R_{gi}^2}{3})$ shows that the Unified Fit model represents all scattering objects as approximately spheres, where $i$ represents the structural level under study, while $i-1$ indicates the previous level. The first term in equation 7 describes the Guinier region, valid for $q \leq q_1$, and the second term, the Porod power law valid for $q \geq q_1$. The requirement is that the Guinier and Porod terms, together with their derivatives must be continuous at $q_1$. $G$ and $B$ are the Guinier and Porod scale factors respectively with $G$ related to the volume of the scatterers and $B$ containing specific scattered surface area information.

We focus on the $R_g$ and $P$ parameters that come out of fitting the data to the Unified Fit model. The systems were discovered to be fractal in nature as observed by a straight line in the $q$-region observed in two or three sections. It is noteworthy that the radius of gyration $R_{g3}$ in the third region was held constant to fit the power-law slope $P_3$ and hence was not used to draw conclusions pertaining the size of the scatterers.

When a fractal interpretation is given to the data, the $P$ value gives information about the fractal dimension of the scatterers. A value of $|P|= 4$ indicates a scatterer or particle with a smooth surface and a fractal dimension $D_s = 2$. If $3 \leq |P| < 4$ then $6 - |P|$ is the surface fractal dimension ($2 < D_s \leq 3$). When $1 \leq |P| < 3$, then the value of $|P|$ is the fractal dimension, $D = |P|$. But if $|P| > 4$, all that is known is that there is diffuse interface. (Beaucage, 1996, 1995)

The other model used for interpretation of the scattering data was the Guinier-Porod one. This model, a variation of equation 7 (Hammouda, 2010), recognizes that the primary particles can have shapes other than spherical, indicated by the terms involving $s_1$ and $s_2$ in equation (8). The value of the parameter $s$ indicates platelets when $s=2$, cylinders or rods when $s=1$ and spheres when $s=0$. Similar to the Unified Fit model, parameters like the radii of gyration and the power law exponents are obtained. The difference is that this model defines a structural level in a wider
\( q \)-region, in that each structural level can have multiple radii of gyration and power law slopes - as long as the scattering comes from one population of primary particles. The fitting functions are

\[
I(q) = \frac{G_2}{q^{2q_2}} e^{-\frac{q^2 R_2^2}{3-q_2}} \quad q \leq q_2
\]

\[
I(q) = \frac{G_1}{q^{3q_1}} e^{-\frac{q^2 R_1^2}{3-q_1}} \quad q_2 \leq q \leq q_1
\]

\[
I(q) = \frac{B}{q^{q_1}} \quad q \geq q_1
\]

where the limits \( q_1 \) and \( q_2 \) are chosen manually by the experimentalist.

### 5.4 Results and discussion

**Figure 5.1** Evidence of ductile (D1) versus brittle (B1) deformation of representative fats during compression. a) views from below a transparent bottom plate for specimens with \( h_0=2 \text{ mm} \), b) side views for specimens with \( h_0=10 \text{ mm} \). A ductile fat (D1) plastically deforms, whereas a brittle fat (B1) fails showing cracks and a cleavage line at \( \Delta h/h_0=-0.10 \). At higher deformations, ductile (D1) also show cracks that onset at the periphery of the test piece possibly triggered by shear stresses.
Fig. 5.1 depicts macrographs of two fat samples lending evidence of ductile (D1) and brittle (B1) material deformation during the application of axial normal force. Similar behaviors were observed for ductile D2 and brittle B2 (See Appendix Fig. A.3). Views from below (Fig. 5.1a) demonstrated that the surface of D1 remained mostly crack-free within the middle of the parallel plate (DIA= 20 mm), unlike B1 where the formation of a number of large cracks was evident throughout the samples. Views from the side (Fig. 5.1b) and stress-strain curves (Fig. 5.2) also revealed that D1 specimens underwent larger plastic deformation, when compressed up to \( \varepsilon_e=0.15 \), whereas B1 test pieces could not sustain the applied compressive strain, showing a non-monotonic in the strain-stress curve (local maximum), and cracked more readily, displaying a cleavage line. The hysteresis in the stress-strain curves (Fig. 5.2) suggests that D1 absorbed more energy due to extensive plastic flow compared to B1, which are hallmarks of ductile and brittle solids, respectively. These observations are in agreement with (van den Tempel, 1958) who suggested that in hard brittle fats shear trigger cracks which are not visible in liquid-like soft fats, but nevertheless did not provide experimental visual evidence of such cracks. In the following sections, we provide further evidence for drawing a parallel between the failure of fats under shear and the fracture of ductile and brittle solids.

**Figure 5.2** Compressive engineering stress (\( \sigma_e = F/A_0 \)) as a function of compressive engineering strain (\( \varepsilon_e = \Delta h/h_0 \)) for a representative ductile (D1) and brittle (B1) fat. The dimensions of the specimens were 20mm×10mm (DIA×height). A thin layer of mineral oil was applied to the parallel plate geometries to diminish frictional force at the edges.
5.4.1 Effect of sample thickness on rheological material functions

During shear rheology, it is assumed that materials deform homogeneously throughout the gap and remain in continuous contact with the plate periphery (Ewoldt et al., 2015). However, non-uniform flow phenomena such as wall slip and shear banding are particularly prevalent in pasty materials, particularly when using parallel plate configurations for rheological characterization (Ewoldt et al., 2015). To ensure that the measured material functions reflect the true behavior of the investigated materials, the effect of sample thickness $T_h$ (and thus gap height) on the average or first-harmonic viscoelastic moduli $G'_1, G''_1$ was determined. The viscoelastic moduli $G'_1, G''_1$ are the most-commonly used descriptors to quantify small-amplitude (SAOS) and large-amplitude oscillatory shear (LAOS) responses, and they refer to the same generic notation $G', G''$ as output by the rheometer. Fig. 5.3a, b, c illustrate stress perspectives of strain-sweep tests with their respective plots of strain ($\gamma_0$) versus the stress of the first harmonic ($\tau_1$) which contrast between the behavior of ductile-like and brittle-like fat materials. For D1, $G'_1, G''_1$ nearly overlap for $T_h=1.3, 1.5$ mm, while for B1, $G'_1, G''_1$ superimpose for all sample thickness except at $T_h=2$ mm (Fig. 5.3a, b). The lack of overlap at different thickness is an indication of slip, internal fracture planes, or other non-ideal kinematics that deviate from homogeneous simple shear. It is observed for D1 that as the sample thickness increases the peak stress and its associated strain decreases dramatically caused possibly due to interplay between slip and shear banding (Thomas, 1961) preceding failure (Fig. 5.3c). In contrast, it is observed for B1 that at $h=2000$ µm the peak strain (but not the magnitude of the stress) shifted to lower strain amplitudes arguably due to wall slip. These trends, albeit not rare to the rheometry of pastes, resonate with the behavior of brittle solids and ductile solids in which slip and shear strain localization are recurrent (Thomas, 1967) Nevertheless, we caution the reader that identifying the true cause of this behavior is not trivial as other factors such as structural changes or additional flow instabilities might also be at play. (Divoux et al., 2015)

5.4.2 Linear to nonlinear viscoelasticity

Based on the aforementioned experiments, we used a thickness $T_h=1.3$ mm for further rheological experiments as the impact of shear instabilities was less prominent. At $T_h=1.3$ mm, it was observed that the linear viscoelastic moduli $G'_1$ and $G''_1$ and the yield stress $\tau_{\text{yield}}$ determined as the maximum of the elastic stress, remained unremarkable, e.g. D1 and D2 have storage
moduli nearly two times smaller than B1 but similar to B2, and yield stress smaller than B1 by \(~400-800\) Pa and larger than B2 by \(~1000\) Pa (Table 5.1). This is agreement with our previous study in which we found that triglyceride shortenings may share similar linear elastic moduli and yield stress irrespective of their bulk functionality (Braulio Macias-Rodriguez and Marangoni, 2016). Pertaining to the nonlinear LAOS behavior, \(G'_1\) and \(G''_1\) decreased indicating that elastic softening and viscous thinning of the crystal network (e.g., disturbance of network interactions) dominate the average stress response. Moreover, when plotted as a function of input strain amplitude (See appendix 1 Fig. A.4), \(G'_1\) also decreased continuously but \(G''_1\) rose initially at \(\gamma_0 \approx 0.09\%\), reached a local maximum at \(\gamma_0 \approx 0.57\%\) and then dropped monotonically, crossing-over \(G'_1\) at \(\gamma_0 \approx 1-2\%\). The \(G''_1\) maxima is typical of type III materials which exhibit a weak strain overshoot or “Payne effect” as termed in filled elastomers (Hyun et al., 2002). In fat crystal networks, the underlying reasons of \(G''_1\) maxima and crossover of \(G'_1 = G''_1\) are unknown, however; these events might be associated to the onset of disruption of intercluster bonds and the onset of material fluidization due to structural network failure, respectively, as observed in other colloidal gels at intermediate volume fractions (Laurati et al., 2011).
Figure 5.3 First-harmonic viscoelastic moduli and stress as functions of increasing sample thickness $T_h=1.3-2$ mm. Stress perspective of strain amplitude sweeps for a) ductile fat D1 and b) brittle fat B1. c) First harmonic stress amplitude $\tau_1$ as a function of apparent strain amplitude $\gamma_0$ for both fats.
At first glance from Fig. 5.3, the behavior of $G'_1$ and $G''_1$ beyond the linear region appeared comparable across the different material classes. Upon careful inspection, it can be noted that $G'_1$ and $G''_1$ for D1 and B1 showed strikingly different failure patterns. As can be seen, D1 $G'_1$ and $G''_1$ displayed a steady decrease starting at $\tau_1 \approx 1000$ Pa. In contrast, B1 $G'_1$ and $G''_1$ showed an initial gradual decrease starting at $\tau_1 \approx 1500$ Pa followed by an abrupt drop and backward bending at $\tau_1 \approx 4000$ Pa, evoking sudden failure as the strain amplitude increases. These markedly different responses can be also visualized in the stress amplitude versus strain amplitude plots (Fig 5.3b, Th=1300µm). Both samples remained in the elastic regime up to small critical strains $\gamma_0 \approx 0.05\%$, which is typical for materials such as fat crystal networks interacting via short-range interparticle forces. (van den Tempel, 1961) It also appeared that D1 displayed more plastic deformation than B1. Both samples reached peak maxima of $\tau_1 \approx 4000$Pa and $\tau_1 \approx 4900$ for D1 and B1, respectively. Beyond the peak maxima, the stress in D1 roughly plateaus as compared to B1 in which the stress suddenly drops (similar to the compression test in Fig. 5.2). Similar findings are reported for D2 and B2 (See Appendix 1 Fig. A.5). These mechanical signatures are similar to those observed for ductile and brittle solids. While ductile solids exhibit significant plastic straining upon failure, brittle solids exhibit little, if any, inelastic deformation prior to catastrophic fracture. (Thomas, 1961) By analogy with solid materials, we thus propose that D1 and D2 act as ductile viscoelastic solids, manifested by larger plastic strains (visualized as the decrease of the local slope in the stress-deformation curve) and a plateau effect, while B1 and B2 resemble brittle viscoelastic solids, evidenced by larger elastic straining and peak stress that dramatically decreases post failure. These behaviors are qualitatively the same to those in Fig. 2, suggesting that yielding of fat crystal networks under compression and oscillatory shear are the consequence of a similar underlying phenomenon.

To provide a physical picture of the mechanisms involved in yielding of ductile (D1, D2) and brittle (B1, B2) fats, we analyzed the LAOS time-resolved stress signals using Lissajous-Bowditch curves, Chebyshev decomposition and the local nonlinear elastic and viscous metrics proposed by Ewoldt et al., (2008). LAOS analysis was performed in a frequency range of $\omega = 0.1-5.9$ rads⁻¹ and strain range of $\gamma_0 = 0.01-10\%$ to map deformation rates relevant to the industrial rolling process and probe sufficiently large deformations, nearly three orders of
magnitude higher than linear deformations. (Chakrabarti-Bell et al., 2010; B. Macias-Rodriguez and Marangoni, 2016a) For illustrative purposes, third-harmonic elastic and viscous Chebyshev coefficients are shown in Fig. 5.4 to denote departure from linearity at a representative frequency $\omega=3.6$ rads$^{-1}$. Elastic and viscous Lissajous-Bowditch (L-B) curves are mapped across the two-dimensional Pipkin space (frequency versus strain amplitude) for each material class (D1 and B1) in Fig. 5.5 and Fig. 5.6. Lissajous-Bowditch curves for all samples and 3D Lissajous-Bowditch curves for two representative samples on absolute scales at $\omega= 3.6$ rad s$^{-1}$ are included in the appendix 1 (Fig. A6-Fig. A10). Corresponding elastic and viscous rheological fingerprints at a representative frequency $\omega=3.6$ rad s$^{-1}$ for all samples are presented in Fig. 5.7 and Fig. A.11 (Appendix 1).

### 5.4.3 Chebyshev coefficients and Lissajous-Bowditch curves

**Figure 5.4** Scaled third order elastic $e_3/e_1$ and viscous $\nu_3/\nu_1$ Chebyshev coefficients as a function of strain input $\gamma_0$ at $\omega= 3.6$ rads$^{-1}$ for ductile D1 and brittle B1 fats in LAOS.

Higher-order Chebyshev coefficients indicate departure from the linear regime and augment the physical interpretation provided by $G_1'$ and $G_1''$ in the LAOS regime. Leading-order Chebyshev coefficients $e_3/e_1$ and $\nu_3/\nu_1$ capture changes in the local elastic and local viscous stresses of the decomposed signal which manifest as the convexity (bending or twisting) in Lissajous-Bowditch curves (See Fig. 5.5 and Fig. 5.6). Most importantly, the signs of these third-harmonics indicate the driving cause of the deviation from linearity in $G_1'$ and $G_1''$ (i.e. whether they are caused primarily by large strains or large strain-rates). (Ewoldt and Bharadwaj, 2013)
Within the linear regime $\gamma_0 \leq 0.03\%$, $e_3/e_1$ and $\nu_3/\nu_1$ did not contribute greatly to the stress response as expected. At $\gamma_0 \approx 0.05\%$, $e_3/e_1$ remained marginal, whereas $\nu_3/\nu_1$ began to rise signaling the onset of nonlinearities and indicating that viscous shear thickening of $G''_1$ was driven by large strain rates (a viscoelastic fluid type of response), since $\nu_3/\nu_1 > 0$. At larger strain amplitudes, $\nu_3/\nu_1$ changes signs. In this regime, there is also a change from thickening to thinning of $G'_1$ (See Fig. S4). Based on the sign of $\nu_3/\nu_1$, large-rates also seem to drive this nonlinearity. (One must be cautious of the sign interpretation beyond the leader order deviation. It requires the third-harmonic to determine the curvature of the viscous stress, which is generally but not always the case for the L-B curves in Fig. 5.5 and Fig. 5.6). For the elastic measures, there is a decrease in $G'_1$ and $e_3/e_1$ is initially positive, indicating that elastic softening was driven also by large instantaneous strain rates. Overall, similar behavior was observed for brittle and ductile fats, however, it appeared that B1 exhibits stronger nonlinearities represented by higher and lower magnitudes of elastic and viscous Chebyshev coefficients, respectively.
Figure 5.5 Steady state Lissajous-Bowditch curves for a ductile fat D1, shown for a selected range of strains and frequencies. a) and b) Normalized 2D projections arranged in a Pipkin space according to the input parameter \( \{ \omega, \gamma_0 \} \), that generated each response curve. The maximum stress is shown above each curve. a) Individual plots of normalized stress (black solid lines) and elastic stress is shown above each curve. a) Individual plots of normalized stress (black solid lines) and elastic stress (green dashed line) vs. strain. b) Individual plots of normalized stress (black solid lines) and viscous stress (green dashed line) vs. strain rate.

Lissajous-Bowditch curves were used to gain qualitative insight into the nonlinear viscoelasticity of ductile and brittle fats. Lissajous-Bowditch figures are parametric plots of strain \textit{versus} stress (elastic perspective) or strain-rate \textit{versus} stress (viscous perspective) which appear elliptical in the linear region, and acquire complex shapes in the nonlinear region, due to the presence of higher harmonic components.
Figure 5.6 Steady state Lissajous-Bowditch curves for a brittle fat B1, shown for a selected range of strains and frequencies. a) and b) Normalized 2D projections arranged in a Pipkin space according to the input parameter \( \{ \omega, \gamma_0 \} \), that generated each response curve. The maximum stress is shown above each curve. a) Individual plots of normalized stress (black solid lines) and elastic stress (blue dashed line) vs. strain. b) Individual plots of normalized stress (black solid lines) and viscous stress (blue dashed line) vs. strain rate.

Elastic and viscous Lissajous-Bowditch curves are depicted in two-dimensional \( \{ \omega, \gamma_0 \} \) Pipkin (Pipkin, 1972) diagrams for ductile (D1) and brittle (B1) fats in Fig. 5.5 and Fig. 5.6, respectively. For both material classes, throughout the frequency range, linear viscoelasticity dominated the stress response at strain amplitudes \( \gamma_0 < 0.05\% \) (not shown), supported by elliptical L-B shapes and linear elastic and viscous stress functions (dotted lines). At strains \( \gamma_0 \geq 0.05\% \), L-B figures began to distort because of periodic variations in the stress response, especially visible at local minima and maxima, with a visibly noticeable onset of nonlinear viscoelasticity in accordance with the trends observed for \( \nu_3/\nu_1 \) and \( e_3/e_1 \) at \( \omega = 3.6 \text{ rads}^{-1} \). At \( \gamma_0 \geq 0.57\% \), D1 and B1 displayed qualitatively similar features, including stress upturn or “twists” in the elastic Lissajous-Bowditch curves at the largest instantaneous strain \( \gamma_0 \) for each oscillatory cycle,
indicating lower elastic energy storage at minimum strain $\gamma_{\text{min}}$ (which is the location of largest strain-rate), compared to elasticity at maximum strain within a cycle. This was concurrent with the appearance of “bends” in the viscous curves also at $\dot{\gamma}_{\text{max}}$ indicating pseudoplasticity or shear-thinning behavior, which was least prominent in D1. Eventually, the nonlinear response is strongly nonlinear $\{\omega=3.6, 5.9 \text{ rads}^{-1}, \gamma_0 \geq 6 \%\}$, as to induce self-intersections and secondary loops in the viscous Lissajous-Bowditch curves at $\dot{\gamma}_{\text{min}}$ which are more apparent in B1. The appearance of secondary loops have been physically related to strongly unloading of instantaneous elastic stresses (which occurs faster than accumulation of new elastic deformations) and competition between network destruction and formation at high shear rates (Ewoldt and McKinley, 2010; Jacob et al., 2014). Secondary loops physically relate to a material that strongly unloads instantaneous elastic stresses (faster than accumulation of new elastic deformations). (Ewoldt and McKinley, 2010) Quantitatively speaking, this translates to negative values on the instantaneous elasticity $G'_M$ or values alternating from positive to negative if multiple loops are present. Qualitatively speaking, self-intersections correspond to strong overshoots ($\gamma_0 \geq 2.34\%$) during yielding which are particularly more pronounced at higher frequencies (i.e. the network becomes more solid-like) in B1 (Fig. 3c). Moreover, at sufficiently high strain inputs ($\gamma_0 \geq 6\%$), plastic deformation became more prominent as demonstrated by larger areas enclosed by the elastic Lissajous-Bowditch curves which is more evident in D1.

5.4.4 Nonlinear viscoelastic metrics

As alluded to earlier, typical mechanical characteristics of ductile solids include greater ability to retain strength during yielding in concert with larger viscous dissipation and plastic deformation than brittle solids. To capture these behaviors, we adopt local (or instantaneous) nonlinear descriptors as proposed by Ewoldt et al. (2008), a selection of which are displayed in Fig. A11 (see Appendix 1) and Fig. 5.7, along with their corresponding graphical representation. To ease comparisons between ductile and brittle fats, measures were also normalized to their linear properties ($\eta'_{LVE}$) when applicable. Based on the qualitative insight gained from L-B curves and the fact that fats do not display marked high elasticity, we anticipated minor differences in elastic properties. These local measures complement average measures as shown in Fig. A4 (Appendix 1), which denote global elastic strain softening and global viscous thickening and thinning, both driven by large strain-rates as previously elucidated. Contrary to van der Vaart et al. (van der
Vaart et al., 2013) and Kim et al. (Kim et al., 2014) who reported time-dependent moduli and cage modulus, we use Chebyshev-stress decomposition measures as they are robust, low dimensional, and adequately describe the bulk rheology, consistent with the macroscopic brittle and ductile nonlinear responses. As described earlier, after failure ($\gamma \approx 2\%$) the strain-stress response is apparent. However, the total energy dissipated and energy stored are true, as measured with loads and displacements at the boundary, which allows for meaningful comparison of material functions between ductile and brittle fats.
Figure 5.7 Dynamic viscosities at a fixed frequency $\omega = 3.6 \text{ rad}^{-1}$ as a function of strain amplitude input $\gamma_0$: a) minimum strain-rate, b) large strain-rate and c) average strain-rate
viscosities. Insets show viscosity metrics normalized by $\eta_{LVE}'$ at $\gamma_0 = 0.01\%$. d) Lissajous-Bowditch curve (viscous perspective) showing normalized shear-rate $\gamma/\dot{\gamma}_0$ versus stress $\tau$ normalized by $\tau_{LVE}$ at $\gamma_0 = 0.01\%$, for a selected data point $\gamma_0 = 1.47\%$ ($\dot{\gamma}_0 = 0.05$ s$^{-1}$), displaying graphical representation of local (instantaneous) and global (average) LAOS viscosity measures.

Nonlinear elastic properties are presented as relative differences between the large-strain or secant modulus $G'_L$ and the minimum-strain or tangent modulus $G'_M$, which indicate more elasticity at the turn-around point $G'_L$ than during flow $G'_M$. This leads to stress upturns within a cycle (or local strain stiffening as referred in the literature), as observed in the elastic L-B curves. It is shown that the general qualitative elastic behavior of ductile and brittle fats was similar, except for B2, which plateaued earlier and then decreased given its much lower yield or peak stress $\tau_y$. It is noteworthy to mention that the magnitudes of $G'_M$ and $G'_L$ give an underestimation of intracycle elasticity as they suffer from plastic strain accumulation since they are calculated post yielding. Nevertheless, based on the qualitative insight gained from L-B curves and the fact that fats do not display marked high elasticity, we conclude that elastic properties do not dominate the nonlinear response (Dimitriou et al., 2013). By contrast, viscous measures showed striking differences, e.g. dynamic viscosities at instantaneous minimum strain-rates $\eta'_M$ and large strain-rates $\eta'_L$ denoted less apparent thinning for ductile D1 and D2 compared to brittle B1 and B2 fats. For instance, in nearly two decades of deformation ($\gamma_0=0.01-0.92\%$), $\eta'_M/\eta'_{LVE}$ and $\eta'_L/\eta'_{LVE}$ decreased 41-53% and $\leq5-8\%$ for D1 and D2, compared to 85-93% and 54-62% for B1 and B2. In agreement with the viscous Chebyshev coefficients $\nu_3/\nu_1$, major differences in the dissipated energy are present at large instantaneous strain-rates, which nearly matched the average intercycle viscous dissipation $\eta'_1$.

The enhanced viscous dissipation of D1 and D2, compared to B1 and B2 is a key hallmark of ductile and brittle solid materials. Here, using LAOS stress decomposition, we can isolate that nonlinear viscous effects change, but nonlinear elastic effects do not, across these material classes. It has been suggested that during deformation, a ductile solid converts the vast majority of the released strain energy into other types of energy, mainly dissipative, associated with plastic flow, whereas a brittle solid expends a large amount of energy for crack growth or formation of new surfaces (Irwin, 1948; Orowan, 1949).
5.4.5 Structural characterization

As earlier mentioned, fat crystal networks feature structural hierarchies from molecular to microscopic dimensions. These multiple length scales determine the rheological behavior of these materials (Marangoni et al., 2012). Irreversible structural changes induced by shear deformations may occur, which in turn will change also the mechanical properties of the material (Marangoni et al., 2012). In this paper, we investigated “quiescent” structural length scales ($L$) ranging from ~20 nm to 6µm using USAXS and SEM techniques, as we had described the molecular length scale of the samples in a previous study. (Macias-Rodriguez and Marangoni, 2016b)

![Figure 5.8](image.png)

Figure 5.8 Absolute scattering intensity $I(q)$ as a function of the scattering vector $q$. Slope values included in the plot serve as guides for the actual values obtained by the Unified Fit model and summarized in Table 5.2.

Fig 5.8 shows absolute intensity $I(q)$ as a function of scattering vector $q$ obtained from USAXS experiments. In general, the USAXS patterns yield hints as to the investigated structure for ductile fats D1 and D2, exhibiting three-hierarchy structures, and brittle fats B1 and B2, displaying two-hierarchy structures. The number of hierarchies is indicated by the power law regions identified in different $q$ ranges, suggesting the studied fat systems conform to a fractal character. (Peyronel et al., 2014b) To characterize these data, we relied on the Unified fit model and Guinier-Porod model, (Beaucage, 1996, 1995; Hammouda, 2010) with their best-fitting parameters shown in Table 5.2, and previous USAXS experiments and computer simulations performed in complex fat systems at intermediate volume fraction (Peyronel et al., 2014d; Pink et al., 2015; Quinn et al., 2014). These parameters and their interpretations collectively describe...
the aggregation mechanisms driving the formation of the crystal network, size, geometry and structural features of the fundamental scatterers (crystal nanoplatelets, CNPs) and crystal aggregates.

**Table 5.2** Selected parameters obtained from Unified Fit and Guinier-Porod models and length scales probed in each structure level of the Unified Fit model. Standard error means for $P$ and $S$ parameters were equal or below 0.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_1$</th>
<th>$R_{g1}$ [nm]</th>
<th>$L_1$ [nm]</th>
<th>$P_2$</th>
<th>$R_{g2}$ [nm]</th>
<th>$L_2$ [nm]</th>
<th>$P_3$</th>
<th>$L_3$ [µm]</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>3.8</td>
<td>53.3±2.4</td>
<td>21-157</td>
<td>2.3</td>
<td>490.2±24.7</td>
<td>157-1571</td>
<td>3.7</td>
<td>0.6-6.3</td>
<td>1.7</td>
</tr>
<tr>
<td>D2</td>
<td>4.0</td>
<td>35.8±0.7</td>
<td>13-78</td>
<td>1.7</td>
<td>358.9±10.7</td>
<td>78-698</td>
<td>4.2</td>
<td>0.1-6.3</td>
<td>1.5</td>
</tr>
<tr>
<td>B1</td>
<td>3.5</td>
<td>399.8±6.6</td>
<td>21-785</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.7</td>
<td>1.3-6.3</td>
<td>2.0</td>
</tr>
<tr>
<td>B2</td>
<td>3.5</td>
<td>167.4±0.0</td>
<td>21-628</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.1</td>
<td>1-6.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Using the Unified Fit model, up to three structural levels or hierarchies were successfully fitted: Level 1 and Level 3, corresponding to high and low $q$ ranges and Level 2 referring to intermediate $q$ values. The slope $P_1$ indicated that the first structural level was made up by CNPs with smooth ($P≈4$) interfaces in ductile fats and rough interfaces ($P<4$) in brittle fats. Nevertheless, estimation of ‘particle’ sizes given by the radius of gyration $R_{g1}$ indicated that the primary scatterers of ductile fats were up to eleven times as small as those of brittle fats. The slope $P_2$ suggested that crystal platelets in ductile fats self-assembled into intermediate hierarchies obeying an interplay between solid condensation and solid diffusion ($P_2>2.1$) or DLCA mechanisms ($P_2≈1.8$), as explained by previous models and computer simulations (Peyronel et al., 2014d; Pink et al., 2015). The crystal clusters had average sizes $R_{g2}=490.2$-358.0 nm. The slope $P_3$ ($P_3>4$) suggested that in most of the cases crystal clusters aggregated having diffuse interfaces.(Beaucage, 1996) Results from the Guinier-Porod model provided insight on the geometry of the scatterers resulting from CNP aggregation. It is suggested that either CNPs assembled at the mesoscopic scale into “supra-platelets” ($S=2$) or structures with shapes intermediate between rods and platelets ($1<S<2$) (Hammouda, 2010).
To further visualize the micro length scales, SEM experiments were performed on nonsheared samples and samples after applying nonlinear oscillatory shear deformations ($\gamma_0=50\%$). Overall, microstructural features shared similarities depending on whether the fat crystal network was ductile or brittle in nature. Fig. 5.9 illustrates SEM micrographs obtained for the presented examples of ductile (D1, D2) and brittle (B1, B2) materials (Refer to Appendix 1 Fig. A12 for similar micrographs at lower magnification). In general, the microstructure of D1 (Fig. 5.9a,b) appeared more homogeneous, composed of well-defined platelet-like crystal aggregates with variable size (~2-10 $\mu$m length) interconnected into elongated layers, roughly parallel to each other, leaving interstitial channels in between, where possibly most of the liquid oil might have been confined. It is conceivable that the three-hierarchy level structure observed in USAXS
enables the creation of such ordered long-layered structures at the micron length scale observed in ductile fats (D1 and D2). By contrast, brittle fats, B1 and B2 (Fig. 5.9c, d), comprised heterogeneous networks made of distorted or “flaky” sheet-like crystal aggregates of comparable size and micro holes or voids (~16 μm diameter) where presumably most of the liquid oil is entrained. The present microstructures are consistent with their processing regimes as substantial cooling and shearing typically result in an uniform, oriented microstructural network such those observed in D1 and D2 but not in B1 and B2. (Maleky et al., 2011) Upon substantial nonlinear deformations, it seemed that shear broke the continuity of the layered microstructure of D1 (Fig. 5.9e), and caused the nearly-parallel array of crystallites to “squeeze” and induced their aggregation into twisting “fiber-like” aggregates with average lengths of ~12μm. These twisted aggregates lend qualitative evidence of ductile deformation. Likewise, the aggregates making up the crystal network of B1 (Fig. 5.9f) fragmented, leading to a more random microstructure with element lengths of ~7μm. It has been previously suggested in fat crystal networks that defect sizes from which cracks nucleate (such as in brittle fats during compression, see Fig. 1) are typically on the order of 8 μm, (Wiliam Kloek et al., 2005) which corresponds to the length scale of the crystal aggregates observed by SEM. Nevertheless, deformation mechanisms at all hierarchical levels will ultimately dictate the nonlinear mechanical response of the material.

Linking rheology and structure and considering that the primary mechanical difference is with the _viscous_ nonlinearities (rather than elastic nonlinearities, as revealed by LAOS), our interpretation is that elastic energies are stored within the hierarchical network in similar ways, but dissipation across the structural levels and crystallite layers is the key difference.

Based on USAXS and SEM results, we postulate that in ductile fats shear loads are better dissipated among the three-hierarchy structures unlike brittle fats where energy is exchanged only between two hierarchy levels. It can also be suggested that the microstructure provides mechanisms of alleviating or constraining local stresses either by allowing controlled sliding motion of the elongated crystallite layers with the liquid phase acting like a lubricant in ductile fats or restricting motion of the “disordered” crystal aggregates in brittle fats. Overall, this provides a tentative explanation for the observed LAOS behavior, and the formation of macroscopic cracks in brittle fats.

Such a picture it is not unreasonable as it has been demonstrated (via computer simulations) at a fundamental level that material toughness (“ductility”) and defect tolerance may vastly increase
solely by introducing \textit{as little as one “extra”} hierarchical structure in biological-like materials with similar constituents and volume fraction (Sen and Buehler, 2011). Additionally, enhanced plasticity and toughening mechanisms in biological materials originates not only from the presence of multiple lengthscales but also from the incorporation of structural means, namely mineral-platelet sliding in seashells, for relieving locally high stresses (Ritchie, 2011).

Since the primary rheological difference is with the \textit{viscous} nonlinearities (rather than elastic nonlinearities, as revealed by LAOS), our interpretation of the hierarchy is that elastic energies are stored within the network in similar ways, and dissipation across the structural levels and crystallite layers is the key difference.

Such a picture it is not unreasonable as it has been demonstrated (via computer simulations) at a fundamental level that material toughness ("ductility") and defect tolerance may vastly increase solely by introducing \textit{as little as one “extra”} hierarchical structure in biological-like materials with similar constituents and volume fraction (Sen and Buehler, 2011). Additionally, enhanced plasticity and toughening mechanisms in biological materials originates not only from the presence of multiple lengthscales but also from the incorporation of structural means, namely mineral-platelet sliding in seashells, for relieving locally high stresses (Ritchie, 2011).

\textbf{5.5 Conclusions}

In previous studies, linear viscoelasticity has been the common explored territory in relating mechanical behavior to macroscopic performance and sensory attributes of fats. However, linking nonlinear viscoelasticity to macroscopic performance may be equally or far more relevant as most processing conditions and application uses of fats typically impose substantial nonlinear deformations. It is possible that fats with comparable linear viscoelastic properties diverge on their nonlinear behavior as supported by our results. Using the LAOS strain protocol, it was possible to quantitatively discriminate between ductile (roll-in) and brittle (all-purpose) fats. LAOS allows for decoupling energy storage and loss mechanisms in nonlinear rheology. Notably, there were not important differences in the moduli of elasticity. Instead, the primary difference was the moduli of viscous dissipation; ductile fats were substantially more dissipative than brittle fats, in accordance with higher resistance to flow and plastic deformation for the ductile systems. Structural investigations indicated that ductile fats featured an additional hierarchy level, and crystal aggregates ordered in elongated crystal layers unlike brittle fats that
showcased only two hierarchy structures and more “disordered” crystal network. It is suggested that the hierarchy levels and spatial distribution of the microstructure play a pivotal role on high energy dissipation (rather than energy storage) and hence superior load-bearing ability of ductile fats to endure mechanically-demanding processes such as “cold-working”. Future work could further explore the relation between rheology and structural states under controlled formulation and processing spaces, and use computer simulations to advance our understanding of ductile versus brittle failure and gain mechanistic insight of the LAOS yielding behavior of fat crystal networks.

5.6 Acknowledgements

The authors are indebted to Dr. Jan Ilavsky and his team at beam line 9ID-C for their invaluable support and help through the data collection and analysis of USAXS. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We also greatly acknowledge Dr. Fernanda Peyronel (Food Science, University of Guelph) for helping with USAXS data reduction and interpretation, Dr. David Pink (Physics, St. Francis Xavier University) for discussions on USAXS, Mr. Gaurav Chaudhary for discussions on LAOS rheology (Mechanical Science and Engineering, University of Illinois at Urbana-Champaign) and Dr. Peter X Chen (Food Science, University of Guelph) for helping with video recording.

5.7 References


CHAPTER 6: THE ROLE OF NONLINEAR VISCOELASTICITY ON THE FUNCTIONALITY OF LAMINATING SHORTENINGS

Braulio A. Macias-Rodriguez\textsuperscript{a}, Fernanda Peyronel\textsuperscript{a} and Alejandro G. Marangoni*\textsuperscript{a}

Under review: Journal of Food Engineering

\textsuperscript{a}Department of Food Science, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. \textit{E-mail}: amarango@uoguelph.ca

6.1 Abstract

The rheology of fats is essential for the development of homogeneous and continuous layered structures of doughs. Here, we define laminating shortenings in terms of rheological behavior displayed during linear-to-nonlinear shear deformations, investigated by large amplitude oscillatory shear rheology. Likewise, we associate the rheological behavior of the shortenings with structural length scales elucidated by ultra-small angle x-ray scattering and cryo-electron microscopy. Shortenings exhibit solid-like viscoelastic and viscoelastoplastic behaviors in the linear and nonlinear regimes respectively. In the nonlinear region, we found that laminating shortenings dissipated more viscous energy (larger normalized dynamic viscosities) than a cake bakery shortening. The fat solid-like network of laminating shortening displayed a three-hierarchy structure and layered crystal aggregates, in comparison to two-hierarchy structure and spherical-like crystal aggregates of a cake shortening. We argue that the observed rheology, correlated to the structural network, is crucial for optimal laminating performance of shortenings.

\textbf{Keywords:} rheology, laminating, puff-pastry, \textit{trans}, saturates, large amplitude oscillatory shear
6.2 Introduction

The study of fats remains a subject of great focus given their many functions in foods, i.e. structuring, mouthfeel and texture, and their nutritional implications (i.e. fats have the highest caloric value among macronutrients 9 kcal g\(^{-1}\)). A large body of research has concluded that the intake of trans fats increases the risk of cardiovascular disease (CVD), whereas some studies have argued that replacing saturated fatty acids with polyunsaturated fatty acids may reduce the risk of CVD (Schwab et al., 2014; Siri-tarino et al., 2010). In view of these findings, strict international regulations have been implemented (i.e. “zero trans” policies) which have prompted processors to develop low-trans and low-saturates alternative products. Nevertheless, reformulation of fats still poses tremendous challenges as removal of hard-stock components (trans and saturates) leads to softening and oil leakage.

An example of specialty fat, high in trans and saturates (as high as 54% altogether) are laminating shortenings (NYC Health 2012). Laminating shortenings are one of the main ingredients (30% by weight) of puff pastry or laminated doughs (Marangoni et al., 2012). In the manufacture of these baked goods, laminating shortenings are co-extruded, sheeted and folded simultaneously with the dough, to form a layered structure. The layered structure is responsible for volume expansion and flakiness of the final product. In achieving an optimal layered structure, the rheology of the laminating shortening is crucial (Renzetti et al., 2015). A shortening must have the ability to remain elastic yet plastic to facilitate dough layering and withstand high stresses without rupturing (hereafter referred to as functionality or performance). For example, a laminating shortening that is too soft will be absorbed into the dough or squeezed out. On the other hand, a shortening that is too hard will break and rupture the dough.

From a mechanical perspective, fats behave as soft viscoelastic solids at small deformations (Narine and Marangoni, 1999b; van den Tempel, 1961). At small deformations, their linear viscoelastic properties can be generally described as similar as those of flocculated fractal colloidal gels (Narine and Marangoni, 1999b). Fats have a hierarchical structure, encompassing nanoscale- and mesoscale- structures). At the molecular level, triacylglycerols (TAGs) stack longitudinally and side-by-side, adopting a specific polymorphic state (\(\alpha, \beta^\prime, \beta\)) and forming bilayers, which then stack to form crystalline nanoplatelets (CNPs). In the mesoscale, CNPs self-assemble to form different structures, according to their processing conditions and their chemical
compositions (Peyronel et al., 2014b, 2013). It has been shown using computer simulations (Pink et al. 2013, Quinn et al. 2014) that diffusion-limited-cluster aggregation (DLCA) and reaction-limited cluster aggregation (RLCA) are two of the mechanism responsible for the self-assembly. It has also been shown using USAXS experiments that CNPs aggregate into fractal clusters which can further aggregate and make up the meso- to micro-scopic crystal network.(Peyronel et al., 2014b)

At large deformations, such as those encountered during industrial processing, fats yield, soften and eventually “flow”. This gradual transition from “solid-like” to “liquid-like” rheological behavior may have important implications in the performance of fats (Refs). Therefore, investigating nonlinear viscoelastic properties due to large deformation and their correlation to structure is of paramount important in the design of healthier yet functional laminating shortenings. In this paper, we probe the rheology of laminating fats using large amplitude oscillatory shear (LAOS). Unlike step-input tests or compression tests, oscillatory shear tests(i) can generate relative easy flows (e.g. gradual increase in deformations or shear-rates), (ii) allow decomposition of elastic and viscous rheological material functions, and (iii) have a better signal-to-noise ratio (Hyun et al., 2011). All these features are important for distinguish the nonlinear viscoelastic properties of materials. In addition, we investigated material structure using Ultra Small Angle X-ray Scattering (USAXS) and Scanning Electron Microscopy (SEM).

6.3 Experimental

6.3.1 Materials
We investigated four commercially-acquired shortenings, the trade names and compositions of which are summarized in Table 6.1. Exact formulations and manufacturing conditions of these shortenings are unknown, it is well known that laminating shortenings “melts” are rapidly cooled and shear-crystallized to promote crystal nucleation, delay crystal growth and impart superior plasticity (Acevedo and Marangoni, 2013). For a detailed description on the molecular composition and other physico-chemical properties of these materials refer to Macias-Rodriguez and Marangoni (2016a).
Table 6.1 Functionality and bulk composition for each material class, linear elastic moduli at $\omega=3.6$ rads$^{-1}$ and $\gamma_0=0.01\%$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Trade name/composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Puff pastry hydrogenated soybean oil and cottonseed oil</td>
</tr>
<tr>
<td>R2</td>
<td>Roll-in hydrogenated vegetable oil and modified palm oil</td>
</tr>
<tr>
<td>R3</td>
<td>Puff pastry palm oil, modified palm oil and soybean oil</td>
</tr>
<tr>
<td>S1</td>
<td>Cake soybean oil interesterified</td>
</tr>
</tbody>
</table>

6.3.2 Sample preparation

6.3.2.1 Rheology
Samples were carefully obtained by piercing a block of shortening with a 30 mm diameter stainless-steel hollow rod to form a cylinder, and then cutting through the fat cylinder with steel wires separated by a distance of 1.3 mm. Prior to cutting, the wires were lubricated with mineral oil to minimize flaw or crack formation that may act as points of stress concentration leading to premature failure. The sample “disks” had approximate dimensions of 30mm×1.3mm (diameter×thickness). The cut cylinder was stored at 16 °C overnight to allow the “healing” of any fracture or damage induced at cutting and to remove any residual stresses. Results are the average of three measurements.

6.3.2.2 Ultra Small Angle X-ray Scattering (USAXS)
A Grace-Bio-Labs (Oregon, USA) circular silicon isolator was used to mount the sample. Prior to this, samples were prepared in a similar way as described above to form fat “disks” with approximate dimensions of 20mm×1mm (diameter×thickness). A microscope cover was attached to each side of the isolator to contain the sample.

6.3.2.3 Scanning Electron Microscope (SEM)
Samples were carefully obtained from the bulk shortening with a spatula. To expose the microstructural features of the fat crystal network, the liquid oil was removed by suspension of the samples in an approximate ratio of 1:25 fat-solvent. Laminating fats (R1, R2 and R3) were suspended in a 8:2 (v:v) isobutyl alcohol-hexane mixture to enhance removal of the more-confined oil phase (preliminary experiments showed that isobutyl alcohol alone was not effective
at removing the liquid oil), whereas (S1) was suspended in isobutyl alcohol. (Chawla et al., 1990) Shortenings were statically deoiled at 20 °C (laminating shortening) and 14 °C (cake shortening) for 48 h, filtered (Whatman No 5) to remove solvent and liquid oil, and finally allowed to stand on filter paper overnight to vaporize any remaining solvent. Removal of oil from laminating shortening R3 using the present protocol was not possible and thus we do not present micrographs for this sample.

6.3.3 Measurements and Analysis

6.3.3.1 Rheology

Preformed samples were carefully transferred onto the lower plate of a rotational rheometer (MCR 302, Anton Paar) and loaded within a parallel plate geometry using 3±0.5 N axial force to avoid the formation of new microstructures and ensure reproducible results. (B. Macias-Rodriguez and Marangoni, 2016a) Sample excess was trimmed with a spatula. After loading, samples were allowed to relax the axial force to a constant value over a zero strain relaxation test for at least 15 min, being equilibrated at 16 °C. This temperature was chosen to resemble thermal conditioning during rolling and layering of fats (B. Macias-Rodriguez and Marangoni, 2016a). Temperature was controlled using Peltier units located in the lower plate and the hood of the rheometer. Experiments were performed with parallel plates (DIA= 20 mm) modified with filter paper (Whatman grade 5, GE Healthcare Life Sciences) attached to the top and bottom plates to improve sample adhesion to contacting boundaries and minimize wall slip during measurements. Parallel plate geometries were selected despite its heterogeneous shear rate field, as it allows for loading of preformed samples.

Small amplitude and large amplitude oscillatory shear experiments (SAOS, LAOS) were performed in strain-controlled mode on the combined-motor-transducer rheometer. Tests involved strain sweeps from the linear region until post-yielding of the material (γ0=0.01-100%) at a fixed frequency ω=3.6 rad s⁻¹ representative of the rolling process (Chakrabarti-Bell et al., 2010). Strain amplitude γ0 represents apparent strain (e.g. deviates from true strain when there is shear-banding or slip at γ0≈10% and beyond).

The average viscoelastic moduli $G'\dot{}$, $G''$ or first-harmonic moduli $G'_1$, $G''_1$ were recorded as reported by the commercial Rheocompass™ software. Linear viscoelastic moduli were
determined at $\gamma_0 = 0.01\%$ were stress response signals are perfectly sinusoidal. Beyond the linear viscoelastic region, at large input amplitudes, complex nonlinear phenomena manifest in the oscillatory stress response as nonsinusoidal waves with higher-order harmonic contributions. If represented via Lissajous-Bowditch (L-B) curves, parametric plots of stress versus strain or strain rate, nonlinearity causes deviation from an elliptical shape of the response. Consequently, the conventional interpretation of the elastic and viscous moduli in the theory of linear viscoelasticity is no longer applicable. Several methods have been developed to interpret nonlinear contributions including Fourier transform (FT) rheology and stress decomposition method described via Chebyshev polynomials (Hyun et al., 2011). In FT rheology, the stress signal is expressed as a Fourier series encoding the amplitude $I_n$ and the phase $\phi_n$ of higher harmonics at each order $n$. In this framework, the extent of nonlinearity can be quantified with a simplified metric of the normalized intensity of the third harmonic $I_3/I_1$ (higher harmonics are also present, but the third-harmonic is dominant at leading order). Although useful, this single approach loses the ability to decompose energy storage and loss concepts, and therefore offers limited insights into the physics of nonlinear viscoelasticity. Several resolutions to this have been proposed including the stress decomposition method proposed by Cho et al., (2005) and extended by Ewoldt et al., (2008), and local measures of elastic and viscous behavior(Ewoldt et al., 2008; Rogers, 2012).

In the stress decomposition framework, the total stress is represented as a superposition of the elastic stress, $\tau'$ and viscous stresses, $\tau''$ using symmetry arguments.(Cho et al., 2005) The elastic and viscous stresses are then unambiguously described by a set of orthogonal Chebyshev polynomials of the first kind, as proposed by Ewoldt et al., (2008)

$$\tau'(x) = \gamma_0 \sum_{n \text{ odd}} e_n(\omega, \gamma_0) T_n(x), \quad (1)$$

$$\tau''(y) = \dot{\gamma}_0 \sum_{n \text{ odd}} v_n(\omega, \gamma_0) T_n(y), \quad (2)$$

Where $T_n(x)$ and $T_n(y)$ corresponds to $n$th-order of the Chebyshev basis functions, $x = \gamma(t)/\gamma_0$ and $y = \dot{\gamma}(t)/\dot{\gamma}_0$, with $\gamma_0$ and $\dot{\gamma}_0$ being the maximum in-cycle strain and shear rate, and $e_n(\omega, \gamma_0)$ and $v_n(\omega, \gamma_0)$ refer to the elastic and viscous Chebyshev coefficients of order $n$. The Chebyshev coefficients are directly related to the higher order Fourier coefficients in the time-domain as:
\( e_n = G_n'(-1)^{(n-1)/2} \) and \( \nu^n = G_n'' \omega = \eta_n' \), respectively. Note that even-harmonic \((n = \text{even})\) Fourier and Chebyshev coefficients are neglected as they are associated with broken shear symmetry, e.g., with responses that have not yet reached the time-periodic state. Just as the third-order Fourier harmonic, the third-order Chebyshev basis function signals depart from linearity and additionally provide physical meaning to the stress response. It is important to emphasize that linear material functions \( G' \) and \( G'' \) (equivalent to \( G_1' \) and \( G_1'' \)), represent average stress responses equivalent to first-order Chebyshev coefficients \( e_1 \) and \( \nu_1 \). Instead, third and higher-order Chebyshev coefficients capture uniquely local responses in the distorted stress signal (i.e., bent, twisted L-B curves). Specifically, the signs of the leading-order elastic and viscous Chebyshev coefficients \( e_3 \) and \( \nu_3 \), reveal the underlying cause driving average changes in the elastic and viscous intercycle stress response as described by (Ewoldt and Bharadwaj, 2013). For example, for \( G_1' \) decreasing, and \( e_3 > 0 \), large instantaneous strain-rates are responsible for the average elastic softening. In the same way, for \( G_1'' \) decreasing and \( \nu_3 < 0 \), large instantaneous strain-rates also drive average viscous thinning. For a full description on how to interpret the leading order Chebyshev LAOStrain nonlinearities, refer to Ewoldt and Bharadwaj (2013).

Local measures of LAOS, interpreted geometrically from L-B curves, provide great insight into nonlinear viscoelasticity. Metrics of elastic energy storage and viscous energy dissipation are determined from characteristic points during the oscillation (at extreme values of strain and strain-rate) as

\[
G_M' = \left. \frac{d\tau}{d\gamma} \right|_{\gamma=0} = \sum_{n: \text{odd}} nG_n' = e_1 + 3e_3 + \ldots, \tag{3}
\]

\[
G_L' = \frac{1}{\omega} \left. \frac{\tau}{\gamma} \right|_{\gamma=\pm\gamma_0} = \sum_{n: \text{odd}} G_n'(-1)^{(n-1)/2} = e_1 + e_3 + \ldots, \tag{4}
\]

\[
\eta_M' = \left. \frac{d\tau}{d\dot{\gamma}} \right|_{\dot{\gamma}=0} = \frac{1}{\omega} \sum_{n: \text{odd}} nG_n''(-1)^{(n-1)/2} = \nu_1 + 3\nu_3 + \ldots, \tag{5}
\]

\[
\eta_L' = \frac{1}{\omega} \left. \frac{\tau}{\dot{\gamma}} \right|_{\dot{\gamma}=\pm\dot{\gamma}_0} = \sum_{n: \text{odd}} \frac{1}{\omega} G_n'' = \nu_1 + \nu_3 + \ldots, \tag{6}
\]
where $G'_M$ is the minimum-strain or tangent modulus at $\gamma_0=0$ and $G'_L$ is the large-strain or secant modulus at $\gamma_0=\gamma_{\text{max}}$. Likewise, $\eta'_M$ is the minimum-rate viscosity and $\eta'_L$ is the large-rate viscosity. These deliberately-chosen material functions reduce to $G'_1$ and $G''_1$ ($\eta_1''=G''/\omega$) in the linear regime.

For LAOS analysis, raw strain-stress data were collected at a sampling rate of 512 points per oscillatory cycle, and extracted from the rheometer software. Due to the thixotropic nature of our samples, a minimum of 20 oscillatory cycles were applied to reach a quasi-steady stress response. Typically, 3-5 waveforms at each coordinate pair $\{\omega, \gamma_0\}$ were input to a custom written MATLAB code. The software processes the signal with a discrete Fourier transform, calculates relevant measures of nonlinear viscoelasticity, and smooths and reconstructs the stress signal by allowing only odd, integer-harmonic components, up to a cutoff such that $I_n/I_1 \geq 0.05$ to avoid noise. Averaging multiple cycles and selecting a cut-off frequency provide increased signal to noise ($S/N$) ratio and greater accuracy by removing random noise masking any real material response respectively. To further minimize the effect of shear artifacts (instabilities, slip, edge fracture) on the LAOS data, we constrained our LAOS analysis to $\gamma_0 \leq 10\%$ as experimental error increased at higher strains and severe slip was even visually observed at $\gamma_0 \approx 30\%$ and above.

6.3.3.2 USAXS

The sample holder was mounted in front of the X-ray beam using an in house support plate provided at the synchrotron facility. During USAXS the scattering intensity is measured as a function of the scattering vector $q$, defined as $q=\frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)$ where $\theta$ is the scattering angle and $\lambda$ the wavelength of the incident X-ray. An estimation of the length scale ($L$) of the material probed can be obtained from the relation $L=2\pi/q$. It is relevant to note that the Bonse-Hart system permits the collection of a sufficient number of data points in only a few minutes to cover the range $\sim 100 \text{ nm} < L < 10-30 \text{ \mu m}$. The scattering patterns were analyzed to find $I(q)$ vs. $q$ regions that either follow Guinier scattering or Porod-power law scattering. The Irena (Ilavsky and Jemian, 2009) IgorPro-based software was used for data interpretation using the Unified fit (Beaucage, 1996, 1995) and the Guinier-Porod model (Hammouda, 2010) Both models,
implemented in the *Irena* software, employ a non-linear regression analysis to find the best fitting parameters.

Equation 5 shows the Unified Fit (Beaucage, 1996, 1995) model expression.

\[
I(q) = G e^{-\left(\frac{q R_g^2}{3}\right)} + B q^P e^{-\left(\frac{q^2 R_g^2}{3}\right)} \left[ \text{erf}\left(-\frac{q R_g}{6^{1/2}}\right) \right]^{3P} \tag{7}
\]

Where \( P \) is the Porod exponent that yields information on the structure of the aggregate and \( R_g \) is the radius of gyration. The exponential term \( \exp(\frac{-q^2 R_g^2}{3}) \) shows that the Unified Fit model represents all scattering objects as approximately spheres, where \( i \) represents the structural level under study, while \( i-1 \) indicates the previous level. The first term in equation 7 describes the Guinier region, valid for \( q \leq q_1 \), and the second term, the Porod power law valid for \( q \geq q_1 \).

The requirement is that the Guinier and Porod terms, together with their derivatives must be continuous at \( q = q_1 \). \( G \) and \( B \) are the Guinier and Porod scale factors respectively with \( G \) related to the volume of the scatterers and \( B \) containing specific scattered surface area information.

We focus was on the two parameters \( R_g \) and \( P \), that come out of fitting the data to the Unified Fit model. The systems were discovered to be fractal in nature as observed by a straight line in the \( q \)-region observed in two or three sections. It is noteworthy that the radius of gyration \( R_g^3 \) in the third region was held constant to fit the power-law slope \( P_3 \) and hence was not used to draw conclusions pertaining the size of the scatterers.

When a fractal interpretation is given to the data, the \( P \) value gives information about the fractal dimension of the scatterers. A value of \( |P|= 4 \) indicates a scatterer or particle with a smooth surface and a fractal dimension \( D_s = 2 \). If \( 3 \leq |P| < 4 \) then \( 6 - |P| \) is the surface fractal dimension \( (2 < D_s \leq 3) \). When \( 1 \leq |P| < 3 \), then the value of \( |P| \) is the fractal dimension, \( D = |P| \). But if \( |P| > 4 \), all that is known is that there is diffuse interface. (Beaucage, 1996, 1995)

The second model used was the Guinier-Porod one. This model, a variation of equation 7 (Hammouda, 2010), recognizes that the primary particles can have shapes other than spherical, indicated by the terms involving \( s_1 \) and \( s_2 \) in equation (8). The value of the parameter \( s \) indicates platelets when \( s=2 \), cylinders or rods when \( s=1 \) and spheres when \( s=0 \). Similar to the Unified Fit model, parameters like the radii of gyration and the power law exponents are obtained. The
difference is that this model defines a structural level in a wider \( q \)-region, in that each structural level can have multiple radii of gyration and power law slopes - as long as the scattering comes from one population of primary particles. The fitting functions are

\[
I(q) = \frac{G_2}{q^{\gamma_1}} e^{-\frac{q^2 R_2^2}{3 \gamma_2^2}} \quad q \leq q_2
\]

\[
I(q) = \frac{G_1}{q^{\gamma_1}} e^{-\frac{q^2 R_1^2}{3 \gamma_1^2}} \quad q_2 \leq q \leq q_1
\]

(8)

\[
I(q) = \frac{B}{q^{\gamma}} \quad q \geq q_1
\]

where the limits \( q_1 \) and \( q_2 \) are chosen manually by the experimentalist.

6.3.3.3 SEM

Deoiled samples were imaged with a Cryo-SEM was used to image the microstructure of the samples. The samples were then attached to the copper sample holder using the Tissue-Tek embedding medium. The sample holder was immersed in a liquid nitrogen slush (-207 °C) using an Emitech K1250x Cryo-preparation unit (Ashford Kent, UK), freeze-fractured and sputter-coated for 2m with gold using a 20 mA deposition current, 7nm min\(^{-1}\) deposition rate. The sample holder was transferred to the SEM stage (Hitachi S-570, Tokyo, Japan) with accelerating voltage of the electron beam of 10 kV. Images were captured digitally using the Quartz PCI imaging package (Quartz Imaging Corp., Vancouver, Canada).

6.4 Results and discussion

6.4.1 Linear viscoelasticity

Fig. 6.1 shows the first-harmonic viscoelastic moduli \( G'_1 \) and \( G''_1 \) as function of strain amplitude \( \gamma_0 \) at a fixed frequency of \( \omega = 3.6 \text{ rads}^{-1} \) for two representatives shortenings (R1 lamination and cake S1). The linear regime encompasses small oscillatory deformations \( \gamma_0 > \gamma_c \), so that material properties are independent of the input strain amplitude. In the linear regime, it was observed that all samples act as soft viscoelastic solids. The magnitudes of the elastic moduli remained
unremarkable: for laminating shortenings $G'_1=1.3-1.6 \times 10^6$ Pa, whereas for a cake shortening $G'_1= 1.3\times10^6$ Pa.

**Figure 6.1** Average storage $G'_1$ and loss moduli $G''_1$ as a function of strain amplitude at $\omega= 3.6$ rads$^{-1}$ for a laminating shortening (R1) and a cake shortening (S1).

### 6.4.2 Nonlinear viscoelasticity

#### 6.4.2.1 Lissajous-Bowditch curves and Chebyshev coefficients

In the nonlinear regime ($\gamma_0 > \gamma_c$), the storage and loss moduli become a function of the strain input and the stress response contains higher-order harmonics in addition to the fundamental harmonic attributed to the frequency of excitation (Hyun et al., 2011)

The incidence of higher harmonics can be appreciated in the so-called Lissajous-Bowditch plots, which serve here as qualitative fingerprints of the transitions from the linear to the nonlinear viscoelastic regime of bakery shortenings. Figs. 6.2(a) and 6.2(b) show elastic Lissajous-Bowditch curves, while Figs. 6.2(c) and 6.2(d) display viscous Lissajous-Bowditch curves. Note, that for small strain amplitudes ($\gamma_0 \leq 0.03\%$ not shown here), the elastic and viscous curves are simple ellipses, representing the linear responses.
Figure 6.2 (a,b) elastic and (c,d) viscous Lissajous-Bowditch plots for selected amplitudes for a laminating shortening (R1) and a cake shortening (S1).

As the strain increases, the ellipses gradually distort into complex nonlinear shapes. Here, we focus on intercycles (average) and intracycle (local) stress responses manifested in the Lissajous-Bowditch curves. At $\gamma_0 \approx 0.36\%$, distinct features are visually evident and persist in the Lissajous-Bowditch plots. Intercycle or global features include the clockwise rotations of the Lissajous-Bowditch plots at increasing deformations, towards the strain or shear-rate axis, which denote average elastic softening and average viscous thinning (as observed in the average viscoelastic moduli $G'_1$ and $G''_1$). Intracycle or local features include upturns or “twists” in the stress of the elastic Lissajous-Bowditch plots occurring at the maximum instantaneous strain $\gamma(t) = \gamma_0$, and downturns or “bends” in the stress of the viscous Lissajous-Bowditch curves visually evident at the maxima strain-rate $\dot{\gamma}_{\text{max}}$. Stress “twists” indicate lower elasticity at the minimum strain $\gamma(t) \to 0$ (which corresponds to the location of the maximum strain-rate $\dot{\gamma}_{\text{max}}$), whereas stress “bends” indicate shear-thinning behavior apparently less prominent in R1. Moreover, at increasing strain inputs ($\gamma_0 \geq 6\%$), the viscous dissipative determined by the area enclosed by the
elastic Lissajous-Bowditch curves, indicated that R1 was more dissipative than S1. Furthermore, the maximum stress associated with each Lissajous-Bowditch curve is larger for laminating (R1) than for cake (S1) shortenings.

**Figure 6.3** (a) elastic stress and (b) viscous stress extracted from Lissajous-Bowditch plots for selected amplitudes for a laminating shortening (R1) and a cake shortening (S1).

These differences can be better visualized in Fig. 6.3, where elastic (Fig. 6.3a) and viscous (Fig. 6.3b) stresses from selected Lissajous-Bowditch curves of R1 and S1 are depicted. As illustrated in Fig 6.3, the decomposition of the total stress into its elastic and viscous components results in single-valued functions that denote the same qualitative features captured by the Lissajous-Bowditch curves. For instance, the maximum instantaneous strain for each increasing strain input is associated with elastic stresses and viscous stresses higher for R1 than for S1 (Especially at $\gamma_0 = 3.57\%$ and $\gamma_0 = 9.54\%$). The elastic and viscous curvatures can be described by a set of Chebyshev polynomials of the first kind as alluded to previously.
Figure 6.4 Scaled third-order elastic $e_3/e_1$ and viscous $v_3/v_1$ Chebyshev coefficients as a function of strain amplitude $\gamma_0$ for a laminating shortening (R1) and a cake shortening (S1).

In Fig. 6.4, we present the leading-order Chebyshev coefficients or harmonics (related to the Fourier coefficients as described in the “Methods” section), $e_3/e_1$ and $v_3/v_1$. These coefficients signal the onset of nonlinear viscoelastic behavior and capture periodic variations in the local elastic and local viscous stress manifested as convexities in the curves (“twists” or “bends” as earlier referred to). The signs of these third harmonics indicate the predominant local driving cause of the nonlinear deviation of the average stress response in $G_1'$ and $G_1''$ (i.e. whether they are triggered by large strains or large strain-rates). To determine this, the third harmonic needs to define the curvature (e.g. “twists” or “bends”) of the elastic or viscous stress, which is generally but not always the case. For a complete interpretation of the intrinsic Chebyshev LAOStrain nonlinearities, the readers are referred to (Ewoldt and Bharadwaj, 2013).

In the linear regime $\gamma_0 \leq 0.03\%$, minimum contributions of $e_3/e_1$ and $v_3/v_1$ to the stress response were observed. For the viscous measures, at $\gamma_0 \geq 0.03\%$, $v_3/v_1 > 0$ marked the onset of nonlinearities and indicated that viscous shear thickening of $G_1''$ was driven by large instantaneous strain rates. Subsequently, $v_3/v_1 < 0$, indicated a transition from shear-thickening to shear-thinning behavior and suggested again that average viscous shear thinning was driven by large strain instantaneous rates. For the elastic measures, at $\gamma_0 \geq 0.05\%$, $e_3/e_1 > 0$ indicated that elastic softening of $G_1'$ was driven also by large instantaneous strain rates.
6.4.2.2 Nonlinear viscoelastic metrics.

The application of nonlinear large deformations disturbs the crystal network inducing elastic softening and plastic viscous deformation as observed qualitatively in the Lissajous-Bowditch curves. To describe quantitatively these events, we used local (or instantaneous) nonlinear viscoelastic as proposed by (Ewoldt et al., 2008), a selection of which are displayed in Figs. 6.5 and 6.6. To capture “residual” local elasticities and local viscosities associated with softening and thinning of the crystal network, we normalized nonlinear measures by their corresponding linear material properties.

Figure 6.5 Local elastic (a) minimum-strain modulus and (b) maximum-strain modulus, both normalized by the linear elastic moduli for laminating shortenings (R1, R2, R3) and a cake shortening (S1). Insets show absolute values of the same elastic measures.

Elastic properties involved the tangent (at minimum strain) and secant (at maximum strain) elastic moduli (Fig. 6.5), whereas viscous properties comprised the tangent (at minimum strain-rate) and secant (at maximum strain-rate) dynamic viscosities (Fig. 6.6). It is shown that elastic measures were similar suggesting they played a minor role in the functionality of the shortenings.
Figure 6.6 Local dynamic (a) minimum-strain-rate viscosity $\eta_M'$ and (b) maximum-strain-rate $\eta_L'$ viscosity, both normalized by the linear dynamic viscosity for laminating shortenings (R1, R2, R3) and a cake shortening (S1). Insets show absolute values of the same viscous measures.

In contrast, viscous measures differed substantially, e.g. dynamic viscosities at instantaneous minimum strain-rates $\eta_M'$ and large strain-rates $\eta_L'$ denoted less thinning for laminating R1-R3 than for a cake shortening S1. Differences appeared to be predominant at the highest strain-rate (which coincides with the minimum strain) in accord with Chebyshev coefficients that indicated that average nonlinearities are driven by instantaneous large strain-rates. To summarize, major differences on the macroscopic rheology of bakery shortenings are due to their ability to dissipate energy in the viscous component of the stress response (i.e. $\eta_M'$ and $\eta_L'$). In line with our previous study (Macias-Rodriguez and Marangoni Chapter), we demonstrate that roll-in shortenings share this “fingerprint” irrespective of bulk composition.

As alluded to earlier, the rheology of fat crystal networks arise from structural hierarchies spanning from the molecular to the microscopic. In a previous work, we found no correlation between the subcell packing of the acyl chains (or polymorphism) and the rheology of shortenings. In the following sections, we investigate larger physical length scales: nano- and micro-structures, to determine their implications on the rheology of shortenings.

6.4.3 USAXS

Larger length scales, ~20 nm to 6μm, were studied using USAXS, a technique that does at the moment does not allow in situ rheological measurements for edible fats. Hence, the results showed here are only values obtain for the bulk material, the one manufacturer in the industry.
Figure 6.7 Absolute scattering intensity $I(q)$ as a function of the scattering vector $q$. Slope values included in the plot serve as guides for the actual values obtained by the Unified Fit model and summarized in Table 6.2.

Fig. 6.7 shows the absolute intensity $I(q)$ as a function of the scattering vector $q$. At first sight, a major qualitative difference between laminating and cake shortenings was that the former presented a three-level structural hierarchy, while the latter displayed a two-level structural hierarchy. Each structural level was represented by a power-law (Porod) region and a “knee” or Guinier region at different $q$-ranges. The scattering patterns were analyzed using Unified fit model and Guinier-Porod model.

Table 6.2 Selected parameters obtained from Unified Fit and Guinier-Porod models and length scales probed in each structure level of the Unified Fit model. Standard error means for $P$ and $S$ parameters were equal or below 0.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_1$</th>
<th>$R_{el}$ [nm]</th>
<th>$L_1$ [nm]</th>
<th>$P_2$</th>
<th>$R_{el}$ [nm]</th>
<th>$L_2$ [nm]</th>
<th>$P_3$</th>
<th>$L_3$ [um]</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>4.0</td>
<td>50.44±3.4</td>
<td>21-157</td>
<td>1.8</td>
<td>370.1±69.5</td>
<td>157-1571</td>
<td>3.6</td>
<td>0.6-6.3</td>
<td>1.5</td>
</tr>
<tr>
<td>R2</td>
<td>4.0</td>
<td>44.0±2.5</td>
<td>13-78</td>
<td>2.1</td>
<td>194.2±12.1</td>
<td>78-698</td>
<td>2.8</td>
<td>0.1-6.3</td>
<td>1.9</td>
</tr>
<tr>
<td>R3</td>
<td>3.8</td>
<td>102.5±0.9</td>
<td>21-157</td>
<td>1.5</td>
<td>106.9±1.2</td>
<td>157-1300</td>
<td>2.8</td>
<td>1.3-6.3</td>
<td>1.5</td>
</tr>
<tr>
<td>S1</td>
<td>3.4</td>
<td>283.2±110.2</td>
<td>21-314</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
<td>0.3-6.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Parameters reported are the best fit and are summarized in Table 6.2. Previous experiments carried out using USAXS (Peyronel et al., 2014b, 2014c, 2013) as well as computer predictions (Pink et al., 2013; Quinn et al., 2014) showed that the CNPs can be seen at the high $q$ values, while their aggregation appeared at the intermediate and smallest $q$-values. These researchers also showed that CNPs can aggregate to form fractal aggregates in either one or two hierarchical levels.
We relied on these previous findings to explain the USAXS patterns obtained for these shortenings. For the laminated shortenings, the Unified Fit model successfully fitted the data using three structural levels: Level 1, Level 2 and Level 3 corresponding to high, intermediate and low $q$ values respectively. Level 1 gave a parameter value $P_1 \approx 4$ for laminating shortenings and $P_1 < 4$ for cake shortening. The first case indicated a smooth CNP surface, while the second one indicated a rough one. The radius of gyration $R_g$, which provides an estimation of the average CNP size, indicated that CNPs of laminating shortenings were up to six times smaller than those of a cake shortening. In level 2, $P_2$ suggested that CNPs of laminating shortenings aggregated into intermediate structures via DLCA ($P_2 = 1.7-1.8$) or RLCA ($P_2 = 2.1$), while $R_g$ indicated that crystal clusters had an average radius of gyration 107-370 nm. It is also conceivable that the smooth morphology of CNPs enabled the creation of an intermediate level of structure in laminating shortenings, which is absent in the cake shortening. The values of $P_3$ in level 3 for the three laminated shortenings indicate that the aggregates are in process to become evenly distributed in space ($P_3 \approx 3$). On the other hand, a value of $P_3 \approx 4.2$ for the cake shortening indicates that the aggregate in this length scale does not have a sharp interface.

The parameters from the Guinier-Porod model are used to find the shape of the scatterer. The structural level defined by this model determines the $S$ parameter which indicates if the scatterer is a sphere, a rod or platelet (Hammouda, 2010). It was found that laminating shortenings had scatterers with platelet morphology ($S \approx 2$) or intermediate shapes between rods and platelets ($S = 1.5$). Instead, a cake shortening had rod-like scatterers ($S \approx 1$).
6.4.5 SEM

Figure 6.8 Cryo-scanning electron images of laminating fats: (a, d) R1, (b) R2, and a cake shortening (c, e) S1. Images a, b, c share the same magnification bar= 30μm. Images d, e share the same magnification bar= 100μm.

Fig 6.8. shows SEM micrographs of shortenings. It was observed that laminating shortenings had a homogeneous microstructure, made up of distinct plate-like crystallites with variable lengths in the range of 2-10 μm which form elongated layered-like clusters, which are roughly parallel to each other. Instead, a cake shortening was composed of distorted spherical-like crystal aggregates with average size 4 μm.

In agreement with our previous study (Macias-Rodriguez and Marangoni Chapter), we show that roll-in shortenings share similar nano- and micro- structural features. In particular, the “smooth” surface morphology of the nanostructure in roll-in shortenings can be attributed to their higher content of trisaturated TAG species (Chapter 3, Physicochemical and rheological characterization of roll-in shortenings) as previously reported for binary mixtures of tristearin in triolein (Peyronel et al., 2013)
Based on the findings from USAXS, SEM and rheology, our interpretation is that the elastic stored energy is stored within the network in similar ways, and viscous dissipated energy across the structural levels and crystallite layers is the key difference. We hypothesize that in laminating shortenings shear loads are better dissipated among the three-hierarchy structures unlike a cake shortening where energy is allocated only between two hierarchy levels. The microstructure might also confer mechanisms of releasing local stresses. For example, slide motion of the elongated crystallite layers in laminating shortenings would facilitate stress dissipation. This scenario seems plausible as it has been proven (via computer simulations) for biological-like materials of similar composition and volume fraction that dissipation and defect tolerance increases vastly by addition of only one additional hierarchical level in their structure. (Sen and Buehler, 2011) In addition, it has been shown that intrinsic structural mechanisms help dissipating high local stresses, e.g. mineral-platelet sliding in seashells (Ritchie, 2011) Finally, we suggest that any fat composition that shares the rheological fingerprint, e.g. high viscous dissipation, will lead to adequate roll-in performance.

6.5 Conclusions

We investigated the rheological response of three laminating shortenings and a cake shortening to oscillatory shear strain deformations. In particular, we utilized LAOS to decouple elastic and viscous mechanisms in the nonlinear regime. We also characterize the materials in the nano to micro length scale using X-ray scattering and Cryo-SEM, to investigate the underlying structure of the fat crystal network.

We found that the major difference between those shortenings used for lamination and the one used for cake applications, is due to the material nonlinear viscous dissipation (rather than nonlinear elasticity). We also found that laminating shortenings displayed a three-hierarchy structure in comparison to two-hierarchy structure of the cake shortening. Moreover, the former also showed a homogenous network made up of layered crystal aggregates, whereas the latter a heterogeneous network comprised of distorted spherical-like crystal aggregates. We argue that enhanced viscous dissipation facilitated by these structural features is crucial for optimal laminating performance of shortenings.

6.6 Acknowledgements
The authors are indebted to Dr. Jan Ilavsky and his team at beam line 9ID-C for their invaluable support and help through the data collection and analysis of USAXS. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We also greatly Dr. David Pink (Physics, St. Francis Xavier University) for discussions on USAXS.

6.7 References


Ilavsky, J., Jemian, P.R., 2009. Irena: tool suite for modeling and analysis of small-angle


CHAPTER 7: BAKERY SHORTENINGS: STRUCTURE-MECHANICAL FUNCTION RELATIONS
Braulio A. Macias-Rodriguez, and Alejandro G. Marangoni

Applied Rheology 27:3 (2017) 33410

Department of Food Science, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. E-mail: amarango@uoguelph.ca

7.1 Abstract

Shortenings are examples of soft viscoelastic materials with important mechanical functions in baking applications. To fully understand their mechanical functionality, it is essential to correlate material microstructure with rheological behavior. We investigated commercial shortenings designed for various applications, with emphasis on those intended for use in laminated doughs. The microstructure of laminating shortenings was characterized by well-defined crystallites arranged in a layer-like fashion, whereas all-purpose and cake shortenings exhibited more distorted crystallites packed in a more heterogeneous manner. Oscillatory and creep shear behavior demonstrated that all shortenings acted as viscoelastic solids, but laminating shortenings had higher viscosities at “rest” in the linear regime. Recovery in the nonlinear regime showed that laminating shortenings lower fractional recovery associated with pronounced plastic irreversible deformations. Extrusion tests also indicated higher viscous dissipation for laminating shortenings. It is argued that the unique layered microstructure is partly responsible for the increased viscous and plastic flow of laminating shortenings, aspects that dictate the ability of these products to endure mechanically demanding processes without apparent catastrophic failure.

Keywords: fat, shortening, rheology, creep, extrusion, microstructure

7.2 Introduction

Fats resemble colloidal gels or colloidal crystals, with rheological properties determined by triglyceride crystal particle concentration in liquid oil, particle size and spatial distribution of mass, and interparticle interactions. (Narine and Marangoni, 1999b; van den Tempel, 1961) At rest, the network is capable of supporting its own weight, however; above a critical deformation,
the network switches from a dense solid-like to a disordered liquid-like structure; that is, it yields and “flow”. Some rheological manifestations of the fat crystal network include viscoelasticity, yielding and thixotropy (i.e., shear thinning and subsequent recovery) (B. Macias-Rodriguez and Marangoni, 2016a; Prentice, 1993; van den Tempel, 1961).

The study of fat rheology began as early as 1930 and it has developed in two major directions: the rheological characterization of fats using multiple techniques and the development of quantitative models that relate structure to linear viscoelasticity (Narine and Marangoni, 1999a; Scott Blair, 1954). A wide array of empirical methods mainly based on indentation or penetration have been proposed (Mortensen, 1983; Scott Blair, 1954). These tests measure the resistance of a material to be pierced by a shaped test body (i.e., sphere, rod and cone) that relates to consistency, yielding and plasticity of butter, margarines and shortenings (Mortensen, 1983; Scott Blair, 1954). Among these, cone penetrometry has become the method of choice for research and industry routine examinations (Haighton, 1959). According to this method, the yield stress of fats can be defined as the force load per unit cross-sectional area of the cone as obtained from \( \text{yield value} = K' W / p^n \), where \( K' \) is a constant dependent on the cone angle, \( W \) is the weight of the cone (g), \( p \) is the penetration depth, and \( n \) is an arbitrary scaling exponent ranging from 1.4 to 2 depending on the type of fat (Haighton, 1959; Tanaka et al., 1971). The difficulty of using this method is that it does not provide well-defined rheological material functions and in some cases it is not sensitive enough to discriminate among the functionality of fats or to correlate with the results of other tests (W. Kloek et al., 2005; B. Macias-Rodriguez and Marangoni, 2016a).

Fundamental methods have involved cutting or “sectility” tests, creep, relaxation and oscillatory shear tests to name a few. Cutting tests measure the force required to cut through a block of butter and have been correlated with “spreadability” and viscosity of fats (Mortensen, 1983; Scott Blair, 1954). Creep and relaxation tests under shear or compression input stress or strain steps and record recoverable and non-recoverable deformations or stresses associated with elastic and viscoplastic components of fats. These tests have revealed rises in viscosity (a type of strain hardening) and drops in viscosity (a type of stress softening) under strain- or stress- controlled respectively for butter (Scott Blair, 1954). Oscillatory shear rheology have demonstrated that fat
crystal networks behave as soft viscoelastic solids and display marked thixotropic behavior (van den Tempel, 1979, 1961, 1958).

Several studies have attempted to link structure to rheology of fats. Fat structure is very complex in nature as it encompasses a hierarchical organization spanning from the molecular to the macroscopic (Marangoni et al., 2012; Narine and Marangoni, 1999a). At the molecular level, triacylglycerols (TAGs) stack in pairs longitudinally, and laterally adopting specific geometrical conformations that define the different polymorphic forms (α, β’, β). At the nano level, translational displacements of the unit cell results in the formation crystal lamella, which in turn gives rise to crystalline nanoplateletes (CNPs). At the submicron and micron levels, CNPs self-assemble into larger crystal aggregates via diffusion-limited-cluster (DLCA) and reaction-limited cluster aggregation (RLCA) to form a space-filling network with solid-like or elastic character (Narine and Marangoni, 1999b; Peyronel et al., 2014b). To provide a quantitative links between structure and elasticity of the network, several microscopic models have been proposed but only a few of them have been partially successful such as the fractal model (Narine and Marangoni, 1999b). The fractal model is based on the assumption that fats self-assemble into self-similar or fractal networks with their elasticity rising as a power of the particle volume fraction $G’ \sim \phi^n$, with the exponent $n$ related to the mass fractal dimension ($D$) (Narine and Marangoni, 1999b, 1999c). For “real” systems ($\phi>0.1$), the crystal network is said to be in the so-called weak-link regime where elasticity of the system arises from the interfloc links rather than the fractal flocs. Despite substantial advances in this area, developing rigorous relationships between rheology and structure remains an ongoing challenge.

In this work, we seek to understand the functionality of shortenings designed for various baking applications as related to their rheology and structure. Shortenings are edible fats used to lubricate, weaken, and “shorten” the dough by preventing gluten-starch particle interactions, which otherwise lead to a firm and tough baked product (Ghotra et al., 2002). We emphasize the rheology of laminating or roll-in shortenings, which shows outstanding functionality when compared to any other type of bakery shortening. A laminating shortening is a material used to provide an optimal multilayered dough structure, responsible for the “lift” (volume expansion) and textural properties of croissants, Danish and puff pastries. During extrusion, sheeting and rolling of laminated doughs, laminating fats are shaped into unbroken micron-thick films that bear stresses and pressures as high as 50kPa (Marangoni et al., 2012).
This raises the scientific question as to which rheological properties confer this material the ability to “survive” the manufacturing process and serve its mechanical function, which we address in the present paper.

7.3 Materials and Methods

7.3.1 Materials

Bulk composition, macroscopic functionality and elastic moduli $G'$ of the investigated samples are described in Table 7.1. Exact molecular TAG composition and other physico-chemical properties have been described previously (B. Macias-Rodriguez and Marangoni, 2016b). All shortenings were of intermediate solid concentration ($\phi_{oc} \approx 0.2-0.3$) and commercially acquired to represent “real” materials since replicating heat and mass transfer conditions imposed by industrial crystallization conditions is extremely difficult at the bench-scale. The only exception was laminating shortening R5 which was formulated and crystallized in house as described elsewhere (Acevedo and Marangoni, 2013). Crystallization of laminating shortenings typically involves the use of votator and working units that impart high degree of cooling and shearing, conditions that promote crystal nucleation and superior plasticity. Instead, processing of non-laminating shortenings generally involves lower cooling rates and mechanical working which favor crystal growth over nucleation. As alluded to earlier, laminating shortenings are highly structured fats used in the manufacture of croissants, Danish and puff pastries. All-purpose shortenings and cake shortenings are designed for multiple bakery applications including cake and icing where air incorporation within the shortening or batter is highly desirable, and for cookies, crackers, etc (only all-purpose shortenings) (Ghotra et al., 2002).
Table 7.1 Functionality, bulk composition and elastic moduli at $\gamma_0=0.005\%$ and $\omega=6.28$ rads$^{-1}$. Adapted from [3]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Functionality–composition</th>
<th>$G'$ ($\times 10^6$ Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Puff-pastry hydrogenated soybean oil and cottonseed oil</td>
<td>1.3±0.1</td>
</tr>
<tr>
<td>R2</td>
<td>Laminating non-hydrogenated canola oil, modified palm and palm kernel oils</td>
<td>2.6±0.1</td>
</tr>
<tr>
<td>R3</td>
<td>Laminating hydrogenated vegetable oil and modified palm oil</td>
<td>1.6±0.1</td>
</tr>
<tr>
<td>R4</td>
<td>Puff-pastry palm oil, modified palm oil and soybean oil</td>
<td>3.8±0.1</td>
</tr>
<tr>
<td>R5</td>
<td>Laminating fully hydrogenated soybean oil, soybean oil and glycerol monopalmitate</td>
<td>2.2±0.1</td>
</tr>
<tr>
<td>S1</td>
<td>All-purpose non hydrogenated palm oil and modified palm oil</td>
<td>4.7±0.2</td>
</tr>
<tr>
<td>S2</td>
<td>All-purpose soybean oil interesterified</td>
<td>0.8±0.1</td>
</tr>
<tr>
<td>S3</td>
<td>Cake soybean oil interesterified</td>
<td>0.6±0.2</td>
</tr>
</tbody>
</table>

7.3.2 Sample preparation

7.3.2.1 Scanning Electron Microscopy

To obtain information of the structure of the shortenings, we used freeze-fracture Cryo Scanning Electron Microscopy (Cryo-SEM). Prior to imaging, liquid oil was removed by suspending sample pieces in a ratio of 1:25 fat-solvent. De-oiling solvent involved a 8:2 (v:v) isobutyl alcohol-hexane mixture for laminating shortenings (R1-R5) in which the liquid oil is better trap in the crystal network, or simply isobutanol for all-purpose and cake shortenings (S1-S3). (Chawla et al., 1990) Shortenings were statically deoiled at 20 °C (laminating shortenings: R1-R5) and 14 °C (all-purpose and cake shortenings: S1-S3) for 48 h, filtered (Whatman No 5) to remove solvent and liquid oil, and finally allowed to stand on filter paper overnight to vaporize any remaining solvent. The samples were then attached to the copper sample holder using the Tissue-Tek embedding medium. The sample holder was immersed in a liquid nitrogen slush (-207 °C) using an Emitech K1250x Cryo-preparation unit (Ashford Kent, UK), freeze-fractured and sputter-coated for 2 min with gold using a 20 mA deposition current, 7nm min$^{-1}$
deposition rate. The sample holder was transferred to the SEM stage (Hitachi S-570, Tokyo, Japan) with accelerating voltage of the electron beam of 10 kV. Images were captured digitally using the Quartz PCI imaging package (Quartz Imaging Corp., Vancouver, Canada). Removal of oil from laminating shortening R3 using the present protocol was not possible and thus we do not present micrographs for this sample.

7.3.2.2 Rheology
Prior to rheological characterization, samples were carefully prepared in the form of cylinders of 30mm×1.3mm (diameter×thickness), and stored at 16 °C overnight to allow for reformation of fractured bonds or local damaged and remove residual stresses induced by cutting. Cutting was performed using a wire lubricated with mineral oil to minimize flaw or crack formation that may act as points of stress concentration leading to premature failure.

7.3.3. Measurements

7.3.3.1 Scanning Electron Microscopy
The samples were attached to the copper sample holder using the Tissue-Tek embedding medium. The sample holder was immersed in a liquid nitrogen slush (-207 °C) using an Emitech K1250x Cryo-preparation unit (Ashford Kent, UK), freeze-fractured and sputter-coated for 2 min with gold using a 20 mA deposition current, 7nm min⁻¹ deposition rate. The sample holder was transferred to the SEM stage (Hitachi S-570, Tokyo, Japan) with accelerating voltage of the electron beam of 10 kV. Images were captured digitally using the Quartz PCI imaging package (Quartz Imaging Corp., Vancouver, Canada).

7.3.3.2 Shear Rheometry
Based on the manufacture (layering and folding) of laminated doughs sample conditioning and rheological characterization for shear oscillatory and creep were conducted at 16 °C (except R4 which was equilibrated to 18 °C, per manufacturer’s recommendation) (Cauvain et al., n.d.).

To probe the linear viscoelastic region (LVR), samples were subjected to small stress oscillatory shear deformations with an AR-2000 (TA Instruments, New Castle, DE). Parallel plates geometry (DIA=20 mm) was used for oscillatory testing. Filter-paper (Whatman No 5) was attached to the top and bottom plates to circumvent slip at the boundaries. Samples were carefully transferred onto the lower plate of the rheometer, and the measuring gap was set using
a 3±0.5 N axial force. Axial normal force where then allowed to relax the axial force to a constant value over a zero stress relaxation test for at least 15 min. This ensured reproducible results and potentially prevented the formation of the new microstructures during loading (B. Macias-Rodriguez and Marangoni, 2016a). To identify a range of stresses in the LVR, stress sweeps were conducted at the low- and high- frequency boundaries of the subsequent frequency sweep. Frequency sweeps were performed at \( \tau_0 = 100 \text{ Pa} \) and \( \omega = 0.1-100 \text{ rads}^{-1} \).

Shear creep and recovery were performed with similar but smaller parallel-plate fixtures (DIA=10 mm). To circumvent residual deformations induced during loading, samples were subjected to 0 Pa stress step until the strain plateaus to approximately 0 while being thermally equilibrated. Subsequently, shear creep and recovery experiments were performed at increasing stress steps applied for \( t = 300 \text{ s} \) necessary to detect sufficient creep motion and reach a steady state. Applied stresses were inside and outside of the linear regime. The maximum shear stress level was constrained by secondary or unstable creep \( (\tau_{\text{max}} = 900 \text{ Pa}) \). Following completion of the creep step, the stress was set to zero and the strain recovery was recorded for 600s. Data was fitted to a 4-element Burgers model (Fig. 7.3). It is noteworthy that due to work softening of fats at increasing stresses, individual samples were used for each stress step.

7.3.3.3 Capillary rheometry

Die extrusion experiments were conducted at room temperature (22 °C) since the rheometer lacked a thermal control. These temperatures fall approximately in the upper range of rolling and folding of pastries (Cauvain and Young, n.d.; Pajin et al., 2011).

Die extrusion was conducted with a capillary rheometry using a 15-mm diameter twin-bore capillary rheometer (Rosand RH-7, Malvern Instruments). Pressure drop as a function of piston speed was measured independently in both barrels. In one barrel, pressure drop was recorded across a capillary die with 8 mm length, 1 mm diameter, and 180° entrance angle, using a 10000 psi pressure transducer. In the other barrel, the same material was run and pressure drop was measured across a 0.25 mm length, 1 mm diameter, and 180° entrance angle capillary die, using a 1500 psi pressure transducer. Capillary pressures were calculated treating the 0.25mm length die as an effective zero-length die. The true shear rate in the die was determined by applying the Rabinowitsch correction to describe non-Newtonian flow behavior of the material, and the shear
viscosity was calculated from the capillary pressure drop (Macosko, 1996). It is noteworthy to mention that we did not ascertain the contributions of wall slip to shear flow.

7.4 Results and discussion
7.4.1 Microstructure

![Image of SEM micrographs of R laminating shortenings and S all-purpose and cake shortenings after deoiling the crystal network. R1 and S2 are included also at lower magnification to visualize the spatial distribution of the crystal aggregates.](image)

Laminating fats should match the consistency of the bulk dough to achieve good rolling and sheeting process performance (Renzetti et al., 2015). If a laminating shortening is too soft and too plastic, it will soak into the dough, squeeze out of the layers and cause dough layer sticking, whereas if it is stiff and brittle, it will tear the dough (Cauvain et al., n.d.). The rheology of laminating shortenings can be thought of as a good balance between strength and plasticity.

The microstructure constitutes the primary structural level responsible for the rheology of fats (Marangoni et al., 2012). The microstructure entails the fat crystal network which encompasses
individual crystallites and clusters of crystallites ranging in the length range between 1 µm and 200 µm (Marangoni et al., 2012). Fig. 7.1 shows SEM micrographs displaying the three-dimensional network of laminating, all-purpose and cake shortenings. It was observed that laminating shortenings shared a uniform microstructure, made up of distinct plate-like crystallites with variable lengths in the range of 2-10 µm which form elongated layered-like clusters, which are roughly parallel to each other. Instead, all-purpose shortenings had a more heterogeneous structure, comprised by less-defined flake-like crystallites of comparable size, which seemed to aggregate more randomly. All-purpose shortenings also displayed microvoids with average diameter 16 µm. A cake shortening was composed of distorted spherical-like crystal aggregates with average size of 4 µm. The described microstructures are in agreement with previous reports that have outlined that shortenings that undergo in-process full shear crystallization (typically the case of laminating shortenings) possess a more homogeneous and oriented structure (Heertje, 1993).

7.4.2 Shear rheometry

![Graph showing shear rheometry](image)

**Figure 7.2** Frequency sweep of selected shortenings at fixed stress \( \tau_0 = 100 \) Pa. Shortenings: S1 All-purpose, R1 Roll-in.

Fig. 7.2 shows representative frequency sweeps laminating (R1) and all-purpose shortenings (S1), within the linear viscoelastic region (LVR, \( \tau_0 = 100 \) Pa). It was observed that shortenings behaved as viscoelastic solids \((G' > G'')\), with elastic and viscous contributions to the complex modulus being weak functions of the frequency. This is a typical behavior of flocculated fat networks in which the solid-like crystal aggregates and crystal interactions govern the linear
viscoelastic response (van den Tempel, 1961). An all-purpose shortening S1 has a storage modulus three times larger \((G' = 3.8 \times 10^6 \text{ Pa})\) than a laminating shortening R1 \((G' = 1.3 \times 10^6 \text{ Pa})\). Despite these quantitative differences, other samples had approximately the same linear elastic moduli (Table 7.1). Likewise, shortenings had comparable critical strains and stresses in the order of \(\gamma_c \approx 0.01-0.02\%\) and \(\tau_c \approx 50-600 \text{ Pa}\) respectively, irrespective of their bulk composition or end functionality (B. Macias-Rodriguez and Marangoni, 2016a). Despite important, lipid composition does not always determine the bulk rheological properties of shortenings (B. Macias-Rodriguez and Marangoni, 2016a).

Creep and recovery tests are particularly useful for probing physical networks (Steffe, 1996). Unlike more traditional strain input experiments, stress inputs experiments also allow for measuring longer timescales of relaxation due to the application of a constant stress. In the creep phase, a constant stress step \((\tau_0 > 0)\) is applied while deformation is monitored over time. The initial stages of creep involve elastic recoverable deformations, whereas the latter stages involve non-recoverable viscous deformations (Fig. 7.3) (Hermida-Merino et al., 2016). In the recovery phase, a zero constant stress \((\tau_0 = 0)\) is input over time, and similar viscoelastic properties are measured (Fig. 7.4). Fig. 7.4 depicts creep and recovery curves for laminating (a) all-purpose and cake shortenings (b). To examine linear viscoelastic properties, all samples were subjected to stress steps \(\tau_0 = 200 \text{ Pa}\) in the creep phase, except for all-purpose (S2) and cake (S3) shortenings that were exposed to \(\tau_0 = 80 \text{ Pa}\) and \(\tau_0 = 50 \text{ Pa}\) respectively, since they yield at higher stresses. Stress inputs of \(\tau_0 < 200 \text{ Pa}\) were not possible as little creep motion and unstable flow at steady state occurred. From these results, it seems that laminating shortenings followed a common trend, which is they accumulated less strain deformations and showed a less steep slope associated with viscous deformations compared to all-purpose and cake shortening. To quantify such behavior, creep and recovery curves were fitted to a generalized 4-element Burgers model that reduces to the following functions (Steffe, 1996):
Figure 7.3 Typical creep and recovery of a linear viscoelastic material under a constant stress and a schematic diagram of the Burgers model, which consists of Maxwell and Kelvin elements in series.

Stress inputs of $\tau_0 < 200 \text{ Pa}$ were not possible as little creep motion and unstable flow at steady state occurred. From these results, it seems that laminating shortenings followed a common trend, which is they accumulated less strain deformations and showed a less steep slope associated with viscous deformations compared to all-purpose and cake shortening.

To quantify such behavior, creep and recovery curves were fitted to a generalized 4-element Burgers model that reduces to the following functions (Steffe, 1996):

$$J(t) = J_0 + J_1 \left(1 - e^{-t/\Lambda}\right) + \frac{t}{\eta_0} \text{ Eq. (1)}$$

$$J(t) = J_{\text{max}} - J_0 - J_1 \left(1 - e^{-t/\Lambda}\right); t_r > t_c \text{ Eq. (2)}$$

Where equations (1) and (2) correspond to the creep and recovery phases with time periods of stress loading $t_c = 5 \text{ min}$ and stress unloading $t_u = 10 \text{ min}$ respectively. The elements of the Burgers model, composed by a combination of a Maxwell ($S_1$ and $D_3$) and Kelvin/Voigt models ($S_2$ and $D_2$), and a typical viscoelastic creep and recovery curve with its corresponding parameters are depicted in Fig. 7.3. The instantaneous compliance $J_0$ and viscosity $\eta_0$ correspond to the elastic deformability and viscosity of the Maxwell element, whereas the retarded compliance $J_1$ and
characteristic retardation time $\Lambda (\eta_i \times J_i)$ represent similar parameters in the Kelvin/Voigt element. The viscosity at “rest” $\eta_0$ (often referred to as zero-shear viscosity in polymers) is indicated by a constant linear slope or shear-rate towards the end of the creep phase. The maximum compliance $J_{\text{max}}$ represents the end of the creep phase.

Figure 7.4 Linear viscoelastic creep and recovery curves for (a) laminating: R and (b) all-purpose and cake shortenings: S. Stress steps of $\tau_0 = 200 \text{ Pa}$ were applied for all samples except for S2 and S3 that were subjected to $\tau_0 = 80 \text{ Pa}$ and $\tau_0 = 50 \text{ Pa}$ respectively. The data are ignored for times $t \leq 100 \text{ ms}$ due to high-frequency creep ringing.

For a linear viscoelastic response, the parameters obtained from the creep period approximate those from the recovery period (Steffe, 1996). The reciprocal compliances are equivalent to elastic moduli $J = 1/G$ within the LVR. Although increasing number of Kelvin-Voigt elements helps to describe a complex spectrum of retardation times, we chose to retain the original parameters to avoid incrementing phenomenology of the model (Scott Blair and Burnett, 1959).
Table 7.2 Creep and recovery parameters obtained from fitting data to a 4-element Burgers model. From left to right: creep or recovery section (C/R), instantaneous compliance ($J_0$), retarded compliance ($J_1$), retardation time ($\lambda$) and maximum compliance ($J_{\text{max}}$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Period</th>
<th>$J_0$ ($\times 10^{-7}$ Pa)</th>
<th>$J_1$ ($\times 10^{-7}$ Pa)</th>
<th>$\lambda$ (s)</th>
<th>$J_{\text{max}}$ ($\times 10^6$ Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>C</td>
<td>9.87</td>
<td>4.51</td>
<td>26.14</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>10.45</td>
<td>5.63</td>
<td>66.50</td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>C</td>
<td>4.59</td>
<td>2.52</td>
<td>21.71</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>4.85</td>
<td>2.48</td>
<td>77.8</td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>C</td>
<td>5.67</td>
<td>2.24</td>
<td>16.18</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>5.62</td>
<td>2.77</td>
<td>66.13</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>C</td>
<td>2.53</td>
<td>1.11</td>
<td>19.85</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>2.99</td>
<td>1.57</td>
<td>77.35</td>
<td></td>
</tr>
<tr>
<td>R5</td>
<td>C</td>
<td>5.43</td>
<td>1.45</td>
<td>14.29</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>6.02</td>
<td>2.41</td>
<td>73.8</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>C</td>
<td>4.86</td>
<td>5.22</td>
<td>25.03</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>4.38</td>
<td>7.69</td>
<td>97.49</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>C</td>
<td>5.56</td>
<td>5.25</td>
<td>34.06</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>6.17</td>
<td>6.54</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>C</td>
<td>26.03</td>
<td>22.32</td>
<td>17.8</td>
<td>6.24</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>7.88</td>
<td>11.8</td>
<td>79.5</td>
<td></td>
</tr>
</tbody>
</table>

In general, the Burgers model describes reasonably well the data ($r^2 > 0.90$) for the creep and the recovery phases, which show similar viscoelastic parameters indicating that the probed stresses were within the LVR (Except S3 that begins to yield at $\tau_0=50$ Pa).

The viscosities at “rest” $\eta_0$ depicted in Fig. 7.5(a) was the most relevant parameter although the retarded elastic compliance $J_1$ and maximum compliance $J_{\text{max}}$ shown in Table 7.2 were also qualitative different to a less extent. The remaining parameters are also provided in Table 7.2, as reference for the reader. Laminating shortenings showed higher steady state viscosities $\eta_0$ which in some cases varied by almost an order of magnitude compared to other samples (i.e., R4=1.1$\times 10^9$ Pa.s, S1=2.6$\times 10^8$ Pa.s). Likewise, laminating shortenings had retarded elastic
compliances and maximum compliances nearly half the values or lower than those of all-purpose shortenings (R1 was the only exception). Similar viscoelastic parameters for cake shortening were substantially different from the other shortenings. Considering that fats do not show marked elasticity, it is concluded that differences in flow properties $\eta_0$ (rather than elastic compliances $J_1$), is what dictates the laminating functionality of a shortening, that is their improved plasticity when compared to other fats. This in agreement with previous reports which have suggested that the “dead” appearance or brittleness of butter and shortenings are caused by inadequate viscous properties, rather than by deficiency of elastic properties (Scott Blair, 1953).

Figure 7.5 Shear (a) Steady shear viscosity and (b) fractional recovery at various shear stresses. Laminating show lower fractional recover than all-purpose and cake shortening.

During processing, shortenings experience large nonlinear deformations and hence we investigated the effect of increasing stress steps on strain deformations. We calculated fractional recovery $\gamma_R/\gamma_C$, defined as the ratio of strains recorded at recovery $\gamma_R$ and creep $\gamma_C$ phases respectively, at similar time periods ($t=5\text{min}$). Tests were constrained to $\tau_{\text{max}}=900 \text{ Pa}$ as secondary creep and unstable creep motion associated were observed which obscured inherent differences among samples. Fractional recovery can be seen as the relative extent to which a material reverses back to its undeformed condition. Fig. 7.5(b) shows that laminating shortenings could be further distinguished from all-purpose and cake shortenings by their fractional recovery upon cessation of imposed shear stress. Throughout the stress range, laminating shortening showed only $\sim$10-40% recovery, whereas all-purpose and cake shortenings showed $\sim$45-70% recovery.
Differences in fractional recovery relate to the rheological functionality of the shortenings. Lower fractional recoveries confer laminating shortenings the ability to maintain their deformation and delay fracture during layering and extrusion operations. On the other hand, all-purpose and cake shortenings do not require such additional process performance and hence tend to have higher fractional recovery and fail more easily. Our interpretation here is that lower fractional recoveries in laminating shortenings attributed to irreversible plastic deformation might originate due to slippage among the nearly-parallel crystal aggregates.

### 7.4.3 Capillary rheology

During processing, laminating shortenings are subjected to cold extrusion and rolling with the dough layers, leading to high nonlinear shear rates in the order of 1-1000 s\(^{-1}\) (Steffe, 1996). The performance of these processes largely depends on the consistency of the laminating shortenings, which present plasticity and shape-retaining ability unlike any other fat (Cauvain and Young, n.d.).

![Macrographs](image)

**Figure 7.6** Macrographs of (a) laminating shortening R5, (b) all-purpose shortening S1 collected at the die exit and (c) laminating shortening R5 collected on a weighing pan. Laminating shortening sustain large shear deformation, remain continuous and produces a thin extrudate compared to all-purpose shortening. Apparent shear viscosity \(\eta_a\) as a function of apparent strain-rate \(\dot{\gamma}_a\).

To capture this rheological behavior, orifice extrusion was conducted with capillary rheometer. Fig. 7.6 displays images of representative laminating (R5) and all-purpose (S1) samples at the die exit of the capillary rheometer, and calculated shear viscosity for selected samples. Apparent shear viscosities were in the order of \(\eta=400-40\) Pa s at relevant apparent shear rates \(\dot{\gamma}_0=10-1000\)
s^{-1}. It was not possible to evaluate the remaining samples due to insufficient and unsteady pressure readings. Nevertheless, qualitatively speaking, laminating shortenings form into continuous fine filaments, whereas all-purpose or cake shortenings fracture showing a more irregular contour and swollen extrudate. It is suggested that a shape-retaining fine extrudate in a laminating shortening might be produced because of extensional orientation of the layered-like microstructure (Refer to Fig. 7.1) at the die entry. Some of this extensional strain energy might be dissipated due to intrinsic slip of the layer-like crystal aggregates, which translates to higher viscous dissipation and plastic flow as the laminating shortening travels through the barrel and exits the capillary. Conversely, a thick extrudate in an all-purpose shortening might result from its heterogeneous microstructure, which allows less energy dissipation and less plastic deformation. Therefore, this type of material tends to regain its shape at the die exit where it is no longer constrained (Stevens and Covas, 1995). This qualitative experimental evidence agrees with the findings on creep and recovery experiments. The postulated physical mechanisms resonate with the macroscopic functionality of the investigated samples although the potential contributions of wall slip to flow behavior during extrusion cannot be ruled out.

7.5 Conclusions

In this paper, we investigated the rheological properties of bakery shortenings as related to their structure. Special attention was devoted to laminating shortenings given their unusual rheological properties, which allows these materials to be extruded, rolled and folded into continuous thin fat layers alternated with dough layers. Creep and recovery revealed that laminating shortenings possessed higher steady-shear viscosity and lower fractional recovery than any other type of fat. In contrast, minor differences were observed in the elastic moduli or creep compliance. Die extrusion provided also evidence of higher viscosity under relevant manufacturing conditions. We argue that higher viscous dissipation and plastic deformation is what confers the ability of laminating shortenings to effectively withstand shear stresses and retain deformations (as manifested in their fractional recovery). The peculiar layered-like crystal network of laminating shortenings provided a possible explanation to the observed rheological properties, e.g. layered-like crystal aggregates slip past each other contributing to energy dissipation and plastic flow. Although bulk compositions of laminating shortenings were heterogeneous, laminating shortenings obeyed a common rheological behavior suggesting that the structure-function
framework is what dictates the desired performance. This means that any composition and processing regimes that match the rheological fingerprint will result in the same product in terms of mechanical function. Finally, although creep and extrusion tests provided valuable information, they impose abrupt stress jumps that do not generate “easy” flow. In future studies, we will use large amplitude oscillatory shear (LAOS) which possess many advantages over these test such as gradual oscillatory yielding, decomposition of elastic and viscous contributions at chosen strain and frequency inputs and higher signal-to-noise ratios. These features will be crucial to further define the mechanical basis for the functionality of shortenings.

7.6 References


Marangoni AG, Acevedo NC, Maleky F, Co E, Peyronel F, Mazzanti G, Quinn B, Pink DA:


CHAPTER 8: UNDERSTANDING THE FUNCTIONALITY OF LIPID-BASED MATERIALS UNDER LARGE-AMPLITUDE NONLINEAR DEFORMATIONS

Braulio A. Macias-Rodriguez\(^a\), and Alejandro G. Marangoni*\(^a\)

Lipid Technology DOI: 10.1002/lite.201700008

\(^a\)Department of Food Science, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. E-mail: amarango@uoguelph.ca

8.1 Abstract

Lipid-based materials meet many functions such as oil binding, lubricity and rheology. In this review, we focus on their rheological function, specifically in nonlinear viscoelastic properties which we characterize using a novel approach known as large amplitude oscillatory shear (LAOS). We summarize recent works on this area and show that this technique has potential for providing insights into the functionality and perception of lipid-based materials during their application process.

**Keywords:** fat, functionality, rheology, nonlinear, laminating

8.2 Introduction

In foods and many commercial products (i.e. shortening, cosmetic cream), fats contribute to nutritional value, and structure which confers many physical functions including oil-binding and rheological properties. Rheology describes the deformation and flow of matter when stresses or strains are applied, e.g. plastic flow of butter during spreading. Rheology is of prime importance to performance, texture and overall consumer acceptability of lipid materials (Marangoni et al., 2012). For example, neither a cosmetic cream (an emulsion) nor a roll-in shortening (a crystal network) have good skin feel or adequate functionality respectively, if they lack certain rheological characteristics.

The rheology of fats is determined by the structural features of the crystal network embedded in the liquid oil phase. At small deformations, fats (e.g. butter at “rest”) exhibit a solid-like linear behavior, whereas at large deformations (e.g. spreading of butter) fats yield and show plastic nonlinear behavior. The structure of fats is hierarchical, that is it comprises substructures ranging
from the molecular to the microscopic. All fats appear to have in common basic building block: crystallized triacylglycerol (TAG) nanoplatelets (CNPs), which assemble in various ways to make up the upper hierarchical levels (Peyronel et al., 2014a). The microstructure is deemed the structural level closest to the macroscopic world and thus it dominates the rheology of fats.

To date, we know more about fat structure than ever before, and we understand to great extent linear viscoelastic properties (i.e., the storage moduli $G'$) and their relationship with structure. However, a question that has remained unanswered in the field (or at least it has not been addressed explicitly in a fundamental fashion), is how to relate rheological properties to “in use” functionality of fats? By “in use” functionality, we refer to the ability of a fat to optimally perform during processing or consumer use, e.g. manufacture of laminated doughs. To the well-seasoned professional or expert baker this sound like a trivial question to which there are two straight answers. The first one is to use tactile perception methods such as the “thumb” or “finger” test as known in industry vernacular. The second one is to use instrumental methods such as cone penetrometry (The official American Oil Chemists’ Society Method AOCS Cc 16-60) and bending tests. While these approaches offer useful and quick feedback for quality control routines, they provide little physical insight that can be used in favor of rational design of existing products (e.g. reformulation of shortenings or use of alternative design materials like organogels).

Given this premise, the purpose of this review is to briefly introduce and discuss a novel protocol: large amplitude oscillatory shear (LAOS), which addresses this issue. We show that LAOS provides insights into the rheological functionality of fatty materials. It is our hope that this framework finds more applications in the lipid research community.

### 8.3 Small amplitude (SAOS) versus Large Amplitude (LAOS) oscillatory shear

Traditionally, researchers have characterized linear viscoelastic properties of fats using SAOS rheology. For a strain-controlled test, SAOS imposes deformations in the order of $\gamma_0 \approx 0.01\%$, which falls within the linear viscoelastic region (LVR) for most fatty materials. Within the LVR, the stress response does not depend on strain $\gamma_0$ or oscillatory frequency $\omega$ inputs. If we look at the raw rheometer data, the sinusoidal strain input triggers a sinusoidal stress response. From the
raw signal, average elastic $G'$ and average viscous $G''$ moduli that relate to the solid-like character and liquid-like character of the network respectively, are calculated and reported by the rheometer. In this regime, the typical behavior for fats is $G'>G''$ with $G'\approx10^5-10^6$ and low-frequency dependence, which are characteristics typical of soft viscoelastic solids (or gel-like systems). One major pitfall of the SAOS regime is that it encompasses strains that do not compare to most processing or product-use deformations. As a result, fats with a variety of macroscopic functionalities can share similar SAOS rheology, but strikingly different LAOS rheology. LAOS rheology probes relevant deformations, manifold higher than those in SAOS (e.g. a strain input of $\gamma_0\approx 10\%$ is 1000-fold higher than a critical strain $\gamma_{\text{critical}}\approx 0.01 \%$). Beyond the LVR, stress responses become non-sinusoidal (See Fig. 8.1a) and variant to changes in $\gamma_0$ or $\omega$. Therefore, $G'$ and $G''$ become insufficient to reflect the richness of the nonlinear response.

Figure 8.1 (a) Strain sweep test at a fixed frequency ($\omega=3.6 \text{ rad s}^{-1}$) showing the linear and nonlinear viscoelastic regimes: small-amplitude oscillatory shear (SAOS, linear) and large-amplitude oscillatory shear (LAOS, nonlinear) for laminating and all-purpose shortenings. Insets depict sinusoidal waves (SAOS) and non-sinusoidal waves (LAOS) for linear and nonlinear strain inputs. Enlarged data points reflect average responses ($G', G''$) calculated from the waveforms. (b) Stress versus strain as obtained from (a) for strain deformations $\gamma_0 \leq 15\%$. Laminating and all-purpose shortenings display contrasting rheological behavior.
8.4 LAOS fundamentals and rheological measures

Several frameworks have been proposed to represent the LAOS response. A simple and convenient way is the use of Lissajous figures, in which the total stress $\tau$ is plotted as a function of the strain input $\gamma_0$ (elastic perspective) or as a function of the shear rate input $\dot{\gamma}_0$ (viscous perspective) within each oscillatory cycle. Lissajous figures can be measured over a range of frequencies and strain inputs, and collapsed in a so-called Pipkin diagram, in which $\omega$ and $\gamma_0$ are positioned on the abscissa and ordinate axes respectively. This method is particularly useful for interpreting the qualitative nonlinear response not only in the context of varying deformations but also of varying relaxation times or processing shear rates ($\dot{\gamma}_0 = \gamma_0 \times \omega$). In the SAOS region, Lissajous curves maintain ellipsoidal shapes, whereas in the LAOS region, they distort (Fig. 8.2). Quantification of these responses can be done via a Fourier transform (FT) analysis, which represents one of the most common methods to quantify the LAOS response. A Fourier series shows the presence of one or “fundamental” harmonic ($n=1=\omega$) in the linear regime, whereas the growth of higher-order odd harmonics ($\omega, 3\omega, 5\omega, \ldots$) appear in the nonlinear regime. Although, FT rheology is mathematically robust and useful for quality-control purposes (i.e. one can assign a Fourier spectrum to a specific shortening functionality), it lacks physical meaning. Therefore, it needs to be complemented by other methods such as stress-decomposition by Chebyshev polynomials (Ewoldt et al., 2008). Chebyshev polynomials are mathematically sound (i.e., eliminate fitting ambiguities), physically-meaningful, and are related to the Fourier coefficients. The stress-decomposition method describes the total stress $\tau'$ sinusoid as the sum of its elastic $\tau'(x)$ and viscous $\tau''(y)$ contributions. Here $x = \gamma/\gamma_0$ and $y = \dot{\gamma}/\dot{\gamma}_0$ are the time-varying strain and time-varying shear-rate normalized by strain and shear-rate inputs respectively (recall that deformation conditions are set by the practitioner and that the rheometer generates an oscillatory time-varying sinusoid that meets the desired deformation criteria). In contrast to the closed-loop Lissajous figures, plotting $\tau'$ vs. $x$ or $\tau''$ vs. $y$ produce single-valued functions. These functions are described by the following equations:

$$\tau'(x) = \gamma_0 \sum_{n \text{ odd}} e_n G(\omega, \gamma_0) T_n(x) \quad \tau''(y) = \dot{\gamma}_0 \sum_{n \text{ odd}} v_n(\omega, \dot{\gamma}_0) T_n(y)$$

where $T_n(x)$ are the $n$th-order Chebyshev polynomial of the first kind (i.e., $T_3(x) = 4x^3 - 3x$ is the third-order polynomial), and $e_n$ and $v_n$ are the elastic and viscous Chebyshev coefficients. Just
like Fourier series, in the LVR \( (n=1) \), \( e_1 \rightarrow G' \) and \( v_1 \rightarrow \eta = G''/\omega \) as commonly output by the rheometer. Beyond the LVR, there are contributions of higher-order terms \( (n>1) \) such as \( e_3 \) and \( v_3 \). It is important to note that these terms refer to local responses, which complement average responses such as the viscoelastic moduli reported by the rheometer \( (G', G'') \). The signs of the higher-order terms provide physical insight into the nonlinear response: i.e., \( e_3 > 0 \) means local strain-hardening and \( v_3 < 0 \) describes local strain-thinning. These characteristics can be also observed visually as stress “upturns” or stress “bends” in the elastic and viscous Lissajous figures respectively. To fully capture this behavior, rheological measures are proposed which incorporate first- and higher-order terms \( (e_1, e_3, \ldots) \) and can be visually appreciated in Fig. 8.3a. The elastic metrics include the minimum-strain modulus or tangent modulus \( G_M' \) and the large-strain or secant modulus \( G_L' \). The viscous metrics include the minimum shear-rate viscosity \( \eta_M' \) and the large shear-rate viscosity \( \eta_L' \).

8.5 A case study: rationalizing the functionality of laminating shortenings

Laminating shortenings are edible fats used in the manufacture of layered doughs such as croissants, Danish and puff pastry. Here, the main role of the fat is to serve as a continuous barrier between sheets of dough and thereby prevent their interaction during co-extrusion, roll-in and layering (the close equivalent processes of kneading and repeatedly folding manually in your kitchen). This process imposes large nonlinear deformations on laminating shortenings. It is obvious that for a fat to bear such high nonlinear deformations, it must possess a good balance of strength and plasticity. If the fat is too soft, it will be soaked into the dough or squeezed out, and if it is too hard and brittle, it will rupture the dough. In any case, this will lead to poor results in terms of process performance, lamination, and product quality: dense pastries with low puff. The remaining question then arises: what rheological characteristics a shortening must meet to achieve the special laminating functionality? To address this, we present LAOS results, which are related to the macroscopic functionality of laminating shortenings (Macias-Rodriguez et al., 2017; B. Macias-Rodriguez and Marangoni, 2016a). Fig. 8.1a shows strain softening as the strain amplitude is increased; however, the response is otherwise unremarkable, that is both shortenings behave as soft elastic solids \( (G'>G'') \). A closer examination of the average strain vs. stress curves (Fig. 8.1b) show markedly contrasting responses for laminating shortening and all-purpose shortening respectively. A laminating shortening reaches a stress maximum, which is
maintained steadily as a function of strain input. In contrast, an all-purpose shortening shows a clear stress overshoot accompanied by larger strain softening. To best represent these discrepancies in rheological behavior, elastic and viscous Lissajous curves at a fixed frequency \( \omega = 3.6 \text{ rads}^{-1} \), are presented for each material in Fig. 8.2.

![Lissajous curves of stress versus strain–elastic projection, and shear rate–viscous projection recorded at \( \omega = 3.6 \text{ rads}^{-1} \) and \( \gamma_0 = 0.01-10\% \) for laminating and all-purpose shortenings. Insets of all-purpose shortening illustrate ellipsoidal elastic and viscous response within the linear viscoelastic region (\( \gamma_0 \approx 0.01-0.05\% \)). Arrows highlight the observed qualitative differences.](image)

**Figure 8.2** Lissajous curves of stress versus strain–elastic projection, and shear rate–viscous projection recorded at \( \omega = 3.6 \text{ rads}^{-1} \) and \( \gamma_0 = 0.01-10\% \) for laminating and all-purpose shortenings. Insets of all-purpose shortening illustrate ellipsoidal elastic and viscous response within the linear viscoelastic region (\( \gamma_0 \approx 0.01-0.05\% \)). Arrows highlight the observed qualitative differences.

In the linear regime, elastic and viscous Lissajous curves display an ellipsoidal shape (Refer to Fig. 8.2 insets); however as the response becomes increasingly nonlinear, the curves distort. Lissajous curves show similar qualitative features; however, it appears that roll-in shortenings
experience less local strain stiffening, i.e. milder stress upturn, and less shear-thinning, i.e. higher viscosity as seen by larger area enclosed by the elastic Lissajous figures and weaker stress bending. To quantify this behavior, elastic and viscous nonlinear rheological measures are also presented in Fig. 8.3.

![Graphs showing elastic and viscous measures](image)

**Figure 8.3** (a) Definition of measures for reporting viscoelastic moduli for a model nonlinear viscoelastic response in the LAOS regime at $\omega = 3.6 \text{ rads-1}$ and $\gamma_0 = 1.4\%$. (b) Nonlinear elastic and viscous measures at $\omega = 3.6 \text{ rads-1}$ and $\gamma_0 = 0.01\text{-}10 \%$ for laminating and all-purpose shortenings. Viscous measures are parametrized by the linear dynamic viscosity $\eta_{\text{LVE}}$ at $\gamma_0 = 0.01\%$. Inset shows absolute values of dynamic viscosities.

Elastic measures show minor differences in strain-stiffening $(G'_L - G'_M)/G'_L$, whereas viscosities at minimum- $\eta_M'$ and maximum- $\eta_L'$ shear rates differed substantially, i.e. laminating shortening showed over two times higher viscosities than all-purpose shortening. Increased viscosities mean
that a laminating shortening dissipates energy more effectively during deformation. We believe this plays a pivotal role on laminating functionality, i.e. a laminating shortening’s ability to withstand high stresses imposed by large nonlinear deformations without rupturing during pastry manufacture. Since, we observed that multiple formulations (e.g. palm-oil based, soybean-oil based, trans-containing, trans-free) achieved the same rheological criteria, the structure-function framework seemed to dictate the unique laminating performance (Macias-Rodriguez et al., 2017; B. Macias-Rodriguez and Marangoni, 2016a).

Finally, for edible fats structured with high solid fat content, it makes the most sense that viscous contributions (which accounts for the plasticity of the crystal network in addition to the viscosity of the liquid-oil) have the largest impact in functionality. For instance, when spreading different commercial butters at refrigeration temperatures, one may not notice big differences in their elasticity (related to “firmness”) but rather in their viscosity (related to “spreadibility”). Indeed, inadequate viscosity or flow properties will give butter a “dead” or brittle consistency!

8.6 Conclusions

In the design of structured lipid-materials, rheology and functionality are intimately related. To assure that a fat meets its desired functionality, one must analyze the full linear and nonlinear rheological response. Particular emphasis must be placed on the nonlinear response as all processing and product uses involve large deformations. In this regard, LAOS tests offer useful insights into the performance of fats as illustrated in this review. The use of this approach is highly advantageous for designing bakery fats, as it will potentially reveal a variety of compositions and alternative lipid-structuring systems (i.e. organogels) that meet the “low trans, low saturates” desirable criteria without sacrificing functionality.

8.7 Acknowledgements

The authors would like to thank Dr. Randy H. Ewoldt (Department of Mechanical Science and Engineering, The University of Illinois at Urbana-Champaign), for his guidance and input on the use of the LAOS protocol.

8.8 References


CHAPTER 9: CONCLUSIONS AND FUTURE WORK

Laminating or roll-in fats are specialty products used in the manufactures of croissant, Danish pastry and other such pastries. Much research efforts have been devoted to develop healthier roll-in fats, lower in \textit{trans} and saturates due to their implications on cardiovascular health. The main role of roll-in fats in laminated doughs is to create uniform and thin layers or barriers to prevent fusion of sheets of dough. Interaction of adjacent dough layers causes increase of strength and decrease of water vapor retention during baking. This results in a “dense” pastry with low tenderness, flakiness and lift. Like any fat, the functionality of roll-in shortenings results from a good compromise of formulation and crystallization conditions during processing. Their formulation typically requires high amounts of “hard” stock fats (\textit{trans} and saturated fatty acids). Their crystallization involves high degrees of supersaturation attained through low-temperature high-shear multi-step processes, which combine scraped-surface heat exchangers, working units, and extrusions valves. These steps maximize in-line crystallization and promote breakage of crystal aggregates and a more homogeneous network. As a result, a set of “ideal” physical properties and consistency are achieved. According to the literature, there are several physical specifications that a fat must meet to achieve the roll-in or laminating functionality. These include adequate melting range, solid fat content, polymorphic, viscoelastic textural attributes. Roll-in fats should have wide- and larger- melting ranges and crystalline solids (SFC) than that of any other bakery fat. Likewise, they should contain preferably “smaller” $\beta'$ polymorphic crystal aggregates associated with plastic and spreadable shortenings. Finally, roll-in should be firm and spreadable (or “plastic”), and match the rheology of the dough, i.e. if a roll-in fat is too soft, it does not bear mechanical stresses and it is absorbed into the dough, whereas if it is too firm, it ruptures the dough during machining. In this thesis, we show that overall of content of “hard” fatty acids (\textit{trans} and saturated fatty acids) between roll-in and other types of shortenings remained comparable (41-52%). Nevertheless, roll-in fats had contents of trisaturated and unsaturated TAGs (12-27 \%; 47-62\%) higher than other shortenings (9-11\%; 6-44 \%). In contrast to the literature, we found that their physical properties including melting profile, SFC, polymorphism and large deformation rheology (penetration and compression), compare to those of any other bakery shortening. Melting peaks fell in the range (42-62 °C) recommended for laminating functionality irrespective of shortening type. Polymorphism comprised metastable, stable or mixed crystal forms ($\beta'$, $\beta$, $\beta'+\beta$) for all samples. SFC profiles of roll-in shortenings
were akin to interesterified all-purpose and interesterified cake shortenings, particularly at 16 °C (relevant of the lamination process), where all mechanical testing was conducted. Differences in yield value $C$, compressive yield stress $\sigma^*$ and apparent Young’s modulus $E_{app}$ were marginal among samples. SAOS showed that all shortenings displayed low-frequency dependence, a behavior reminiscent of viscoelastic solids where the storage elastic modulus $G'$ is higher than the loss viscous modulus $G''$. Linear elastic moduli, critical strains and critical stresses were on the order of $0.6-3.8 \times 10^6$ Pa, $0.01-0.03\%$ and $50-600$ Pa respectively and were unremarkable. Although these material rheological functions are believed to designate fat functionality alone, we observed that it is not case. In contrast, shear creep tests, which probe relaxation phenomena at longer time scales, showed that roll-in shortenings had higher viscosities “at rest” ($4.9 \times 10^8$-$1.1 \times 10^9$ Pa.s) than other type of shortening ($6.4 \times 10^7$-$2.6 \times 10^8$ Pa.s).

Sheeting and folding of the multiple fat-dough layers subject roll-in shortenings to large deformations that exceed critical strains and trigger viscoelastic responses, which may be relevant for laminating functionality. Initial experiments on LAOS rheology revealed strikingly different nonlinear viscoelastic behavior, e.g. raw data in the form of Lissajous-Bowditch curves qualitatively suggested less intracycle strain stiffening (stress “upturns”) and less average intercycle strain softening (“tilting” towards the strain axis). The third-harmonic $I_3/I_1$ of the FT spectra indicated a more gradual transition into the nonlinear regime for roll-in shortenings. Oscillatory thixotropic tests indicated less shear-sensitivity that leads to less network “breakup” and prompt structural recovery ($G'/G'0=0.56-0.71$) for roll-in shortenings. Further experiments on LAOS revealed that the nonlinear rheology of roll-in shortenings stand apart from any other type of bakery fat. Elastic and viscous Lissajous-Bowditch curves showed that roll-in shortenings presented less dramatic yielding with larger viscous dissipation (i.e. higher local viscosities). The LAOS Chebyshev stress decomposition method decoupled energy storage and loss mechanisms in the nonlinear response. Notably, there were not important differences among the moduli of elasticity of bakery shortenings. Instead, the primary difference was the moduli of viscous dissipation; roll-in shortenings were substantially more dissipative than all-purpose and cake shortening, in accordance with higher viscous dissipation and plastic deformation for ductile solids. This behavior was also reflected in lower nonlinear fractional recovery for roll-in shortenings ($\gamma_R/\gamma_C \approx 10-40\%$). Capillary rheology showed that roll-in
shortenings were shaped into continuous fine extrudates with apparent shear viscosities in the order of $\eta=400$-40 Pa s at relevant apparent shear rates $\dot{\gamma}=10$-1000 s$^{-1}$.

Structural investigations by USAXS and SEM revealed that roll-in shortenings featured smooth and smaller CNPs, an additional hierarchy level, and crystal aggregates ordered in elongated crystal layers unlike all-purpose fats that showcased rough larger CNPs, only two hierarchy structures and a more random crystal network. These structures are consistent with the formulation and processing of shortenings. High fractions of trisaturates and high shear conditions maximize degree of supersaturation (and thus crystal nucleation), removal of the heat of crystallization that lead to smooth and smaller CNPs, and more uniform crystal aggregates in roll-in shortenings. It is plausible that the use of extrusion steps (passage through a slot or other form of constriction) prior to filling induce microstructural orientation as demonstrated by layered-like crystal aggregates. On the other hand, lower trisaturates and static crystallization decreases supersaturation, and thus promote rough CNPS, growth of large crystal aggregates and random microstructures in all-purpose and cake shortenings.

We suggest that the additional hierarchy level and spatial distribution of the microstructure play a pivotal role on energy dissipation (rather than on energy storage) of roll-in shortenings during mechanically demanding processes such as layering, sheeting and folding in the production of laminated doughs.

To sum up, physical properties including melting, SFC, polymorphic behavior and large-deformation mechanical properties from penetration and compression tests were similar among shortenings independent of baking application. Despite important, lipid composition (TAGs) which was different for roll-in shortenings cannot be used to understand laminating performance of fats. This motivated the use of other physical indicators of functionality concerned with the nonlinear rheological behavior of shortenings (the hypothesis of this dissertation). Rheological material functions obtained from LAOS, which was introduced for the first time in fat rheology, provided insights into laminating performance of fats. Elastic properties of roll-in shortenings were similar to those of other types of shortening, considering that fats in general do not show marked elasticity. In contrast, viscous properties of roll-in shortenings were substantially higher. The observed rheology correlated with additional microstructural hierarchies and layer-like crystal aggregates. We postulate that these structural features contribute to higher viscous dissipation during lamination of layered doughs to achieve the desired roll-in performance. We
argue that healthier (no \textit{trans} and lower saturates) and functional roll-in shortenings can be obtained as long as alternative formulations or lipid-structuring systems (i.e. organogels) match the unique rheological “fingerprint”. This formulation/design route is commonly applied to materials with complex microstructures such as ice cream, chewing/bubble gums where the desired macroscopic behavior is defined by the structure-function framework, rather than by specific bulk composition (Martinetti et al. 2014). Finally, we demonstrate that LAOS rheology is a powerful tool to understand the physics of the nonlinear viscoelasticity of roll-in fats and has the potential to provide similar insights on other lipid-based materials.

Suggested future work

Throughout this thesis, the physico-chemical properties of roll-in shortenings have been investigated. Emphasis has been placed on rheological properties given their major role on roll-in functionality. Nonlinear viscoelasticity has been studied in detail using LAOS to simulate large deformations encountered during processing and application uses of fats. Despite the findings previously described, there remains much work to be done on the reformulation of roll-in shortenings and more generally in the rheology of fats. The first step is to construct a constitutive model that describes quantitatively the range of nonlinear rheological phenomena observed in laminating shortenings. The next obvious step is to survey composition-processing space or alternative lipid-structuring materials (i.e. organogels) that meet rheological material functions (i.e. high viscous dissipation) associated with the desired roll-in performance. In the field of LAOS rheology, there are broader and more exciting opportunities to study fundamental aspects of the structure-rheology relationships of sheared crystal networks. To my opinion, the most promising areas for future research include the use of oscillatory rheological measurements complemented with time- and space- resolved scattering techniques (i.e. rheo-USAXS) and computer simulations. The combination of these techniques will provide a more detailed structural picture of the physical nonlinearities (stress localization, viscous dissipation) leading to yielding as observed in the LAOS response.
APPENDIX 1: SUPPLEMENTARY MATERIAL (CHAPTER 5)

Figure A.1 Modified parallel plate geometries used for oscillatory shear experiments. Filter paper (Whatman grade 5) was glued to the upper and lower plates.

Figure A.2 Filter performance for \( \gamma_0 = 6\% \) at \( \omega = 5.9 \) rads\(^{-1} \) for a) ductile (D1) and brittle fat (B1). The nonlinearities are described by harmonic contributions lower than \( n=7 \) (\( e_9/e_1, \nu_9/\nu_1 < 0.05 \)). Secondary local minimums at high strains in the stress response are a consequence of data processing.
Figure A.3 Side view for ductile (D2) and brittle (B2) with \( h_0 = 10 \text{ mm} \) under compression. A ductile fat plastically deforms, whereas a brittle fat breaks or "crumbles" at \( \Delta h/h_0 = -0.10 \).

Figure A.4 First-harmonic moduli as a function of apparent strain amplitude \( \gamma_0 \) at \( \omega = 3.6 \text{ rads}^1 \) for ductile (D1) and brittle fats (B1).
Figure A.5 First harmonic stress amplitude $\tau_1$ as a function of apparent strain amplitude $\gamma_0$ at $\omega=3.6 \text{ rads}^{-1}$ and sample thickness $\text{Th}=1.3\text{mm}$, for ductile D2 and brittle B2 fats.

Figure A.6 Un-normalized steady state Lissajous-Bowditch curves for a ductile (D1) fat at $\omega=3.6 \text{ rads}^{-1}$. (a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\dot{\gamma}$ (viscous perspective).
**Figure A.7** Un-normalized steady state Lissajous-Bowditch curves for a ductile (D2) fat at $\omega = 3.6 \text{ rads}^{-1}$. (a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\dot{\gamma}$ (viscous perspective).

**Figure A.8** Un-normalized steady state Lissajous-Bowditch curves for a brittle (B1) fat at $\omega = 3.6 \text{ rads}^{-1}$. (a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\dot{\gamma}$ (viscous perspective).
Un-normalized steady state Lissajous-Bowditch curves for a brittle (B2) fat at $\omega = 3.6 \text{ rads}^{-1}$. (a) Individual plots of absolute stress $\tau$ vs. strain $\gamma$ (elastic perspective). (b) Individual plots of absolute stress $\tau$ vs. strain rate $\dot{\gamma}$ (viscous perspective).

Un-normalized 3D Lissajous-Bowditch curves obtained at $\gamma=2.34\%$ and $\omega=3.6 \text{ rads}^{-1}$ for (a) ductile (D1) and (b) brittle (B1) fats.

Figure A.9
Figure A.10
Figure A.11 Normalized difference between local elastic measures: minimum strain ($G_M'$) and large strain modulus ($G_L'$) as a function of strain input $\gamma_0$ at $\omega=3.6$ rads$^{-1}$ for ductile (D1, D2) and brittle fats (B1, B2). (b) Lissajous-Bowditch curve (elastic perspective) showing strain $\gamma_0$ versus stress $\tau$ for a selected data point $\gamma_0 = 1.47\%$, displaying graphical representation of local (instantaneous) and global (average) LAOS elastic measures.
Figure A.12 Cryo-scanning electron images of ductile (D1, D2) and brittle (B1, B2) fats: a) D1, b) D2, c) B1, d) B2. All images share the same magnification bar= 60μm.