Macromolecules **1996,** *29,* 5493−5496

Homopolymer Interfaces Reinforced with Random Copolymers

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Received March 14, 1996; Revised Manuscript Received May 23, 1996⊗

ABSTRACT: The strengthening of the interface between polystyrene (PS) and poly(methyl methacrylate) (PMMA) using a random copolymer $P(S_f\text{-}r\text{-}MMA_{1-f})$, where f is the fraction of styrene in the copolymer, was investigated. The maximal fracture toughness, measured by crack propagation, was found when $f = 0.68$. Neutron reflectivity measurements showed that this value of f corresponded to the point where the interfacial broadening on the PS and PMMA sides of the interface was symmetric. The symmetry of broadening and the optimization of the toughness at $f = 0.68$ are attributable to a composition-dependent segmental interaction parameter.

Introduction

Diblock copolymers can be used for the compatibilization of two immiscible polymers or, at least, limit the size of phase separation. In this use, diblock copolymers serve two distinct functions. First, they work as surfactants to stabilize the microstructure and secondly as adhesion promoters to establish a strong coupling between the phases. The origins of these unique functions arise from the ability of one block to reside preferentially in one component and the other block in the second, as shown schematically in Figure 1a. Each block entangles with the homopolymers on either side of the interface and forms a covalent coupling between them. Numerous studies now exist on the interfacial activity of diblock copolymers.[1−6]

Diblock copolymers, however, represent only one possible architecture for copolymers. Consider a triblock copolymer. Studies have shown that triblock copolymers form "hairpins" at interfaces[7] with the two end blocks located on one side of the interface and the central block residing preferentially on the other side, as shown schematically in Figure 1b. With a triblock architecture, the copolymer crosses the interface twice, which increases the number of couplings per copolymer molecule joining the two immiscible homopolymers. In the case of a random copolymer, a single polymer chain may make multiple crossings at the interface.[2,8−11] Hence, the number of times one chain crosses the interface can be large, as shown in Figure 1c, and, thus, the copolymer may effectively "stitch" the two immiscible homopolymers together. However, the effectiveness of each stitch is unknown since the loop may not be long enough to entangle well with the homopolymers.

Here, we report studies on the behavior of a polystyrene (PS) and poly(methyl methacrylate) (PMMA) random copolymer, denoted $P(S_f\text{-}r\text{-}MMA_{1-f})$, where f is the fraction of styrene units in the copolymer, at the interface between PS and PMMA. In contrast to previous studies,[8] it is shown that the maximal toughness of the interface is not achieved when $f = 0.50$ but, rather when $f = 0.68$. This difference, demonstrated by the compatibility of the $P(S_f\text{-}r\text{-}MMA_{1-f})$ with PS and PMMA homopolymers, can be attributed to a composition-dependent segmental interaction parameter, χ. Neutron reflectivity studies have shown that a styrene fraction of 0.68, where the fracture toughness is greatest,

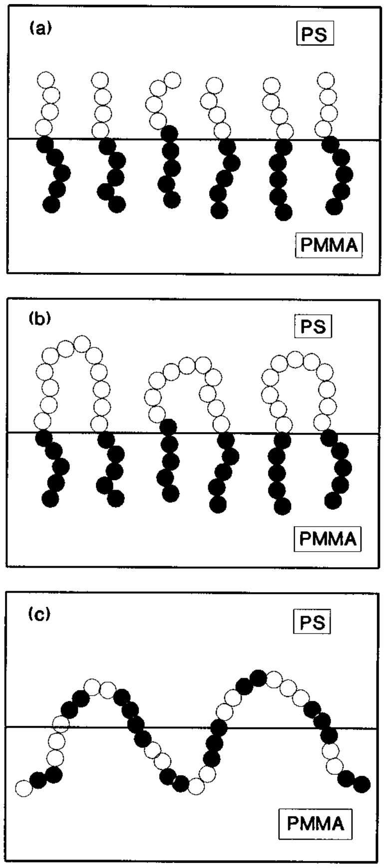

Figure 1. Schematic diagram of the organization of copolymers at the interface between homopolymers comprised of the same basic units: (a) a diblock copolymer; (b) a triblock copolymer; (c) a random copolymer. Note the increase in the number of crossings of the copolymer chain as the sequence distribution of the monomers in the chain is varied.

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⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.

Table 1. Polymer Characteristics

polymer	M_w ($\times 10^{-3}$)	M_w/M_n
PS	96	1.01
d-PS	104	1.02
PMMA	107	1.02
d-PMMA	127	1.04
P($S_{0.30}$-*r*-$MMA_{0.70}$)	250	1.95
P($S_{0.55}$-*r*-$MMA_{0.45}$)	125	1.62
P($S_{0.68}$-*r*-$MMA_{0.32}$)	160	1.51
P($S_{0.78}$-*r*-$MMA_{0.22}$)	173	1.26
P($S_{0.89}$-*r*-$MMA_{0.11}$)	180	1.40

corresponds to the point where the broadening of the interface is symmetric.

Experimental Techniques

The P(S_f-*r*-MMA_{1-f}) used in this study were prepared by a "living" free radical polymerization process.[12] The molecular weights, polydispersities, and styrene content of the copolymers are shown in Table 1. The random nature of the copolymer, in terms of the triad and tetrad sequences, was confirmed by ^{13}C NMR. We also expect, from the synthesis, that all the copolymer chains will be compositionally the same. Details on the synthesis and characterization of the copolymer can be found elsewhere.[13] The characteristics of the homopolymers used for the neutron reflectivity studies are also shown in Table 1. Samples for the reflectivity studies were prepared by spin coating an ~800 Å layer of either PMMA or d-PMMA onto a 5 cm diameter Si substrate. Subsequently, a layer of the P(S_f-*r*-MMA_{1-f}) having a thickness of ~150 Å was prepared on a glass slide, floated onto the surface of deionized water, and retrieved with the coated substrate, forming a bilayer. This bilayer was dried and, in a similar manner, an ~800 Å layer of either d-PS or PS was placed on top of the bilayer to form a trilayered structure. The trilayers were heated to 170 °C for 12 h and quenched to room temperature for the reflectivity measurements. Neutron reflectivity measurements were performed on GANS, the neutron reflectometer at the Missouri University Research Reactor,[14] using neutrons of wavelength $\lambda = 2.35$ Å. Analysis of reflectivity profiles has been discussed elsewhere.[15,16] Fracture toughness measurements were performed on trilayers prepared by melt pressing a 1.6 mm thick slab of PMMA ($M_w = 120\,000$, $M_w/M_n = 2.0$) and then spin coating a layer of P(S_f-*r*-MMA_{1-f}) onto the surface of the PMMA. A melt-pressed slab of PS ($M_w = 355\,000$, $M_w/M_n = 3.0$), having a thickness twice that of the PMMA, was placed on top, sandwiching the random copolymer. This trilayer was annealed at 165 °C for 1.5 h under slight pressure to ensure good contact and then slowly cooled to room temperature. The fracture toughness, G_c, was determined by propagating a crack at the interface between the two homopolymers.[3] Studies were performed as a function of f and of the thickness of the P(S_f-*r*-MMA_{1-f}) layer between the homopolymers (ranging from 76 to 3800 Å).

Results and Discussion

It is important, first, to determine the miscibility of the P(S_f-*r*-MMA_{1-f}) in both the PS and PMMA homopolymer. To this end, mixtures of the homopolymer with PS and PMMA were prepared in toluene where the concentration of the copolymer relative to the homopolymer ranged from 0.5 to 15% by weight and f was varied from 0.30 to 0.89. The solutions were left to evaporate at 160 °C, well above the glass transition temperature of the PS and PMMA. Owing to the refractive index difference between the PS and PMMA, phase separation was determined from the opacity of the resultant films. P(S_f-*r*-MMA_{1-f}) and PS were miscible for all concentrations when $f \geq 0.78$. For $f = 0.78$ the two were miscible only for low concentrations of the random copolymer. In all other cases, the two phase separated. PMMA and P(S_f-*r*-MMA_{1-f}) were miscible for all concentrations when $f \leq 0.60$, though some phase separation was evident for concentrations greater than 15%. Therefore, P(S_f-*r*-MMA_{1-f}) is more miscible with PMMA than PS. Both PS and PMMA are immiscible with P(S_f-*r*-MMA_{1-f}) over a narrow range of f centered around 0.68. The immiscibility of the random copolymer with both homopolymers suppresses the diffusion of the copolymer away from the interface. This lack of symmetry in the solubility has been observed before.[17,18]

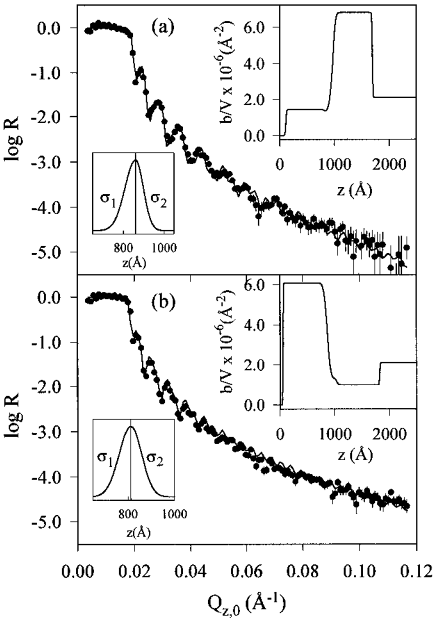

Figure 2. Neutron reflectivity as a function of the neutron momentum transfer, $Q_{z,0}$, for P($S_{0.68}$-*r*-$MMA_{0.32}$) at the interface between (a) PS and d-PMMA and (b) d-PS and PMMA. The scattering length density profiles in the insets were used to calculate the best fit to the reflectivity data. Shown in the second inset is the asymmetric Gaussian function that was used to calculate the scattering length density profile.

Typical neutron reflectivity profiles for the trilayered structures are shown in Figures 2a and 2b where ~160 Å of P($S_{0.68}$-*r*-$MMA_{0.32}$) was placed at the interface between PS and PMMA. The data in Figure 2a were obtained using d-PMMA and the data in Figure 2b were obtained using d-PS. Evident in both sets of data are the Kiessig fringes which characterize the thickness of the perdeuterated homopolymer layer. Shown in the insets are the scattering length density, b/V, profiles which were used to calculate the best fit to the reflectivity data using a nonlinear least squares regression. Since there is little difference between the scattering length densities of the random copolymer and the hydrogenated homopolymer, the gradient profiles reflect the variation in the concentration of the deuterated homopolymer. In general, the *b*/*V* profiles could not be described by a simple error function. To fit the data, a roughness, defined by merging two Gaussian functions having different half-widths, σ_1 and σ_2, as shown in the lower inset of Figure 2, were used. Comparing the results for the two different labelings of the homopolymer, it can be concluded that the penetration of the random copolymer into the homopolymers is not equal, in keeping with the solubility data. An average interfacial width, a_I, can be defined as $(2\pi)^{1/2}(\sigma_1 + \sigma_2)$. Shown in Figure 3 are the values of a_I for d-PS (solid) and d-PMMA (open) experiments as a function of f where the thickness of the random copolymer was ~160 Å. In all cases, a_I was greater than that for the 50 Å interface between PS and PMMA homopolymers.[6,19-21] In the

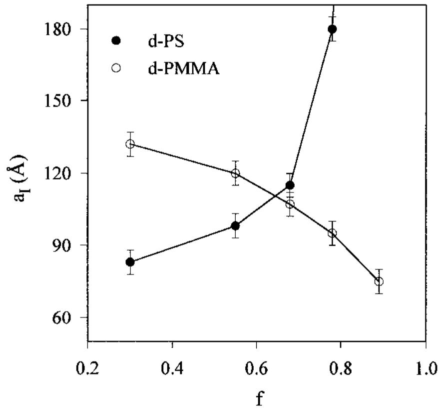

Figure 3. Interfacial widths obtained from neutron reflectivity measurements as a function of *f*, the styrene fraction in the random copolymer, for (solid) d-PS/P(S_f-*r*-MMA_{1-f})/PMMA and for (open) PS/P(S_f-*r*-MMA_{1-f})/d-PMMA. The solid line is a guide for the eye.

case of PMMA, as the concentration of styrene in the copolymer increases, the penetration of the PMMA homopolymer into the interfacial region decreases. In the case of PS, the reverse is true, i.e. as more styrene is incorporated into the random copolymer, the PS can penetrate more deeply into the interfacial region. At *f* ~ 0.65, the interfacial widths are equal and, therefore, there is an equal amount of penetration of PS and PMMA into the interfacial region. Also, even though P($S_{0.68}$-*r*-$MMA_{0.32}$) is immiscible with both homopolymers, the presence of the random copolymer produces a substantial broadening of the interface. At this point, it is not possible to determine how much of the random copolymer is remaining at the interface or how much is dissolved in the homopolymer. The neutron reflectivity data clearly demonstrate the broadening of the interface due to the presence of the copolymer.

The fracture toughness G_c was calculated using a model derived by Kanninen[22] in which a crack is propagated along an interface between a beam and an elastic foundation. Here,

$$G_c = \frac{3\Delta^2 E_1 h_1^{\,3} E_2 h_2^{\,3}}{8d^4}\left[\frac{E_1 h_1^{\,3} C_2^{\,2} + E_2 h_2^{\,3} C_1^{\,2}}{(E_1 h_1^{\,3} C_2^{\,3} + E_2 h_2^{\,3} C_1^{\,3})^2}\right] \quad (1)$$

where

$$C_i = 1 + \frac{0.64 h_i}{d} \quad (2)$$

The subscripts 1 and 2 denote PS and PMMA, respectively. h_i is the thickness of layer *i* having a Young's modulus of E_i, Δ is the thickness of the razor edge, and *d* is the crack length. Shown in Figure 4 is G_c as a function of *f* for thicknesses of the copolymer layer ranging from 76 to 3800 Å. Each point in this figure represents an average of 50 independent measurements. The magnitude of the error in each measurement (one standard deviation) is indicated only for the data where there was a 155 Å layer of P(S_f-*r*-MMA_{1-f}) at the interface.

One surprising feature of these data is that the maximum in G_c occurs for *f* ~ 0.68 and not at 0.50 as seen in the PS–poly(2-vinylpyridine) (P(2VP)), system.[8] From the solubility data, it is apparent that this asymmetry in *f* arises from a concentration-dependent χ parameter, whereas for PS and P(2VP) χ is not concentration dependent. From the solubility data, 0.68 is also the value of *f* where the P(S_f-*r*-MMA_{1-f}) was immiscible with both homopolymers. It also corresponds to the point where the penetration of both PS and PMMA into the copolymer was equal. This result suggests that, for a P(A_f-*r*-B_{1-f}) random copolymer between A and B homopolymers, maximal G_c is achieved when the copolymer/homopolymer interface is symmetrically broadened. For PS and PMMA, the point of symmetry occurs at *f* ~ 0.68, whereas for PS and P(2VP), it occurs when *f* ~0.50.

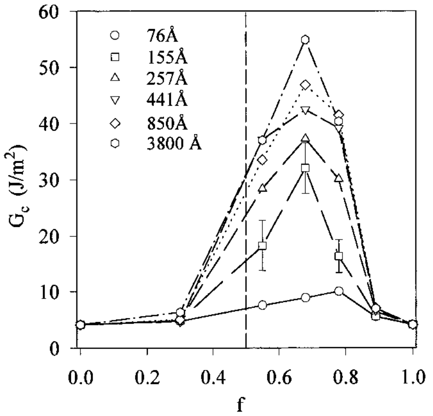

Figure 4. Fracture toughness G_c as a function of *f*, the styrene fraction in P(S_f-*r*-MMA_{1-f}), and as a function of the thickness of the random copolymer layer between the PS and PMMA homopolymers. The error bars on the 155 Å random copolymer layer represent one standard deviation of the values obtained in the G_c measurements. The error bars on the remaining data have been suppressed for clarity. The solid line is a guide for the eye.

For the thinnest copolymer layer, 76 Å, only minimal, if any, strengthening of the interface was found. It was not until sufficient copolymer was placed at the interface, forming effectively a separate layer of copolymer, that any significant adhesion promotion was achieved. By this point, perhaps coincidentally, the thickness of the P(S_f-*r*-MMA_{1-f}) exceeds the radius of gyration of the copolymer (~122 Å based on data for PS and PMMA homopolymers). With increasing thickness, G_c increases, albeit more gradually. However, at 55 J/m^2 for the 3800 Å thick copolymer layer, the increase in G_c with thickness has not fully saturated. This result suggests that the toughening process is related either to the deformation of the P(S-*r*-MMA) or to the interaction between the weak interfaces on either side of the random copolymer layer.[23]

It would be possible to compare the toughness results presented here with results obtained previously using PS–PMMA diblock copolymers. However, such a comparison would not be valuable. In some recent experiments, we have found that the test geometry used here with a PS to PMMA thickness ratio of 2 to 1 is not optimum in the sense that it does not give the minimum toughness. Also, we found that the measured toughness of interfaces coupled with a random copolymer is more sensitive to sample geometry than in the case where the interface is coupled with a diblock copolymer. Hence the direct comparison needs to be made at the optimum sample geometry, which is currently under investigation.

Conclusions

In conclusion, it has been shown that the maximum toughness of the interface between PS and PMMA reinforced with P(S_f-*r*-MMA_{1-f}) occurs when *f* ~ 0.68.

It has also been found that P($S_{0.68}$-*r*-$MMA_{0.32}$) is not miscible with either PS or PMMA homopolymers. Nevertheless, the interface between the homopolymers is markedly broadened and this broadening is symmetric. No saturation in the interfacial toughness was observed as a fraction of the amount of P(S_f-*r*-MMA_{1-f}) placed at the interface. This suggests that the toughening is related to the deformation of the P(S_f-*r*-MMA_{1-f}) or to the formation of a layer of P(S_f-*r*-MMA_{1-f}) between the PS and PMMA having two distinct interfaces.

Acknowledgment. This work was partially supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract FG03-88ER 45375.

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MA960382M