Supplementary Information

Micromechanical finite element modeling of crystalline lipid-based materials: monoglyceride-based oleogels and their composites

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1 Polymorphic form of pure monoglyceride and powder-XRD verification

The thermal treatment protocol presented in Section 2.2.2 of the main article was selected to expedite the transition from the α/sub-α -polymorphic form to the desired β-polymorphic form of samples containing 100% MG. It was found to be important that the samples were allowed to rest at room temperature for overnight before starting the heat treatment, as preliminary powder-XRD measurements showed that starting the heat-treatment immediately after the sample had crystallized proved ineffective at expediting the transition. We suspect that there is a degree of seeding of the β-polymorphic form that occurs for some hours after the initial crystallization. Higher temperatures either stop or slow down this initial seeding. The long duration of heat-treatment (94 hours) was used to ensure that the sample had completely transitioned into the β-polymorphic form. After the heat-treatment, powder-XRD measurements were carried out for the treated samples, untreated samples and reference samples. We used as reference one-and-a-half-year-old 100% Myverol 18-04K samples, which were presumed to be in the β-polymorphic form.

The powder-XRD was carried out using the Malvern Panalytical (England, Malvern) Empyrean diffractometer with a 2θ range of 5–35 degrees and a step size of approximately 0.013° (2285 points). The device was operated in transmission mode using a copper generator, with K-Alpha1 wavelength of 1.5406 Å, K-Alpha2 wavelength of 1.54443 Å, generator voltage of 45 kV and operating current of 40 mA. The results from the powder-XRD shown in Fig. S1 reveal that the MG polymorphic form depends on the applied heat-treatment. A fresh MG

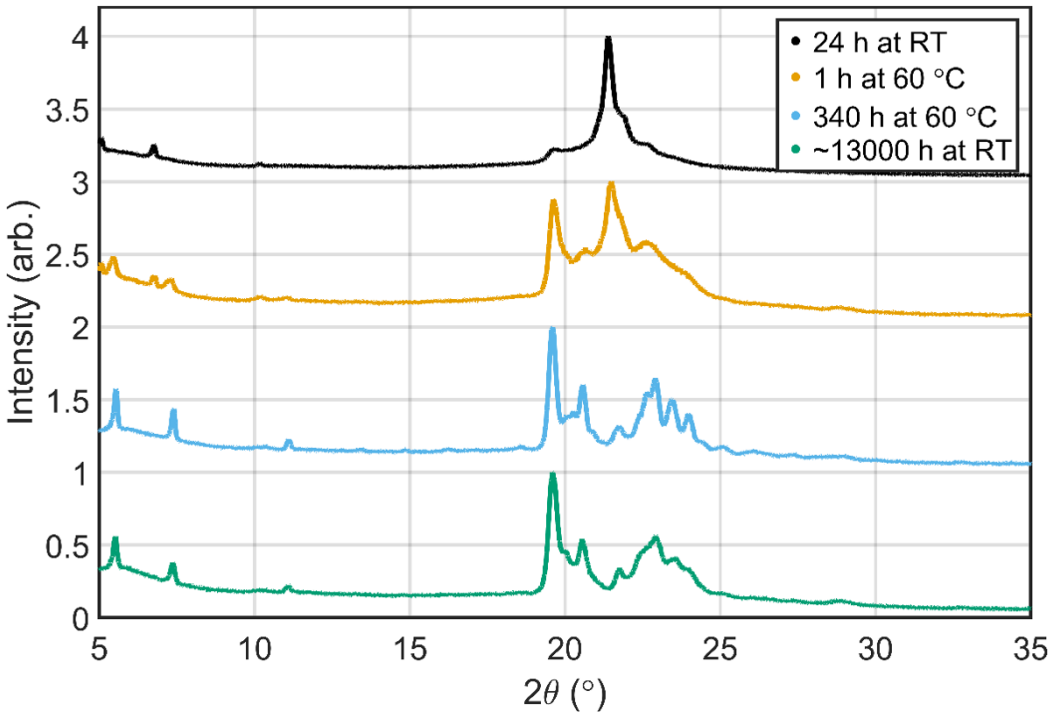

Fig. S1 Intensity as a function of diffraction angle obtained by powder-XRD of monoglyceride samples. 1) The black curve shows the intensity distribution for a fresh sample with no heat-treatment applied. 2) The orange curve is for a sample treated at 60 °C for 1 hour. 3) The cyan-blue curve is for a sample treated at 60 °C for 340 hours. 4) The lime-green curve is for a sample stored at room temperature (RT) for approximately 1.5 years. Constant offsets were added to the curves for improved readability.

sample (Fig. S1, black curve) shows an intense diffraction peak at 21.4°, with smaller peaks observable at 5° and 6.8°. In comparison, a reference MG sample (Fig. S1, lime-green curve) which was stored for approximately one-and-a-half years (13000 h) shows a region of low-intensity at around 21° with the small-angle peaks shifting to 5.5° and 7.4°, respectively. In addition, multiple diffraction peaks appear between 19–25°, with the most intense peak at 19.6°. As it is presumed that the 1.5-year-old sample is entirely in the desirable β-polymorphic form,[1] a successful heat treatment of fresh samples can be expected to result in a similar diffraction pattern. In Fig. S1, the orange curve shows the diffraction pattern for a sample that was heat treated at 60 °C for 1 hour, and the cyan-blue curve shows the pattern for a sample treated at 60 °C for 340 hours. The 1-hour treatment results in a polymorphic change to some extent, but parts of the sample clearly remain in the α/sub-α -polymorphic form. This is evident from the fact that the diffraction pattern has peaks at the locations matching both the fresh sample and the old reference sample. In comparison, the sample treated for 340 hours (cyan-blue curve) shows a diffraction pattern very similar to the old reference sample (lime-green curve). We conclude that a complete polymorphic transition can be achieved using heat treatment at 60 °C with a treatment time within the range between 1 and 340 hours.

2 Torsional measurement results for pure monoglyceride

The storage and loss moduli were measured for three samples of pure monoglyceride using small-amplitude-oscillatory-shear. The oscillation frequency was 1 Hz. The results shown in Fig. S2 show that the modulus is constant in the range between 0.001% and 0.01% strain. As the strain approaches 0.1%, the storage modulus decreases slightly. The small-amplitude storage moduli are approximately 610, 630 and 680 MPa in the linear region. The average value, 640 MPa is taken as a representative value for the modeling in the main article. Losses are not included in the models but are shown in Fig. S2 for sake of completeness. The small-amplitude loss moduli are approximately 16, 15 and 14 MPa for the three samples, respectively.

It should be emphasized that the high modulus of 640 MPa is only seen for pure monoglyceride that is completely in the β-polymorphic form. For comparison, we also measured the storage and loss moduli for three samples of pure monoglyceride that had only been heat-treated for 1 hour. As observed by the orange curve in Fig. S1, such a sample consists of domains in α and β-form. The measured moduli for these mixed-form samples are shown in Fig. S3. The small-amplitude storage moduli are approximately 100 MPa, 141 MPa, and 146 MPa. These are significantly lower values compared to the samples that are fully in β-form. Since monoglyceride-based oleogels crystallize in β-form, the values for mixed-form samples should not be used. We conclude that future research involving finite element modeling of lipid-based materials needs to ensure that material data is obtained from the correct polymorphic form.

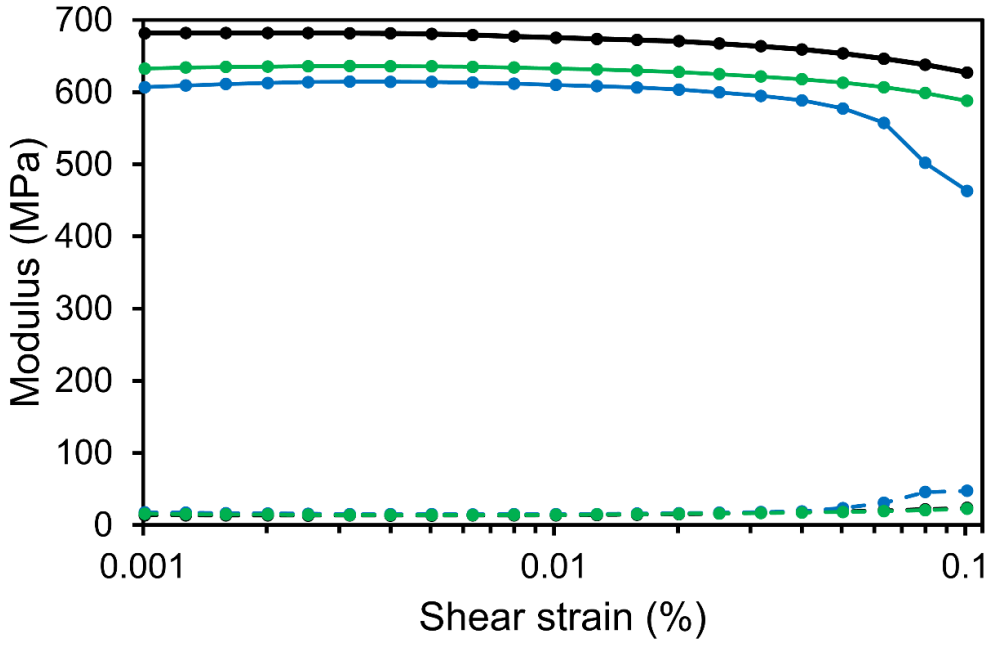

Fig. S2 Storage modulus (solid lines) and loss modulus (dashed lines) measured for 94-hour heat-treated Myverol 18-04K using small-amplitude-oscillatory-shear. The results for three samples are specified by blue, green, and black curves.

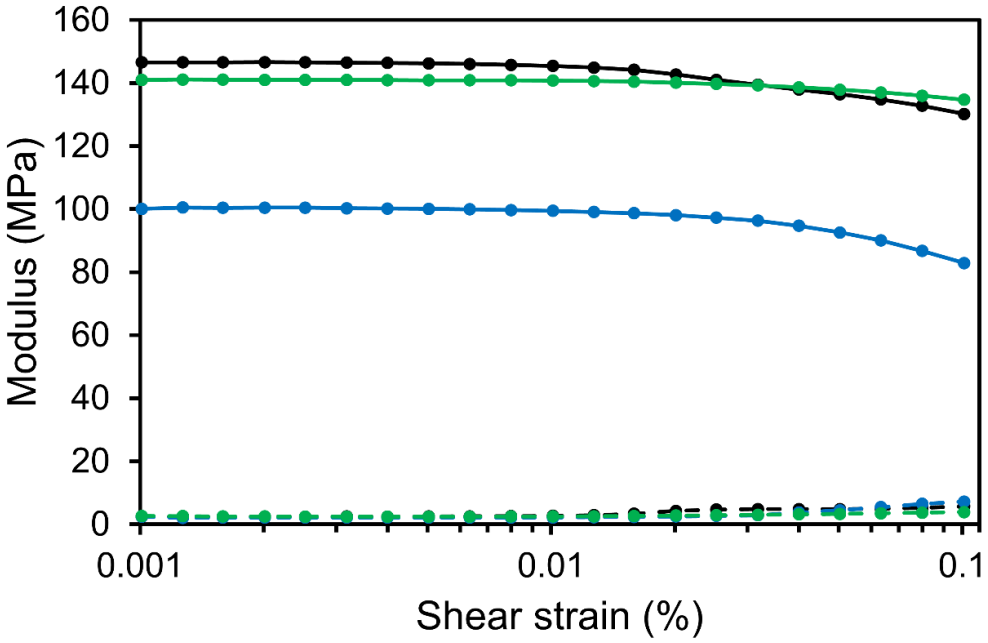

Fig. S3 Storage modulus (solid lines) and loss modulus (dashed lines) measured for 1-hour heat-treated Myverol 18-04K using small-amplitude-oscillatory-shear. The samples are in mixed-polymorphic form. The results for three samples are specified by blue, green, and black curves.

3 Box counting analysis of tomography data

The tomography data consists of 999 greyscale image files, each containing 998-by-998 pixels. As the data is limited to a cylindrical volume, each file contains empty regions outside the cylinder. Thus, as a first step, we import a subset of the image data consisting of the central 512-by-512 pixels for the central 512 image files into MATLAB. This gives us a matrix of size 512-by-512-by-512. The image data is binarized by selecting a threshold for the color. Many different values for threshold were tried and the results presented here are obtained using the same threshold value as was used to create the representative volume elements (RVEs) in the main article.

The binarized matrix was provided as argument for the MATLAB function 'boxcount'.[2] The function returns the number of boxes n needed to cover the image as a function of box size r. The local dimension s is evaluated by the equation $s = -d(\log(n))/d(\log(r))$. The local dimension as a function of box size is shown in Fig. S4. At small box sizes, the local dimension should demonstrate a plateau equal to the fractal dimension. The calculated local dimension fails to demonstrate any plateau, suggesting that the image data is not fractal. Fig. S4 shows the local dimension calculated both prior and posterior to applying the DeepReconPro algorithm. This algorithm was used to reduce noise and improve contrast, such that a 3D-mesh could be generated.[3] Neither the raw image data nor the algorithm-processed data reveal a fractal dimension with the box counting.

4 References

1 F. Valoppi, S. Calligaris, L. Barba, N. Šegatin, N. Poklar Ulrih and M. C. Nicoli, *European Journal of Lipid Science and Technology*, 2017, **119**, 1500549.

2 F. Moisy, Boxcount (version 1.0.0.0) https://www.mathworks.com/matlabcentral/fileexchange/13063-boxcount 2008.

3 Advanced reconstruction technologies for X-ray microscopy and microCT, https://www.zeiss.com/microscopy/en/products/software/advanced-reconstruction-toolbox.html, (accessed November 17, 2024).

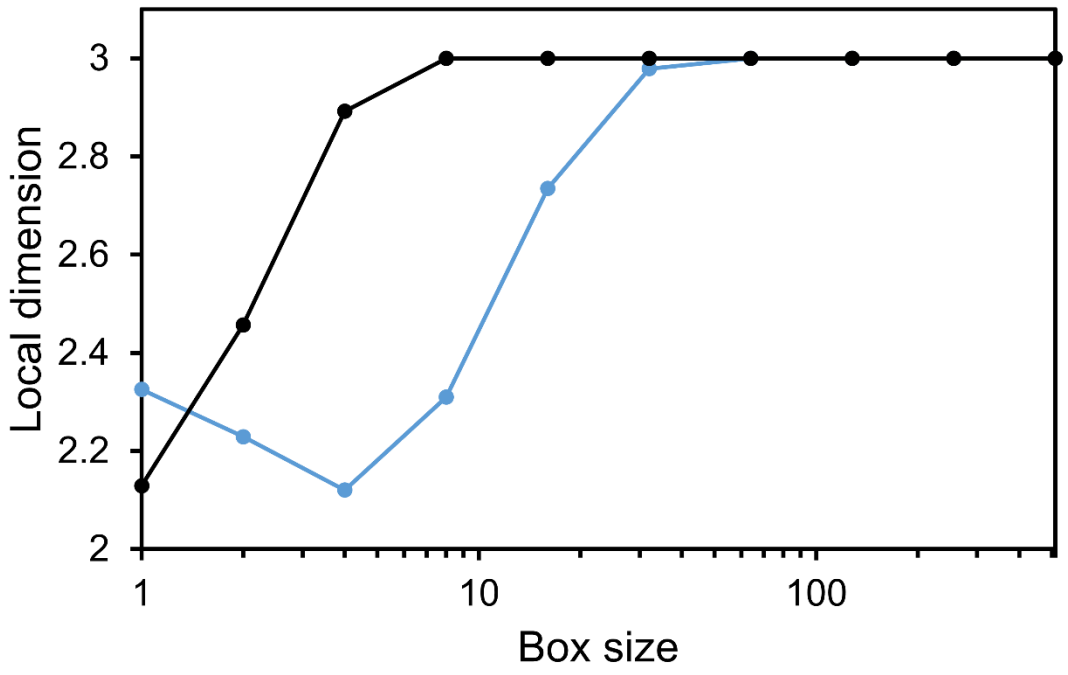

Fig. S4 Local dimension as a function of box size for 3D tomography data of a plain oleogel. The blue curve uses data that has been de-noised and improved by the DeepReconPro algorithm. The black curve uses raw data without having applied the algorithm.