Chain Pullout Fracture of Polymer Interfaces[†]

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ABSTRACT: We have examined the fracture toughness as well as the deformation and fracture mechanisms of planar interfaces between polystyrene (PS) or blends of PS and poly(2,6-dimethylphenylene oxide) (PPO) and poly(2-vinylpyridine) (PVP) polymers. These interfaces were reinforced with various deuterated polystyrene/poly(2-vinylpyridine) (dPS/PVP) block copolymers, each of which had a short PVP block (shorter than, or just above, the entanglement molecular weight M_e of PVP); the dPS block in all cases was substantially longer than the M_e of PS. The fracture mechanism is found to be pure pullout rather than crazing followed by craze breakdown by chain pullout. When the fracture toughness, G_c, was plotted against $N_{PVP}{}^2\Sigma$, where Σ represents the areal chain density of a block copolymer, all data points (both for PS/PVP and PS(PPO) blend/PVP interfaces) fell on a single line, indicating that, in the pullout regime, only a single parameter, the friction coefficient between the PVP block segments and the PVP homopolymer, determines G_c. The upper limit N^* of the PVP block polymerization index above which chain scission occurs rather than pullout was investigated experimentally using a 420/270 block copolymer; the numbers represent the polymerization indices of the dPS and the PVP block, respectively. The PVP block is slightly longer than the polymerization index of PVP between entanglements, $N_{e;PVP}$ (=255). We found the upper limit, N^*, to be $N^* \approx N_{e;PVP}$, which is smaller than the estimate from the static friction force between PVP segments under the assumption that the friction force depends linearly on N_{PVP}. This fact indicates that there is an extra friction due to entanglements in the glass.

Introduction

The fact that block copolymers can strengthen interfaces between immiscible homopolymer phases is now well-known, and the conditions for such strengthening have been explored by a number of experiments.[1–12] Concurrently, theoretical models[7,8,13,14] have been developed to explain the reinforcement effect of these block copolymers and a failure mechanism map has been developed, based in part on these models, which attempts to predict the mechanism of interface failure as N, the polymerization index of each block, and Σ, the number of block copolymer chains per unit area, are changed.[13] According to the failure mechanism map, outlined in the appendix, the interface fails by crazing followed by chain scission when N and Σ are large,[8] while fracture takes place by chain scission of block copolymer at the joint when N is large and Σ is small.[8,15] On the other hand, for block copolymers with at least one short block, chain pullout is the mechanism for the interface fracture when Σ is small.[8,10]

For the molecular design of block copolymers for interfacial reinforcement, precise knowledge of the chain pullout regime, particularly the minimum polymerization index of the block to avoid pullout, is necessary. Two somewhat different mechanisms have been proposed for interface failure by chain pullout. The first is pure chain pullout[13] where one block is pulled out from the bulk under conditions where no crazing occurs. In the second a craze first occurs and craze breakdown takes place by chain pullout.[6,8,10] The objective of this work is a quantitative investigation of the chain pullout regime, with special emphasis on which of the chain pullout mechanisms is operative and on the determination of the upper limit of N above which chain scission rather than pullout takes place at small values of Σ.

We have chosen polystyrene (PS), as well as the blends between PS and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), and poly(2-vinylpyridine) (PVP) homopolymers as the immiscible polymer pair and dPS/PVP block copolymers as the compatibilizer to reinforce the interface between PS or the PS(PPO) blends and PVP. The advantage of these systems is that those materials deform plastically by crazing,[6,8–10] which can be easily investigated by transmission electron microscopy (TEM).[9,10] In addition, the crazing stress can be controlled by changing the composition of the PS(PPO) blend, which will allow us to determine which chain pullout mechanism (pure chain pullout or crazing followed by chain pullout) is active for the fracture of the interface.

We will use an asymmetric double cantilever beam method to measure the fracture toughness, G_c, of planar interfaces between immiscible polymers.[3–5,8] Use of this technique will allow us, from forward recoil spectrometry (FRES) of the two surfaces produced by the fracture, to determine the areal chain density Σ of the block copolymer at the interface, as well as to derive important clues as to the failure mechanism.

Experimental Section

(1) Materials. PS and PVP homopolymers purchased from Aldrich Chemical Co. Inc. were of commercial grade with weight-average molecular weights of 250 000 and 200 000, respectively. The PPO homopolymer had a weight-average molecular weight of 35 000. The dPS/PVP block copolymers listed in Table 1 were synthesized by anionic polymerization in tetrahydrofuran using cumylpotassium as the initiator at −55 °C in an argon atmosphere. The PS block is labeled with deuterium so that the quantity of the dPS block at the interface can be analyzed with forward recoil spectrometry (FRES).[16,17] The molecular weight and the composition of the block copolymers were characterized using FRES, gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR). The polydispersity indices of these

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Table 1. Polymerization Indices of the Block Copolymers

code	dPS block	PVP block
580/220	580	220
680/100	680	100
625/49	625	49
420/270	420	270

block copolymers were 1.1 or less. The various block copolymers will be designated by their polymerization indices; i.e., the block copolymer whose polymerization index of the dPS block is 580 and that of the PVP block is 220 will be denoted as 580/220. More details of the polymerization and the characterization can be found elsewhere.[18]

(2) Sample Preparation. A thin film of the block copolymer was spun cast from a toluene solution on a PVP slab. The areal density of block copolymer chains at the interface, Σ, was controlled by varying the concentration of the block copolymer in solution (0.1–0.4%), which in turn determined the thickness of the initial block copolymer layer. For the PS(PPO) blends, a PS(PPO) = 75/25 w/w film was cast from chloroform solution onto a glass plate. The polymer blend film was then transferred on top of a PS slab. The PVP slab was then joined to the PS slab (or PS(PPO)-clad PS slab) and annealed in a mold at 160 °C for 2 h. In this annealing process, some block copolymer chains organize as a brush at the interface. The resulting sandwich was cut with a diamond saw to obtain strips for the subsequent fracture toughness measurement. The dimensions of the strips were 50.8 mm long × 8.7 mm wide × 4.0 mm thick (2.3 and 1.7 mm for PS and PVP, respectively).

(3) Measurement of Fracture Toughness. The fracture toughness of the interface, G_c, which is defined as the critical energy release rate of an interfacial crack, was measured using an asymmetric double cantilever beam geometry (ADCB).[8] The measurement was performed by inserting a single-edge razor blade at the interface and pushing it at a constant rate of 3×10^{-6} m/s using a servo-controlled motor drive at room temperature in the air. The steady-state value of the crack length, a, along the interface ahead of the razor blade was measured at a regular interval. The fracture toughness, G_c, which is proportional to a^{-4},[8] was computed using these values of a. The error bars reported subsequently for G_c represent ±1 standard deviation of at least 16 measurements of crack length. After the G_c measurement, the halves of the fracture surfaces were examined with FRES to determine the areal density of block copolymer chains on both PS and PVP sides (Σ(PS) and Σ(PVP), respectively). The total areal chain density, Σ, of block copolymer was calculated by summing these two measurements; i.e., $\Sigma = \Sigma(\text{PS}) + \Sigma(\text{PVP})$. More details about the ADCB fracture test can be found elsewhere.[4,5,8,9]

Results and Discussion

(1) Fracture Toughness of the Interface between PS or PS(PPO) Blend and PVP. The fracture toughness, G_c, of the PS/PVP interface reinforced with the 580/220, 680/100, and 625/49 block copolymers is plotted as a function of Σ as open symbols in parts a, b, and c of Figure 1, respectively. For the 680/100 and 625/49 block copolymers, G_c increased linearly with increasing Σ, while the 580/220 block copolymer showed a discontinuous jump by ~10 J/m^2 at $\Sigma^* \approx 0.040$ chains/nm^2 and remained approximately constant for $\Sigma > \Sigma^*$;[10] only points below Σ^* are shown in Figure 1a.

The fraction of the dPS block found on the PS side after fracture, $\Sigma(\text{PS})/\Sigma$, is shown as a function of Σ as the open symbols in Figure 2. It is obvious that for the PS/PVP interface all the dPS block was found on the PS side of the interface for the 680/100 and 625/49 block copolymers, while the 580/220 block copolymer showed a discontinuous drop from $\Sigma(\text{PS})/\Sigma = 1$ to 0.2–0.4 at Σ^*. These discontinuous changes in G_c and $\Sigma(\text{PS})/\Sigma$ are due to a transition in the fracture mechanism from chain pullout ($\Sigma < \Sigma^*$) to crazing followed by craze failure by

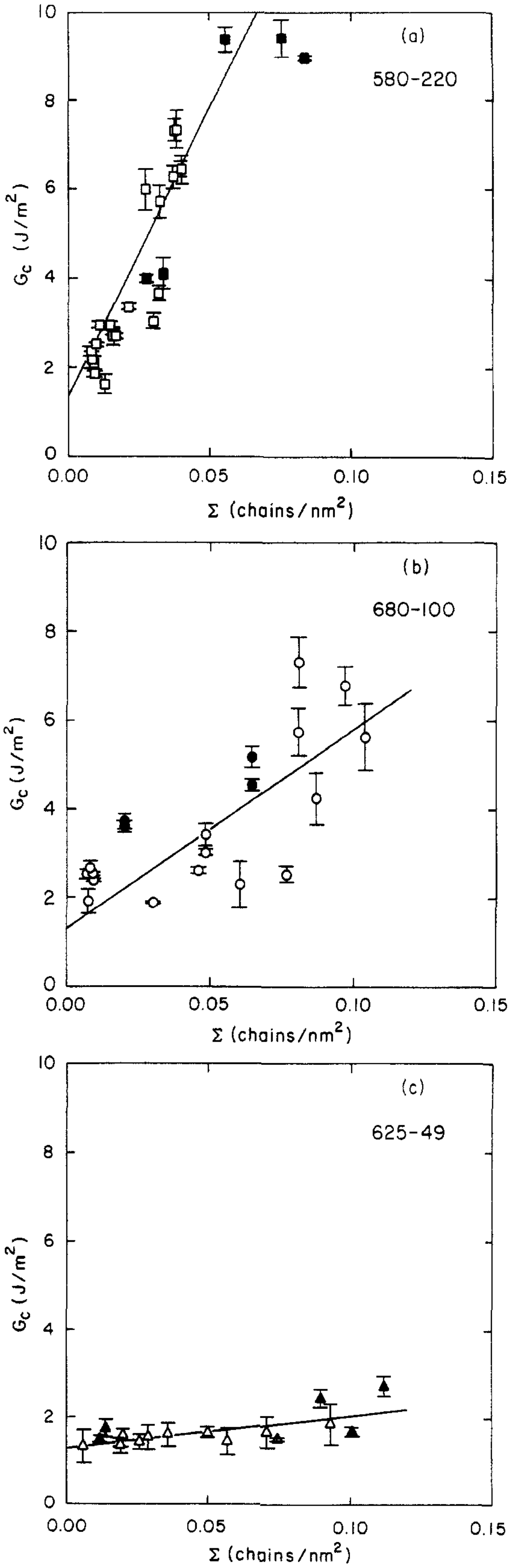

Figure 1. Fracture toughness, G_c, plotted as a function of areal chain density Σ of various block copolymers, at the PS/PVP interface (open symbols) or the PS(PPO)/PVP interface (filled symbols). (a) 580/220 block copolymer; (b) 680/100 block copolymer; (c) 625/49 block copolymer. Note that for all block copolymers G_c increases linearly with Σ in the small Σ regime. For the 580/220 block copolymer at the PS/PVP interface G_c shows a discontinuous increase (not shown) by ~10 J/m^2 at $\Sigma^* \approx 0.040$ chains/nm^2; for the same block copolymer at the PS(PPO)/PVP interface there is no discontinuous increase at this value of Σ.

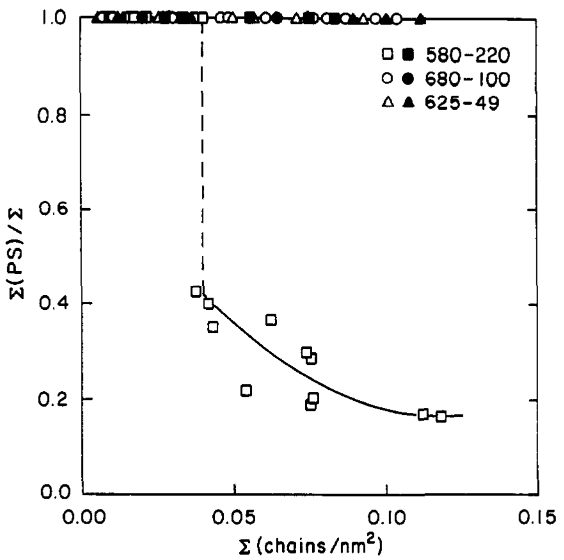

Figure 2. Fraction of the dPS block found on the PS side, $\Sigma(PS)/\Sigma$, plotted as a function of Σ of various block copolymers for the PS/PVP interface (open symbols) and for the PS(PPO)/PVP interface (filled symbols). Note that all the dPS block was found on the PS or PS(PPO) side of the interface for the 680/100 and the 625/49 block copolymers for both PS/PVP and PS(PPO)/PVP interfaces, while for the 580/220 block copolymer there is a discontinuous transition at Σ^*, above which $\Sigma(PS)/\Sigma$ started to decrease, for the PS/PVP interface only; all the dPS block is found on the PS(PPO) side of the PS(PPO)PVP interface for all values of Σ.

chain scission ($\Sigma > \Sigma^*$).[10] These results indicate that the interface fractured by chain pullout for all block copolymers at low enough Σ. While one might argue that chain scission exactly at the joint in the block copolymer would result in all the dPS block being found on the PS side, such chain scission exactly at the joint is very unlikely and experiments on block copolymers with large N show that when chain scission near the joint occurs, about 5–10% of the dPS block is found on the opposite side of the fracture.[8] Since all the dPS is found on the PS side for these block copolymers at the PS/PVP interface, we conclude that the pullout is the operative mechanism.

For the interfaces between the blend of 75% PS and 25% PPO and PVP, the fracture toughness (solid points in Figure 1) and $\Sigma(PS)/\Sigma$ (solid points on Figure 2) showed similar features to these same quantities for PS/PVP interfaces as a function of Σ. For all the block copolymers, G_c linearly increased with increasing Σ, and all the dPS block was found on the PS side of the interface. These results indicate that the fracture mechanism of the interface is chain pullout. It should be noted that the 580/220 block copolymer at the PS(PPO)/PVP interface showed no discontinuous jump in G_c nor drop in $\Sigma(PS)/\Sigma$ when Σ exceeded Σ^*, indicating that, in contrast to the PS/PVP system, no wide craze was able to propagate for these values of Σ at this interface. This behavior can be understood by realizing that the addition of PPO to PS increases the crazing stress above σ_{craze} for the pure PS, shifting to larger values the critical areal chain density of block copolymer necessary to produce crazing on the PS(PPO) side of the interface. Under these conditions we expect the crazing stress of PVP (75 MPa) to be lower than that for PS(PPO). The increase in the minimum stress for crazing from 55 MPa for PS to 75 MPa for PVP should produce an increase in Σ^* from 0.04 if Σ^* is limited by the crazing stress of PS to 0.055 if Σ^* is limited by the crazing stress of PVP. For the PS(PPO)/PVP interface when $\Sigma > 0.055$, it seems likely that a craze started to form on the PVP side of the interface. Such a craze will break down by PVP block pullout before it can widen significantly, and thus it will not contribute significantly to the measured G_c. All the dPS will still be on the PS side of the interface as observed. The fact that G_c for the PS(PPO) interface with the largest Σ falls somewhat below the linear increase observed at lower Σ may also be a result of this failure mechanism. To prove this point definitely, we would need a way to detect very narrow crazes on the PVP side of the interface, a capability that is beyond the current state of the art.

(2) Mechanism for Chain Pull-Out. Two different mechanisms are possible for chain pullout failure of the interface. For the first, pure chain pullout,[13] no crazing is produced prior to pullout, and for the second a craze forms first, followed by craze breakdown by chain pullout.[7] Both of them can account for the results in Figure 2.

For the pure one-sided chain pullout model (where only one block pulls out of its side of the interface with no significant prior crazing), G_c scales as:[13]

$$G_c \sim f_{mono} N_{PVP}^{\,2} \Sigma \tag{1}$$

where f_{mono} is a static monomer friction coefficient and where N_{PVP} denotes the polymerization index of the PVP block.[19] (Note that in this case the PVP block is pulled out from the PVP homopolymer.) It should be noted that G_c is independent of the crazing stress. For the craze breakdown by chain pullout model, G_c scales as:[7]

$$G_c \sim f_{mono}^{\,2} N_{PVP}^{\,2} \Sigma^2 / \sigma_{craze} \tag{2}$$

This scaling equation is derived based on Brown's model for craze breakdown,[7] where the threshold force for the craze breakdown is replaced by the maximum friction force ($=f_{mono}N_{PVP}\Sigma$) on the PVP block instead of bond scission force as reported in Brown's paper. A more thorough analysis of Brown's model[14] shows that the Σ^2 dependence of eq 2 only strictly holds if the craze width is much larger than craze fibril spacing; otherwise, the continuum approximation used to derive this equation breaks down. Since the scaling of G_c with $1/\sigma_{craze}$ should not be affected to the same extent by the continuum approximation, for our purposes here we will use eq 2 even though we know that from the magnitude of G_c any craze which forms prior to failure must be narrow. The scaling law for G_c when a craze is formed (eq 2) is completely different from that for the pure one-sided pullout failure (eq 1). The difference will provide a way to identify which pullout mechanism is active.

In Figure 3, ΔG_c is plotted as a function of $N_{PVP}^2\Sigma$ for the interface between PS and PVP for all $\Sigma < \Sigma^*$, conditions where pullout is the operative mechanism, and where ΔG_c is given by:

$$\Delta G_c = G_c - G_c(0) \tag{3}$$

Here, $G_c(0)$ corresponds to the fracture toughness of a bare PS/PVP or PS(PPO)/PVP interface (without block copolymer; $\Sigma = 0$). It is obvious from Figure 3 that all data points for the interface fall close to a single line. This observation indicates that the pure one-sided chain pullout is the mechanism for the interface fracture and that the chain pullout process is characterized by a single value of the friction coefficient per monomer.

The magnitude of the friction coefficient f_{mono} can be estimated using the value of $\Sigma^* = \sigma_{craze}/f_{mono}N_{PVP}$ at which the transition from chain pullout to crazing takes place for the interface between PS and PVP for the 580/220 block copolymer. A value of $f_{mono} \approx 6 \times 10^{-12}$ N/monomer

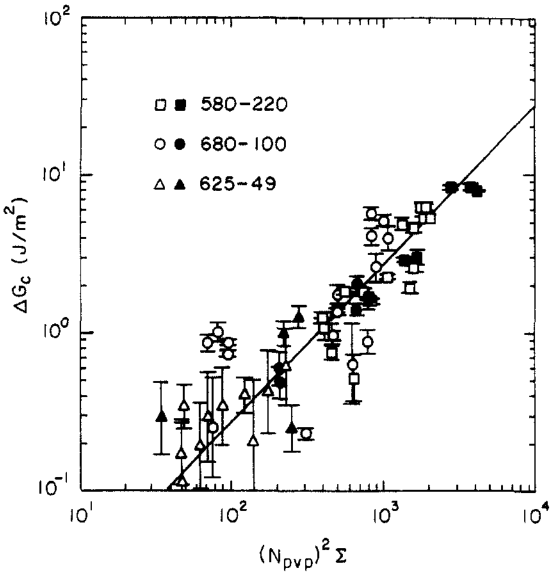

Figure 3. ΔG_c plotted as a function of ΣN_{PVP}^2 for both the PS/PVP and the PS/PPO blend/PVP interfaces reinforced with the block copolymers in the chain pullout regime. Note that both sets of data fall close to a single line of slope 1, indicating that ΔG_c is independent of the crazing stress.

was obtained.[10] In the large Σ regime ($\sim$0.103 chains/nm^2) of the 680/100 block copolymer, crazing on the PS side of the PS/PVP interface has been observed by a cross-sectional TEM technique.[9,10] The chain pullout stress for this system can be estimated to be $\sigma_{pullout} \approx 60$ MPa, which is larger than the crazing stress of PS ($\approx$55 MPa.)[8] The observation of crazing at large Σ for this block copolymer is thus consistent with the failure mechanism map.[10,13]

It should be pointed out that some polymer chains break during craze propagation in order to form the craze fibril structure.[20,21] Therefore, Σ required to support propagation of a stable craze is somewhat larger than Σ required to allow an unstable (narrow) craze to initiate. This difference would cause f_{mono} to be underestimated if it is calculated from the condition for stable craze propagation, i.e., from the Σ^* at which a jump in G_c is observed. For the G_c measurements we have used an asymmetric double cantilever beam geometry to force the craze tip to propagate at the interface,[8] thus causing breakage of chains during craze formation in the region of the dPS block/PS hompolymer interface. The Σ required for the stable (wide) craze propagation should therefore be greater than that required to support the stress to initiate craze widening.

In contrast, in the TEM experiments reported by Washiyama et al., an interfacial craze propagated parallel to, but offset from, the interface[9] and grew in width both away from and toward the interface. The sample geometry of the TEM specimen is symmetric, and the smaller Young's modulus of the PS causes a mode II stress intensity factor K_{II} which tends to force the craze tip away from the interface and into the PS phase. In this case, no entanglement loss occurs at the block copolymer/homopolymer interface until the craze widens enough that the craze/bulk boundary reaches the block copolymer region. Indeed, a craze was observed at the interface in the TEM experiments,[9] under conditions where no evidence for crazing was observed from G_c from the asymmetric double cantilever beam fracture tests or from an optical microscopic study of the fracture surfaces produced by this test.[8]

It is possible to estimate f_{mono} by analyzing G_c in the chain pullout regime from eq 4 by assuming no extra energy dissipation except chain pullout takes place during fracture.[13] Namely

$$\Delta G_c = (1/2) f_{mono} N_{PVP}^2 \Sigma l_0 \qquad (4)$$

where l_0 denotes the monomer length ($\approx 2.3 \times 10^{-10}$ m). By fitting eq 4 to ΔG_c vs $N_{PVP}^2\Sigma$, one obtains $f_{mono} \approx 2.5 \times 10^{-11}$ N/monomer. This number is about 4 times as large as that from the transition.[10] At least two possible reasons for this discrepancy can be given. The model proposed above ignores any viscoelastic dissipation in the PS or PVP homopolymer outside the pullout zone. The effect of such dissipation will be to multiply the G_c of the pullout model by a factor greater than 1.[22] This mechanism gives larger G_c without changing the scaling law for the pure chain pullout model. Another reason for that discrepancy is underestimation of the crazing stress of PS, where we have used the craze propagation stress instead of the craze initiation stress which may be higher.[10] While the latter error may contribute as much as a 20% increase in G_c and thus f_{mono}, it cannot account for most of the 4-fold increase actually observed, and we believe that viscoelastic dissipation outside the pullout zone is the major cause of the discrepancy.

(3) Limits of Chain Pull-Out. According to the failure mechanism map, chain pullout should be observed under certain conditions. The first is that Σ cannot be larger than Σ^* where the transition from the chain pullout to crazing occurs. This transition has been already discussed above and elsewhere.[10] The second is that so much force cannot be applied to the block copolymer chains that they break. When $\sigma_{pullout}$ is greater than the chain scission stress, $\sigma_{scission}$, chain pullout can no longer take place and chain scission is the operative fracture mechanism. This condition produces an upper limit on N, N^*, for chain pullout. Although this upper limit is one of the most important parameters required for the molecular design of block copolymers for interfacial reinforcement, it is not known precisely for any system. Assuming that the pullout force on a single chain continues to increase linearly with N, i.e.

$$f_{pullout} = f_{mono} N_{PVP} \qquad (5)$$

holds to large values of N, Washiyama et al.[10] have estimated the upper limit, N^*, for the chain pullout for the interface between PS and PVP reinforced with dPS/PVP block copolymer and obtained $N^* \approx 350$. This number is larger than the N between entanglements, $N_{e;PVP} \approx 255$, and for an N between $N_{e;PVP}$ and N^* some PVP blocks would thus form entanglements with PVP homopolymer. Any localized extra friction at an entanglement might be expected, however, to drastically increase the chain pullout force, so that the simple linear relationship between $f_{pullout}$ and N_{PVP} may break down for N_{PVP} somewhat above $N_{e;PVP}$. Consequently, $N^* = N_{e;PVP}$ has been expected.[10]

In order to clarify this point, experiments on a dPS/PVP block copolymer, with N_{PVP} satisfying the condition of $N_{e;PVP}$ (=255) $< N_{PVP} < 350$, are necessary. The critical test for this system is to examine an interface with an areal chain density of block copolymer in the small Σ regime ($\Sigma < 0.05$ chains/nm^2) to determine the location of the dPS block after fracture. If chain pullout were active, one would find *all* dPS on the PS side, and if chain scission were the mechanism one would find the majority (but *not all*) of dPS on the PS side. We used a 420/270 block copolymer for this investigation, the PVP block of which

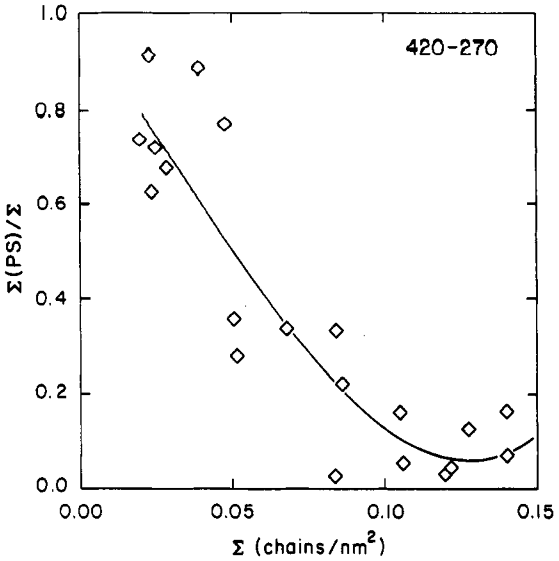

Figure 4. Fraction of the dPS block found on the PS side, $\Sigma(PS)/\Sigma$, plotted as a function of Σ of the 420/270 block copolymer at a PS/PVP interface. Note that the majority, but not all, of the dPS block is found on the PS side of the interface, indicating that the failure mechanism is chain scission prior to crazing at low Σ and crazing and craze failure by chain scission at higher Σ.

is slightly greater than $N_{e;PVP}$, so that this block copolymer will provide a critical test for the value of N^*.

Figure 4 shows the fraction of dPS block found on the PS side, $\Sigma(PS)/\Sigma$, as a function of Σ. In contrast to the results for the 580/220 block copolymer, it is clear that at low Σ the majority (80–90%) but not all of the dPS block is found on the PS side and that fraction decreases with increasing Σ. A similar decrease in $\Sigma(PS)/\Sigma$ is observed for symmetric dPS/PVP block copolymers of larger N_{PVP} where it marks the transition from chain scission to crazing.[8,23] We also observed, by optical microscopy, the remnants of a broken craze on the PS side of the fracture surfaces for $\Sigma > 0.05$ chains/nm^2. These observations indicate that N_e dictates the upper limit of N for the chain pullout; i.e., $N^* \approx N_e$. This point can be demonstrated more dramatically by plotting the pullout force for the various block copolymers vs N_{PVP} as shown in Figure 5. (The point for $N_{PVP} = 220$ was determined from Σ^*, and forces for the lower N_{PVP}'s were computed based on the scaling relation of eq 5 which is consistent with the results shown in Figure 3.) For $N_{PVP} = 270$, the pullout force must be larger than the force f_b to break a C–C bond estimated previously from the transition from chain scission to crazing to be approximately 2.2×10^{-9} N. The pullout force must increase much more rapidly with N_{PVP} than linearly between $N_{PVP} = 220$ and 270. This result indicates that there is an extra friction or constraint associated with entanglements in the glass, supporting inferences drawn previously from deformation and fracture studies of polymer glasses [e.g., refs 20 and 21].

Conclusions

We have investigated the chain pullout mechanism and an upper limit of N_{PVP} of planar interfaces between PS or PS(PPO) and PVP, reinforced with a series of PS/PVP block copolymers which have short PVP blocks.

Chain pullout mechanisms, pure pullout, and crazing followed by craze breakdown by pullout were investigated. When the fracture toughness, G_c, is plotted against $N_{PVP}{}^2\Sigma$, where Σ represents the areal chain density of the block copolymer, all data points (both for PS/PVP and PS(PPO)/PVP) fell on a single line. This result indicates that pure chain pullout is the mechanism for the interface fracture and that, in the pullout regime, only a single parameter, the friction coefficient between the PVP block segments and PVP homopolymer, determines G_c.

The upper limit, N^*, of the polymerization index of a PVP block for the chain pullout was investigated using a 420/270 block copolymer. We found $N^* \approx N_{e;PVP}$, which is smaller than the value estimated from the static friction force under the assumption of the linear dependence between friction force and N_{PVP}, indicating that there is an extra friction due to entanglements in the glass.

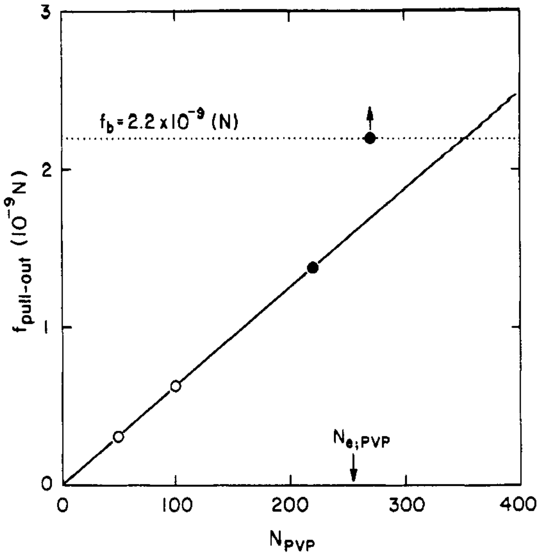

Figure 5. Pullout force, $f_{pullout}$, plotted as a function of N_{PVP}, where the slope of the straight line was determined from the solid point found from the transition from pullout to crazing in the 580/200 block copolymer. The $f_{pullout}$ at $N_{PVP} = 270$ must be larger than the point with the arrow since chain scission, not pullout, was observed. The two open points for lower N_{PVP} are inferred from the success of the scaling relation (eq 4) for ΔG_c. Note that the pullout force increases much more rapidly than linearly with N_{PVP} between $N_{PVP} = 220$ and $N_{PVP} = 270$.

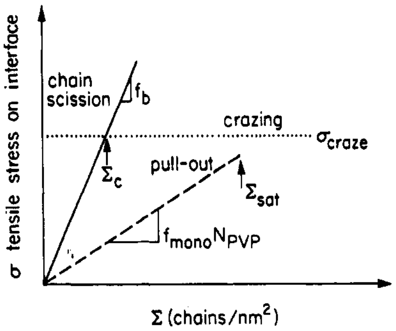

Figure 6. Failure mechanism map proposed by Xu et al.[13]

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Appendix: The Failure Mechanism Map

A brief summary of the failure mechanism map, developed previously[10,13] and shown in Figure 6, follows. The map describes the relationship between the maximum tensile stress, σ, ahead of the crack tip and normal to the interface and the areal density of block copolymer Σ, where at least one of the materials is capable of deforming plastically by crazing.

The horizontal line $\sigma = \sigma_{\rm craze}$ represents an upper limit which is independent of Σ, since we assume a craze widens into one polymer phase (in this case PS) under constant stress, $\sigma_{\rm craze}$. The saturation areal chain density, $\Sigma = \Sigma_{\rm sat}$, provides an upper limit of areal chain density above which the interface becomes saturated with block copolymers so that additional block copolymer chains can no longer organize as a brush at the interface but form other phases, such as micelles or lamellae, near the interface.[24]

The stress for chain scission and the stress for block pullout both increase from zero linearly with Σ so only one of these fracture mechanisms can operate, the one with the smaller slope on the σ vs Σ map. The stress required to cause chain scission of block copolymer chains at the interface $\sigma_{\rm scission}$ is given by eq A-1:

$$\sigma_{\rm scission} = \mathbf{f}_{\rm b}\Sigma \qquad \text{(A-1)}$$

where $\mathbf{f}_{\rm b}$ denotes the force to break a single C–C bond. (Note that for the dPS/PVP block copolymer, all main-chain bonds consist of C–C bonds.) The value of $\mathbf{f}_{\rm b}$ has been determined from both theoretical[25] and experimental[7,8,26] studies.

The block pullout stress, $\sigma_{\rm pullout}$, arising from the frictional force between the copolymer block and the bulk polymer chains surrounding it, is assumed to be given by eq A-2, viz.

$$\sigma_{\rm pullout} = f_{\rm mono}N\Sigma \qquad \text{(A-2)}$$

where $f_{\rm mono}$ denotes a static (velocity independent) friction coefficient per monomer, and N is the polymerization index of a block which is subjected to pullout. This simple form of eq A-2 can only be expected to hold for blocks shorter than $N_{\rm e}$; for $N \gg N_{\rm e}$, $\sigma_{\rm pullout}$ will increase with N more strongly than linearly, as demonstrated above.

The $\sigma_{\rm pullout}$ line can fall in one of three different regimes depending on the value of N: we define such regimes as regimes I–III. The conditions to achieve these three regimes are given by the following:

$$N > \sigma_{\rm craze}/f_{\rm mono}\Sigma_{\rm c}\ (=\mathbf{f}_{\rm b}/f_{\rm mono}) \qquad \text{regime I} \qquad \text{(A-3)}$$

$$\sigma_{\rm craze}/f_{\rm mono}\Sigma_{\rm sat} < N < \sigma_{\rm craze}/f_{\rm mono}\Sigma_{\rm c} \qquad \text{regime II} \qquad \text{(A-4)}$$

$$N < \sigma_{\rm craze}/f_{\rm mono}\Sigma_{\rm sat} \qquad \text{regime III} \qquad \text{(A-5)}$$

Regime I. Regime I corresponds to large N. From Figure 6 there is a critical chain density at $\Sigma_{\rm c}$ given by eq A-6, at which a fracture mechanism transition would be expected.

$$\Sigma_{\rm c} = \sigma_{\rm craze}/\mathbf{f}_{\rm b} \qquad \text{(A-6)}$$

When $\Sigma < \Sigma_{\rm c}$, chain scission would be the dominant fracture mechanism, since $\sigma_{\rm scission} < \sigma_{\rm craze}$ in this range of Σ, while when $\Sigma > \Sigma_{\rm c}$, crazing would be the dominant mechanism. It is emphasized that this transition is dictated by the bond strength (for example, C–C bond) and, hence, should be universal.

Regime II. The second regime corresponds to an intermediate N. In this regime, a transition in the fracture mechanism would be expected at Σ^*, given by eq A-7, from chain pullout ($\Sigma < \Sigma^*$) to crazing ($\Sigma > \Sigma^*$).

$$\Sigma^* = \sigma_{\rm craze}/f_{\rm mono}N \qquad \text{(A-7)}$$

Regime III. When a block is extremely short, the $\sigma_{\rm pullout}$ cannot exceed $\sigma_{\rm craze}$ over the entire range of $\Sigma < \Sigma_{\rm sat}$, and hence chain pullout would be the fracture mechanism throughout this whole regime.

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