Thickness Dependence of the Glass Transition Temperature in Thin Polymer Films

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Introduction

Recently, focus is given to the study of the glass transition temperature (T_g) in thin polymer films due to its importance in technology and in science. Keddie et al. gave the first direct evidence for reduction in T_g with decreasing thickness for Polystyrene thin film coated on Si wafer. When the thickness of the film was below $400\,\text{Å}$, the reduction in T_g was apparent and the measured T_g was not dependent on the molecular weight. It was suggested that the reduction of T_g is caused by the presence of a liquid layer at the surface. On the other hand, other experiments show rather contradictory. T_g in the thin polymer film coated on a strongly favorable substrate increases with decreasing film thickness. These results revealed that both surface and interface affect the T_g in thin films.

Experimental

Thin films of different thickness were prepared by spin-coating polymer solutions of various concentrations at a speed of 2000 rpm on the clean native-oxide surface of a Si wafer (100). Ellipsometric angles were continuously monitored while the sample was being heated or cooled at a constant rate of 2K/min. X-ray reflectivity measurements were performed at the Pohang Accelerator Laboratory in order to measure the thickness of very thin film. Below and above T_g, the thickness of the film linearly increases, and the two straight lines intersect at T_g. The investigated systems are listed in Table 1.

Table 1. Investigated samples

Homopolymer	Poly(α-methylstyrene)
Random Copolymer	Poly(styrene-co-methyl methacrylate) Poly(2-vinyl pyridine-co-styrene)
Blend	1) Poly(2,6-dimethly-p-phenylene oxide)/Polystyrene 2) Poly(styrene-co-methyl methacrylate)/ Poly(2,6-dimethly-p-phenylene oxide)

Results and discussion

The thickness dependence in T_g was shown for all studied systems. Figure 1 shows the measured T_g of poly(α-methylstyrene) plotted against film thickness.
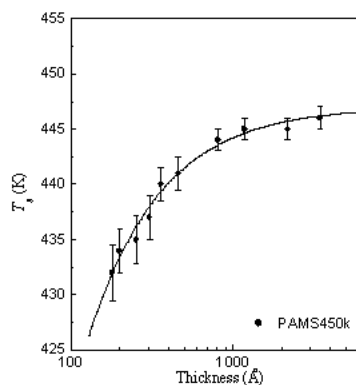

Figure 1. Measured glass transition temperature (T_g) vs film thickness for the PAMS thin film. The solid line is a fit of the measured T_g by eq. 1

The measured T_g pattern with thickness can be fitted by empirical equation 1.

$$T_g(t) = \frac{T_{g,\infty} t}{\xi + t} \qquad (1)$$

In equation 1, t is the thickness of polymer film and $T_g(t)$ is the thickness dependent T_g of the film. $T_{g,\infty}$ is the saturation level with increasing thickness, ξ decides the saturation rate of growth in this function. As t decreases to $0\,\text{Å}$, T_g converges to zero degree, and as t increases, $T_g(t)$ approaches to $T_{g,\infty}$. The best fit parameter values are $T_{g,\infty} = 446.8 \pm 0.4\text{K}$, and $\xi = 6.3 \pm 0.6\,\text{Å}$ for Poly(α-methylstyrene)

To explain the thickness dependence, a continuous multilayer model was proposed. T_g of polymer surface is much lower than that of the bulk, and it gradually converges to a bulk values with increasing distance from the surface of the film. Based on continuous multilayer model, the depth-dependent T_g, $S_g(x)$, can be derived.

$$S_g(x) = T_{g,\infty} \frac{x(2\xi + x)}{(\xi + x)^2} \qquad (2)$$

In equation 2, the variable x is the distance from the extreme edge of the film surface and the magnitude of the constant $T_{g,\infty}$ is the bulk T_g. The fitting parameter ξ can be replaced by the statistical segmental length of the polymer. For a given polymer, this statistical length can be calculated from an assumption that two rotatable parts in the chain are a unit segment.

ξ also reveals a composition dependence in thin PS/PPO miscible blend films. ξ in miscible blend follows linear additive behavior $\xi = w_1 \cdot \xi_1 + w_2 \cdot \xi_2$. ξ in random copolymer might follow linear additive behavior.

Polymer may experience the restrict mobility at the interface region. For the case where a specific interaction between polymer and substrate exists, the restrict mobility at the interface region might be taken into consideration in describing the T_g behavior of thin polymer films. The form of T_g profile at the interface region would be similar to that of the surface. The thickness dependent T_g function including the effects from the surface can be proposed in equation 3.

$$T_g(t) = T_{g,\infty} \frac{t(2k+t)}{(\xi + t)^2} \qquad (3)$$

Here, an adjustable parameter (k) is needed, and this parameter k can be obtain from fitting this equation with the measured T_g versus the thickness data at given polymer–substrate pair. If there is no specific interaction between polymer and substrate, parameter k value is $\xi/2$, and the equation3 becomes equation 1. For free standing films, parameter k value becomes 0.

When PMMA or P(2)VP is coated on the strongly favorable substrate, T_g shows increasing tendency with decreasing film thickness. At surface and interface region, there exist T_g different region with the bulk values, respectively, and T_g of the thin film can be determined by both contributions. The free surface act to lower T_g, while the substrate raises T_g depending on the interaction between the polymer and the surface of the substrate. In the case of P(2)VP, the effect of interface in much higher than that of the surface, so the measured T_g shows an increasing tendency with decreasing film thickness. T_g of thin poly(styrene-co-methyl methacrylate) and poly(2-vinyl pyridine-co-styrene) film coated on a native oxide surface of Si wafer (100) can be properly fitted by equation 1. The interaction parameter k is dependent on the composition of random copolymers. For the estimation of k values of thin random copolymer film, a parallel type additive function was proposed.

References

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