

Polymer Communication

Random copolymer/homopolymer interfacial widths as a function of copolymer composition

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Abstract

Neutron reflectivity experiments were performed on bilayer samples to determine interfacial widths between poly(styrene-*ran*-methyl methacrylate) copolymers (P[S-*ran*-MMA]) and deuterated polystyrene (dPS) or deuterated poly(methyl methacrylate) (dPMMA) as a function of copolymer composition. The copolymer composition, f_s , varied from 0.49 to 0.85 mol% styrene. After a 4 h anneal at 150°C, the interfacial width between the compositionally symmetric random copolymer ($f_s = 0.49$) and dPS was smaller than with dPMMA. Equal interfacial widths for the copolymer with dPS and with dPMMA was found at $\langle f_s \rangle \approx 0.6$. These reflectivity results are consistent with work by Kulasekere et al. and are discussed in relation to our previously published results on the fracture toughness of PS/PMMA joints reinforced with P[S-*ran*-MMA]. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The use of copolymers as reinforcing agents in homopolymer blends and at interfaces continues to be of widespread interest. Random copolymers offer potential benefits over block copolymers for such applications as they are generally cheaper, easier to synthesize, and offer a larger degree of design flexibility. Previously, we reported on the ability of a compositionally symmetric random copolymer of styrene and methyl methacrylate (P[S_{0.49}-*ran*-MMA]) to segregate from a miscible blend with deuterated poly(methyl methacrylate) (dPMMA) to an immiscible interface between dPMMA and deuterated polystyrene (dPS) [1]. This segregation to the boundary between immiscible homopolymers broadens the interface and thereby should increase the interfacial fracture toughness and reduce phase coalescence.

Once the copolymer is in the interfacial region, the question remains as to how well it will increase the fracture

toughness of a joint. Currently the strengthening abilities of random copolymers are not as well understood as those of their block counterparts, as fracture toughness experiments involving random copolymers at homopolymer joints provide inconclusive results. Kramer and coworkers [2] used the asymmetric double cantilever beam (ADCB) test and found that a compositionally symmetric random copolymer of styrene and 2-vinyl pyridine strongly reinforces the interface between polystyrene (PS) and poly(2-vinyl pyridine) homopolymers. The fracture toughness measured for this system decreases as the molar styrene fraction of the copolymer varies from 0.5. Kulasekere et al. used a static ADCB test to study the strengthening properties of P[S-*ran*-MMA], where f is the mole fraction of styrene in the copolymer [3]. However, these authors note that their test geometry was not optimal, which complicates the interpretation of their measurements.

In our own fracture toughness experiments using P[S-*ran*-MMA] between PS and PMMA, we found that a 50 nm film formed a discrete layer so that two interfaces must be considered, PS/copolymer and PMMA/copolymer [4]. Using a dynamic ADCB experiment and carefully selecting the optimal geometry, we found that a copolymer of $f = 0.48$ did not significantly strengthen the interface

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Table 1
Materials description

Material ^a	M_w^b	M_w/M_n	$(b/V) \times 10^{-6}$ (\AA^{-2})
P[S _{0.49} - <i>ran</i> -MMA]	361,000	2.23	1.22
P[S _{0.73} - <i>ran</i> -MMA]	446,000	1.86	1.30
P[S _{0.85} - <i>ran</i> -MMA]	531,000	1.92	1.34
hPMMA	285,000	1.09	1.06
hPS	315,000	1.07	1.41
dPMMA	310,000	1.05	7.02
dPS	690,000	1.09	6.46

^a Mol% MMA and styrene in the copolymers determined by ¹H NMR. Copolymerizations were terminated at less than 5% conversion to prevent composition drift and to ensure reasonable polydispersities. All homopolymers were purchased from Polymer Laboratories.

^b Determined by size exclusion chromatography (SEC), using four mixed columns in series and THF as the solvent at room temperature.

relative to that for the bare joint. A copolymer of $f = 0.73$ produced a slightly stronger joint by creating oblique crazes in the PS. For both copolymer compositions fracture occurred at or near the PS/copolymer interface.

One hypothesis is that measuring the interfacial width between the copolymer and the two homopolymers could be a viable alternative to fracture toughness experiments. Fracture toughness is expected to increase with interfacial width, because the load can be distributed through a larger volume of material and thereby create a larger volume of plastic deformation prior to failure. Measuring interfacial width can avoid the complications of crack instability and the influence of the mechanical testing technique and geometry on the measured fracture toughness. In order to test this hypothesis, we have used neutron reflectivity to determine the interfacial width in bilayer thin films of P[S_{*f*}-*ran*-MMA] and either dPMMA or dPS. Three random copolymer compositions ($f = 0.49, 0.73$ and 0.85) were used. Although insufficient to establish equilibrium interfacial widths, samples were prepared with an annealing history similar to that of our ADCB specimens for fracture tests: 4 h at 150°C. Polymers of the same molecular weights as in the ADCB specimens are used, with the exception of dPS, thereby maintaining comparable processing conditions and materials. Asymmetric behavior of the compositionally symmetric copolymer was observed, in that P[S_{0.49}-*ran*-MMA] exhibits a broader interface with dPMMA than with dPS.

We can compare our results to those of Kulasekere et al., who performed neutron reflectivity experiments to investigate similar interfaces [3]. Our results confirm overall trends in interfacial width as a function of f which they reported. Their measured interfacial widths were consistently higher than ours, a result most likely attributable to the fact that they used polymers of lower molecular weights (96–250K) than we did (285–531K). Another difference worth noting was the sample geometry used in their experiments and in ours. Their trilayer samples contained two homopolymer/copolymer interfaces:

Si/80 nm (d)PMMA/15 nm P[S_{*f*}-*ran*-MMA]/80 nm (d)PS, where (d)PMMA and (d)PS represent either deuterated or hydrogenated species. We used an asymmetric bilayer sample geometry of Si/40 nm deuterated homopolymer/200 nm P[S_{*f*}-*ran*-MMA]. We have found that this geometry improves resolution and simplifies data interpretation, resulting in lower uncertainty in interfacial width measurements. The error in our measurements was determined to be ± 0.2 nm, compared to Kulasekere's reported error of ± 0.5 nm. One further difference is that our samples were annealed for 4 h at 150°C, which we determined to be insufficient time to reach equilibrium. Kulasekere's samples were annealed for 12 h at 170°C, but the question of whether their annealing conditions were sufficient to reach equilibrium is not addressed in their paper. We selected annealing conditions that mimic those used to prepare interfacial fracture toughness specimens, so that we can compare the two experiments.

2. Experimental

Table 1 summarizes the polymers used for this study. Random copolymers were synthesized via methods described previously [5]. Thin film bilayers were prepared using the following geometry to optimize reflectivity data resolution and deter dewetting: Si/40 nm deuterated homopolymer/200 nm P[S-*ran*-MMA]. Placing the hydrogenated polymer layer at the surface decreases surface scattering interference, as its scattering length density, (b/V) , is similar to that of air. The thick hydrogenated layer deters dewetting, and the asymmetry in the layers' thicknesses simplifies interpretation of the reflectivity results. Light microscopy confirmed the absence of dewetting in all samples.

Reflectivity measurements were performed upside down on the NG7 neutron reflectometer at NIST, so that the incident neutron beam traversed the silicon wafer. Having the beam pass through the Si/polymer interface improves resolution, as this interface is smoother and results in less surface scattering than the polymer/air interface. Instrumental resolution was taken as $\Delta q/q = 0.04$, $\Delta\theta = 1 \times 10^{-6}$ and $\Delta\lambda = 0.035$. Results were analyzed by fitting data to algorithm-generated reflectivity curves, created from model profiles of (b/V) as a function of sample depth, z . Hyperbolic tangent profiles were used to model the polymer/polymer interface. Full Width Half Maximum interfacial widths are calculated as

$$w = \frac{(b/v)_1 - (b/v)_2}{m} \quad (1)$$

where $(b/v)_1$ and $(b/v)_2$ are the scattering length densities of the pure components 1 and 2 and m is the slope of the hyperbolic tangent interfacial profile at its midpoint. Surface roughnesses were estimated for the silicon/polymer and polymer/air interfaces and varied from 0.3–1.5 nm.

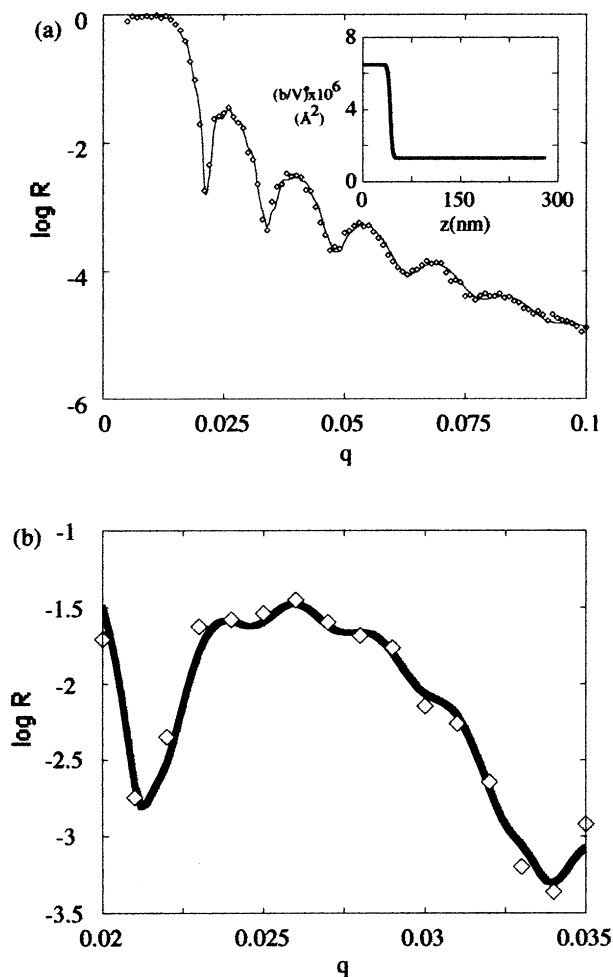


Fig. 1. (a) Neutron reflectivity data for Si/dPS/P[S_{0.73}-ran-MMA], shown as diamonds. The solid curve is the simulated reflectivity from using the scattering length density profile shown in the inset. The silicon/polymer interface corresponds to a z value of 0 nm. Interfacial width is calculated to be 7.7 ± 0.2 nm. (b) Expansion of above reflectivity curve for $q = 0.02$ – 0.035 .

3. Results and discussion

Representative reflectivity data and the corresponding algorithm-generated fit are shown in Fig. 1. The asymmetric layers of the sample result in distinct oscillation periods for the deuterated and hydrogenated films, which significantly aids in determining accurate layer thicknesses. Interfacial widths could be calculated within ± 0.2 nm. The interfacial width for dPMMA/P[S_{0.49}-ran-MMA] is 6.6 nm after 4 h annealing at 150°C. In comparison, the dPS/P[S_{0.49}-ran-MMA] interfacial width is 3.6 nm after 4 h at 150°C. Both samples were then annealed for an additional 4 h at 150°C. The interfacial width for dPMMA/P[S_{0.49}-ran-MMA] remained unchanged, whereas $w_{\text{dPS/P[S}_{0.49}\text{-ran-MMA}]}$ increases to 4.8 nm, establishing that 4 h is insufficient to reach equilibrium for this bilayer.

Previously, TEM studies found that a P[S_{0.48}-ran-MMA] copolymer of $M_w = 286\text{K}$ exhibits a wider range of

miscibility with PMMA ($M_w = 32\text{K}$) than with PS ($M_w = 22\text{K}$) [6]. The copolymer was immiscible for the range 6–72 vol% copolymer blended with PMMA, but immiscible for the range 0–100 vol% copolymer when blended with PS. Systems with lower bulk miscibility are expected to show narrower interfacial widths, therefore we would expect, assuming the effect of deuterium labeling is minor, $w_{\text{dPS/P[S}_{0.49}\text{-ran-MMA}]} < w_{\text{dPMMA/P[S}_{0.49}\text{-ran-MMA}]}$. This behavior is what we have observed in our measured interfacial widths. Similarly, asymmetric bulk miscibility and asymmetric interfacial width have been reported by Kulasekera et al. using neutron reflectivity.

Fig. 2 shows the interfacial widths after 4 h annealing as a function of random copolymer composition. As expected, increasing the styrene content of the copolymer increases $w_{\text{dPS/P[S}_f\text{-ran-MMA}]}$ and decreases $w_{\text{dPMMA/P[S}_f\text{-ran-MMA}]}$. Note, however, that $w_{\text{dPMMA/P[S}_f\text{-ran-MMA}]} = w_{\text{dPS/P[S}_f\text{-ran-MMA}]}$ at a copolymer composition between 0.6 and 0.7 mole fraction of styrene. Kulasekera et al. observed that interfacial width varied with copolymer composition, with symmetric widths occurring at $f \sim 0.68$.

We can directly compare our interfacial width and fracture toughness measurements, as both experiments used similar annealing conditions and materials of similar molecular weights (except for the dPS used in the reflectivity samples, which is of a higher molecular weight than the PS used in the fracture samples) [4]. Fracture occurring at the PS/P[S_{0.48}-ran-MMA] interface within the PS/P[S_{0.48}-ran-MMA] joint is consistent with $w_{\text{dPS/P[S}_{0.49}\text{-ran-MMA}]} < w_{\text{dPMMA/P[S}_{0.49}\text{-ran-MMA}]}$, as a wider interface can dissipate stresses and resist failure better than a narrow interface. However, for $f = 0.73$ crack propagation persists at or near the PS/copolymer interface, although $w_{\text{dPS/P[S}_{0.73}\text{-ran-MMA}]} > w_{\text{dPMMA/P[S}_{0.73}\text{-ran-MMA}]}$. It appears that factors in addition to interfacial width must be considered when determining the locus of failure within the joint, because the PMMA/copolymer interface is resisting failure even when it is narrower than the PS/copolymer interface. We also observe that $w_{\text{dPS/P[S}_{0.49}\text{-ran-MMA}]} < w_{\text{dPS/P[S}_{0.73}\text{-ran-MMA}]}$, which does appear related to the higher fracture toughness of the joint with P[S_{0.73}-ran-MMA] at the interface. The styrene-rich copolymer has an increased ability to transfer stress to the PS sheet, causing deformation of the material into oblique crazes. At some $f > 0.73$, we can expect the PMMA/copolymer interface to become the weak link in the joint and the locus of failure, but that value of f has yet to be determined.

4. Conclusions

Neutron reflectivity experiments were performed on bilayer samples to determine interfacial widths within ± 0.2 nm between P[S-*ran*-MMA] copolymers and dPS or dPMMA homopolymers as a function of copolymer composition. A compositionally symmetric random copolymer

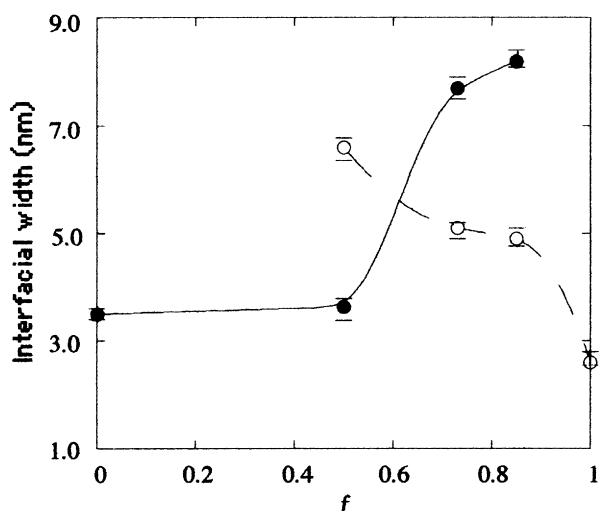


Fig. 2. Interfacial width as a function of styrene content, f , in P[S_ran-MMA]. Open circles are for dPMMA/P[S_ran-MMA] bilayers, filled circles are for dPS/P[S_ran-MMA] bilayers. End points at $f = 0$ and 1.0 were determined from Si/dPS/hPMMA and Si/dPMMA/hPS bilayers, respectively, and differ due to isotope effect by less than 0.7 nm.

exhibits a narrower interface with dPS than with dPMMA, which is consistent with both our previous blend miscibility and interfacial fracture toughness studies. Also consistent with Kulasekere's results, increasing the styrene content of the random copolymer increases the random copolymer/dPS interfacial width until it surpasses that of the random copolymer/dPMMA interface at $f > \sim 0.6$. However, contrary to expectations, these interfacial width

measurements fail to correlate directly with interfacial fracture toughness.

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