

Examination of Thin Film Modulus for a Series of Poly(alkyl methacrylates)*

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INTRODUCTION

The thermal behavior of polymer thin films has been studied extensively over the past decade.[1] Dependencies of the glass transition temperature (T_g) of polystyrene thin films on molecular mass [2] and interfacial interactions [3] have been elucidated. In these experiments T_g has been shown to have gradient properties as one moves away from the interface [4]. These studies have provided an improved understanding of the physical properties of thin polymer films, but the origins of the nanoconfinement effect are still unclear [1,5]. Much of the motivation towards understanding the thermal behavior (especially variations in T_g) has been related to the mechanical stability of polymeric nanostructures, as proximity to T_g in bulk polymers is known to correlate with mechanical properties through superposition principles [6]. Experimental difficulties have limited the measurement of the modulus of ultrathin polymer films, but recently the development of a wrinkling based metrology to determine the modulus of thin films [7] has allowed the mechanical properties of polymer films as thin as 5 nm to be assessed [8].

In this work, the modulus of polymer thin films for a homologous series of poly(n-alkyl methacrylate)s will be discussed. In particular, the impact of the degree of undercooling from bulk T_g on the deviations will be explored as T_g is significantly impacted by alkyl chain length [9]. Bohme and de Pablo predicted that the modulus of nanoconfined polymers decrease even at temperatures well below T_g [10]. Additionally as T_g is approached, the size scale at which the decreased modulus occurs increases [10]. This work will experimentally examine these predictions.

EXPERIMENTAL[†]

Materials and Film Preparation. Poly(methyl methacrylate) (PMMA) was purchased from Polymer Source ($M_w=91k$ g/mol $M_w/M_n=1.3$, where M_w and M_n are weight- and number-average molecular mass, respectively)[‡]. Two other alkyl methacrylate polymers, poly(ethyl methacrylate) (PEMA) ($M_w=250k$ g/mol) and poly(n-propyl methacrylate) (PnPMA) ($M_w=70k$ g/mol), were purchased from Scientific Polymer Products. Polymer films of uniform thickness were spin-cast from dilute polymer solutions onto mica. Mica was used as the substrate to facilitate film transfer to poly(dimethylsiloxane) (PDMS). PDMS was prepared at a ratio of 20:1 by mass of base to curing agent (Sylgard 184, Dow Corning) and allowed to gel at room temperature for 3 h before curing at 100 °C for 2 h. After cooling the PDMS sheet was cut into 25 mm X 75 mm X 1.5 mm. The modulus of the bulk PDMS sheets was determined using an Instron with a strain rate of 0.01 mm/s. To test the modulus of the polymer films, the PDMS was prestrained to 4 % and the supported polymer film was placed in contact with the strained PDMS. From differential adhesion in water, the polymer film is transferred from the mica onto the PDMS. The pre-strain on the PDMS was released at a rate of 0.1 mm/s and at ambient temperature (23 °C).

Characterization. The wrinkling morphology was quantified with optical and atomic force microscopy (AFM). AFM images were acquired at ambient temperature on an Agilent Technologies 5500 System in tapping mode. Optical images were acquired on a Mitutoyo

Ultraplan FS-110. The images were analyzed using a 1D Fast Fourier Transform (FFT) to obtain the wavelength of the wrinkles.

Ellipsometry. The thickness and refractive index of the polymer films were determined directly on the pre-strained PDMS using a spectroscopic ellipsometer (M-2000, J.A. Woollam Co., Inc.). A fixed incident angle of 70° was utilized while the ellipsometric angles (Ψ and Δ) were determined over the wavelength range from 250 nm to 1700 nm. The measured Ψ and Δ data were fit recursively using a Cauchy model to describe the polymer film to yield the film thickness and refractive index of the poly(n-alkyl methacrylate) film.

RESULTS AND DISCUSSION

The modulus of polymer thin films was determined from the wrinkling instability of poly (n-alkyl methacrylate) films on PDMS [7]. In order for wrinkling to occur, the pre-strain must be greater than the critical strain of each material. The critical strain, ε_c , depends upon the ratio of the plane strain modulus of the elastic film, \bar{E}_f , and the soft substrate, \bar{E}_s , as:

$$\varepsilon_c = -\frac{1}{4} \left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{2/3} \quad (1)$$

The negative sign in equation (1) denotes compression. When $\varepsilon > \varepsilon_c$, a bifurcation occurs that results in the stable equilibrium state of the film being wrinkled in a sinusoidal form. If the soft substrate is significantly thicker than the elastic film, the wrinkling can be simplified by considering the soft substrate as semi-infinite. Then the equilibrium wrinkling wavelength, λ_{eq} , is only dependent upon the modulus ratio (\bar{E}_f/\bar{E}_s) and the film thickness, h_f , as:

$$\lambda_{eq} = 2\pi h_f \left(\frac{\bar{E}_f}{3\bar{E}_s} \right)^{1/3} \quad (2)$$

Since all the variables except the film modulus are easily measurable, wrinkling provides a facile route to elucidate the moduli of thin films. The wrinkle wavelength, λ_{eq} , should be directly proportional to the film thickness if the film modulus is independent of thickness and should intersect at the origin. Figure 1 illustrates the dependence of the wavelength on the film thickness for PMMA, PEMA, and PnPMA.

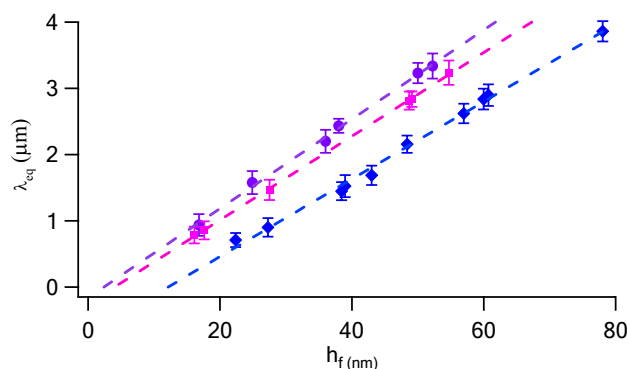


Figure 1. Wrinkling wavelength as a function of film thickness for PMMA (●), PEMA (■), and PnPMA (◆). The extrapolated wavelength-thickness correlation deviates from the origin, consistent with thickness dependent moduli. The dashed lines are linear fits to the data, and the error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

The PDMS substrate is similar in all cases so \bar{E}_s is nominally constant. The slopes of the linear fits to the wavelength data decrease as the alkyl chain length is increased, consistent with a progressively

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smaller modulus from PMMA to PEMA to PnPMA. Additionally, the extrapolated wavelength does not extend through the origin. Instead, there appears to be finite thicknesses where the film will be intrinsically stable (zero wavelength). This behavior has been previously reported for polystyrene thin films [8] and is attributed to a decrease in the modulus of the polymer as the film thickness decreases.

Rearrangement of equation (2) enables the modulus of the films to be calculated from the equilibrium wavelengths. The moduli as a function of film thickness for a series of poly(n-alkyl methacrylate)s is shown in Figure 2. The modulus of the PMMA decreases significantly as the thickness of the film is decreased below ≈ 60 nm in agreement with previous reports [8]. This result is also consistent with previous reports that showed the fractional change in the moduli as a function of film thickness to be polymer independent for polystyrene (PS) and PMMA [8]. Therefore since for this series of poly(n-alkyl methacrylate)s the chemistry difference is far less than between PMMA and PS, any difference in the mechanical behavior should be primarily attributed to changes in T_g of these systems. The modulus of PEMA appears to begin to deviate at slightly larger thicknesses (≈ 65 nm), but due to statistical variation, there is no significant difference in the thickness dependence on the modulus of thin films of PMMA and PEMA. Both polymers are well into the glassy regime with bulk T_g of 105°C and 70°C for PMMA and PEMA, respectively. However, the moduli of the PnPMA films deviate from the bulk at ≈ 80 nm. This result is consistent with molecular simulations that suggest the 'critical' thickness for a decrease in the polymer modulus increases as T_g is approached [10]. However, the length scale for the deviation in the moduli from the bulk does not appear to correlate with reported thickness-dependent deviations in T_g for PnPMA [11].

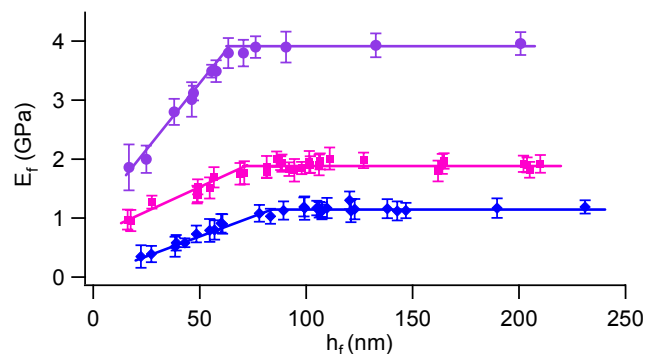


Figure 2. Elastic moduli of PMMA (●), PEMA (■), and PnPMA (◆) thin films as a function of film thickness. The solid lines are meant to guide the eye, and the error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

CONCLUSIONS

The wrinkling instability was utilized to determine the moduli of thin films of poly(n-alkyl methacrylate)s. All polymers examined showed a decrease in modulus when the film thickness decreased below a critical value. However, the length scale for the deviation in the moduli from the bulk did not appear to correlate with the reported thickness dependence of T_g for PnPMA. These results are consistent with simulations from Bohme and de Pablo [10].

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[†] Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the products identified are necessarily the best available for this purpose.

[‡] According to ISO 31-8, the term "molecular weight" has been replaced by "relative molecular mass," M_r . The conventional notation, rather than the ISO notation, has been employed for this publication.