EFFECT OF CHAIN ARCHITECTURE ON THE VISCOELASTIC PROPERTIES OF POLYMER FILMS MEASURED VIA THERMAL WRINKLING[†]

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Introduction

The viscoelastic properties of a material are a key determinant in the performance of a soft adhesive, providing energy dissipation through chain rearrangement and other relaxation processes. The viscoelasticity (modulus and viscosity) of an adhesive is known to be highly dependent on temperature. Thus, the materials' cohesive strength changes with temperature. One way to counter this change in performance is to lightly crosslink the material, imparting more elastic characteristics to the material. For bulk materials, there are many established techniques for measuring the viscoelastic properties, such as dynamic mechanical analysis. For films, the viscoelastic properties can be indirectly assessed through peel tests and probe tack tests. But as the thickness of the adhesive decreases, these tests become less reliable due to secondary effects such as bending of the backing layer or substrate interactions.

We recently developed a measurement strategy based on surface wrinkling that allows us to deduce the elastic properties of thin films and coatings [1]. Subsequently, we extended this technique to measure the viscoelastic properties of thin polymer films above their bulk glass transition temperature (T_g) [2]. By confining the polymeric film between a rigid substrate and rigid superstrate, heating the sample leads to a net compressive thermal stress due to mismatches in thermal expansion coefficients of the materials. This compressive stress leads to the development of surface wrinkles characterized by an isotropic morphology that can be approximated as a sinusoidal surface profile (Fig. 1) with defined wavelength and amplitude [2,3]. If the film is elastic, the wavelength and amplitude would remain constant over time; alternatively, if the film is viscoelastic, the wrinkling profile evolves with time as the material creeps under the applied stress. By following the evolution of the wrinkle wavelength and amplitude with small angle laser light scattering (SALS), we can determine the rubbery modulus and shear viscosity of the polymer film with the aid of a theoretical model [4]. In this paper, we use thermal wrinkling to quantify the effects of crosslinking on the viscoelastic properties of amorphous polymer films.



Figure 1. (a) Schematic of thermal wrinkling, which occurs when a polymer film confined by both a superstrate and substrate is heated to elevated temperatures. The wrinkle pattern has both a wavelength [d(t)] and amplitude [A(t)] that grow with time. (b) Optical profilometry image of a thermally-wrinkled surface. The wrinkling pattern is isotropic as a result of the isotropic thermal stress.

Experimental[‡]

Poly(*p*-hydroxystyrene) [PHOST] was chosen as a model crosslinkable system. It has been widely studied due to its use as a negative-tone chemically amplified photoresist for microelectronics applications. The relative number average molecular mass of the PHOST was 2,400 g/mol. Solutions of PHOST were spin coated on silicon wafers, followed by a post-apply bake. The thickness of the PHOST was \approx 700 nm. To induce crosslinking, the films were exposed to ultraviolet light having a wavelength of 248 nm. Aluminum was then deposited by thermal evaporation, and the thickness of the aluminum capping layer was \approx 50 nm. Both crosslinked and uncrosslinked samples were measured via thermal wrinkling.

After evaporation, the samples were diced into 1 cm × 1 cm specimens. These composite films were placed on a heating stage at a predetermined annealing temperature, and the temporal evolution of the wrinkling pattern was captured using a custom-built SALS apparatus [4]. The 2-D scattering patterns were used to calculate the wavelength (*d*) and amplitude (*A*) of the wrinkles at a time interval of ≈ 0.5 s. The amplitude of the wrinkles is related to the scattering intensity of the first order peak as $A \sim I^{1/2}$. For simplicity purposes, we present the intensity data from SALS rather than the absolute amplitude of the wrinkles.

Results and Discussion

Figure 2 shows representative scattering patterns from thermal wrinkling of both the crosslinked and linear PHOST. From the scattering patterns, the wrinkling wavelength (d) and scattered intensity can be determined as a function of annealing time. The crosslinked PHOST films behaved elastically, displaying no temporal evolution of the scattering pattern. The wavelength and amplitude were selected immediately upon heating and did not change over the course of the experiment. Conversely, the linear PHOST films displayed a wavelength and amplitude that changed with time, indicative of a viscoelastic response. At long times, the wavelength and amplitude plateau at an equilibrated value. rate of change in intensity (dI/dt) of the scattering at initial times (for details of this analysis, see ref [4]). Shown in Figure 3 are the modulus and viscosity of the PHOST films. The modulus for the linear PHOST decreases with increasing temperature, as expected for amorphous polymers above T_{g} . Conversely, the crosslinked PHOST exhibited a relatively constant modulus with increasing temperature, indicative of a crosslinked elastic material. The shear viscosity calculated from the intensity data decreased with increasing temperature for the linear PHOST system. Since the crosslinked PHOST films did not show any change in intensity with time, we could not deduce a shear viscosity for those films.



Figure 2. Representative scattering patterns (top) and the resulting wavelength and intensity (bottom) as a function of time for (a) crosslinked and (b) uncrosslinked (linear) PHOST.

The modulus of the film in the rubbery regime can be calculated from the equilibrated wavelength at long times. Additionally, the shear viscosity can be estimated from the



Figure 3. (a) Modulus and (b) shear viscosity as a function of annealing temperature for PHOST films measured via thermal wrinkling. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

Conclusions

We demonstrated that thermal wrinkling can be used to measure the viscoelastic properties of thin polymer films before and after crosslinking. Future work will include a systematic study of the effect of crosslink density and film thickness on the rubbery modulus and shear viscosity of films under substrate and superstrate confinement.

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[‡]The equipment and instruments or materials are identified in the paper in order to adequately specify the experimental details. Such identification does not imply recommendation by NIST, nor does it imply the materials are necessarily the best available for the purpose.

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