Influence of Cross-Link Density on the Thermal Properties of Thin Polymer Network Films

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Introduction

The properties of thin polymer films are known to be different than the properties of bulk polymers. Both dewetting studies^{1,2} and temperature-dependent thickness measurements³ showed that thin polystyrene films can exhibit polymer mobility even at temperatures well below that of the bulk-polymer glass transition (T_g) . Subsequent work by a wide range of groups has shown that the thermal properties in thin polymer films can be different than those of the bulk and will depend on the polymer/substrate interactions.⁴⁻²⁰ With favorable polymer/substrate interactions, $T_{\rm g}$ can increase and the coefficients of thermal expansion (CTE) can decrease. $^{4-11}\ For\ weak\ polymer/$ substrate interactions, T_g can decrease and CTE can increase.^{4,5,8,10,12,13} For free-standing films, T_g decreases dramatically.¹⁴

Most of the work to date probing the thermal properties of ultrathin polymer films has focused on low-polydispersity thermoplastic polymers [predominantly polystyrene-based polymers and poly(methyl methacrylate)].

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However, one class of polymer films that has not been as thoroughly studied is cross-linked polymers. The interfacial properties of cross-linked polymers are important in technical applications such as fiber-reinforced composites, nanocomposites, artificial tissue scaffolds, electronics packaging, antireflective coatings, and general adhesive applications.

In this work, we use X-ray reflectivity to probe the thermal properties of thin cross-linked polymer films adhered to silicon wafers. Networks with two different cross-link densities were used. The network was composed of an epoxy monomer cross-linked by a diamine hardener (see Figure 1). The cross-link density of the network was varied by adjusting the length, *n*, of the propylene glycol spacer in the diamine hardener.

Experimental Section

Unless otherwise stated, all chemicals were used as obtained from Aldrich Chemical Co. (Milwaukee, WI).²¹ Silane coupling agents were used as received from Gelest (Tulleytown, PA).

The cross-linked polymer network was an amine-hardened epoxy system composed of a stoichiometric ratio of diglycidyl ether of bisphenol A (DGEBA, Tactix 123, Dow Chemical Company) mixed with poly(propylene glycol) bis(2-amino propyl ether) (Jeffamine D400 or D230, Aldrich Chemical Co.). The molecular mass of the hardener was 400 or 230 g/mol for the D400 and the D230, respectively. The resin monomers are shown in Figure 1. The epoxy films were spun-cast onto a silicon wafer from propylene glycol methyl ether acetate (PGMEA). Before the monomers were dissolved in PGMEA, the resin was partially cured to build up the polymer viscosity. This was necessary because the uncured epoxy will dewet the substrate. Once cast onto the silicon wafer, the films were cured at 20 °C for 12 h under vacuum. For the DGEBA/D400 system, this was followed by curing under vacuum at 40, 60, 80, and 100 °C for 3 h at each temperature. Finally, the resin was postcured at 150 °C for 3 h under a vacuum of 10^{-4} to 10^{-5} Pa. The vacuum was required to completely remove the residual PGMEA, which has a boiling point near 140 °C. For the DGEBA/D230 system, the initial cure at 20 °C for 12 h under vacuum was followed by subsequent curing at 40, 60, 80, 100, 120, 140, 160, 180, and 200 °C under vacuum. The slow cure cycle was used to allow ample time for the relaxation and cure of the spun-cast network. The postcure temperature was chosen to be above the highest measurement temperature. The cured films were smooth with a roughness less than 10 Å in all cases, as was determined by X-ray reflectivity.

The silicon wafer surface was treated in a variety of ways, as is discussed elsewhere.²² One treatment left an oxide-coated surface (SiO_x) with a water contact angle less than 5°. Another treatment was a wafer coated with a thin layer of propyltriethoxysilane (PTS) having a contact angle greater than 90°. The third treatment was a wafer coated with a thin layer of aminopropyltriethoxysilane (APS) having a water contact angle ranging from 45 to 55°.

Thermal expansion measurements were conducted on an X-ray reflectometer (Scintag) with 1.54-Å radiation from a Cu Ka source. For the DGEBA/D400 films, the samples were held at 140 °C under a vacuum of 10⁻⁶ Pa for 6 h prior to any measurements. For the DGEBA/D230 films, the samples were held at 180 °C under a vacuum of 10^{-6} Pa for 6 h prior to any measurements. The thickness was then measured at increments of 10 °C, starting at the elevated temperature through cooling to 20 °C. A subsequent heating cycle was then performed back to the elevated

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⁽²¹⁾ Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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Figure 1. Structure of the resin monomers. The top is DGEBA, and bottom is D400.



Figure 2. Rubbery CTE plotted as a function of the film thickness for DGEBA/D230 epoxy films, illustrating a lack of dependence between the CTE and the film thickness. In the inset, the normalized thickness as a function of temperature for DGEBA/D230 polymer films of different thicknesses on SiO_x-coated wafers is plotted, further illustrating the independence of both the apparent glass transition temperature and the CTE with the film thickness. The relative standard uncertainty in the film thickness is represented by the data scatter in the inset. The error bars were estimated from the data scatter for each particular thickness-versus-temperature plot.

temperature. For all the films, the cooling and heating cycles overlapped, indicating a stable polymer film. Before each thickness measurement, the sample was annealed at the measurement temperature for 1 h.

Results and Discussion

Figure 2 plots the rubbery CTE for the DGEBA/D230 films as a function of the film thickness, illustrating that the rubbery CTE for these tightly cross-linked polymer films is independent of the film thickness. The inset in Figure 2 shows the thickness-versus-temperature plots for the DGEBA/D230 films of various thicknesses on SiO_x wafer surfaces. The film thickness, Z, is normalized with the film thickness at 20 °C. The bulk-glass transition of the network is demarcated by the arrow and ranged from 85 to 90 °C, as was measured by differential scanning calorimetry. The inset in Figure 2 illustrates that the thin epoxy films do not exhibit any change in either the glassy or the rubbery CTE. In addition, if we define the apparent glass transition of the thin films as the discontinuity in the slope of the thickness-versus-temperature plots, the thin films do not exhibit a change in apparent glass transition temperature. This result is different than what has been observed for thermoplastic films [such as polystyrene and poly(methyl methacrylate)], where both the glass transition temperature and CTE can either increase or decrease with the film thickness depending on the strength of the polymer/substrate interactions.



Figure 3. Thermal expansion (for temperatures between 40 and 140 °C) plotted as a function of the film thickness for the DGEBA/D400 films on the three different surface treatments. The filled circles show the CTE for epoxy films on a SiO_x-coated wafer surface. The triangles show the CTE for epoxy films on an APS-coated wafer surface. The squares show the CTE for epoxy films on a PTS-coated wafer surface. The decrease in the rubbery CTE is independent of the wafer surface treatment. Error bars reflecting the uncertainty in the thermal expansion were estimated from the scatter in the thickness-versus-temperature plots for each film. In the inset, the normalized thickness as a function of temperature for typical DGEBA/ D400 films is plotted. The top curve is for an 830-Å thick film on the PTS-coated wafer. The middle curve is for a 120-Å film on the PTS-coated wafer. The bottom curve is for a 75-Å film on the APS-coated wafer. The arrow in the inset demarcates the bulk-glass transition temperature for DGEBA/D400. The line in the inset represents a typical glassy CTE for thin polymer films.

Generally, for linear-chain polymers with a favorable polymer/substrate interaction, $T_{\rm g}$ will increase and the expansion coefficients will decrease.^{4–11} Here, we have a silicon oxide layer on the wafer surface, which contains hydroxyl groups. The hydroxyl groups on the substrate will have a favorable interaction with the epoxy resin through either hydrogen bonding with residual hydroxyl groups in the cured polymer or covalent bonding between the epoxy in the resin and the silicon surface hydroxyl. Despite this favorable interaction, the thermal properties of the thin epoxy films remain unchanged. We propose that, for polymer networks, the cross-link structure will dominate or dampen the influence of the polymer/substrate interactions.

If the cross-linking screens the influence of the polymer/substrate interactions, then the effectiveness of this screening should be dependent on the cross-link density. As the cross-link density decreases, the polymer/substrate interaction will have an increasing impact on the thin-film thermal properties. The inset in Figure 3 shows thickness-versus-temperature plots for DGEBA/D400 films of various initial thicknesses. The thickness is normalized with the film thickness at 20 °C. The arrow demarcates the bulk-polymer $T_{\rm g}$. As the film thickness decreases, the rubbery CTE is decreasing. The line

represents a typical glassy CTE value for polymer films of $0.8 imes 10^{-4}$ K $^{-1}$. Even though the apparent $T_{
m g}$ values of these films cannot be accurately determined as a result of the small number of data points below the bulk $T_{\rm g}$, the thin epoxy films clearly exhibit glassy expansion values at temperatures greater than the bulk T_{g} . In a previous publication, we demonstrate that ultrathin DGEBA/D400 films exhibit glassy expansion behavior 20-40 °C above the bulk-polymer T_g , suggesting an increase in the apparent T_g for these thin films.²² Qualitatively, this increase in the apparent T_g was independent of the silicon wafer surface treatment.²² Figure 3 plots the total thermal expansion, over the temperature range from 40 to 140 °C, versus the thickness of the DGEBA/D400 epoxy films at 20 °C. A transition occurs from "bulklike" to "confined" expansion near 200 Å, with the thinner films displaying smaller expansions. Neutron scattering studies on a similar epoxy resin provide a length scale of 20 Å for the end-to-end distance between cross-links.^{23,24} Figure 3 illustrates that the transition from "confined" expansion to "bulk" expansion corresponds to a range of 10 crosslink junctions.

Figure 3 emphasizes that the thermal expansion of the epoxy films was *independent* of the wafer surface treatment. The epoxy films exhibited the same decrease in the rubbery CTE with decreasing film thickness whether the wafer surface was coated with SiO_x, APS, or PTS. As is mentioned in the Introduction section of this paper, the thin-film thermal properties for linear-chain polymers dramatically depend on the substrate/polymer interactions. This clearly illustrates that network films can behave differently than thermoplastic polymer films and supports the hypothesis that for polymer networks the cross-link structure will dominate or dampen the influence of the polymer/substrate interaction.

A possible explanation for the decrease in the CTE for the DGEBA/D400 films is that the cross-link density of the thin epoxy films is different than the cross-link density for the thick films. However, swelling thick and thin epoxy films in deuterium-labeled acetone showed that both exhibited the same acetone uptake, thickness change, and uniform acetone profile, as were measured by neutron reflectivity, illustrating that both thick and thin epoxy films have similar cross-link densities. In addition, because the thick and thin epoxy films were from the same resin formulation (progressively diluted with PGMEA), segregation of one of the resin monomers or small molecularmass fractions of the resin to an interface during curing is the only potential cause for variations in the film crosslink density. With the epoxy films in this study, the polymer viscosity was increased by partially curing the network before spin casting, making it unlikely that significant monomer segregation occurs. In addition, segregation of monomers to the interfacial region would lead to off-stoichiometric network curing and likely cause a larger thermal expansion and decrease in $T_{\rm g}$. If segregation was an issue, we would expect the surface treatment to influence this segregation, but there was no such effect. Because the resin monomers are relatively monodispersed, in the absence of significant segregation the interfacial cross-link density will not change, as is suggested by the neutron reflectivity swelling data.

Another possible explanation for the confined expansion in low cross-link density thin films is the orientation of the network molecules. This would allow the hydroxyl

groups on the reacted epoxy monomers to hydrogen bond more effectively with each other and constrain the mobility. The higher cross-link density films may not have enough local mobility to allow for this orientation and hydrogen bonding. It is well-known that increasing the cross-link density or chain stiffness in polymer films will increase the glass transition temperature.^{25,26} It has also been demonstrated that segmental relaxation in highly cross-linked polymers requires greater cooperativity than that in loosely cross-linked systems.^{27–29} It is, therefore, more likely that a loosely cross-linked polymer will be perturbed by the substrate interface in such a way that the chain segments can order, pack, orient, or hydrogen bond more efficiently, resulting in the observed increase in the apparent $T_{\rm g}$ and decrease in the thermal expansion for the loosely cross-linked thin films.

The epoxy films used in this study were partially cured before dissolving the polymer in PGMEA and spin casting to build up the resin viscosity and prevent dewetting. We believe that the predominant impact of the partial curing is to eliminate significant monomer segregation at the interfaces in the film. Although the spinning process could potentially induce deviations in the stress, strain, and orientation of the polymer films, we believe that these deviations were annealed away during the slow curing cycle for the films. Evidence supporting this is that the DGEBA/D230 films had apparent T_g values similar to that of the bulk resin, suggesting that deviations in the film structure from spin casting did not influence the thinfilm thermal properties.

Conclusions

X-ray reflectivity was used to characterize the thermal expansion of thin cross-linked polymer films. Changing the molecular mass of the hardener varied the cross-link density of the network. When the smaller-molecular-mass hardener was used (high cross-link density), no changes in the apparent glass transition temperature or CTE were observed in the thin films. When the larger-molecularmass hardener was used (low cross-link density), a transition from "bulk" to "confined" expansion occurs near 200 Å, where thinner films exhibit smaller rubbery expansion coefficients. For the lower cross-link density network, the thermal expansion behavior of the films was *independent* of the substrate surface treatment, which varied in both the surface energy and the strength of the bonding interactions with the polymer. We propose that the cross-link structure in polymer networks dominates or screens the influence of the polymer/substrate interactions on the properties of the polymer films. This screening effect will be increasingly important with higher cross-link densities. The results show that cross-linked polymer films can behave differently than thermoplastic polymer films, where the thermal properties can be strongly dependent on the film thickness and substrate surface treatments.

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