

Measuring the viscoelastic properties of confined polymer films by thermal wrinkling

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Introduction

With the increasing utilization of polymer thin films in technological applications ranging from optics¹ to microelectronics,^{2,4} it is important to understand and control the viscoelastic properties of confined polymer films. While there are approaches capable of measuring the viscoelastic properties of confined polymer films,⁵⁻⁹ they are limited by 1) the inability to measure both the temperature-dependent modulus and viscosity, and 2) the lack of applicability to small length scales due to their complexity.

One interesting strategy to measure the viscoelastic properties of confined polymer films is to take advantage of thermal wrinkling, which is a thermally-induced instability that develops when a polymer film is sandwiched between substrate and superstrate layers that are stiffer in comparison with the polymer layer. Due to the differences in coefficients of thermal expansion (α) between the polymer and inorganic layers ($\alpha_{\text{polymer}} > \alpha_{\text{inorganic}}$), a net compressive stress develops at the polymer-superstrate interface when this composite layer is heated to temperatures that promote mobility of the polymer layer. At a critical compressive stress, surface wrinkles develop on the superstrate surface characterized by an isotropic morphology that can be approximated as a sinusoidal profile.

Based on this approach, we demonstrate that thermal wrinkling can be utilized to measure the rubbery modulus and shear viscosity of polystyrene (PS) thin films as a function of temperature.¹⁰ Specifically, we use surface laser-light scattering (SLS) to characterize the wrinkled surface in real-time in order to monitor the changes in morphology as a function of annealing time at fixed annealing temperatures. The results from such experiments are compared to a theoretical model,¹¹ from which the viscoelastic properties of the PS thin film are extracted.

Experimental

Materials and Instruments. PS thin films were prepared by spin-casting a 600,000 g/mol PS (Polymer Source, Inc^{††}) solution in toluene onto silicon substrates. The films were then annealed under vacuum for 24 h at 180 °C to remove residual solvent and mitigate the residual stress from processing history. The film thickness was determined to be 270 nm \pm 3 nm via interferometry (Filmetrics F20 UV, Filmetrics, Inc^{††}). An aluminum (Al) film was then thermally evaporated onto the PS film to form the final composite film. The Al film thickness was determined to be 54 nm \pm 1 nm measured via atomic force microscopy step height measurements. The composite films were used for thermal wrinkling without additionally processing.

A schematic of the thermal wrinkling process is illustrated in **Fig. 1a**. The Al/PS composite thin film is heated to elevated temperatures until 1) a significant compressive stress develops in the composite film due to the thermal expansion mismatch of the layers, and 2) the polymer gains sufficient mobility that results from heating above its glass transition temperature. At this critical temperature, wrinkles develop on the aluminum film surface characterized by random surface relief patterns with a dominant wavelength, d , and amplitude, A .

SLS was performed using a custom-built instrument. The composite film was placed on a hot stage (Linkam TMS94, Linkam Scientific Instruments^{††}), and held at a predetermined annealing temperature from 120 °C to 135 °C in 5 °C increments. This temperature range is above the glass transition temperature of PS ($T_g \approx 100$ °C),¹² which promotes mobility of the polymer and facilitates wrinkle formation. The 2-dimensional (2D) scattering images were collected using a charge-coupled device (CCD) camera (Apogee kx260e, Apogee Instruments, Inc^{††}). Each 2D image was radially averaged to determine the scattering intensity as a function of the scattering vector, k . The peak intensity was fitted as a Gaussian and the corresponding scattering vector was determined.

Results and Discussion

Representative time-resolved SLS images for PS annealed at 125 °C are shown in **Fig. 1b**. We observe that both the wrinkle amplitude and wavelength increase with annealing time, t . During early times, A grows exponentially with time at a growth rate, S . As time progresses, the wrinkle amplitude grows significantly, characterized by an isotropic morphology of a dominant wavelength, d , and amplitude, A . This dominant wavelength is captured by SLS as the scattering vector, $k = (4\pi/\lambda)\sin\theta \approx 2\pi/d$. To a first-order approximation, the wrinkle amplitude is related to the peak intensity, I , and the wavelength of incident light, λ , as $A \approx I^{1/2}(\lambda/2\pi)$.

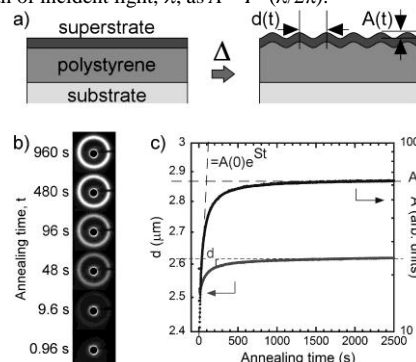


Figure 1. a) Schematic of thermal wrinkling approach to measure the rubbery modulus and viscosity of a confined PS thin film capped by an aluminum superstrate and a silicon substrate. Heating this composite film above the T_g of PS leads to the development of surface wrinkles on the aluminum surface. Both the amplitude, $A(t)$ and wavelength, $d(t)$ of the wrinkles evolve with annealing time of the experiment. b) Representative results for confined PS film thermally wrinkled at 125 °C. Time-evolved scattering patterning as captured by the SLS. c) Time-evolved wrinkle wavelength, d , and amplitude, A , for the PS thin film.

The key parameters measured from the SLS that reflect the viscoelastic properties of the PS film are d_r and S (**Fig. 1c**). Specifically, the rubbery modulus and shear viscosity of the confined PS film can be inferred with the aid of a theoretical model that is based on linear perturbation analysis.

At long annealing times, the wrinkle wavelength reaches an equilibrium value of d_r . Thus, measurement of this parameter allows for the interpolation of rubbery modulus of PS, $E_{i,r}$:

$$E_{i,r} = \frac{(1-2\nu_i)(1+\nu_i)}{12(1-\nu_i)} \left(\frac{h_i}{h_f} \right) \left(\frac{2\pi h_f}{d_r} \right)^4 \frac{E_f}{1-\nu_f^2} \quad (1)$$

where ν_i and η_i correspond to the Poisson's ratio and film thickness of PS, and ν_f , η_f , and E_f correspond to the Poisson's ratio, film thickness and elastic modulus of Al.

At short annealing times, measurement of S allows for the interpolation of η_i . Specifically, S is determined at the very initial time of the annealing process when an initial value of k is observed:

$$\eta_i = \frac{\frac{1-2\nu_i}{1-\nu_i} \left(\frac{h_i}{h_f} \right) \left(\frac{-E_f}{12(1-\nu_f^2)} \left(\frac{2\pi h_f}{d} \right)^4 - \sigma \left(\frac{2\pi h_f}{d} \right)^2 \right) - \frac{E_i}{1+\nu_i}}{2S} \quad (2)$$

where σ corresponds to the thermal stress required to cause wrinkling.

Using eq. (1) and (2), we determined the $E_{i,r}$ and η_i values of the confined PS film as function of annealing temperatures, respectively (**Fig. 2**). Both material properties decrease with annealing temperature, which we attribute to an enhanced softening of the confined PS layer. Specifically, we assumed that PS is a physically-entangled polymer network with sufficient mobility that behaves rubber-like above its T_g . Unlike a chemically-crosslinked elastomer whose entanglements are permanent crosslinks, the entanglements for PS can be described as a dynamic network of physical associations, or constraints that restrict polymer motions. Above T_g , the entanglement life-time and density are expected to decrease with increasing annealing temperature, which leads to a subsequent decrease in the rubbery modulus and shear viscosity. Thus, this softening reduces $E_{i,r}$ as reflected by an increase in d with annealing temperature, but also reduces the critical stress

for wrinkling, σ_c . Additionally, increasing the annealing temperature leads to a reduction in the shear viscosity and an increase in the thermally-induced compressive stress in the Al film, σ . Therefore, the reductions in η_s and σ_c , coupled with the increase in σ contribute to the observed increase in S with temperature.

Finally, to validate the accuracy of our technique, we compared our results with traditional parallel-plate rheometry. Specifically, we measured the rubbery modulus and shear viscosity of bulk PS samples using parallel-plate shear rheometry and the results are quite comparable (on average, within 50% of the value from bulk rheometry) to the values obtained from thermal wrinkling measurements. The results of both measurement techniques will be discussed in the presentation.

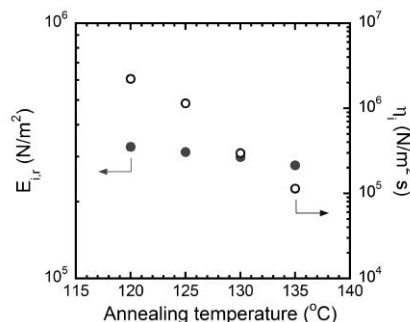


Figure 2. Summary of rubbery modulus, $E_{i,r}$, and shear viscosity, η_s , as a function of temperature and comparison with bulk rheology.

Conclusions

Thermal wrinkling, combined with SLS, provides a new approach to measure the viscoelastic properties of confined PS thin films above its glass transition temperature. We showed that by employing the equations established for theoretical buckling mechanics, it is possible to quantify the rubbery modulus and the shear viscosity of a PS thin film under confinement. This technique will provide a new measurement platform in quantifying the temperature-dependent viscoelastic relaxation behavior of a variety of confined polymer systems. Although we have demonstrated this measurement technique for confined PS films, it can be extended to polymers with other forms of phase transitions, such as such as melting or order-disorder transitions.

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†† Equipment and instruments or materials are identified in this work in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology (NIST), nor does it imply that the materials are necessarily the best available for the purpose.

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