Influence of Molecular Mass on the Modulus of Thin Polystyrene Films

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INTRODUCTION

There are conflicting results on the effect of confinement on T_g as a function of molecular weight as well as a limited understanding on the correlation between mechanical properties and T_g at the nanoscale [1]. For example, the rheological properties of thin poly(vinyl acetate) films do not correlate with changes in thin film T_g [2]. Furthermore, Bohme and de Pablo used simulations to predict significant stress relaxation occurring at the air-polymer interface even at temperatures deep in the glass where a deviation in mechanical properties would not be expected [3]. These results bring into question common assumptions regarding the relationship between the observed deviations in T_g and the expected modulus of polymer thin films.

In this work, we examine the influence of relative molecular mass (M_n, or the number average molecular mass) of PS on the thickness-dependent moduli using a wrinkling based instability of a stiff film on an elastic substrate. This wrinkling based metrology allows for the determination of elastic moduli for film thicknesses down to ≈ 5 nm [4]. We have previously shown that the modulus of PS being independent on molecular mass, for M_n> 100 kg/mol [5]. However, lower molecular masses have not been examined. It might be expected that confinement effects would be reduced for low molecular weight films (as R_g is reduced), if the intrinsic size of the polymer is partially responsible for the size dependent behavior. Conversely, molecular simulations suggest the critical length scale is proportional to quench depth ($T_{g,bulk}$ -T) into the glass. Experiments are carried out at room temperature, thus the quench depth is decreased for low molecular mass PS, due to the lower $T_{g,bulk}$ of these materials. We demonstrate that above a critical threshold of M_n> 3.1 kg/mol the modulus remains statistically independent of molecular mass, while lower molecular mass PS films exhibit a decrease in modulus at a larger film thickness, which appears to scale with quench depth into the glass.

EXPERIMENTAL[†]

Materials and Film Preparation. PS having a range of molecular mass, from 1.1 kg/mol to 990 kg/mol, were purchased from Polymer Laboratories. Table 1 lists the molecular mass of the different samples, as measured by gel permeation chromatography. The T_g of the PS samples was determined via differential scanning calorimetry and also listed in Table 1. Silicon wafers, cleaned with ultraviolet/ozone (Model 42, Jelight), were used as substrates for the spin cast PS films. Poly (dimethylsiloxane) (PDMS) was prepared at a 20:1 ratio by mass of base to curing agent (Sylgard 184, Dow Corning). The PDMS was allowed to gel on float glass for 3 h at room temperature before curing at 100 °C for 2 h. A 25 mm × 75 mm × 1.5 mm slab of PDMS was mounted onto a custom built stage and pre-strained to 4 %. The silicon wafer-supported polymer film was placed in contact with the PDMS and immersed in water to transfer the PS film to the PDMS. The pre-strained system was released at ambient temperature (23 °C) after drying.

Characterization. The modulus of the PDMS substrate was determined using a texture analyzer, TA.XTPlus, (Texture Technologies Corp., Scarsdale, NY/Stable Microsystems, Godalming, Surrey, UK) with a strain rate of 0.1 mm/s. The wrinkling morphology was determined by atomic force microscopy (5500 System, Agilent Technologies) in tapping mode or optical micrscopy (Ultraplan FS-110, Mititoyo). The thickness and refractive index of the polymers films were determined using a spectroscopy ellipsometer (M-2000, J.A. Woollam) over wavelengths from 250 nm to 1700 nm at incident angles of 65°, 70°, and 75°. The ellipsometric angles (Ψ and Δ) were fit using a Cauchy model to describe the PS films. The thickness of the PS films on the silicon wafer was unchanged (within the uncertainty of the measurement) after transfer to the PDMS.

RESULTS AND DISCUSSION

The elastic modulus of the thin PS films was determined by exploiting a wrinkling instability of a stiff film on a compliant elastic substrate [4,6]. A sinusoidal wrinkling instability is induced above a critical strain, which is dependent on the ratio of the elastic modulus of the substrate to the film. The observed wrinkling wavelength, λ, is dependent on the ratio of the film to the substrate plane-strain moduli ($\overline{E}_f / \overline{E}_s$) and the film thickness, h_f, as [4]:

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

Through the rearrangement of eq (1) the elastic modulus of the film can be determined as a function of readily measurable variables, such as film thickness. Figure 1 shows the modulus as a function of film thickness for a range of PS with varying M_n. For M_n > 3.1 kg/mol the moduli as a function of film thickness is statistically invariant with a critical length scale of ≈50 nm where deviations from the bulk modulus are observed. This independence of the mechanical properties of thin PS films on molecular mass is consistent with recent reports of T_g for supported PS films [7]. However as M_n is reduced to 1.3 kg/mol and 1.1 kg/mol, the bulk modulus is reduced to ≈1.1 GPa and the critical length scale at which deviation from the bulk occurs is increased to ≈ 80 nm and ≈ 100 nm, respectively. The enhancement of nanoconfinement effects with decreasing polymer size is inconsistent with finite size arguments [8]. Rather, it appears as though interfacial effects are responsible for the observed size dependent behavior [9].
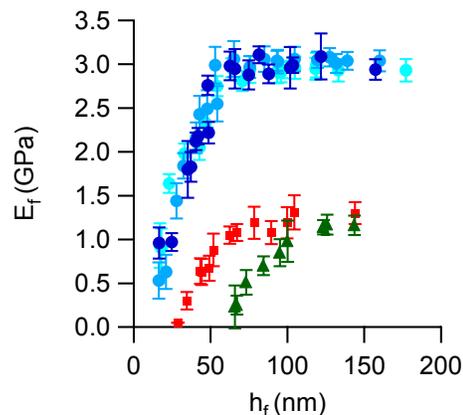
Figure 1. Elastic moduli of PS M_n>3.1 kg/mol (●), M_n=1.3 kg/mol (■), M_n=1.1 kg/mol (▲) thin films as a function of film thickness. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

A gradient in T_gs emanating from the free surface has been demonstrated by the fluorescence labeling experiments of Ellison and Torkelson [9]. However from the mechanical measurements presented here, there is no way to *a prioi* predict the shape of a gradient in modulus from the free surface that might be responsible for the thickness dependence of the PS modulus. In an attempt to simplify the near surface modulus, a bilayer model consisting of total thickness, h, a bulk layer of modulus, $\overline{E}_f$, and a free surface layer of fixed thickness, h^*, with a modulus that deviates from bulk, $\overline{E}_f^*$, has been proposed and is shown in Equation 2 [10]. This surface layer thickness is independent of the total film thickness, but dependent upon the choice of polymer.
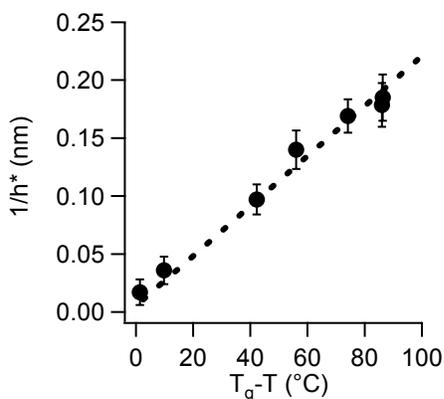
$$\overline{E}_{f,Stretching} = \overline{E}_f\left(1-\frac{h^*}{h}\right) + \overline{E}_f^*\left(\frac{h^*}{h}\right) \qquad (2)$$

This simple model is able to accurately capture the thickness dependent moduli for the different PS films using the parameters shown in Table 1. As M_n is reduced, the elastic modulus of the free surface is decreased and the thickness of the free surface layer increases. Statistically, the thickness of the surface layer is independent of molecular mass for $M_n > 3.1$ kg/mol. These PS samples are deep in the glass at ambient temperature where the wrinkling is performed. For the 1.3 kg/mol and 1.1 kg/mol samples, the T_g of PS approaches room temperature and the thickness of the free surface layer obtained from fitting rapidly increases.

Table 1. Physical Properties and Bilayer Fit Data for PS Thin Films

M_n (kg/mol)	$T_{g, bulk}$(°C)	$\overline{E}_f^*$ (MPa)	h^* (nm)
990	106.3 ± 2.0	170 ± 40	5.4 ± 1
492.5	106.1 ± 2.5	140 ± 50	5.6 ± 1.2
10.2	94.1 ± 2.3	95 ± 79	5.9 ± 1.6
3.1	76.1 ± 2.2	86 ± 46	7.0 ± 1.9
1.3	29.9 ± 3.1	46 ± 10	27.5 ± 1.6
1.1	21.3 ± 3.2	26 ± 3	59.1 ± 2.5

The thickness of the surface layer is determined by fitting the moduli data as a function of film thickness for a given M_n PS to the bilayer model. It appears that the quench depth into the glass (T_g-T) is related to the thickness of a soft surface layer. This is consistent with predictions from Bohme and de Pablo [3]. Figure 2 shows the inverse of the free surface layer as a function of quench depth. The data suggests there is a linear correlation between the quench depth and the thickness of the free surface layer for these different M_n PS films. This result is consistent with recently reported thickness dependent modulus of a series of poly(alkyl methacrylate) films [11].

behavior to the presence of this surface layer. An earlier onset of deviation in the modulus from the bulk value as film thickness is reduced is found for low molecular mass PS films. However, the simplified model utilized here does not provide insight into possible local distribution of moduli in these films. Experimental and theoretical work is required in order to gain further insight into nature of the near surface moduli in polymer films.

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Figure 2. Impact of quench depth into the glass on the thickness of soft free surface layer. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement.

The results suggest that the modulus deviations observed in thin glassy polymer films are significantly influenced by the quench depth into the bulk glass (T_g - T). Additionally as the quench depth of the film into the glassy state decreases, the thickness of a soft surface layer increases. We attribute the observed differences in thin film modulus