Interfacial Rheology of a Glassy Polymer

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Introduction

Complex fluid-fluid interfaces comprise surface-active materials that occupy air-liquid or liquid-liquid interfaces and impart a nontrivial response to flow and deformation. They play major roles in a variety of natural and industrial systems, such as biological (lung surfactant, lipid membranes, saliva, eye tear films), topical (skin creams, gels, lotions), food (emulsions, gels, foams) and biopharmaceutical (monoclonal antibodies, peptides). Despite their prevalence, obtaining accurate rheological information on such interfacial systems remains challenging to this day. The standard Langmuir-Pockels trough applies a mixed-flow deformation, and separation of the shear and dilatational contributions are non-trivial to obtain, and the radial trough applies pure dilatational deformations, but no shear.[1-3] Utilizing a square interface, it is possible to perform an entire rheological and thermodynamic characterization (dilatational and shear, steady and dynamic) of an interface in one instrument without requiring sample change.[4] Here, we demonstrate the capabilities of the RheoSurfR™ instrument on a model system of the glassy polymer, poly(tert-butyl methacrylate) (PtBMA, 170,000 g·mol⁻¹, Sigma Aldrich).
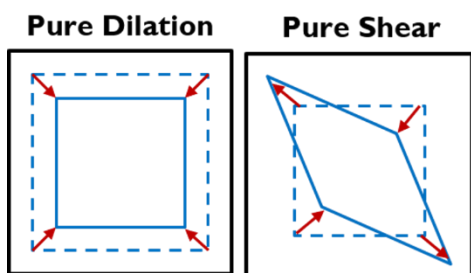

Figure 1. Pure dilatational and pure shear deformation profiles that can be performed by RheoSurfR.

Constant strain rate pressure-area isotherm

A standard measurement in interfacial rheometry is to perform a pressure-area isotherm. Measurement of the surface pressure as a function of molecular area can provide information both about the phase transitions of the interface, and its mechanical properties. A pressure-area isotherm obtained by compressing at 4 mm²·s⁻¹ for PtBMA is shown in Fig. 2. The interface was prepared by adding 50 μL of 0.27 mg·mL⁻¹ PtBMA in a chloroform spreading solution to an air-water interface with an area of 12,000 mm².
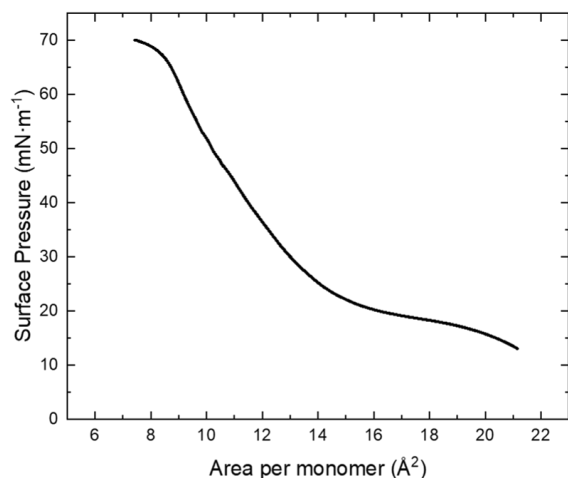

Figure 2. A pressure-area isotherm for PtBMA (170,000 g·mol⁻¹) performed at the air-water interface. The measurement was performed at 22 °C and at a constant rate of area change of 4 mm²·sec⁻¹. The starting area was 12000 mm² and the final area was 4000 mm².

The apparent steady dilatational modulus can be obtained by the following:

$$K_{app}^s = -\frac{d(\Pi - \Pi_0)}{dln\left(\frac{A}{A_0}\right)}$$

Where Π and Π_0 are surface pressure (mN·m^{-1}) and surface pressure at a reference molecular area and A and A$_0$ are molecular area and reference molecular area. A similar analysis can be performed on data from a step compression measurement to obtain the Gibbs elasticity (K$_{Gibbs}$) i.e., compress to multiple molecular areas and allow the interface to relax at each area. Then the steady dilatational moduli can be calculated:

$$K^s = K^s_{app} - K_{Gibbs}$$

Steady interfacial shear rheology

Measurements of the steady shear modulus can be performed by applying a small, unidirectional strain in either direction, at any molecular area. Orientation of the Wilhelmy plate perpendicular to or parallel to the major extensional axis dictates whether a positive or negative strain is applied, and good alignment along this axis is necessary for accurate measurements.
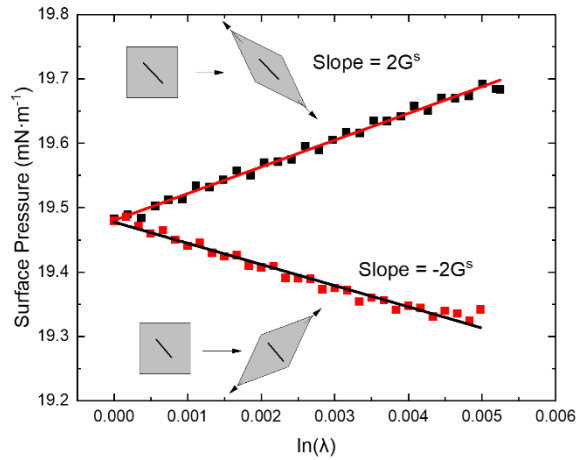

Figure 3. Surface pressure as a function of ln(λ). The black squares represent a positive strain applied and the red squares represent a negative strain. The measurements were performed at a molecular area of 13.3 Å^2 and at a temperature of 22 °C.

The steady shear moduli can be determined with either plate orientation as follows:

$$\Pi_\perp = \Pi(\Gamma) - 2G^s \ln \lambda$$

$$\Pi_\parallel = \Pi(\Gamma) + 2G^s \ln \lambda$$

Where λ is the ratio of the length of the diagonal of the square to the length of the major extensional axis.

Dynamic interfacial rheology

The viscoelasticity of the interfacial layers can be probed by dynamic dilatational and shear interfacial rheology. Applying a small amplitude oscillatory shear/dilatational strain at a fixed amplitude probes the interface's response to deformation as a function of frequency. The analysis is analogous to bulk rheology measurements, and is briefly presented below for shear. A sinusoidal oscillatory strain (γ^s) is applied with an oscillation frequency (ω) and strain amplitude (γ^s_0):

$$\gamma^s(t) = \gamma^s_0 \sin(\omega t)$$

The sinusoidal stress response is composed of both elastic and viscous components, and the measured stress amplitude (σ^s_0) is used to calculate the complex moduli using the following equation:

$$|G^{s*}| = \frac{\sigma^s_0}{\gamma^s_0}$$

For viscoelastic materials in the LVR, the complex interfacial modulus can be decomposed into its elastic (interfacial shear storage modulus, $G^{s'}$) and viscous components (interfacial shear loss modulus, $G^{s''}$) using the phase angle (δ) between oscillatory strain and the stress response from the interface:

$$G^{s'} = |G^{s*}| \cos(\delta)$$

$$G^{s''} = |G^{s*}| \sin(\delta)$$

The same analysis can be performed for dynamic dilatational rheology to obtain interfacial dilatational storage and loss moduli ($K^{s'}$ and $K^{s''}$). Below, the stress and strain profiles are shown vs time.
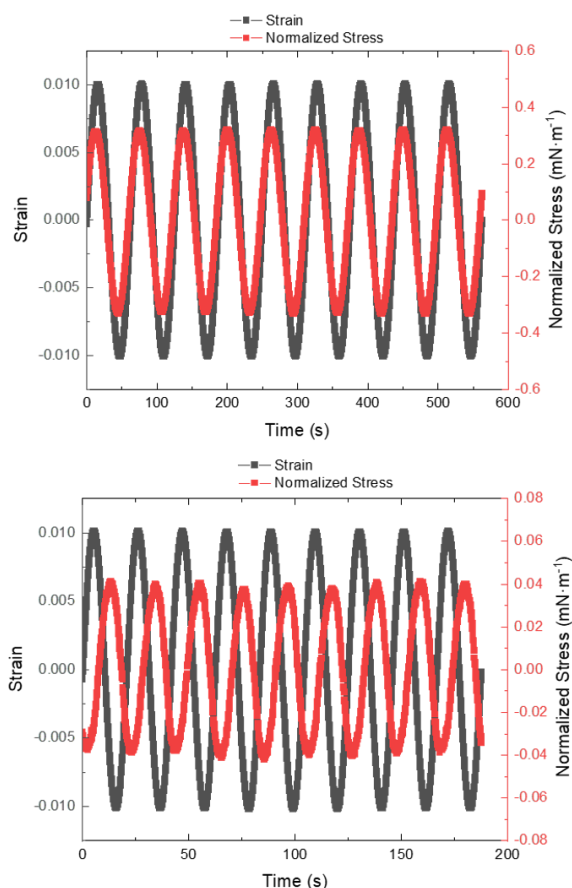
Figure 4. The top graph shows the measured stress response (red) and the applied <u>dilatational</u> strain (grey) as a function of time (ω = 0.1 rad·s^{-1}). The bottom graph shows the measured stress response (red) and the applied <u>shear</u> strain (grey) as a function of time (ω = 0.3 rad·s^{-1}). Both measurements were performed at a molecular area of 19 Å^2 and at 22 °C.

It is shown in Fig. 4. that the stress response is in phase with the dilatational strain, demonstrating a more elastic-like response of the interfacial layer to applied dilatational strain. The stress response is out of phase with shear strain, which is evidence that the interfacial layer behaves viscous-like under shear strain at this molecular area. Dilatational and shear frequency sweeps were performed at multiple molecular areas and are presented in Fig. 5. It was found that both the dilatational moduli and the shear moduli increased with decreasing molecular area. Furthermore, upon compression from a

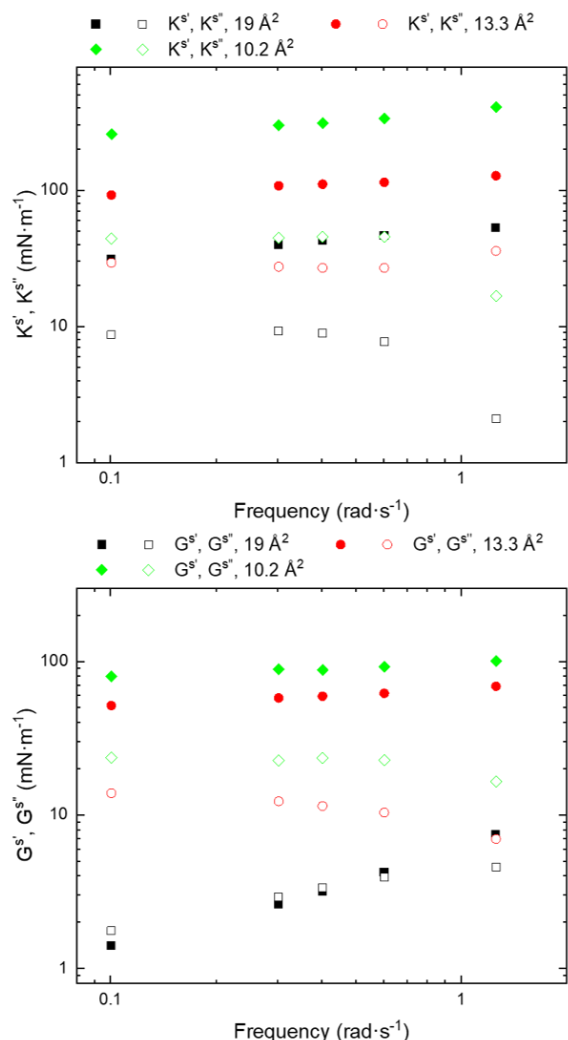molecular area of 19 Å^2 to 13.3 Å^2 the shear response changed from viscous-like to elastic-like.

Figure 5. Dilatational frequency sweeps (top) and shear frequency sweeps (bottom) for PtBMA at multiple molecular areas (19 Å^2, 13.3 Å^2 and 10 Å^2). All measurements were performed on the same interface. The amplitude was 1% and the temperature was 22 °C.

The full analysis of steady and dynamic shear and dilatational rheology for PtBMA at the air-water interface is presented in Fig. 6.
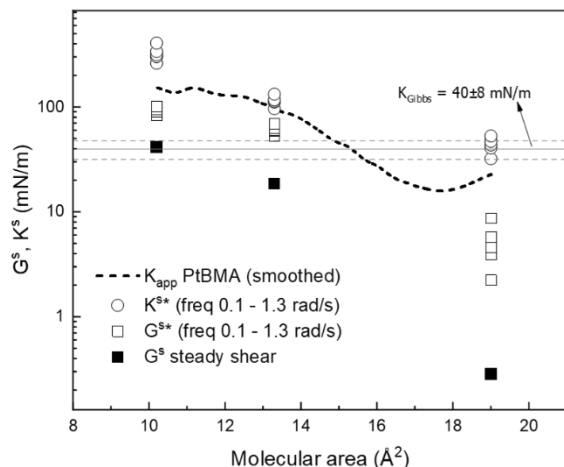
Figure 6. Steady dilatational (dashed black line), dynamic dilatational (empty circles), steady shear (black squares) and dynamic shear (empty squares) rheology data for PtBMA at the air-water interface at various molecular areas. Gibbs modulus (K_{Gibbs}) is shown as the horizontal line, with the dashed lines as the standard deviation.

Conclusions

Utilizing the RheoSurfR™ instrument, we have demonstrated a complete rheological and thermodynamic characterization of the glassy polymer PtBMA at the air-water interface. By deforming the quadrangular interface with well-defined, high-fidelity control schemes, we performed both steady and dynamic, shear and dilatational, interfacial rheology. It was found that both the dynamic shear and dilatational moduli increase with decreasing molecular area, and that the shear response transitions from viscous-like at large areas, to elastic-like under compression.

References

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Additional Information

For more information on the RheoSurfR™ instrument, or to request a product quote, please contact sales@stf-technologies.com, or visit www.stf-technologies.com.