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The role of nonlinear viscoelasticity on the functionality of laminating shortenings

Braulio A. Macias-Rodriguez, Fernanda Peyronel, Alejandro G. Marangoni*

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

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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 exhibited solid-like viscoelastic and viscoelastoplastic behaviors in the linear and nonlinear regimes respectively. In the nonlinear region, 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.

1. 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 a specialty fat, high in *trans* and saturates (as high as 54% altogether) are laminating shortenings (NYC Health 2012). Laminating shortenings (or margarines as commonly utilized in Europe) 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., 2016). 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, 1999; van den Tempel, 1961). Their linear viscoelastic properties can be generally described as similar as those of flocculated fractal colloidal gels (Narine and Marangoni, 1999). Fats have a hierarchical structure, encompassing nanoscale- and mesoscale-structures. At the molecular level, triacylgycerols (TAGs) stack longitudinally and side-by-side, adopting a specific polymorphic state (α, β', β) 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., 2014a, 2013). It has been shown using computer simulations (Pink et al., 2013; Quinn et al.,

* Corresponding author.
E-mail address: amarango@uoguelph.ca (A.G. Marangoni).

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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 to make up the microscale crystal network (up to 6 μm) (Peyronel et al., 2014a).

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 (Macias-Rodriguez and Marangoni, 2016a). Therefore, investigating nonlinear viscoelastic properties under large deformations, 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 distinguishing nonlinear viscoelastic properties of materials. In addition, we investigated material structure using Ultra Small Angle X-ray Scattering (USAXS) and Scanning Electron Microscopy (SEM).

2. Experimental

2.1. Materials

We investigated four commercial shortenings, the trade names and compositions of which are summarized in Table 1. Exact formulations and manufacturing conditions of these shortenings are unknown. However, we found in a previous study that these laminating shortenings had higher content of trisaturated (13–16%) and unsaturated (43–46%) TAGs, than a cake shortening (10% trisaturated TAGs, 21% unsaturated TAGs) (Macias-Rodriguez and Marangoni, 2016b). In addition, it is well known that the crystallization of laminating shortenings involves high degrees of supersaturation attained through low-temperature high-shear multistep processes, which combine scraped-surface heat exchangers, working units, and extrusions valves. Such formulation and processing steps maximize crystal nucleation, breakage of large crystal aggregates, homogeneous crystal network and removal of the heat of crystallization (Acevedo and Marangoni, 2013).

2.2. Sample preparation

2.2.1. 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 30 mm × 1.3 mm (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.

Table 1
Functionality and bulk composition for each material class.

Sample	Trade name/composition
R1	Puff pastry hydrogenated soybean oil and cottonseed oil
R2	Roll-in hydrogenated vegetable oil and modified palm oil
R3	Puff pastry palm oil, modified palm oil and soybean oil
S1	Cake soybean oil interesterified

2.2.2. 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 20 mm × 1 mm (diameter × thickness). A microscope cover was attached to each side of the isolator to contain the sample.

2.2.3. 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.

2.3. Measurements and analysis

2.3.1. 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 (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, while being re-equilibrated at 16 °C (the only exception was R3 that was conditioned at 18 °C based on manufacturer's recommendations). This temperature was chosen to resemble thermal conditioning during rolling and layering of fats (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 ($\gamma_0 = 0.01$–100%) at a fixed frequency $\omega = 3.6$ rad s^{-1} representative of the rolling process (Chakrabarti-Bell et al., 2010). Strain amplitude γ_0 represents apparent strain (e.g. deviates from true strain when there is shear-banding or slip at γ_0~10% and beyond).

The average viscoelastic moduli G', 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.

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