MEASURING MODULUS OF GRADIENT POLYMER FILMS BY STRAIN-INDUCED BUCKLING INSTABILITIES

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Introduction

We present a high-throughput technique to rapidly measure the tensile modulus of thin polymer films. This technique exploits a strain-induced buckling instability in elastomer-supported films[1] that produces a modulus-dependent wavelength. The thin film modulus is then calculated using the buckling wavelength and mechanical properties of the elastomer.[2]

Experimental

Materials. All materials were used as received without further purification. Atactic polystyrene (PS) was obtained from Aldrich[3] (M_r = 2.80x10^5, M_r/M_n = 3.07).[4] The polymer was dissolved in toluene at 2 % mass fraction and filtered using a 0.2 μm filter prior to coating. Polydimethylsiloxane prepolymer (PDMS, Sylgard 184) was obtained from Dow Corning. The prepolymer and curing agents were mixed at a ratio of 10:1, spread on a glass plate, allowed to flow and level overnight, and cured fully at 70 °C for 3 h. This results in a PDMS sheet having a uniform thickness of 1 mm that was cut into 25 mm x 75 mm strips.

Sample Preparation. Polystyrene films with continuous thickness gradients ranging from 70 nm to 140 nm were prepared by flow coating onto silicon wafers, as described elsewhere.[5] The above PDMS strip was applied to the PS-coated wafer and the resulting sandwich was immersed in water. Water preferentially wets the hydrophilic silicon wafer, which allows the PDMS/PS bilayer to lift off of the substrate, thus transferring the PS film from the silicon wafer onto the PDMS.

Measurement. Bilayers were secured between supports on a custom-built strain stage that was then mounted on an x-y translation stage (Ludl Electronic Products, Ltd). A tensile strain of 12.5 % was used for all reported data here. The strained sample was placed in the normal transmissive path of a low-power He-Ne (λ= 6328 Å) laser and the diffraction pattern was projected onto a diffusing screen, that was then imaged by a conventional CCD camera of 8 bit pixel depth. The diffraction pattern was used to measure the dominant wavelength of the buckling as a function of PS film thickness.

Results and Discussion

Unstrained samples were clear and without structure as observed by optical microscopy and/or light scattering, except for spurious cracks introduced by sample handling. However, upon application of a threshold strain, a buckling abruptly developed (Figures 1 and 2) that was invariant upon increasing strain. As Figure 3 shows, the wrinkling wavelength was strongly dependent on local film thickness. Over a thickness range of 70 nm to 140 nm, the wrinkling wavelength changed proportionately (3.5 μm to 6.8 μm). The modulus of the polystyrene film was calculated from the dominant periodicity by the following equation:[2]

$$E_p = 4E_m(1-\nu_p)\left(\frac{\lambda}{2\pi h}\right)^{-3} \qquad (1)$$

where E_p is the Young's modulus of the PS film, E_m is the Young's modulus of the PDMS substrate (1.3 MPa ± 0.1 GPa), ν_p is the Poisson's ratio of the thin film (0.35), λ is the wavelength of the buckling instability, and h is the PS film thickness. Figure 3 shows that the measured modulus (2.6 GPa ± 0.1 GPa) is both independent of film thickness and comparable to reported values (3.3 GPa).[6]

Conclusions

We have demonstrated that a strain-induced buckling instability can be used to measure the modulus of thin polystyrene films. The technique is robust over a thickness range of 70 nm to 140 nm for which a modulus of 2.6 GPa ± 0.1 GPa is measured. The appeal of this method is its simplicity. A given strain above a threshold induces a buckling wavelength that can be measured rapidly by light scattering, enabling the calculation of the modulus of the film. We are currently expanding the technique to investigate the effect of fillers and composition on the modulus of polymer films.

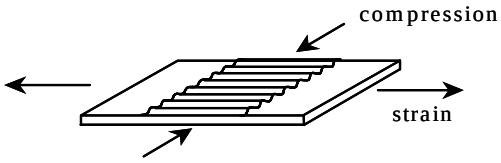

Figure 1. Schematic showing buckling instability of a PDMS/PS bilayer resulting from the compressive forces exerted on the sample upon application of strain. Periodicity of undulations (not to scale) is on the order of a few microns, ideal for measurements via light scattering.

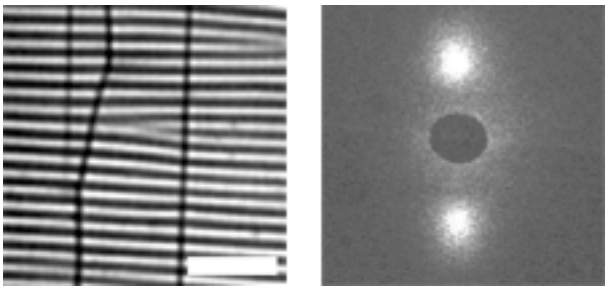

Figure 2. Representative optical micrograph and corresponding diffraction pattern of buckling instabilities exhibited by the PDMS/PS bilayer under compression. Contrast in the optical image originates from sample topography; vertical lines are a result of cracks in the film upon elongation. Scale bar = 10 μm.

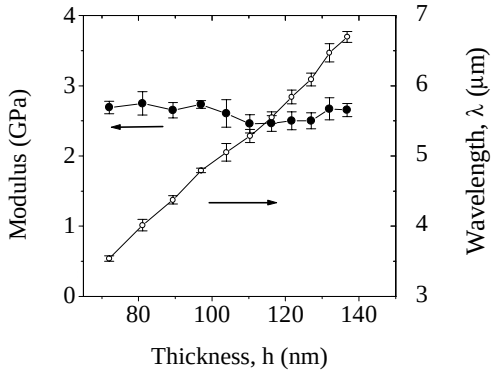

Figure 3. Plot showing the buckling wavelength (right axis) as a function of film thickness and the corresponding calculated modulus (left axis). The error bars represent one standard deviation of the data, and are taken as the experimental uncertainty of the measurement.

References

(1) Bowden, N.; Brittain, S.; Evans, A.G.; Hutchinson, J.W.; Whitesides, G.M. *Nature* **1998**, *393*, 146.
(2) Groenewold, J. *Physica A* **2001**, *298*, 32.
(3) 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.
(4) According to ISO 31-8 the term "molecular weight" has been replaced by "relative molecular mass", M_r. The number average molecular weight is given by M_n.
(5) Meredith, J.C.; Karim, A.; Amis, E.J. *Macromolecules* **2000**, *33*, 5760.
(6) Brandrup, J.; Immergut, E.H.; Grulke, E.A. *Polymer Handbook*, 4th Ed.; John Wiley & Sons: New York, **1999**.