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Ultrasonic-Standing-Wave-Crystallized Oleogels Characterized via Oscillatory Rheology

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***Abstract*—Ultrasonic standing waves, have been shown by our research group, to change the mechanical properties of crystallizing monoglyceride oleogels, which are viscoelastic lipid-based materials featuring a 3D network of structuring molecules. Oleogels are a potentially healthier alternative to traditional fats, such as butter, margarine, and shortenings. Here, we continue our research on ultrasonic-standing-wave-treated oleogels by investigating their mechanical properties through linear and non-linear oscillatory shear rheology. We found that the mechanical response of the treated oleogels is more elastic at lower strains and more viscous at higher strains when compared to reference samples, while the overall shape of the response curves remains similar. Through characterization of ultrasound-standing-wave-treated oleogels, we expand the previous knowledge of the state-of-the-art lipid-based materials.**

***Index Terms*—Ultrasonic Standing Waves, Oleogels, Rheology**

I. Introduction

Traditional fat products such as butter, margarine, and other animal fats often contain considerable amounts of saturated fatty acids, which provide the necessary structural integrity required from solid fats. Much research has been done to understand the health effects of saturated fats, leading to a consensus that saturated fatty acids are a factor in the modern rise of obesity and consequently diabetes, as well as cardiovascular diseases [1], [2]. As such, solid fat alternatives which contain more of the healthier unsaturated fatty acids are of great interest [3]–[5]. Oleogels are structured lipids with high concentrations of unsaturated fatty acids. The structuring network of oleogels consists of an interlinked network of gelling molecules such as polysaccharides and proteins. Or of self-assembled small molecules (monoglycerides, fatty alcohols, fatty acids, waxes, or phytosterols and their esters) [3], [5]. The structural properties of oleogels and traditional solid fats affect their end use as e.g., spreads, shortenings, or creams. For oleogels, the mechanical properties arise from the network of gelling molecules, and the surrounding lipid-media. Their properties can be tailored by modifying the concentration of the gelling molecules or the solvent (oil), as well as the production process parameters such as cooling rate, mechanical mixing during oleogel formation or the application of ultrasound. High-intensity ultrasound (HIU)-induced cavitation has been shown to influence oleogel microstructure and fat-crystal formation, and consequently their mechanical properties [6]–[8]. However, concerns over the negative effects of HIU such as the generation of free radicals which initiate oxidation in oils, have been raised [9]. Ingestion of oxidized oils can increase levels of oxidative stress in the human body, which can lead to pathologies, such as cancer, cardiovascular-, and inflammatory diseases [10]. The negative health effects caused by structural modification through cavitation can be avoided by using low-intensity ultrasound, such as in the case of low-intensity ultrasonic standing waves (USW). Our research group was the first to apply low-intensity USW to control the structure formation of crystallizing oleogels, and to show that application of USW affects the mechanical properties of oleogels [9], [11], [12].

Many foodstuffs (including fats) are commonly characterized using oscillatory rheology to study their viscoelastic material properties. However, food rheology is often limited to small deformations within the linear viscoelastic region (LVR), which does not effectively represent the end use. The end uses often involve the application of large shear stresses (e.g. spreading) which produces a non-linear mechanical response to the applied shear. This response cannot be sufficiently understood by measurements performed in the LVR, and thus need to be studied in the non-linear viscoelastic region. Understanding the mechanical behavior of structured lipids in the non-linear region is crucial for improving the functionality of the ingredients in food products manufacturing. In this work we expand upon our previous research by studying the effect of USW on the rheological properties of 10 wt% monoglyceride (MG) oleogels using linear and non-linear oscillatory shear rheology.

II. Methods

The objective of the study was to investigate the effect of USW on 10 wt% MG oleogels, through large and small amplitude oscillatory shear (LAOS and SAOS, respectively) measurements. Reference and treated samples were produced in a previously developed experimental chamber [12]. To prepare the samples, rapeseed oil (purchased from the local grocery store) and 10 wt% monoglycerides (Myverol™ saturated monoglyceride (fatty acid composition 1.4% C14:0,

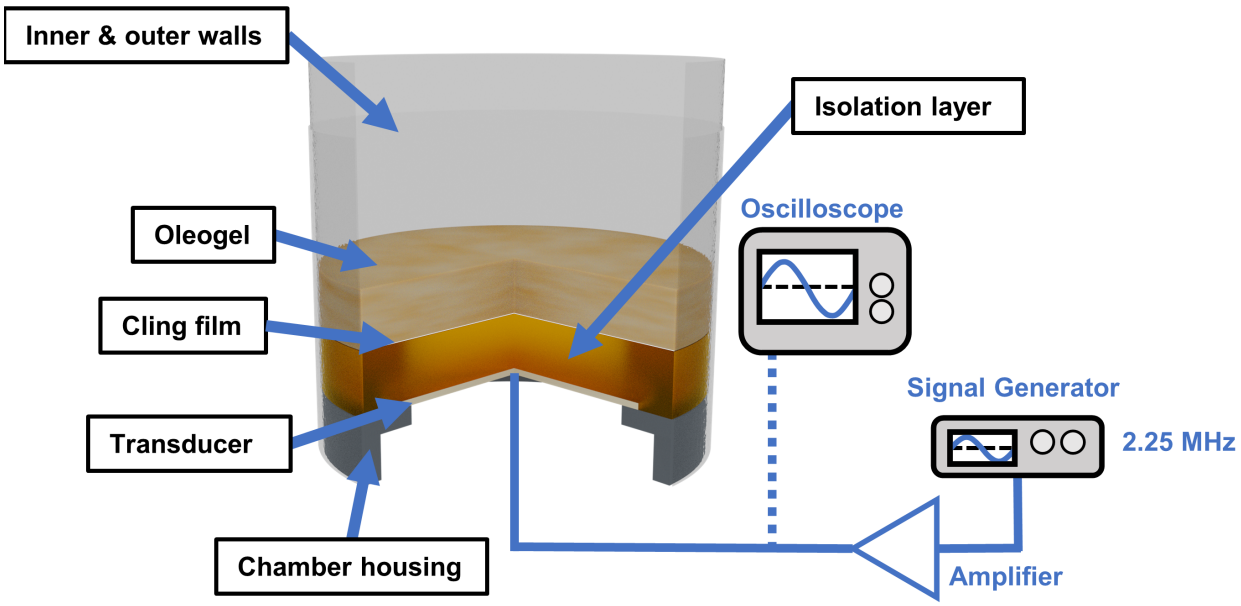

Figure 1. Schematic of the experimental setup.

59.8% C16:0, 38.8% C18:0; melting point 68.0 ± 0.5 °C), donated by Kerry Ingredients and Flavour, Bristol, United Kingdom) were mixed using a magnetic stirrer, and heated to 80 °C. Samples were mixed for at least 15 minutes after crystalline material had dissolved. Following, 30 mL of sample was transfer to the experimental chamber (Fig. 1). Reference oleogels were allowed to cool to room temperature and crystallize, while treated oleogels were sonicated at 2.25 MHz until sample was crystallized i.e. after the oleogel had turned opaque. The sonication chamber chamber was designed the open-source 3D computer graphics software Blender (Blender foundation) and printed using the 3D printer Ultimaker 3 (Ultimaker B.v., Utrecht, The Netherlands). A isolation layer of rapeseed oil was added between the transducer and oleogel to avoid complications relating to ultrasonic near-field effects. The sonication chamber was mounted on a tilt-stage (KM200B/M, Thorlabs, Newton, NJ, USA) with which the oleogel-air interface was aligned to be parallel with the piezoelectric transducer, wherein the transducer was actuated using a HV pulser/receiver (Olympus Corporation, Shinjuku, Tokyo, Japan). For the sonication treatment, the transducer was driven using an arbitary waveform generator (Hewlett Packard, Palo Alto, California, USA) and RF power amplifier (Tomco Technologies, Stepney SA, Australia). Samples were left to crystallize in the chamber overnight before extraction.

Four duplicates of reference and sonicated samples were produced and measured. Samples were extracted from the experimental chamber and cut into 20 mm diameter cylinders, using thin copper pipe of the same diameter. Cut samples were transferred to a Discovery Hybrid Rheometer 2 (TA-instruments, New Caste, DE, USA). A 20 mm parallel plate geometry on top of a Peltier heated plate was used. On both plates, a piece of sandpaper with an average grit of 600 was glued to reduce the slipping of the sample. To further ensure no-slip conditions the plate was set to exert a force of 1 N on the oleogel. Oscillatory rheology was performed on the samples at 22 °C in the SAOS and LAOS regime (0.001%-1000% strain), at an angular frequency of 2 rad/s. Data was collected with Trios software version 4.1 (TA instruments) and exported as text files for further analysis in MATLAB R2020 (MathWorks, Natick, MA, United States). From the stress-strain response data, storage (G'), and loss (G'') moduli were determined. The moduli measure the amount of energy stored, and lost as heat, in the material. The end of the LVR of the samples was determined as the 5% drop-off point from the plateau stress. The crossover point was determined as the intersection point of the storage and loss moduli. Lissajous-Bowditch curves were acquired through recording the transient stress-strain signal and plotting it in the Pipkin diagram [13]. The microstructure of the samples was imaged using a digital microscope (Q-scope model QS.80200-P, Euromex Microscopen BV, Amsterdam, The Netherlands).

III. Results and Discussion

Fig. 2A shows the cross-sectional micrographs of reference (Fig. 2A1) and treated (Fig. 2A2) oleogels. Treated oleogels were visibly altered and showed a band-like structure, while reference samples exhibited a homogeneous structure. This was also observed previously [12]. The band structure indicates a denser region of the crystalline material (darker horizontal bands), due to the application of the USW which generates a force acting on the forming crystals directed towards the standing wave nodes [9], [12]. The height of the samples was 3260 ± 90 µm for the reference, and 2610 ± 80 µm for the sonicated sample. The dense bands of the treated

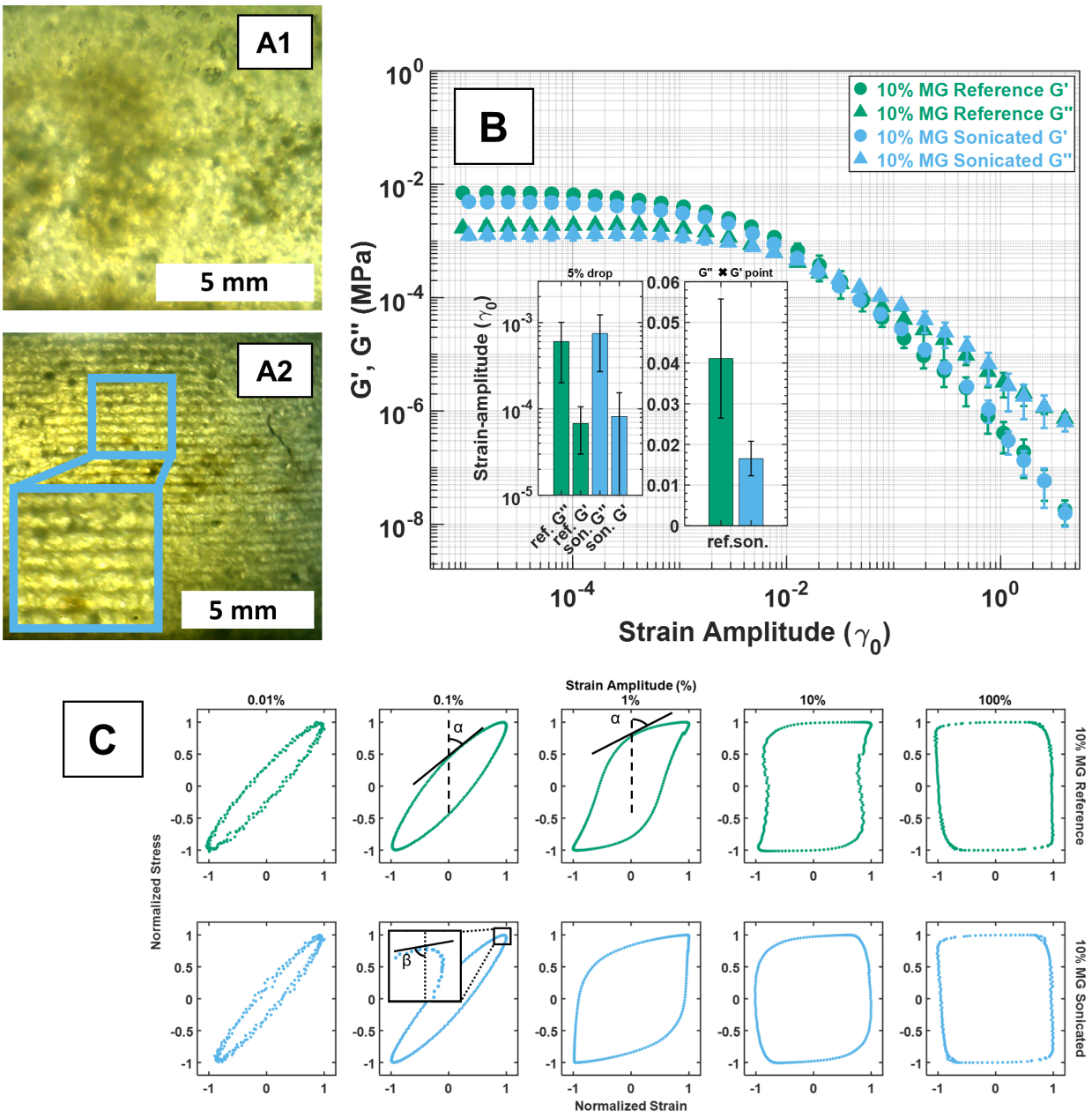

Figure 2. Micrographs of oleogel cross-sections for (A1) reference and (A2) sonicated samples. (B) Oscillatory shear reference and USW treated storage (G') and loss (G'') moduli for 10 wt% MG samples. Insets show the 5% drop from maxima for the reference- and sonicated oleogel G'' and G', and the G' and G'' crossover point for 10 wt% MG reference- and sonicated oleogels. (C) Normalized Lissajous-Bowditch plots for reference and treated 10 wt% MG oleogels, showing stress-strain response. Error bars indicate the 95% confidence interval.

samples cause the contraction as the crystalline structure of treated samples are more densely packed.

The mechanical properties of oleogels were studied under oscillatory shear in the linear and non-linear regimes. Fig. 2B shows the oscillatory stress-strain curves for both reference and treated 10 wt% MG oleogels. The stress-strain sweep curve for the reference oleogel starts with a LVR (up to $5{\cdot}10^{-4}$ strain-amplitude), followed by a transition-zone indicating the transition from a solid-like to a more liquid-like material behavior, and ending in the non-linear region where the sample experiences structural breakdown due to the applied stress. The oscillatory stress-strain response for the treated sample follows a similar behavior and does not significantly differ in the shape of the curve, which follows a similar trend seen in previous research [12]. Comparing the calculated end points of the LVR, one can observe that the application of USW during oleogel formation does not alter the LVR significantly (Fig. 2B, cf. 5% drop points for reference- and sonicated oleogels respectively). However, it can be observed from Fig. 2B that for treated samples, breakdown of the overall gel structure

occurs at a lower strain (Fig. 2B, cf. G' and G'' crossing points for reference- and sonicated oleogels respectively). This is due to the increased concentration of the gelator and crystalline mass at the dense bands (Fig. 2A2), which leaves less material for the sparser bands. The sparser bands are therefore weaker (due to the lower concentration of structuring molecules) than the homogeneous structure of the reference gels, and thus rupture at lower stresses. That is, at lower stresses the denser crystalline bands withstand the stresses and translate them to the sparser bands which are weaker compared to the reference gel structure, and as such the stress-strain response of the treated samples is dominated by sparser bands at lower stresses.

Lissajous-Bowditch curves provide a qualitative method of observing and interpreting nonlinearities in rheological measurements. The curves in Fig. 2C show plots of normalized strain vs. normalized stress captured during a single oscillatory sweep. Observing the change in curve shape as the strain amplitude is increased provides information about the elasticity and rupturing of the structure of materials. Fig. 2C shows elastic softening in both reference and treated cases, indicated by the clockwise rotation in the slope α of the curve at zero cycle strain with increasing strain. Close to cycle strain maxima, area indicated by the inset in 10 wt% MG sonicated 0.1% strain, both samples show no upturn in stress as slope β only increases near strain maxima. This indicates that the plastic deformation of the samples remains uniform and no local stiffening occurs. The shape of the Lissajous-Bowditch curve at the strain maxima is dominated by the material at the vicinity of the oscillating plate geometry. As such, the structural properties of the monoglyceride crystals (elastic properties, crystal size and shape) have a larger effect on what is observed than the amorphous reference material. That being the case, the comparable behavior at the strain maxima between the samples suggest that USW treatment does not affect the crystal structure at the micrometer-scale. The Lissajous-Bowditch curves show that treated samples are more elastic than reference samples at strains of 0.001% and 0.1% (indicated by the tighter oval shape of the curve), while at strains greater than 1%, treated samples show a more liquid like behavior compared to the reference samples as the curves appear more rectangular. This behavior at lower strains is due to the domination of the stress-strain response by the denser crystalline bands, which are more elastic than the amorphous reference material. As the sparser structures starts to rupture in the transition zone, the stress-strain response from the sparser structure becomes dominant, which can be observed as the treated sample appearing more viscous. This is because the bands of denser and sparser crystalline material are parallel to the oscillating plate, wherein the denser bands experience elastic deformation. Similar behavior at the strain maxima, and divergent behavior at lower strains indicate that USW treatment can be used to modify the material properties in the mesostructure without affecting the microstructural formation of monoglyceride crystals.

IV. Conclusions

In this paper, we investigated the oscillatory rheology of 10 wt% monoglyceride reference and sonicated oleogels. USW was found to alter the viscoelastic properties of MG oleogels. Sonicated oleogels showed similar behavior to reference oleogels, however, the crossover point between the storage and loss moduli of treated oleogels was higher. The mechanical behavior of treated oleogels was dominated by an elastic response at lower strains, and a viscous response at higher strains. The observed difference between the samples can be attributed to the microstructural changes caused by the application of USW. The presented work expands the understanding of USW effects on oleogels through a detailed characterization of the rheological response, taking a step towards applying USW treatment in food, pharmaceutical, and cosmetic industries.

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