ULTRATHIN ADHESIVES: CONFINEMENT EFFECT ON MODULUS

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Introduction

The modulus of polymeric materials is a critical parameter in assessing their utility as adhesives. The improved properties of some materials when confined to the nanometer length scale, such as graphene sheets which are molecularly thick in one dimension [1], provide motivation for development of nanolaminates that are held together by polymeric adhesives, where the adhesive layer would be desired to be <100 nm thick. Similarly to improve the profitability of pressure sensitive adhesives, minimization of the thickness of the adhesive layer is desired. In all these examples, the mechanical properties of a polymeric adhesive at the nanoscale are critical for performance.

In general, the modulus of a polymer near the glass transition temperature (T_g) is strongly dependent upon the quench depth into the glass, which is simply the difference between the temperature of interest (T) and T_g. It is well known that in the bulk, the modulus of a polymer scales with ($T-T_g$) according to the theory proposed by Williams-Landau-Ferry (WLF). However, it is unclear whether the macroscopic WLF theory based upon the quench depth into the glass is valid at the nanoscale. It has been shown that the T_g of thin polymer films can deviate from the bulk as films are confined to thicknesses <100 nm [2]; unfortunately the fundamental origins of this behavior are poorly understood and still actively debated [3]. Therefore, it is of interest to determine how confinement impacts the modulus of polymer coatings and how this varies with the polymer chemistry. 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 [5] has allowed the mechanical properties of polymer films as thin as 5 nm to be assessed [6].

In this work, we will employ this wrinkling metrology to extract the modulus of polymer thin films for a homologous series of poly(n-alkyl methacrylate)s. In particular, we take advantage of the decrease in T_g as the alkyl chain length increases for these methacrylates [7]. Since our wrinkling measurements are conducted at room temperature, the quench depth ($T-T_g$) in the polymer film is varied by using different polymers. This systematic series allows us to ascertain the effect of quench depth into the glass on the modulus of these ultrathin films. Bohme and de Pablo predicted that the modulus of nanoconfined polymers decreases even at temperatures well below T_g [8]. Additionally as T_g is approached, they predict an increase in the length scale at which the decreased modulus occurs [8]. This study aims to 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)[‡]. Four other methacrylate polymers, poly(ethyl methacrylate) (PEMA) (M_w=250k g/mol), poly(n-propyl methacrylate) (PnPMA) (M_w=70k g/mol), poly(benzyl methacrylate) (PBzMA) (M_w=70k g/mol), and poly(isobutyl methacrylate) (PiBMA) (M_w=200k g/mol) were purchased from Scientific Polymer Products.
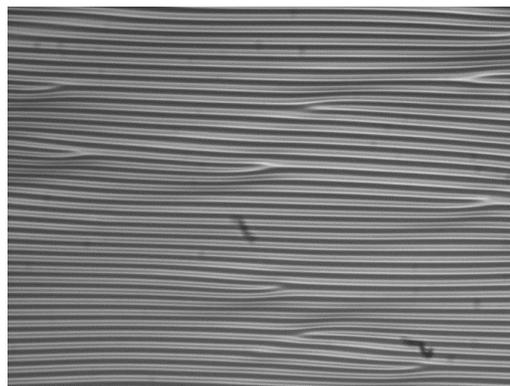

Figure 1. Optical micrograph of a wrinkled PMMA film on supported on a PDMS substrate.

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 × 75 mm × 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. The sample was then immersed in water. As water wetted the high-energy mica surface, the polymer film is transferred from the mica onto the PDMS. The prestrain on the PDMS was released at a rate of 0.1 mm/s at

ambient temperature (23 °C). This resulted in the applied polymer film wrinkling in a periodic fashion as illustrated in Figure 1.

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

Results and Discussion

Wrinkling Mechanics. The modulus of polymer thin films was determined from the wrinkling instability of poly (n-alkyl methacrylate) films on PDMS [5]. In order for wrinkling to occur, the pre-strain must to 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, $\overline{E}_f$, and the soft substrate, $\overline{E}_s$, as:

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

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 ($\overline{E}_f/\overline{E}_s$) and the film thickness, h_f, as:

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

Since all the variables except the film modulus are easily measurable, wrinkling provides a facile route to elucidate the moduli of thin films.

Modulus of poly(n-alkyl methacrylate) 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. However as shown in Figure 2, the wavelength dependence upon the film thickness extrapolates to a finite film thickness. The PDMS substrate is similar in all cases so $\overline{E}_s$ 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 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). From T_g measurements in thin films, it has been established that a gradient in T_g's exist and generally the surface T_g is significantly depressed [9]. This combined with the data in Fig. 2 suggest the presence of a liquid-like layer on the surface of the polymer films that would be of sufficiently low modulus to resist wrinkling. From an adhesion perspective, the presence of a low modulus layer at a free surface for polymers could be advantageous in pressure sensitive adhesives especially as it appears that the thickness of this layer is directly related to proximity to bulk T_g.
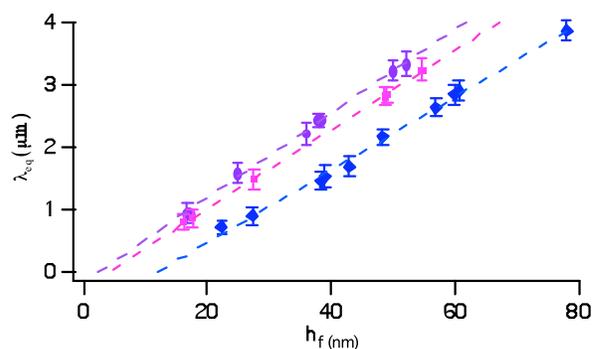

Figure 2.   Wrinkling wavelength as a function of film thickness, h_f, for PMMA (●), PEMA (■), and PnPMA (♦). The extrapolated wavelength-thickness correlation deviates from the origin, consistent with thickness dependent moduli. The dashed lines are linear fits to the data, and the error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

Rearrangement of equation (2) enables the modulus of the films to be calculated from the equilibrium wavelength. The moduli as a function of film thickness for a series of poly(n-alkyl methacrylate)s are shown in Fig. 3.   The modulus of PMMA decreases significantly as the thickness of the film is decreased below ≈60 nm in agreement with previous reports [6]. 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 [6]. Since chemistry difference for this series of poly(n-alkyl methacrylate)s 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, we cannot argue that there is a 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 a bulk T_g of 105 °C and 70 °C for PMMA and PEMA, respectively. T_g for PMMA and PEMA thin films does not appear to decrease from the bulk until ≈40 nm [10]. However the T_g of a polymer sur-

face is actually decreased,[9] thus a low modulus surface layer could be responsible for the depressed modulus in the thin films [6]. However, the moduli of the PnPMA films deviate from the bulk at ≈90 nm, but the T_g of PnPMA films also deviate from the bulk only at ≈40 nm [10]. This difference in length scales for this series of poly(n-alkyl methacrylate)s suggests that the T_g of thin films and mechanical properties are not directly correlated, but this result is consistent with molecular simulations that suggest the 'critical' thickness for a decrease in the polymer modulus increases as r T_g is approached [8].
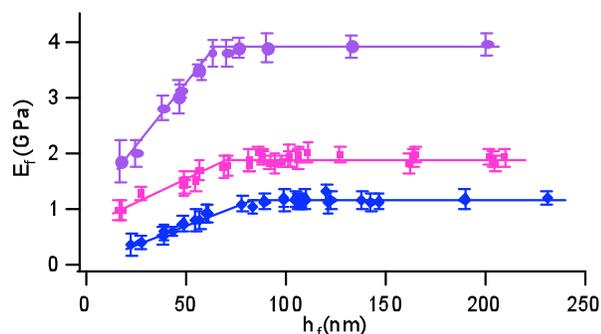
Figure 3. Elastic moduli of PMMA (●), PEMA (■), and PnPMA (♦) thin films as a function of film thickness (h_f). The solid lines are meant to guide the eye, and the error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.
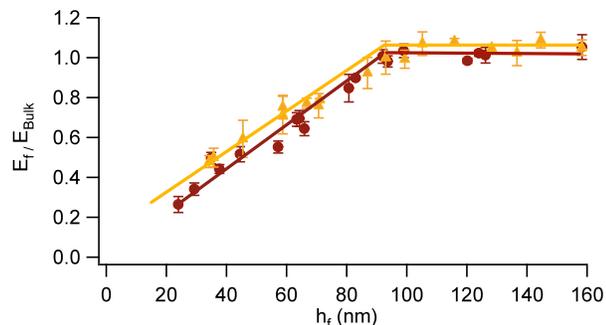

Figure 4. Reduced elastic moduli (E_f/E_{bulk}) of PiBMA (▲) and PBzMA (■) thin films as a function of film thickness (h_f). The solid lines are meant to guide the eye, and the error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

Decoupling Modulus and T_g effects. One problem with the previous series is that both modulus and T_g decrease with alkyl chain length, thus it is not clear if the correlation in length scale for thin film moduli deviations from the bulk is due to the changes in bulk T_g or modulus. To investigate these effects, two polymers with similar T_g, but different moduli are used: PiBMA (E_{bulk} = 2.5 GPa, T_g = 47 °C) and PBzMA (E_{bulk} = 3.25 GPa, T_g = 54 °C). Interestingly, both polymers appear to show deviations from bulk modulus at ≈ 85 nm as shown in Fig. 4; this is consis-

tent with the quench depth into the glass for the bulk being correlated with the length scale where a decrease in the polymer modulus is observed for thin films [8]. Future work will examine non-methacrylate polymer systems to assess the universality of these findings.

Conclusions

Wrinkling instabilities were utilized to determine the moduli of thin films of different poly(methacrylate)s. All polymers examined showed a decrease in modulus when the film thickness decreased below a critical value. These results are consistent with simulations from Bohme and de Pablo [8]. Moreover, finite thickness effects can be present in coatings as thin as 100 nm; the decreased modulus of the adhesive at this length scale could have detrimental effects on the performance of nano-adhesive joints, but also suggest that a glassy bulk polymers could function as rubbery thin film adhesive due to the decrease in both Tg and modulus for thin films.

Acknowledgements

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