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Thickness and Composition Dependence of the Glass Transition Temperature in Thin Homogeneous Polymer Blend Films

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Introduction

Nowadays there is much interest in thin polymer films due to their importance in science and technology.¹ Studies on T_g in thin polymer films have revealed that it is dependent on film thickness and that such dependence increases with decreasing film thickness.^{2–13} As for the case where the interaction between the polymer and the substrate is not large enough to affect the glass transition, T_g usually decreases with decreasing thickness.^{2,6,12} On the other hand, T_g of films coated on a strongly favorable substrate increased with decreasing film thickness due to a strong interaction between polymer and substrate.^{3,5,7} Although many experimental works have been performed on T_g in typical homopolymer thin films, there has been no work dealing with polymer blend systems. The concept of physically blending two or more existing polymers to obtain new products has been attracting widespread interest and commercial utilization.¹⁴ This blending method can be used as a good way to control the basic properties of polymers without sacrificing many attractive properties of each polymer. One of the most attractive compatible blends is that of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS). Perhaps the most unambiguous criterion of polymer compatibility is the detection of a single glass transition temperature whose temperature is intermediate between those corresponding to the two-component polymers. For the bulk blend systems, PPO and PS are known to be compatible in all compositions.^{14–16}

In this study, to find out the thickness dependence of T_g depression in the compatible PPO and PS blend thin films, the T_g 's of the films are measured as functions of thickness (200–1200 Å) and composition and compared

with the calculated T_g by the equation, which has been proposed to describe the thickness dependence of the glass transition temperatures of homopolymers.^{12,13}

Experimental Section

The investigated sample consists of a thin polymer film coated onto the clean native oxide surface of a Si wafer (100). Poly(2,6-dimethyl-*p*-phenylene oxide) (PPO) used was purchased from Scientific Polymer Products and has $M_w = 244\,000$ g/mol and $M_n = 32\,000$ g/mol. Polystyrene (PS) used was purchased from Pressure Chemicals and has $M_w = 90\,000$ g/mol and $M_n = 87\,000$ g/mol. Films of different composition blends of PPO and PS were prepared by solution blending and spin casting these solutions at 0, 30, 50, and 70% PPO weight contents. Thin films of different thicknesses were prepared by spin coating toluene solutions of various concentrations at a speed of 2000 rpm for about 40 s on a Si wafer. To ensure that all experiments were done on samples with equivalent and well-defined thermal histories, samples were annealed for 10 min at about 30–60 K above the bulk T_g before the experiments. Before and after T_g measurement, optical microscopy and atomic force microscopy (AFM) were used to observe the morphology of the samples. There were no remarkable changes in sample morphology before or after the T_g measurement experiment, so it can be confirmed that dewetting¹⁶ did not occur in this experimental condition. The heating stage, devised in our laboratory, was used in conjunction with an ellipsometer. A single-wavelength null-type ellipsometer (Rudolf Research; AutoEL II) was used, and the ellipsometric angles (ψ , δ) were continuously monitored while the sample was being heated or cooled at a constant rate of 2 K/min. DSC (Perkin-Elmer; DSC-7) was used to measure the bulk T_g of each composition sample, and the scanning rate (2 K/min) was controlled at the same rate as that used with the ellipsometric experiment.

Results and Discussion

The variable temperature ellipsometric technique has been widely used for measuring T_g in thin polymer films by detecting volumetric changes in temperature dependence between the glassy and rubbery states.^{2,3,17,18} The experimental details of the usual ellipsometric method to measure T_g have already been published elsewhere.^{12,13} For the usual ellipsometric scans, there was only one observable T_g of these films in the intermediate between those corresponding to the two-component polymers, as can be seen in Figure 1. For similar thicknesses, the T_g of blend films decreases with increasing the content of PS. Although the PPO homopolymer could decompose approaching its T_g (483 K) in air, the blends of PPO and PS are known to be suitably stabilized against thermal oxidation.^{19,20} To avoid the possibility of degradation in the sample films, the temperature was not raised over 460 K. Shifts in T_g in heating and cooling scans were not found throughout the entire experiment. Figure 2 shows the glass transition temperatures of the PPO and PS blend thin films as functions of composition and thickness. As can be seen in this figure, the T_g of these samples is dependent

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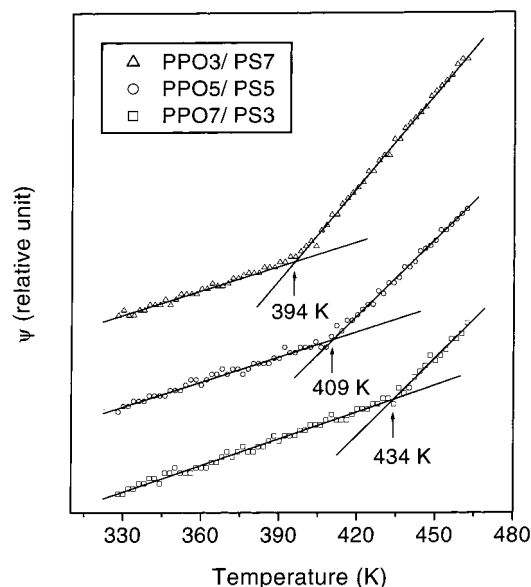


Figure 1. Typical ellipsometric cooling scan for PPO and PS blend thin films. The thicknesses of PPO3/PS7, PPO5/PS5, and PPO7/PS3 are 477, 464, and 457 Å, respectively. The vertical arrow indicates T_g for the film. The angle of incidence of radiation is 70° , and its wavelength is 6328 Å. These data points are obtained every minute during the cooling process at a rate of -2 K/min.

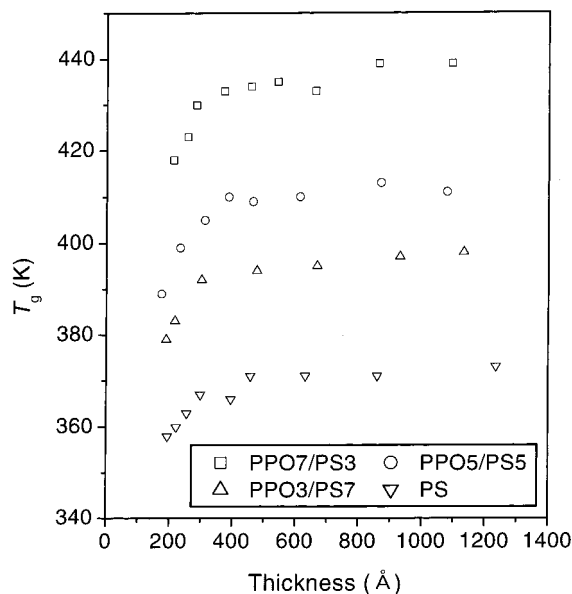


Figure 2. Measured glass transition temperatures of the PPO and PS blend thin films as functions of composition and thickness.

on the thickness of the samples as well as on their composition. As the thickness of the films or the PPO content increases, the measured T_g of the thin films increases.

To determine the composition dependence for the same dimensions, the T_g 's of thin films whose thicknesses are similar are plotted in Figure 3. A number of equations have been proposed for relating the T_g of miscible blends to the composition and T_g of its constituents. One of them is the Fox equation:²¹

$$1/T_g = w_1/T_{g,1} + w_2/T_{g,2} \quad (1)$$

where the T_g is the glass transition temperature of the

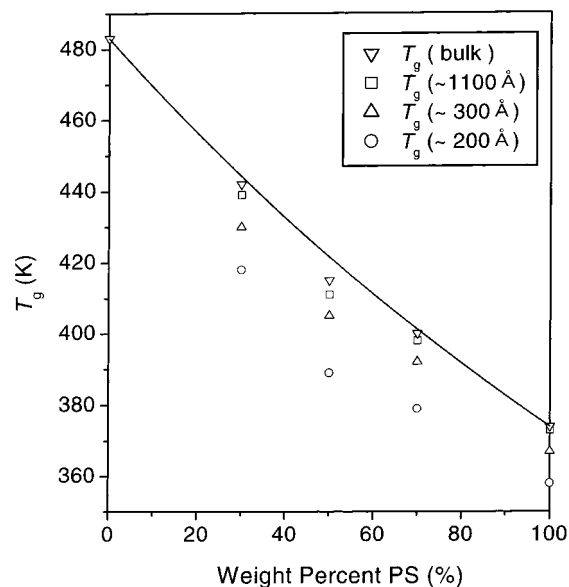


Figure 3. Measured glass transition temperatures of PPO/PS blend thin films as a function of blend composition for three films thickness. The bulk T_g (down triangle) is measured by DSC, and the solid line is constructed by the Fox equation ($1/T_g = w_1/T_{g,1} + w_2/T_{g,2}$).

binary blends, $T_{g,1}$ and $T_{g,2}$ are the glass transition temperatures of polymers 1 and 2, and w_1 and w_2 are the mass fractions of polymers 1 and 2. This eq 1 was used to construct a solid line for the bulk T_g measured by DSC. For the thickest films (1100–1200 Å) of each composition, the T_g of these films shows a similar value with that of the bulk. Because the T_g of PPO homopolymer thin films could not be obtained, the Fox equation was not applied to the case of thin films. However, as shown in Figure 3, the composition dependence of T_g in thin films whose thicknesses are similar seems to be like that of the bulk. Therefore, it is known that the composition dependence of T_g in thin polymer films does not change with its thickness, and the Fox relationship still holds.

To find out the thickness dependence of T_g for the same composition, eq 2 was used.

$$T_g(t) = \frac{T_{g,\infty}t}{\xi + t} \quad (2)$$

This equation was used to describe the thickness dependence of T_g in polymer thin films, where there is no specific interaction between the polymer and the substrate.^{12,13} In eq 2, t is the thickness of the polymer film and $T_g(t)$ is the thickness-dependent glass transition temperature of the polymer film. The magnitude of the constant $T_{g,\infty}$ was the bulk T_g , and the parameter ξ could be obtained by fitting the measured T_g data in thin films with this function. The measured T_g data for each composition sample, presented in Figure 2, were fitted by eq 2, where $T_{g,\infty}$ is the bulk T_g . The parameter ξ was obtained from this fitting. The bulk T_g measured by DSC and the fitted parameters (ξ) are summarized in Table 1. As the content of PPO increased, the fitted values also increased. The parameter ξ is a material-dependent parameter and defines the degree of thickness dependence of T_g in thin films.¹² According to the previous results, the statistical segment length (l) (the calculated value in an assumption that two rotatable parts in the chain are a unit segment) corresponds to

Table 1. Physical Parameters of PPO, PPO7/PS3, PPO5/PS5, PPO3/PS7, and PS

sample	bulk T_g^a (K)	ξ^b (Å)	l^c (Å)
PPO	483		10
PPO7/PS3	442	9.5	
PPO5/PS5	415	9.1	
PPO3/PS7	400	8.4	
PS	374	7.0	6.9

^a T_g is measured by DSC, and the scanning rate was controlled at the same rate as with the ellipsometric experiment. This bulk T_g was used as $T_{g,\infty}$ in eqs 1 and 2 in the text. ^b ξ is the parameter fitted by eq 1 in the text with the experimentally measured T_g data in thin films. ^c l is the statistical segment length for each sample. $\langle R_0^2 \rangle = nl^2$ is used to obtain this segment length. Two-rotatable parts in the polymer chain are regarded as the basic unit for this segmental length. The $\langle R_0 \rangle$ of each polymer was obtained from previous experimental literature (PPO,²² PS²³).

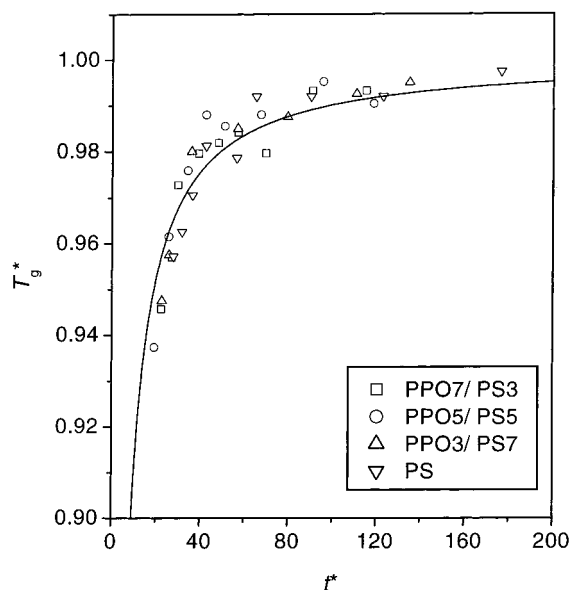


Figure 4. Master curves for glass transition temperatures in the PPO/PS blend and PS thin films. T_g^* ($=T_g(t)/T_{g,\infty}$) is the normalized $T_g(t)$, and t^* ($=t/\xi$) is the normalized film thickness. The solid line is the master curve for thickness-dependent T_g , which is drawn by eq 3. The open square, circle, up-triangle, and down-triangle represent the normalized data points of PPO7/PS3, PPO5/PS5, PPO3/PS7, and PS, respectively.

the fitted parameter ξ .¹² These calculated segmental lengths (l) of PPO and PS are added in Table 1 for comparison. Therefore, the larger value for PPO can be estimated from the larger length scale due to its longer statistical segment length, and it is reasonably expected that the blends have an intermediate average value for their ξ .

Equation 2 can be expressed as a general form, as shown in eq 3, and this relationship holds regardless of the kinds of polymers.¹²

$$T_g^* = \frac{t^*}{1 + t^*} \quad (3)$$

In the above equation, T_g^* ($=T_g(t)/T_{g,\infty}$) is the normalized T_g , and t^* ($=t/\xi$) is the normalized film thickness. Both T_g^* and t^* are dimensionless parameters and

independent of the kinds of samples. Figure 4 exhibits the master curve that is drawn by eq 3, and the measured T_g data are added for comparison after thickness and T_g normalization by their own ξ and $T_{g,\infty}$ at each data point. Regardless of their blend composition, all the measured T_g data are well superimposed in one curve. This means that the origin of T_g depression in thin films may have the same ground between each composition sample. Our previous results concerning the thickness dependence of thin homopolymers also showed this kind of universality in the T_g depression.¹² Therefore, it is confirmed that PPO and PS blends are completely miscible and that molecular miscibility is not affected by their dimensions down to 200 Å. In addition, T_g reduction in thin films with decreasing thickness is a universal phenomenon, and the origins for this phenomenon of homopolymers and miscible blends may be the same.

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