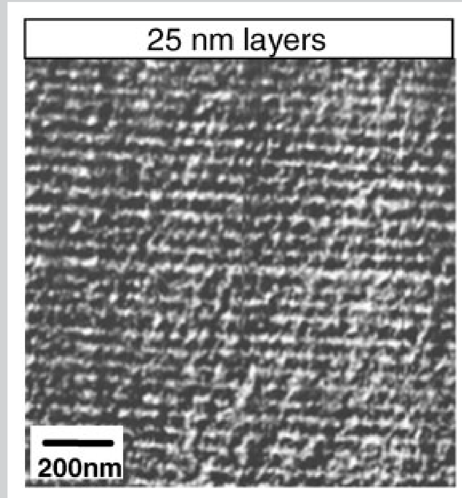
Communication: When two immiscible polymers are brought into intimate contact, highly localized mixing of polymer chains creates an ‘‘interphase’’ region. Materials that are entirely interphase are fabricated by forced-assembly using layer-multiplying coextrusion to form assemblies of thousands of nanolayers. Analysis of the interphase materials with conventional methods of polymer analysis confirms certain theoretical predictions for the first time. The unique properties of the new interphase materials result from lower free volume than the constituents.



Atomic force microscopy phase image from the cross-section of a PC/PMMA nanolayer film with 4096 layers and average layer thickness of 25 nm.

Probing Nanoscale Polymer Interactions by Forced-Assembly

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Introduction

It has been recognized for some time that when two polymers are brought into intimate contact, the interface between them is not perfectly sharp. Highly localized mixing of polymer chains creates an ‘‘interphase’’ region. A vast amount of literature attests the importance of the interphase for polymer adhesion and for compatibility of polymer blends and alloys.[1] Indeed, it is reasonable to consider the interphase of immiscible polymer blends as a third phase with its own characteristic properties.[2] The interphase takes on new significance as nanotechnology and microelectronics drive the fabrication of increasingly thin polymer layers. Under these conditions, as bulk polymers become thinner and more interphase-like, departures in physical properties are expected. Changes in segmental mobility as the thickness scale approaches the size scale of the polymer molecule[3,4] will have consequences for the glass transition temperature (T_g), thermal stability, adhesion, and transport characteristics.[1,4–6] Understanding interphase properties is crucial if polymers are to be integrated effectively into modern technology.

The origin of interfacial mixing is the entropic advantage for chains to diffuse across the boundary. Halving in the conformational entropy of chains at a surface is ameliorated if the chains cross the interface. The entropic advantage for crossing the interface is offset by the negative effect of the interaction energy between incompatible chain segments. The generalized theory developed by Helfand and co-workers is the basis of a quantitative relationship between interphase thickness and the thermodynamic interaction parameter.[7] However, experimental determination of interphase properties has challenged the field. Even measurement of the interphase dimension is difficult and requires extreme care. Nevertheless, existing theoretical and experimental results agree that the dimension of the interphase for immiscible polymers is in the range of 5–10 nm.[8]

Nanolayer processing facilitates the creation of new hierarchical systems. Although this type of polymer nanoprocessing is still far removed from the unique behavior of living cells – in which both complex synthesis and nanoprocessing take place concurrently – layer multiplication is a highly flexible tool for fabricating unique structures of otherwise incompatible polymers. In contrast to the well-known concept of self-assembly,[9] layer-multiplying coextrusion uses forced-assembly to create thousands of alternating layers of the two polymers.[10] Each layer can be less than 10 nm in thickness.[11,12] Although the amount of material in a single interphase between two polymer layers is very small, the layer thickness can be made comparable to the interphase dimension, and the properties of the interphase are multiplied a thousand-fold by the number of identical interphases in the assembly. This enables us to use conventional methods of polymer analysis to probe size-scale-dependent properties as nanolayers became thinner and more interphase-like.

We propose that when the layer thickness becomes comparable to the interphase dimension, the layers lose their identity and a new composition is created that is totally interphase. To test this possibility, we chose an immiscible glassy polymer pair, polycarbonate (PC) and poly(methyl methacrylate) (PMMA) for forced-assembly into nanolayers, and used thermal analysis, gas transport, and positron annihilation lifetime spectroscopy to probe the effect of layer thickness.

Experimental Part

The schematic drawing of layer-multiplying coextrusion in Figure 1 shows how a series of n multiplying elements combines two dissimilar polymers as $2^{(n+1)}$ alternating layers.[11,12] Polycarbonate (PC, $\overline{M}_w = 62$ kg mol^{-1}) and poly(methyl methacrylate) (PMMA, $\overline{M}_w = 132$ kg mol^{-1}) are believed to be immiscible although good adhesion of the pair suggests some level of compatibility.[13,14] Coextruded films of PC and PMMA with different layer thickness were obtained by increasing the number of alternating PC and PMMA layers from 8 to 4 096. Based on total film thickness (200 to 20 μm), the number of layers (8 to 4096), and 1:1 (vol:vol) composition ratio, the average thickness (d) of individual layers ranged from 25 μm to 5 nm. The smallest average layer thickness was less than the end-to-end distance of a polymer molecule (ca. 20 nm).

Embedded films were microtomed through the thickness and cross-sections were examined with an atomic force microscope (AFM) in order to visualize the layers. Glass transition temperatures were determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1}. The density was measured at 23 °C using a density gradient column with a solution of calcium nitrate and water. The detailed procedures were described previously.[15] The oxygen and carbon dioxide transport characteristics at 23 °C and 1 atm pressure were characterized with commercial instruments from Modern Controls, Inc., using procedures described previously.[15] The average free volume hole size was determined by positron annihilation lifetime spectroscopy (PALS) as described previously.[16]

Results and Discussion

Continuous uniform layers are well-resolved in AFM images of films with an average layer thickness of 100 nm and 25 nm (Figure 2). The PC layers are smooth and bright, the PMMA layers are hackled due to brittle fracture during microtoming. Layer thickness measured from the images corresponds well with the calculated average thickness. A different texture is seen in the image of the film with average layer thickness of 10 nm. Instead of distinct layers with straight boundaries, the image shows an irregular periodicity of about 20 nm, or about twice the expected layer thickness.

Micron-sized domains in a mixture of immiscible polymers prepared by conventional melt blending are usually large enough that the blend exhibits a characteristic glass transition for each constituent. Similarly, DSC thermograms of films with layers thicker than 100 nm contain two

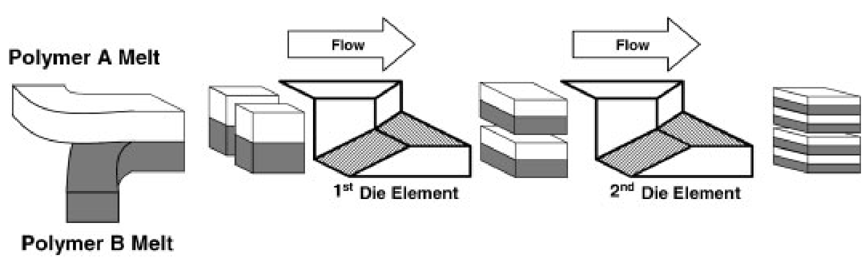

Figure 1. Layer-multiplying coextrusion for forced-assembly of polymer nanolayers. After the polymer melts are combined in the feedblock, the melt stream flows through a series of layer-multiplying die elements; each element splits the melt vertically, spreads it horizontally, and finally recombines it with twice the number of layers. The figure illustrates how two elements multiply the number of layers from 2 to 8. An assembly of n die elements produces $2^{(n+1)}$ layers. Eleven die elements produce 4096 layers. Finally, the melt is spread in a film die to further reduce the layer thickness.

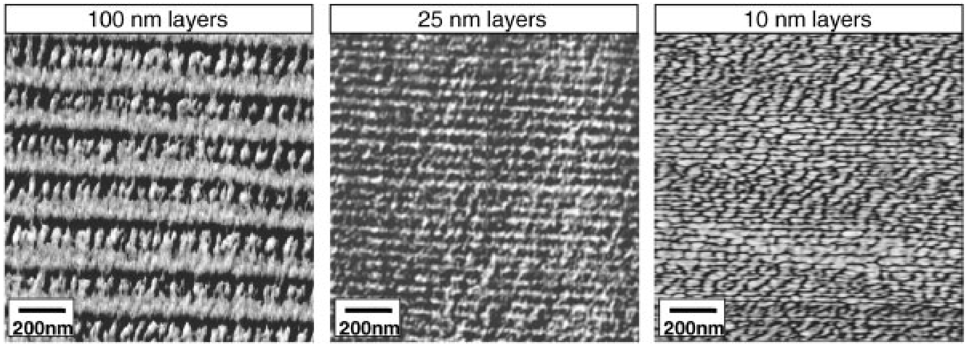

Figure 2. Atomic force microscopy (AFM) phase images of microtomed cross-sections of PC/PMMA nanolayer films. Films with average layer thickness 100 nm and 25 nm show continuous, uniform layers of PC (smooth and bright) and PMMA (hackled). The film with a 10-nm average layer thickness shows an irregular periodicity about twice the average layer thickness.

inflections in heat capacity at 112 °C corresponding to the T_g of PMMA and at 144 °C corresponding to the T_g of PC (Figure 3). However the glass transition temperatures gradually shift closer together as layer thickness decreases below 100 nm. When the layer thickness is 10 nm or less the two inflections merge into a single inflection at a temperature that is intermediate between the glass transition temperatures of PC and PMMA. The breadth of the glass transition, measured as ΔT between the onset and finish of the heat capacity inflection, is about 8 °C for the individual constituents but broadens considerably to about 15 °C when a single inflection is observed.

A single glass transition is contrary to conventional understanding of immiscible polymer blends. A single glass transition is generally taken as evidence of constituent miscibility. Under certain circumstances, blends of PC and PMMA appear to form a miscible blend, however this occurs after prolonged mixing and homogenization is thought to result from transesterification reactions between the constituents.[17] To prevent exchange reactions, we minimize the resident time in the coextrusion multiplying elements to 3 min at about 270 °C. This time is much too short to produce significant transesterification based on melt blending studies.[18] However it is more than sufficient time for achieving an equilibrium interphase.[19] Two additional experiments demonstrate that transesterification is not a significant factor. First, the films easily dissolve in tetrahydrofuran (THF). If exchange reactions were extensive enough to produce a single glass transition, the film would be highly crosslinked and would swell but not dissolve in THF.[17] Second, nanolayer films that exhibit a single T_g on the first heating to 180 °C, exhibit two T_gs corresponding to those of the constituent polymers on the second heating. Interfacial tension-driven breakup destroys the layers and results in a coarse phase-separated morphology with two T_gs. If exchange reactions were extensive enough to produce homogeneity there would be no driving force for interfacial tension-driven breakup of the layers.

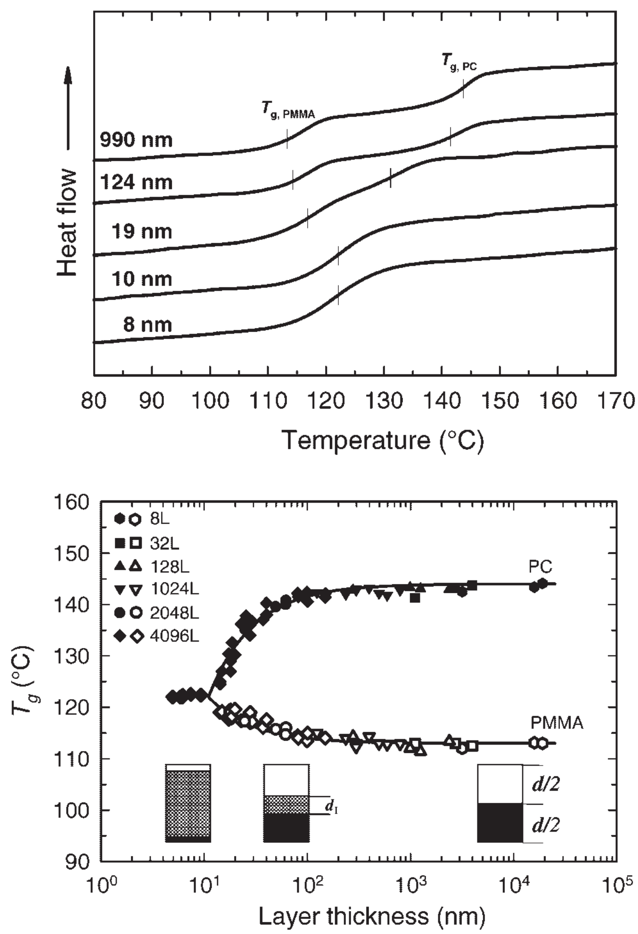

Figure 3. Glass transition behavior of PC/PMMA nanolayer films. In the upper plot, heating thermograms show convergence of the heat capacity inflections corresponding to T_gs of the constituent polymers into a single inflection as the layers become thinner. In the lower plot, the dependence of T_g on layer thickness is described by the three-layer interphase model as illustrated schematically in the figure and as formulated in Equation (1) for $d \geq d_I$ (solid lines).

The convergence to a single glass transition is not symmetrical (Figure 3). The T_g of PMMA increases only about 10 °C, whereas the T_g of PC decreases by 22 °C. The glass transition of a miscible blend usually is described by either the Fox law ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$) or the additive law ($T_g = T_{g1}w_1 + T_{g2}w_2$), where w_1 and w_2 are the weight fractions of the blend constituents. The calculated T_g of a miscible PC/PMMA (1:1 vol:vol) blend is 126 °C from the Fox law and 128 °C from the additive law. In nanolayers the glass transition temperatures of PC and PMMA converge asymmetrically to 122 °C, which is 4–6 °C lower than the calculated values.

Nanolayer films with layers less than 100 nm thick exhibit higher density than films with thick layers. The additive law for a 1:1 (vol:vol) mixture of PC ($\rho = 1.1934$ g cm^{-3}) and PMMA ($\rho = 1.1923$ g cm^{-3}) predicts a density of 1.1928 g cm^{-3}, which accurately describes films with layers more than 100 nm thick within an experimental error (± 0.0003 g cm^{-3}). The density gradually increases to 1.1945 g cm^{-3} in films with a layer thickness less than 10 nm, which is an increase of 0.0017 g cm^{-3} or 0.14 wt.-% over the additive value.

Based on free volume arguments,[20] a density change should be manifest as a T_g shift with ΔT_g given as $\Delta T_g = \Delta v/\Delta\alpha$, where Δv is the change in specific volume and $\Delta\alpha$ is the difference in rubber and glass thermal expansion coefficients ($\Delta\alpha = \alpha_l - \alpha_g$) taken as 2.8×10^{-4} cm^3 g^{-1} K^{-1} from average values for PC and PMMA.[21] A change of 0.14 wt.-% in density corresponds to a change in T_g of 4.3 °C, which is in excellent agreement with the DSC observation of 4–6 °C.

The size of free volume holes can be estimated by positron annihilation lifetime spectroscopy (PALS) even if the total amount of free volume in a polymer glass cannot be reliably accessed by this method. The constituents have average free volume hole sizes of 2.71 ± 0.01 Å (PMMA) and 2.82 ± 0.01 Å (PC) as determined by PALS. In films with layers thicker than 100 nm, the hole size of 2.76 ± 0.01 Å appears to be the additive result for the constituents. However, the hole size is smaller, 2.71 ± 0.01 Å, in the film with a layer thickness of 10 nm. Assuming that the number of holes remains constant and taking the fractional free volume (FFV) as 0.03, a simple calculation shows that the observed decrease in free volume hole size of 5% satisfactorily accounts for the observed increase in density.

Gas transport, like the glass transition, is a molecular scale probe of glassy polymer structure that is amenable to interpretation based on free volume concepts.[15,22] Oxygen permeability (P) and diffusivity (D) of nanolayer films were extracted from the nonsteady state oxygen flux following established procedures,[15] and the oxygen solubility (S) was calculated as $S = P/D$. The series model for permeability of a stack of infinite layers gives $1/P = \phi_{PMMA}/P_{PMMA} + \phi_{PC}/P_{PC}$, where ϕ is the volume fraction of the constituent. If the layers are thicker than 100 nm, P, D and S at 23 °C and 1 atm pressure are independent of layer thickness (Figure 4), and P satisfactorily conforms to this relationship. A substantial increase in P is observed for films with layers less than 100 nm thick. Permeability more than doubles from 0.72 to 1.62 cc (STP) cm m^{-2} day^{-1} atm^{-1}. Gas permeability of a miscible blend is expected to follow the relationship $\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2$.[1] The calculated P for oxygen of a miscible 1:1 (vol:vol) blend of PC ($P = 9.91$ cc (STP) cm m^{-2} day^{-1} atm^{-1}) and PMMA ($P = 0.371$ cc (STP) cm m^{-2} day^{-1} atm^{-1}) is 1.92 cc (STP) cm m^{-2} day^{-1} atm^{-1}, which is significantly higher than the value observed for nanolayers of 1.62 cc (STP) cm m^{-2} day^{-1} atm^{-1}.

The change in P with layer thickness comes mainly from D whereas S remains almost constant. Therefore the increase in D is less than expected for a miscible blend. Apparently the change in hole free volume affects the

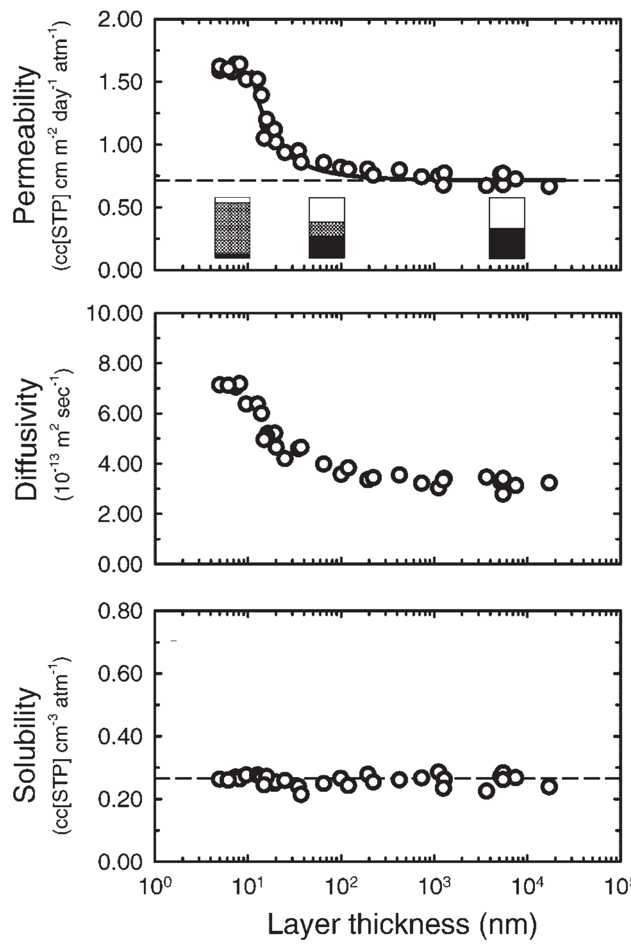

Figure 4. Oxygen transport parameters of PC/PMMA nanolayer films. The effect of layer thickness on oxygen permeability is due to a change in diffusivity rather than a change in solubility. The dependence of permeability on layer thickness is described by the three-layer interphase model as illustrated schematically in the figure and as formulated in Equation (2) for $d \geq d_I$ (solid line).

dynamic component of permeability, however the reason for this is not clear at the moment. Oxygen solubility in glassy polymers at low pressure is determined primarily by excess hole free volume.[15] Lower free volume of nanolayers as demonstrated by higher density and smaller free volume hole size should decrease oxygen solubility according to $\Delta S = \beta \Delta v$, where $\beta = 3.6$ cc (STP) g cm^{-3} atm^{-1}.[22] A density increase of 0.14 wt.-% produces a decrease in S of approximately 5%, which is comparable to experimental uncertainty (2%). Thus S is not sensitive enough to detect the change in free volume, and S is adequately described by the additive law, $S = w_1 S_1 + w_2 S_2$. Similar results are obtained with CO_2 transport. Nanolayer films become more permeable as the layer thickness decreases below 100 nm with P for CO_2 increasing from 4.5 to 9.6 cc (STP) cm m^{-2} day^{-1} atm^{-1}. Again, the increase in P is due to increasing D, whereas S remains constant.

We propose that when the layer thickness in nanolayer films becomes comparable to the interphase dimension, the layers lose their integrity as constituent layers, and the film becomes essentially totally interphase. The composition profile is not homogeneous, but rather undulating with a period that is twice the layer thickness. The composition gradient accounts for the width of the heat capacity inflection at the single T_g (see Figure 3), and also accounts for the irregular periodicity of about twice the average layer thickness in AFM images (see Figure 2). Furthermore, film properties are no longer additive combinations of constituent properties, and instead film properties are dominated by interphase properties. For the PC/PMMA pair, nanolayers with average layer thickness of 10 nm or less present properties of the interphase.

To describe the dependence of physical properties on layer thickness and to obtain a better estimate of interfacial thickness, layers thicker than the interphase are assumed to possess a symmetrical interphase of constant thickness d_I. The dependence of T_g on layer thickness is given by a simple three-layer model, in which constituent layers of thickness $d - d_I$ (d is the average layer thickness) are sandwiched between interphase layers of thickness $d_I/2$ [Equation (1)].

$$T_{g,i} = \frac{(d - d_I)}{d} T^o_{g,i} + \frac{d_I}{d} T_{g,I} \qquad (1)$$

where i refers to either PMMA or PC; $T_{g,I}$ is the glass transition temperature of the interphase and is taken as 122 °C, and $T^o_{g,i}$ is the glass transition temperature of the i constituent, taken as 112 °C for PMMA and 144 °C for PC. The model has d_I as the single adjustable parameter. The best fit of Equation (1) to the data for $d \geq d_I$, included in Figure 3 as solid lines, is obtained with $d_I = 10 \pm 1$ nm.

The three-layer model also applies for gas permeability. The series model formulated for permeability of a 1:1 (vol:vol) composition is calculated by Equation (2).

$$P = 2\left[\frac{(d - d_I)}{d}\left(\frac{1}{P^o_{PC}} + \frac{1}{P^o_{PMMA}}\right) + 2\frac{d_I}{d}\left(\frac{1}{P_I}\right)\right]^{-1} \qquad (2)$$

where P^o_{PC} and P^o_{PMMA} are the permeabilities of PC and PMMA taken as 9.91 and 0.371 cc (STP) cm m^{-2} day^{-1} atm^{-1}, and P_I is the permeability of the interphase taken as 1.62 cc (STP) cm m^{-2} day^{-1} atm^{-1}. The best fit of the data for $d \geq d_I$ is obtained with $d_I = 10 \pm 1$ nm. The fit is included in Figure 4 as a solid line. The CO_2 permeability also conforms to Equation (2) with $d_I = 10 \pm 1$ nm.

The experimental result for d_I can be compared with the theoretical prediction of Helfand and co-workers.[23] For the interphase between immiscible polymers of infinite molecular weight, the equilibrium interpenetration depth, or interphase thickness d_I, with respect to the Flory–Huggins interaction parameter (χ) is given as Equation (3).

$$d_I = \frac{2b}{(6\chi)^{0.5}} \qquad (3)$$

where b is the statistical segment step length and is taken as 6 Å for PC and PMMA. The interaction parameter χ is estimated from the solubility parameters δ of the constituents according to the expression [Equation (4)].

$$\chi = \frac{V}{RT}(\delta_{PC} - \delta_{PMMA})^2 \qquad (4)$$

where V is the molar volume, T is the processing temperature of 543 K, and δ_{PC} and δ_{PMMA} are taken as 19.6 and 19.9 J$^{0.5}$ cm$^{-1.5}$, respectively.[24] The calculated interphase thickness of 9 nm is comparable to d_I determined experimentally from nanolayers, 10 ± 1 nm. The small discrepancy may originate from the infinite molecular weight assumption of the theory as compared with polydisperse ''real'' polymers which contain low-molecular-weight fractions.

This finding suggests that mixing of two dissimilar polymers from the melt can be achieved by forced-assembly. A simple three-layer model describes the layer thickness dependence of the glass transition and the gas permeability. We demonstrate in this communication that the layered nanostructures prepared by forced-assembly using layer-multiplying coextrusion technology provide a model structure to probe interphase structure-property relationships. Experiments with other polymer–polymer pairs demonstrate the generality of this approach and reveal the dependence of interphase thickness on chemical structure of the constituents.

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