

# Structure-property-processing relationships of soft viscoelastic materials

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To design the next generation of ‘smart’ soft materials, researchers must first understand how rapidly-changing flow conditions affect model materials. Soft viscoelastic materials, such as synthetic and biological polymers, tend to generate complex material responses. The link between macroscopic flow and molecular-level microstructural rearrangements has long been sought but has remained elusive. We show, by experimentally combining new rheological techniques with time-resolved rheo-small-angle neutron scattering (rheo-SANS), such links can now be made, forming nonlinear structure-property-processing relations, by considering the evolution of the recoverable component of the strain [1].

Oscillatory shearing has been widely used to study a wide array of soft materials. In particular, rapidly-changing flow conditions that are often encountered in processing and manufacturing soft materials can be accurately simulated by large amplitude oscillatory shear (LAOS) because of the independent control of length and time scales it affords. As such, LAOS has been commonly employed as a model transient flow protocol capable of eliciting nonlinear responses. In spite of the wide adoption of LAOS, the underlying physics and resulting structural rearrangements have remained difficult to interpret [2]. In a recent study, we show that the recoverable strain, a rheological metric first proposed by Weissenberg [3] and Reiner [4], is a key to understanding oscillatory shear rheology, in not only complex macroscopic responses such as shear and normal stresses, but also in how the microstructure reacts to dynamic flows.

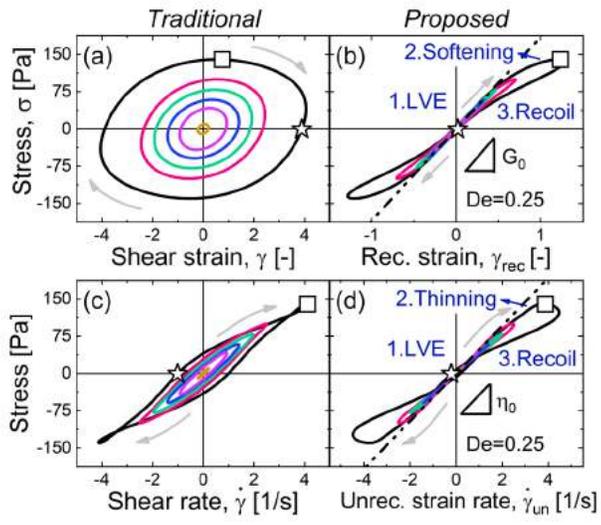
We investigate two distinct polymeric materials, including an industrial entangled worm-like micelle (WLM) solution and a fibrin network. The LAOS responses from WLMs across a wide range of amplitudes at a normalized frequency (Deborah number) of 0.25 are presented in Fig. 1. Traditionally, the stress response is plotted against the shear strain (Fig.1(a)) or shear rate (Fig.1(c)), forming the so-called elastic and viscous Lissajous curves. The distorted ellipses and the secondary loops are typical features of LAOS in these presentations. These presentations, however, view the responses from the perspective that the reference state remains fixed at zero strain, and ignores the fact that the reference state (or “ground state” originally referred by Weissenberg [3]) can be shifted by external flow conditions.

Strain can be experimentally decomposed into recoverable and unrecoverable components by unloading stresses. Recoverable strain is elastic, while viscous properties are dictated by the rate at which strain is acquired unrecoverably. The natural presentation to display elastic and viscous responses is therefore stress versus recoverable strain (Fig.1(b)) and stress versus unrecoverable strain rate (Fig.1(d)). Significant differences are observed from the traditional Lissajous curves. The curves collapse into a straight line at small strains and rates, where the slopes naturally correspond to the plateau modulus (Fig.1(b)) and zero-shear viscosity (Fig.1(d)) of the WLMs, which are traditionally thought not determinable from a single LAOS test. Further, the instant when the total strain is maximal (star in Fig.1(a)), which is traditionally considered to be the most-strained state, actually corresponds to the point of zero recoverable strain, indicating there is little-to-no deformation from a microscopic perspective. This finding explains the origin of observations made in numerous studies of colloidal and polymeric materials, where researchers have noted the existence of linear elasticity close to total strain extrema (See [1] for references). In short, in these new experiments and their associated proposed presentations, LAOS naturally presents a sequence of physical processes: linear viscoelasticity (LVE) is observed when the recoverable strain is small, softening and thinning with larger recoverable strains and higher unrecoverable strain rates, followed by a recoil process that returns the material to the original state. The same sequence occurs twice per oscillation, as the materials respond to shearing in a symmetric manner.

While the macroscopic physics is more clearly discerned by recovery-based rheology, we complete the structure-property relationship using time-resolved SANS to monitor the microstructural evolution. Shown in Fig. 2(a) is the stress versus recoverable strain with a color scale reflecting the degree of alignment observed in the 2D SANS patterns in Fig. 2(b). Given that a natural state of the entangled micellar system is isotropic, aligning the micellar segments is entropically unfavorable, leading to a macroscopic elastic response. The alignment factors in the velocity-gradient (1-2) and velocity-vorticity (1-3) planes are presented as functions of recoverable strain in Fig. 2(c) and Fig. 2(d), where a linear proportionality with a constant prefactor is manifested. A clear physical picture therefore emerges. When

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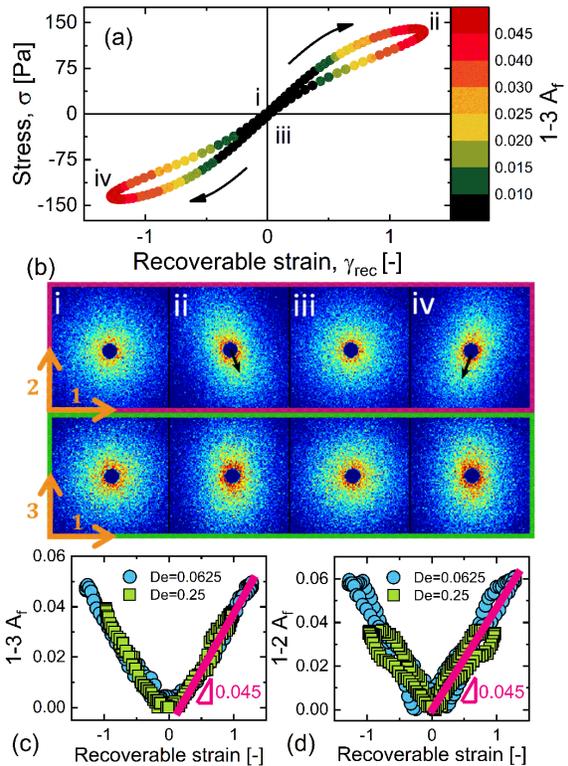
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**FIGURE 1:** LAOS results presented in the traditional ( $\sigma$ - $\gamma$ ,  $\sigma$ - $\dot{\gamma}$ ) and proposed ( $\sigma$ - $\gamma_{rec}$ ,  $\sigma$ - $\dot{\gamma}_{un}$ ) frames from WLMs. The lines in the proposed elastic and viscous views have slopes equal to the plateau modulus  $G_0 = 180$  Pa and the zero-shear viscosity  $\eta_0 = 48$  Pa·s. The stars and squares correspond to zero and maximum recoverable strain at the largest amplitude, respectively.

the recoverable strain is small, linear viscoelastic responses are seen, even under LAOS, and we observe an isotropic scattering pattern that is identical to equilibrium conditions with no alignment. As the magnitude of the recoverable strain increases, so too does the alignment factor. Even when the modulus begins to drop at large recoverable strains (points ii and iv in Fig. 2(a)), the alignment is still linearly dependent on the magnitude of the recoverable strain.

In summary, we have provided key insights into the understanding of dynamic flows and how molecular-level structure reacts during changing flows. We have shown that, by monitoring the evolution of the recoverable component of strain, the material physics under dynamic flows can be identified as a sequence of processes. Combining with experimental evidence from neutron scattering, we have established structure-property-processing relationships, providing new design criteria for soft materials. Armed with such new understandings, researchers now have a clearer path for developing advanced materials for a variety of biomedical, industrial and environmental applications.



**FIGURE 2:** Correlation between macroscopic rheology and microscopic structure. (a) Proposed elastic Lissajous figure ( $\sigma$ - $\gamma_{rec}$ ) coupled with 1-3 alignment factor  $A_f$  denoted by the color scale. (b) 2D SANS patterns at zero (i and iii) and maximum (ii and iv) recoverable strain in both velocity-gradient and velocity-vorticity planes. Alignment factors in the 1-3 (c) and 1-2 (d) planes are plotted as functions of the recoverable strain, showing the same proportionality constant of 0.045.

**References**

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