Strengthening Polymer Phase Boundaries with Hydrogen-Bonding Random Copolymers[†]

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ABSTRACT: We have used a random copolymer of deuterated styrene and *p*-hydroxystyrene [dPS$_{(1-f)}$-*r*-PPHS$_f$], where f is the molar fraction of PHS, to strengthen the weak phase boundary between PS and poly(2-vinylpyridine) (PVP). The fracture toughness (G_c) of the phase boundary was measured using an asymmetric double cantilever beam method, and the areal chain density (Σ) of copolymer at the phase boundary was determined by forward recoil spectrometry (FRES). The interfacial strength was extremely sensitive to the composition of the random copolymer with an optimum value found for $f \approx 0.03$. The maximum measured fracture toughness was around 250 J/m^2 at $f = 0.022$, while no significant strengthening was observed at $f = 0.01$ and $f = 0.066$. Such a strong composition dependence of G_c is in marked contrast to the case of dPS$_{(1-f)}$-*r*-PVP$_f$ copolymers, for which the maximum strengthening is seen at $f \approx 0.5$ with significant strengthening still observed at $f = 0.4$ and $f = 0.6$. The differences in the compositions for optimum strengthening and in the composition sensitivity of strengthening in these two cases are attributed to the hydrogen bonding between different PHS units and between PHS units and the PVP homopolymer as well as the absence of composition drift in our dPS$_{(1-f)}$-*r*-PPHS$_f$ random copolymers. Using FRES, we determined the fracture mechanism to be chain pull-out for $f = 0.01$ and $f = 0.066$ over the entire range of Σ probed. For copolymers with $f = 0.022$ and $f = 0.045$, a mixture of chain scission and chain pull-out prevailed at low areal chain densities while craze formation followed by craze breakdown was observed at higher areal chain densities.

Introduction

Recent studies on the strengthening of the phase boundaries between immiscible glassy homopolymers A and B have focused on the use of A−B diblock copolymers[1−11] as the strengthening agent. In general, two conditions must be met for the strengthening to be effective: (i) each block of the copolymer has to be long enough to entangle effectively with the corresponding homopolymer[5−12] and (ii) the areal chain density of the copolymer at the phase boundary must be sufficiently large[5,7−12] that the stress borne by the interface is large enough to cause a craze to form in one of the homopolymers. However, when block copolymers are mixed with homopolymers, the long block copolymer molecules tend to form micelles in the bulk material, which substantially slows down the kinetics of the segregation of the block copolymer to phase boundaries. Such slow segregation kinetics may prevent equilibrium conditions from being attained and therefore limit the strengthening effect achievable in practice. To circumvent this problem, copolymers have been made in situ using end functional polymers,[13−15] e.g., A−X in which the end group −X can chemically bond to B while the A chain can entangle sufficiently with A. Alternatively, a block copolymer A-*b*-C, in which C can form hydrogen bonds with B,[16] may be used. Both approaches have demonstrated effective strengthening of the phase boundary with a lower molecular weight copolymer than would be required for the A-*b*-B case. The reason is as follows. If the end-functionalized polymer becomes grafted at the interface via covalent bonding to polymer B, mechanical strengthening can be achieved merely by entanglement of A−X with the polymer A. Similarly, in the case of the A-*b*-C block copolymer, only short blocks of C are required if C forms strong H-bonds with polymer B, and therefore, the A block only needs to be long enough to entangle with homopolymer A. Consequently, shorter copolymer chains can be used for interfacial toughening. The use of a lower molecular weight strengthening agent facilitates much faster segregation to the phase boundaries.

Recent experiments[8,9,17,25] have shown that random copolymers A-*r*-B can be quite effective in strengthening an A/B phase boundary. Compared to A-*b*-B diblock copolymers, A-*r*-B random copolymers have the following advantages: first, they can be prepared easily by radical polymerizations, which are cheaper and more accessible than the anionic polymerizations required to make the diblock copolymers; second, they can achieve a high fracture toughness of the phase boundary at about 10 times lower areal chain density. The exact mechanism by which random copolymers strengthen the phase boundary, however, is still not clear.[18−20]

We have combined the advantages of hydrogen-bonding interactions and random copolymers by making a series of random copolymers of perdeuterated styrene and *p*-hydroxystyrene [dPS$_{(1-f)}$-*r*-PPHS$_f$] with different molar fractions, f, of *p*-hydroxystyrene (PHS) units in the copolymer.[21] These copolymers were then tested in the strengthening of the phase boundary between polystyrene (PS) and poly(2-vinylpyridine) (PVP) with the goal of measuring their effect and elucidating the possible strengthening mechanisms.

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Table 1. Preparation of Precursor Polymers via Bulk Polymerization at 105 °C

copolymer	f^a	initiator[b] (mol % × 10^4)	conversion (%)	$10^{-5}M_w$ precursor[c]	M_w/M_n	$10^{-5}M_w$, calc deprotected
1	0.010	8.21	88	7.11	3.69	7.05
2	0.022	8.05	91	6.79	3.08	6.72
3	0.045	8.67	93	7.88	3.46	7.58
4	0.066	7.71	87	5.16	3.11	4.99

[a] Molar fraction of *p*-hydroxystyrene in copolymer. [b] Amount of dicumyl peroxide used relative to monomer. [c] Molecular weight from polystyrene calibration.

Experimental Section

Materials. The polydisperse polystyrene (PS) with M_w = 280 000 was purchased from Aldrich. The polydisperse poly(2-vinylpyridine) (PVP) with M_w = 200 000 was purchased from Polysciences. Both homopolymers were used as received. Styrene-d_8 was obtained from Cambridge Isotopes Laboratories. The monomer was simply distilled for use in the polymerizations. 4-[(*tert*-Butoxycarbonyl)oxy]styrene (tBOC styrene) was used as obtained from Kodak. Dicumyl peroxide (DPO) and trifluoroacetic acid were obtained from Aldrich. DPO was further purified by recrystallization from 95% ethanol. Tetrahydrofuran (THF), methanol, pyridine, and methylene chloride were used as received from Fisher Scientific.

Methods. Molecular weights of the precursor polymers were determined by SEC on a liquid chromatograph equipped with two parallel detectors: a Viscotek 110 differential viscometer and a differential refractometer (refractoMonitor, Milton Roy). THF at 40 °C was used as the mobile phase at a nominal flow rate of 1 mL/min. Four 5 μm PL Gel columns with porosities of 10, 50, and 100 nm and Mixed C were used to achieve separations. The system was calibrated with 30 monodisperse polystyrene standards. Infrared spectra were recorded on a Nicolet IR/44 spectrophotometer as a suspension of the copolymers in a KBr film. Thermogravimetric analysis (TGA) was performed on a Seiko Instruments TG/DTA 220.

Preparation of Poly(styrene-d_8-*ran*-tBOC styrene). In a typical polymerization styrene-d_8 (5.0 g, 0.0446 mol) and tBOC styrene (0.10 g , 4.54×10^{-4} mol) were combined with dicumyl peroxide (10 mg, 3.7×10^{-5} mol). The solution was stirred under nitrogen for 30 min before being placed in a heating bath at 105 °C. The polymerization was carried out in the bulk under nitrogen and stopped after 20 h. The resulting polymer was dissolved in THF and precipitated into excess methanol. The polymer powder was filtered off and dried in vacuo. Conversions were between 87 and 93%. The compositions of the random copolymers were determined using TGA from the relative weight loss due to the thermal hydrolysis of the tBOC group.

Preparation of Poly(styrene-d_8-*ran*-*p*-hydroxystyrene). For the deprotection of the tBOC group, the precursor copolymer (4.0 g) was dissolved in methylene chloride (150 mL) and trifluoroacetic acid (TFA) (12 mL) and refluxed for 12 h. The extent of deprotection was monitored by the decrease of the carbonyl absorption at 1759 cm^{-1} and appearance of a broad hydroxyl absorption (3300−3500 cm^{-1}) in the FTIR spectrum. The methylene chloride and TFA were removed on a Rotovapor; then the copolymer was redissolved in pyridine and precipitated into excess water. After drying in vacuo at 50 °C in the presence of P_2O_5, the copolymer was reprecipitated from a THF solution into excess methanol. The copolymer was dried again in vacuo. Yields were 94−97%.

Preparation of Fracture Toughness Samples. For the preparation of the fracture toughness samples, PS and PVP plates were made by compression molding. The PS plate (2.3 mm) was made thicker than the PVP plate (1.7 mm) to keep the crack at the interface. A film of the random copolymer was spun-cast from toluene onto the optically smooth surface of the PVP plate. The residual solvent was removed by heating the coated plate in a vacuum oven at 80 °C for 2 h. This plate was then welded to a PS plate at 160 °C for 2 h to form a layered assembly of PS/random copolymer/PVP. This process promotes the diffusion of the random copolymer into the respective homopolymers to form chain entanglements. The annealed sample was then cut with a diamond saw into strips for the subsequent fracture toughness measurements. The dimensions of the strips were 50 mm long × 8.7 mm wide × 4.0 mm thick.

The fracture toughness of the phase boundary, G_c, which is defined as the critical energy release rate of an interfacial crack, was measured using an asymmetric double cantilever beam method (ADCB). The measurement was performed by inserting a single-edge razor blade at the phase boundary and pushing it at a constant rate of 3×10^{-6} m/s using a servo-controlled motor drive at room temperature. The steady-state value of the crack length, *a*, along the phase boundary ahead of the razor blade was measured at regular time intervals. The fracture toughness G_c, which is proportional to a^{-4}, was computed[7] using these values of *a*. The error bars reported subsequently for G_c represent the standard deviation of at least 16 measurements of the crack length. More details about the ADCB fracture test can found elsewhere.[5,7] After the G_c measurement, the two surfaces of the fracture were examined with FRES to determine the apparent areal density of copolymer chains on both PS and PVP sides (Σ_{ps} and Σ_{pvp}, respectively). The total areal chain density, Σ, of the copolymer was calculated by summing these two measurements; i.e., $\Sigma = \Sigma_{ps} + \Sigma_{pvp}$. The fraction of copolymer remaining on each surface was also calculated from the FRES measurements in order to evaluate the fracture mechanism.

Results and Discussion

As shown in Table 1, high molecular weight precursor copolymers were obtained in good yields using dicumyl peroxide as initiator. As expected for bulk radical polymerization, copolymers had broad molecular weight distributions ($M_w/M_n \approx 3$). The acidic deprotection of the precursor was found to go to completion only at sufficiently high concentrations of TFA and long reaction times, as described above. This observation is in stark contrast to the facile deprotection of lower molecular weight homopolymers of tBOC styrene in earlier work.[22] The deprotected copolymers were not characterized by SEC since the presence of specific interactions can cause difficulty in data interpretation. The molecular weights of the deprotected copolymers were calculated from the relative weight loss upon hydrolysis, measured by TG/DTA, and the precursor molecular weight.

For the fracture toughness samples, the difference in the thickness of the PS and PVP plates was necessary to produce a mechanical phase angle, $\psi \approx -6°$, which produces a small tendency for the crack to propagate into the more craze resistant PVP. (The actual crack propagates right along the interface, as shown by the FRES results below.) Also, such a phase angle has been previously shown[23] to minimize G_c, so our measurements are expected to reflect the minimum values of the interfacial fracture energy. We compare the results for copolymers with different PHS molar fractions, *f*, by plotting both G_c and the fraction of ^{2}H on the PS side as functions of Σ. In all plots the star represents the fracture toughness of the phase boundary in the absence of copolymer. The open circles represent the results

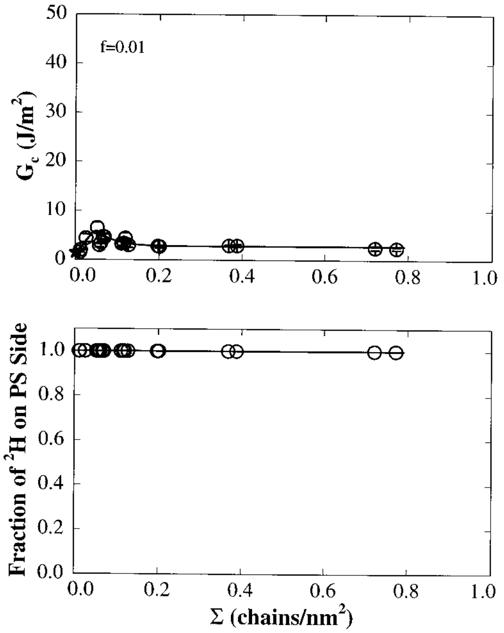

Figure 1. PS/PVP interface reinforced by a $dPS_{(1-f)}$-*r*-$PPHS_f$ random copolymer with $f = 0.01$. Fracture toughness G_c (a) and the fraction of dPS on the PS side of the interface after fracture (b) as a function of areal chain density Σ. The open symbols represent experimental data and the solid lines are guides to the eye.

from our experiments, and the solid line is our qualitative interpretation of the data trend.

For the copolymer with $f = 0.010$, there is clearly only a minor enhancement in the fracture toughness (Figure 1). The G_c data show a weak maximum value of 6 J/m^2 at $\Sigma^* = 0.04$ chains/nm^2. When Σ is increased further, G_c decreases to a constant value of 2 J/m^2. Since all the deuterium is found on the polystyrene side after fracture, Figure 1b, it is reasonable to assume that all the copolymer chains have been pulled out of the PVP side. This observation is consistent with the fact that only 1% of the units bear hydroxyl groups and therefore only very few hydrogen bonds to PVP can be formed. It should be noted that for Σ values above 0.3 chains/nm^2 some of the copolymer diffused so deeply into the PS that the value of Σ could only be obtained with time of flight FRES (TOF-FRES). This technique allowed us to probe beyond the depth limit of conventional FRES (about 0.5 μm) to distances as far as 3 μm below the surface. A similar procedure was followed in all cases where the copolymer was at significant depths below the fracture surface. In these cases the copolymer is clearly no longer localized on the interface. This complication occurred only at large areal chain densities where the fracture toughness had reached a constant (saturated) value.

Throughout the whole range of Σ for $f = 0.066$ (Figure 2), G_c increases only slightly, but in this case all of the random copolymer was on the PVP side after fracture. For this copolymer the phase boundary fails by pull-out from the PS homopolymer. Therefore, if the random copolymer of $dPS_{(1-f)}$-*r*-$PPHS_f$ can significantly strengthen the phase boundary, such strengthening will only occur in the range between these two extreme cases of chain pull-out (between $f = 0.010$ and $f = 0.066$).

The results observed when the PHS molar fraction is decreased to $f = 0.045$ are shown in Figure 3. The fracture toughness increases only slowly with Σ up to a critical value of $\Sigma^* = 0.09$ chains/nm^2. Above this value, there is an almost discontinuous jump in G_c to a value exceeding 100 J/m^2, which then remains relatively constant as Σ is increased further. Examination of the fracture surface by optical microscopy reveals evidence of crazing above Σ* but little evidence of crazing below this value. Below $\Sigma^* = 0.09$ chains/nm^2, 3−10% of the copolymer was found on the PS side of the fracture surface. Above Σ*, all of the copolymer is found on the PVP side. If pull-out were the mechanism of phase boundary failure below Σ*, however, there would be no deuterium on the PS side. Consequently, we believe that the mechanism of failure at low Σ involves some chain scission. It is easy to demonstrate that not all copolymer chains break, even once, in this regime. For long diblock copolymers[7] or long end-grafted chains,[15] which must break once if chain scission is the phase boundary failure mechanism, the chain scission-to-crazing transition is seen at $\Sigma^* = 0.03$ chains/nm^2. Thus, if each random copolymer chain of the $f = 0.045$

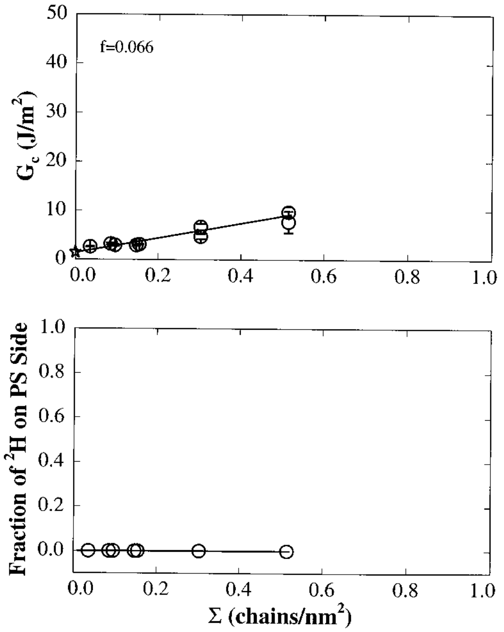

Figure 2. PS/PVP interface reinforced by a $dPS_{(1-f)}$-*r*-$PPHS_f$ random copolymer with $f = 0.066$.

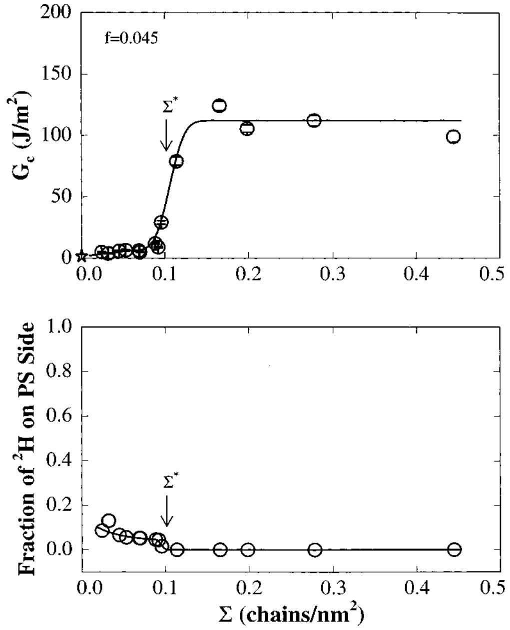

Figure 3. PS/PVP interface reinforced by a $dPS_{(1-f)}$-*r*-$PPHS_f$ random copolymer with $f = 0.045$.

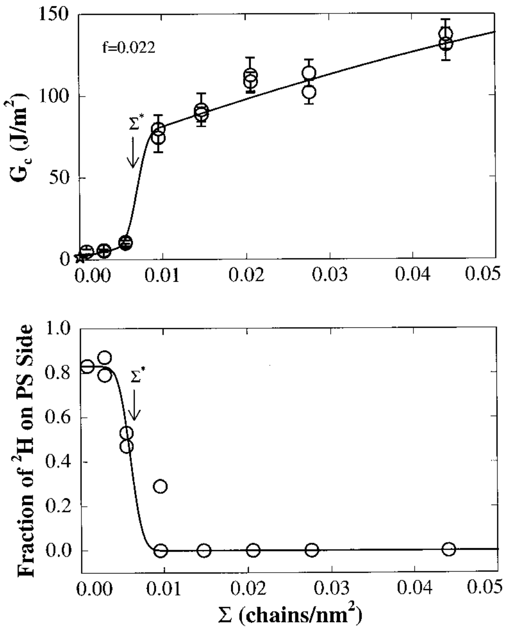

Figure 4. PS/PVP interface reinforced by a $dPS_{(1-f)}$-*r*-$PPHS_f$ random copolymer with $f = 0.022$, at low areal chain density.

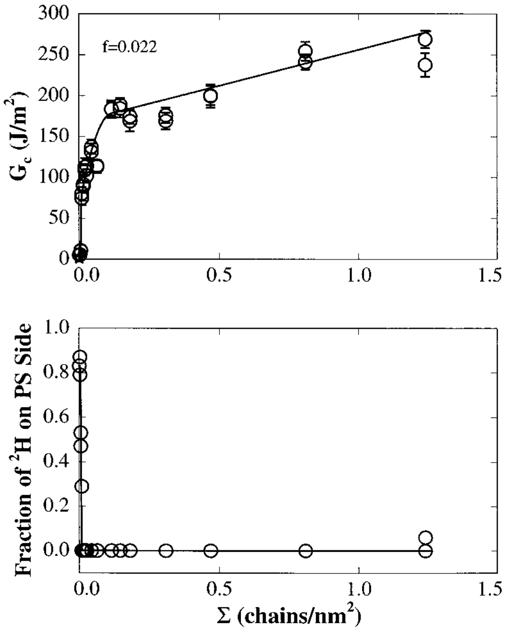

Figure 5. PS/PVP interface reinforced by a $dPS_{(1-f)}$-*r*-$PPHS_f$ random copolymer with $f = 0.022$, at high areal chain density.

copolymer broke once in the low-Σ regime, we should see the chain scission-to-crazing transition also at $\Sigma^* = 0.03$ chains/nm^2. Instead, we observe the transition at $\Sigma^* = 0.09$ chains/nm^2. This result implies that at least two-thirds of the random copolymer chains are not broken, i.e., are pulled out from the PS side of the interface for $\Sigma < \Sigma^*$. This inference is consistent with the rather small fraction of deuterium found on the PS surface. Nevertheless, the small fraction of chains that break strengthens the interface sufficiently so that a craze can form for $\Sigma > \Sigma^*$. Subsequent widening of the craze causes fracture toughness values exceeding 100 J/m^2. The craze fibrils at the crack tip eventually fail by disentanglement of the copolymer from the PS homopolymer, which accounts for the large fraction of deuterium on the PVP surface.

As f is decreased further to $f = 0.022$, the phase boundary is further strengthened, as shown in Figure 4. In Figure 4a, G_c increases only slowly with Σ when Σ is below a critical value, $\Sigma^* = 0.006$ chains/nm^2. In this regime most (80%), but not all, of the random copolymer is found on the PS side after fracture. As Σ is increased beyond Σ*, the fraction of copolymer found on the PS side drops rapidly to zero. This indicates that at low $\Sigma < \Sigma^*$ the phase boundary fails by scission of the random copolymer along a plane that is close to the PVP. Once crazing occurs for $\Sigma > \Sigma^*$, as indicated by the strong increase in G_c, the craze fails close to the boundary between the PS homopolymer and the random copolymer. At even higher Σ (Figure 5) the fracture toughness continues to increase to values as high as 250 J/m^2. Such high values of fracture toughness are comparable to those for PS/PVP phase boundaries reinforced with large areal chain densities of a long PVP−dPS−PVP triblock copolymer[24] and are much larger than the maximum fracture toughness obtained for PS/PVP phase boundaries reinforced with either long diblock copolymers (dPS-*b*-PVP) or dPS-*r*-PVP random copolymers.[17,25]

By comparing the critical areal densities of the PHS random copolymers with those of long block copolymers and grafted chains, further insight on the strengthening mechanism can be gained. For the $f = 0.022$ copolymer, the critical density ($\Sigma^* \sim 0.006$ chain/nm^2) is considerably less than the value for long block copolymers and grafted chains (0.03 chains/nm^2).[7,15] This critical value of Σ* is expected to be the same for all strengthening copolymers that undergo one scission per chain during fracture since the craze resistance remains constant for the PVP and the PS. These data suggest that multiple covalent bonds across the interface break for each random copolymer chain of $dPS_{(1-f)}$-*r*-$PPHS_f$. By comparing the transition values of the random copolymers and the block copolymers, we can estimate that about five bonds must be broken for each random copolymer chain.

To compare the current results with those obtained previously by Dai et al.[25] for the $dPS_{(1-f)}$-*r*-PVP_f, we plotted the G_c values at high values of Σ as a function of f in Figure 6a. The corresponding distribution of ^2H as a function of f in the low areal chain density regime is shown in Figure 6b. In both plots the data are plotted as open circles and the solid lines are our interpretation of the trend shown by the data. In contrast to the $dPS_{(1-f)}$-*r*-PVP_f case where optimum strengthening was obtained at $f = 0.5$ and the strengthening remained effective over a broad range of f, our data show that for the $dPS_{(1-f)}$-*r*-$PPHS_f$ copolymer the maximum strengthening is obtained at a fraction $f \approx 0.03$ and the strengthening effect drops drastically as f deviates from the optimum value. The maximum toughness of 250 J/m^2 obtained for the PHS copolymers, however, is considerably higher than that for the $dPS_{(1-f)}$-*r*-PVP_f copolymer (150 J/m^2). The distribution of random copolymer on the PS side after fracture at low areal chain density is similar to that observed for $dPS_{(1-f)}$-*r*-PVP_f, ranging from 1 to 0 as f increases, except that the drop occurs over a narrower range of f, corresponding to the range where the peak in G_c is observed.

The observed shift in the toughness maximum from $f \approx 0.5$ for the $dPS_{(1-f)}$-*r*-PVP_f to $f \approx 0.03$ for the $dPS_{(1-f)}$-*r*-$PPHS_f$ is associated with both the formation of hydrogen bonds between the PHS units and the PVP homopolymer, and the repulsion of PHS units from the PS homopolymer. If too much PHS is present in the copolymer, strong hydrogen bonding between the PHS

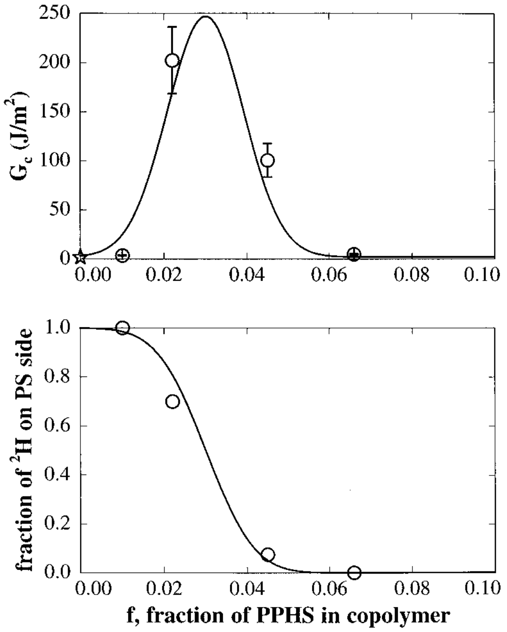

Figure 6. PS/PVP interface reinforced by a dPS$_{(1-f)}$-*r*-PPHS$_f$ random copolymer. (a) Fracture toughness G_c at high areal chain density ($\Sigma > \Sigma^*$) as a function of *f*. (b) Fraction of dPS on the PS side of the interface after fracture at low areal chain density ($\Sigma < \Sigma^*$) as a function of *f*.

and PVP is capable of "pulling" relatively large runs of styrene units into the PVP side. As a result, only short styrene-rich loops are left on the PS side, which are unable to entangle effectively with the PS homopolymer. At even higher PHS contents, the copolymer, in fact, becomes soluble in the PVP phase and no longer resides near the phase boundary. The strong repulsion between PHS and PS units reinforces this tendency.

For practical applications of these copolymers as strengthening agents, it would be convenient to predict the molar fraction, *f*, at which a maximum interfacial toughness value occurs. If we treat the random copolymer as a distinct, separate phase, the molar fraction that provides for a strong interface with both the PS and PVP homopolymers can be obtained in a straightforward manner. For this problem three interaction parameters are involved ($\chi_{PS-PPHS}$, χ_{PS-PVP}, and $\chi_{PPHS-PVP}$), which give rise to the effective interaction parameters between the random copolymer (rcp) and PS:[26]

$$\chi_{rcp-PS} = f^2\chi_{PS-PPHS} \tag{1}$$

and between the random copolymer and PVP:

$$\chi_{rcp-PVP} = (1 - f)\chi_{PS-PVP} + f\chi_{PPHS-PVP} - f(1 - f)\chi_{PS-PPHS} \tag{2}$$

In the large Σ limit, the random copolymer/PS interface becomes strong enough to support a craze only below $f \approx 0.05$. Therefore, below this composition, the χ_{rcp-PS} becomes comparable in magnitude to the interaction parameter for a relatively weak dPS$_{(1-f)}$-*r*-PVP$_f$ /PS interface ($\chi \sim 0.015$).[25] This condition sets an approximate lower limit for $\chi_{PS-PPHS} \approx 6$ according to eq 1. In our small *f* regime, $1 - f \approx 1$ and eq 2 for $\chi_{rcp-PVP}$ can be simplified to

$$\chi_{rcp-PVP} \approx \chi_{PS-PVP} + f(\chi_{PPHS-PVP} - \chi_{PS-PPHS}) \tag{3}$$

Using eq 3 we can estimate the *f* value at which $\chi_{rcp-PVP} < 0.015$. Using values of $\chi_{PS-PVP} \sim 0.1$,[27] and $\chi_{PPHS-PVP} \sim -0.28$,[28] and $\chi_{PS-PPHS} \sim 6$, our analysis gives a value $f > 0.018$ to produce a sufficiently strong interface between the random copolymer and PVP to support a craze. This estimate is in good agreement with the results shown in Figure 6. The analysis does not take account of the possibility of composition drift which is thought to be important in the dPS$_{(1-f)}$-*r*-PVP$_f$ random copolymer.[25] The reactivity ratios for the copolymerization of styrene and 4-[(*tert*-butoxycarbonyl)oxy]styrene (the precursor for PPHS) have been reported[29] to be both equal to 1, and thus no composition drift is expected in these copolymers.

Interestingly, the analysis also suggests that the large, positive $\chi_{PS-PPHS}$ is primarily responsible for the strong random copolymer/PVP interface (and a contributor to the good solubility of the copolymer in PVP at large *f*s) via the well-known copolymer effect.[20,26] The hydrogen-bonding attraction between PHS and PVP is relatively small compared to these repulsion effects. Since a large contribution to $\chi_{PS-PPHS}$ is derived from the self-hydrogen-bonding between PHS segments, hydrogen-bonding interactions still play the most important role in determining the range of *f* values for which interfacial strengthening is observed.

Conclusion

We have investigated the strengthening of the phase boundary between the pair of immiscible polymers PS and PVP using random copolymers of perdeuterated styrene and *p*-hydroxystyrene, dPS$_{(1-f)}$-*r*-PPHS$_f$, with different molar fractions, f. We found that the random copolymers are effective in strengthening the phase boundary only when *f* lies between 0.01 and 0.066. The highest G_c value obtained was near 250 J/m^2, which is not only higher than that obtained with dPS-*b*-PVP or dPS$_{(1-f)}$-*r*-PVP$_f$ copolymers but also close to the fracture toughness of the bulk PS material. The copolymer with which the maximum toughness was obtained contained only 2.2 mol % *p*-hydroxystyrene ($f = 0.022$). In the fracture studies, phase boundary failure was observed to occur through several different modes depending on the degree of functionalization of the random copolymer. For the two compositional extremes, the failure mechanism was chain pull-out from the PVP side (for copolymers with $f = 0.010$) and from the PS side (for copolymers with high functionality, $f = 0.066$). For each copolymer with intermediate composition ($f = 0.022$ and $f = 0.045$), a critical areal chain density, Σ^*, exists, which indicated the transition between failure mechanisms. Below Σ^*, failure occurred by a combination of chain scission and chain pull-out, while above this value, craze formation and craze breakdown via disentanglement was the predominant mechanism.

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