Influence of Chain Entanglement on the Failure Modes in Block Copolymer Toughened Interfaces

C. Creton, H. R. Brown,* and V. R. Deline

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

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ABSTRACT: We have investigated the toughness and failure mechanism of the interface between poly(methyl methacrylate) (PMMA) and poly(phenylene oxide) (PPO) homopolymers reinforced with varying amounts of a PMMA–polystyrene (PS) block copolymer. The block copolymer was found to increase the interface fracture toughness, G_c, by up to 2 orders of magnitude. G_c increased with the areal density of block copolymer, Σ, and then showed a maximum at a copolymer layer thickness equal to about $0.75L$, where L is the long period of the neat copolymer. SIMS analysis of the fracture surfaces revealed that the block copolymer was well organized at the time of fracture and that, when the surface coverage was below $L/2$, the block copolymer fractured in the middle. When Σ was larger than the value corresponding to $L/2$, patches of a lamella of pure block copolymer were formed at the interface and the locus of fracture shifted to the center of the PS lamella. These results suggested that, at low coverage, the interface failed by fracture of the block copolymer chains near their junction points without any significant amount of plastic deformation. At higher Σ, but below the saturation value, the interface failed by forming a craze, the maximum thickness of which was controlled by the fracture of the block copolymer chains again near their junction points. No fracture in the brush between the block copolymer and the homopolymer was observed. When PS lamellas formed, at high coverage, the locus of fracture shifted to the center of the lamellas as the entanglement in a PS layer is significantly lower than that between PS and PPO or in a PMMA layer.

Introduction

It has been known for some time that the presence of a suitable block copolymer can greatly improve the mechanical properties of a blend of immiscible polymers.[1-5] This improvement has been attributed to the emulsifying effect of the block copolymer producing both better adhesion between the phases and a smaller phase size. To reduce the overall free energy, a block copolymer that is blended into the system will tend to segregate at the interfaces and organize itself with each of its blocks mixed with a compatible or nearly compatible homopolymer. The experiments of Creton et al. on the blends of polystyrene (PS) and poly(2-vinylpyridine) (PVP)[6] demonstrated that, while this interfacial block copolymer is always effective in reducing the interfacial tension, certin criteria must be met to obtain a mechanical reinforcement. Recently, a great deal of attention has been given to the study of the interfacial adhesion of such systems. An instrumental tool in the recent work has been the extensive use of a combination of an asymmetric double cantilever beam test designed to measure the fracture toughness of interfaces with samples that contain a controlled amount of block copolymer at the interface.[7] This test method combined with surface analysis techniques such as secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS), and X-ray photoelectron spectroscopy has produced a reasonably good understanding of the effect of block copolymers on the interfacial adhesion.

The fracture toughness of an interface, G_c, defined as the energy that must be dissipated to split a unit area of the interface, is large when crack propagation causes the material close to the interface to experience a large amount of plastic deformation. This deformation occurs when the interface can sustain a high enough stress to activate a major energy dissipation mechanism such as crazing or yielding to form deformation zones.[8] In this context, the addition of a suitable block copolymer is a technique to raise the maximum acceptable stress at the interface to a level high enough to trigger the plastic deformation mechanisms in the bulk polymers.

In a series of recent studies, the interfacial adhesion was found to be dependent on the degree of polymerization of each block (N), the areal density of block copolymer chains at the interface (Σ), and the average degree of polymerization between entanglements (N_e) of the two homopolymers.[9-12] In these experiments the diblock chains at the interface are normally present in quantities less than saturation but, even when the interface is saturated, the chains are not expected to be seriously stretched away from the interface. Hence it is reasonable to use the standard homopolymer value for N_e. Several microscopic deformation mechanisms were identified and can be summarized in the following manner: If N of one of the blocks is lower than N_e for the homopolymer with which it is blended, the interface failed by pullout of this shorter block without any significant amount of plastic deformation. The measured fracture toughness G_c was low and increased linearly with Σ and approximately with N^2, consistent with some recently proposed models based on a frictional resistance to chain pullout. The N^2 form follows directly from the fact that both the frictional resistance and the length of the pulled-out chain increase linearly with N. When N was raised above N_e, two distinct regimes were identified. At low Σ, the measured G_c was low and varied linearly with Σ, and the interface failed without any significant amount of plastic deformation. In this regime, surface analysis revealed that the block copolymer underwent chain scission near the joint between the two blocks. At higher Σ, the interface failed at much higher levels of G_c by first forming a wide craze in the material with the lower crazing stress, which then subsequently failed by fracture or pullout of the copolymer chains.

As the high N and high Σ regime is the most interesting for anyone wishing to design a block copolymer system, it is worthwhile to review in more detail what is known both theoretically and experimentally. In his recent

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model,[13] Brown argues that the last fibril in a craze (the one closest to the crack tip) experiences a stress which is dependent on the width of the craze and much higher then the average craze stress. This model, subsequently developed more rigorously in mechanical terms by Hui et al.,[14] predicts that G_c should be proportional to σ_f^2, where σ_f is the critical stress of failure of the last fibril. If the fibril fails by chain scission, $\sigma_f = \Sigma f_b$, where f_b is the force to break a C–C bond. Brown's results on interfaces between PPO and PMMA in a regime where $N \gg N_e$ are consistent with σ_f being independent of N and varying with Σ. However, the results on the PS–PVP system in a range where $N \approx 1$–$4.5N_e$ showed a clear dependence of σ_f on N as well as on Σ. In a generalization of Brown's model to a disentanglement case, de Gennes[15] argues that the fibril fails in a softened active zone, the size of which depends on the stress. When the softened zone reaches a critical size larger than the size of a random coil of the block copolymer, the interface fails. Such a model, which can be applied to explain the molecular weight dependence of the toughness of homopolymers, yields a dependence on N^2 for G_c which is qualitatively consistent with experimental results. Some additional information is provided in this regime by the surface analysis; in the PS–PVP system, FRES and cross-sectional TEM results show that the craze does indeed fail in the active zone and that the interface fails not at the joint between the two blocks of the copolymer, as was seen at low Σ, but in the brush region between the PS homopolymer and the PS block (note this is not a stretched brush). By contrast, Brown et al.[16] found by SIMS that, in the PMMA–PPO system, the interface failed in the joint area. However, this latter result was only a particular value of Σ, and so they had no information on whether any transition from joint to brush failure, similar to that observed in the PS–PVP system, occurred in their system.

In this paper, we investigate the fracture mechanisms of interfaces between poly(methyl methacrylate) (PMMA) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) reinforced with PS–PMMA block copolymers. The use of copolymers with comparable molecular weights but having the PS block or the PMMA block respectively perdeuterated allowed us to determine precisely the locus of fracture and to compare our results with those obtained by Creton et al. in the polystyrene–poly(2-vinylpyridine) (PS/PVP) system. The PS–PMMA block copolymers are known to organize at the interface between PPO and PMMA[17] in a similar fashion as the PS–PVP copolymers do but the average molecular weight between entanglements of PPO, PS/PPO mixtures, and PMMA is much smaller than those of PS and PVP. This difference between the two systems allowed us to test the validity of some recently proposed analysis on the role of entanglements in the reinforcement effect.[11,17]

Experimental Section

Materials. The PMMA homopolymer was purchased from DuPont (ELVACITE 2021) and had a M_w of 118 000 while the PPO homopolymer was purchased from General Electric (646–111) and had a M_w of 55 000. For both homopolymers the polydispersity was fairly broad, in the range of 2–2.5.

The PS–PMMA block copolymers were purchased from Polymer Laboratories and were nearly monodisperse. They were prepared by anionic polymerization, and the residual amount of precursor was removed by successive extractions in cyclohexane. Both copolymers used here were nearly symmetric. The polymers will be referred to by their respective degrees of polymerization so that a block copolymer with a PS degree of polymerization (N_{PS}) of 400 and a PMMA degree of polymerization (N_{PMMA}) of 450 will be referred to as 400–450. The 472–480 copolymer had a deuterated PS block, while the 541–602 copolymer had a deuterated PMMA block. More details about the copolymers and their characterization can be found in ref 18.

Sample Preparation. PMMA and PPO homopolymers were compression molded into sheets of dimensions 57 mm × 51 × t, where t varied from 0.8 to 3.2 mm. The molding was done at a temperature above the respective glass transition temperature of each polymer, namely, at 155 °C for PMMA and 225 °C for PPO. A thin film of PS–PMMA copolymer was then spun cast from a toluene solution on the PMMA sheet. Although one could think that this procedure would bury the block copolymer in the PMMA homopolymer, previous experiments comparing results from as-spun films with floated-on films which gave identical results showed this was not the case.[17] The thickness of the deposited copolymer film was controlled by the concentration of the solution and was checked by ellipsometry on silicon wafers where the film was cast using spinning conditions identical to those used on the PMMA sheets. The sheet was then dried at 70 °C for 1 h and joined to the PPO sheet in a press at 190 °C for 2 h. A temperature below the glass transition of PPO was chosen for the joining because it was the highest temperature that could be sustained by the PMMA without degradation. Previously published SIMS results have shown that 2 h at 190 °C is long enough to allow the organization of a 3 times larger block copolymer at the interface.[19] Little change in diblock organization was observed on increasing the joining time to 24 h. The favorable enthalpy of mixing between PS and PPO caused the PS part of the larger diblock to stretch by about a factor 2 away from the interface, but insignificant stretching was seen for the small diblocks used in the current experiment. After the joining process, the sample was fractured using the asymmetric double cantilever beam test developed by Brown.[7] The basic idea of this test (to be discussed in more detail below) is to choose the asymmetry of the sample, and hence the crack tip stress state, that gives the minimum toughness. This minimum is obtained by driving the crack toward the material with higher craze resistance, thereby suppressing multiple crazing close to the crack tip.

Samples for Dynamic SIMS. After fracture, one sample for each amount of copolymer was cut up to a square of ~1 cm², and the fracture surface was covered with a PS film ~500 Å thick. This additional layer, the purpose of which is to protect the fracture surface from contamination and provide a film to contain the initial SIMS sputtering transition, was deposited by first spin coating the PS film on a glass slide and then floating it off in a water bath and picking it upon the fracture surface. The sample was then dried and analyzed.

A Perkin-Elmer 6300 secondary ion mass spectrometer was used to analyze the prepared SIMS samples. A 2-keV O_2^+ sputtering ion beam was used. The impact angle was 60° from the surface normal and the ion current was ~190 nA. The beam was rastered over an area 600 μm × 600 μm, and the secondary ions of $^1H^-$, $^2H^-$, and $^{12}C^-$ were collected from the center 20% of the raster. The $^1H^-$ and $^2H^-$ profiles were normalized to the $^{12}C^-$ depth profile at a counting rate of 5×10^4 $^{12}C^-/s$. Details of SIMS profiling in polymer films can be found elsewhere.[20]

Fracture Toughness Test. After molding, the sandwich test specimens were cut into strips 100 mm wide and 50 mm long. A razor blade was inserted at the interface and pushed in until the crack was clearly seen to be moving, at which point the sample was set aside and the length of the crack ahead of the razor blade was measured after 24 h to obtain a value characteristic of a crack arrest toughness. The results were then analyzed to obtain G_c according to the beam on elastic foundation model[21] adapted for asymmetric interfaces.[11]

Before we present our results, it is worth commenting on the test method which was used. When a crack propagates at the interface between two materials with different elastic constants, although the far-field applied stress pattern may be quite symmetric about the crack plane and so exclusively in opening mode or mode I, the crack tip will see a certain amount of shear (mode II) and hence propagate in a mixed mode (mode I and mode II).[22] Therefore the direction of maximum tensile stress will no longer be normal to the interface plane and there will be a driving force for the crack to deviate from the interface. Such effects have been extensively studied both theoretically and

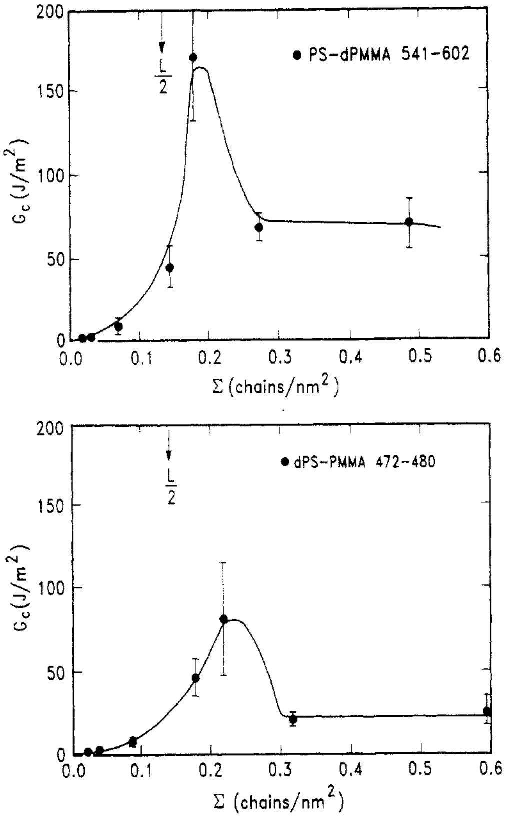

Figure 1. Variation of the interface toughness with block copolymer density Σ for (a, top) the PS–dPMMA copolymers and (b, bottom) the dPS–PMMA copolymers.

experimentally in the metal ceramic interfaces.[23-25] In the case of interfaces between polymers which deform mainly by crazing, if the crack tends to deviate toward the material which has the lowest resistance to plastic deformation, a significant amount of crazing in the bulk polymer can take place giving therefore much higher G_c values than expected for a purely adhesive failure.[10] Such an effect has been seen in various systems but always interpreted as an inherent property of the interface.[26,27] Only recently it has been demonstrated both theoretically and experimentally that the ratio of mode I to mode II can be controlled by the experimental geometry and that it can have a big influence on the measured fracture toughness.[7,11,23,28] In this study we used a thickness ratio of PMMA:PPO of 2:1. This was designed to drive the crack toward the material with the highest crazing stress (namely, the PPO) and to prevent any cohesive failure in the PMMA.

Results

The measured fracture toughness of the interface, G_c, is plotted in Figure 1 as a function of the nominal areal density of the copolymer, Σ. The value of Σ was obtained from ellipsometry as described previously, and it is assumed that no block copolymer is lost by diffusion in the bulk. The validity of such an assumption was confirmed by the fact that the SIMS experiments detected no copolymer that had diffused away from the interface into the bulk material. As the two block copolymers had very similar molecular weights well above M_e, it is not suprising that the plot of G_c vs Σ for both polymers shows very similar features. As was previously reported,[17] the presence of the block copolymer greatly increases the fracture toughness G_c. We measured fracture toughness values up to 80 J/m^2 for the 472–480 copolymer and up to 170 J/m^2 for the 541–602 polymer, which represent an increase of 2 orders of magnitude relative to the bare interface value of 2 J/m^2. Such high values of G_c imply that a major plastic deformation mechanism was active during fracture. It should also be noted that there appear to be two regimes in the portion of the plots where G_c increases: at low Σ, G_c increases linearly with Σ while at higher Σ, G_c appears to increase more rapidly up to a maximum value corresponding to a layer of thickness of 0.75*L*, where *L* is the long period of the neat copolymer. This result shows that the interface saturates at a layer thickness greater than *L*/2 (which corresponds to a Σ of 0.14 chains/nm^2 for these polymers), perhaps because of the favorable enthalpy of mixing between PPO and PS. For both copolymers, when Σ is further increased above the value corresponding to 0.75*L*, G_c decreases to a constant value that is much lower than the maximum, suggesting the occurrence of a "weak plane" at the interface. This "equilibrium" value of G_c is of the order of 25 J/m^2 for the 472–480 polymer and 70 J/m^2 for the 541–602 polymer.

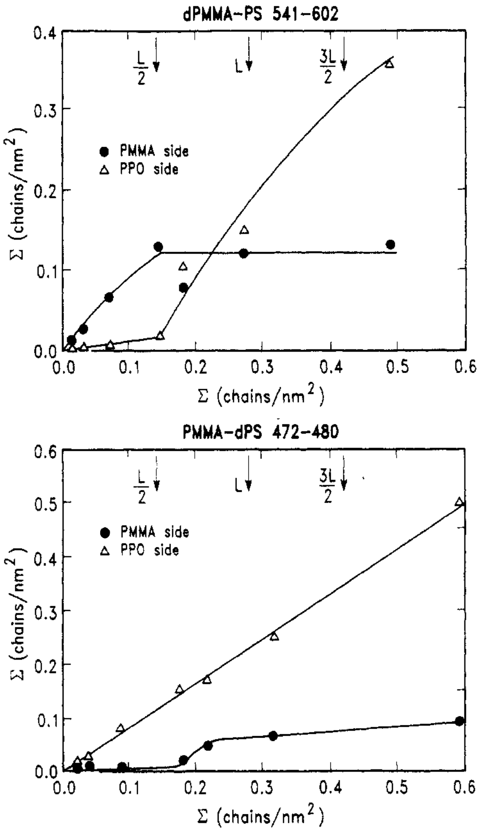

Figure 2. Quantity of the deuterated half of the copolymer, measured in chains per unit area, on the two fracture surfaces, the PMMA side and the PPO side, for (a, top) the PS–dPMMA copolymer and (b, bottom) the dPS–PMMA copolymer.

The most important advantage of our experimental system is the capability to analyze the fracture surfaces using surface analysis techniques and hence determine independently and quantitatively the location of each block of the diblock after fracture, gaining therefore an understanding of the precise locus of fracture. The areal density of the deuterated PMMA block of the 541–602 copolymer found on the two fracture surfaces is shown in Figure 2a, while the areal density of the dPS block of the 472–480 copolymer is shown in Figure 2b. The values of Σ_{PMMA} and Σ_{PPO} were obtained in the folloing manner: the relative amount of deuterium on each fracture surface was determined by integrating the $^2H^-$ signal from the SIMS depth profile which was then multiplied by the total areal density of chains at the interface as obtained by ellipsometry.[17]

The SIMS results show two distinct regimes. In the first regime, for $\Sigma_{TOT} \leq$ the value corresponding to a layer thickness of *L*/2, each block remains on its respective ("correct") side of the fracture plane and so fracture takes

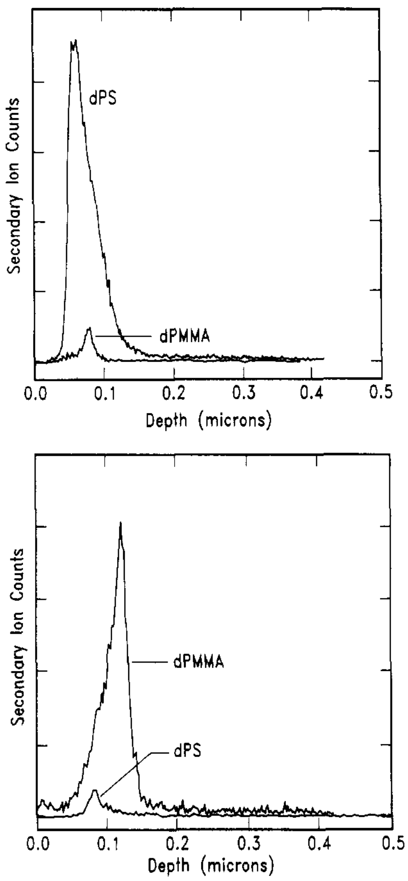

Figure 3. Deuterium depth profiles beneath two fracture surfaces for both diblock copolymers taken at a value of Σ of 0.075 chains/nm^2, a value that is below $L/2$ but sufficient to cause crazing. Clearly, the copolymer molecules fail near their junction points.

place very close to the junction point between the two blocks of the diblock. Such fracture can only occur if all the diblock molecules break close to their junction points. A SIMS spectrum for each of the two copolymers at Σ = 0.075 chains/nm^2 is shown in Figure 3 to illustrate this regime. It should be noted that such results also constitute a proof that the block copolymer was organized at the interface before fracture as was reported previously by Brown et al.[16] In the second regime, at higher Σ, the situation ceases to be symmetric. For the case of the dPMMA-PS copolymer, the amount of dPMMA on the "correct" side, Σ_{PMMA}, remains constant at a value of 0.12 chains/nm^2, corresponding approximately to $L/2$ for that polymer, while the amount of dPMMA on the "wrong" side, Σ_{PPO}, increases very rapidly for $\Sigma > 0.12$ from a very small value and becomes greater than Σ_{PMMA} at high coverage. On the other hand, for the dPS-PMMA polymer, the amount of dPS on the "correct" side, Σ_{PPO}, continues to increase with increasing coverage while the amount of dPS on the "wrong" side, Σ_{PMMA}, slowly increases to a value of 0.1, corresponding roughly to a layer thickness of $L/2$ for that polymer. The situation at high coverage is illustrated in Figure 4 for Σ = 0.3 chains/nm^2. It is immediately evident from the double peak in Figure 4a that the diblock was organized into multiple lamellae at the interface. These results show that, as the coverage was increased above saturation ($L/2$) the diblock formed patches where the organized layer had a thickness of $3L/2$. In these thick patches the failure ran through the center of the PS lamella that was closest to the PMMA homopolymer. The situation is illustrated in Figure 5.

Effect of Asymmetry. Before we conclude the Results section, a comment is necessary concerning the effect of crack mixity. If our results are directly compared with the results of Char et al.[17] on the same system, they are lower by ~40%. The discrepancy can be explained by the difference in ratio of mode I and mode II loading at the crack tip between the two experiments. In Char's experiments, a very asymmetrical sample configuration was chosen where the PMMA was glued down to an aluminum substrate, as it was assumed that such a configuration would minimize plastic deformation in the PMMA without causing any plastic deformation in the PPO. However, in the present set of experiments, several degrees of asymmetry were tested and it was found that the best, by which it is meant the one giving the lowest

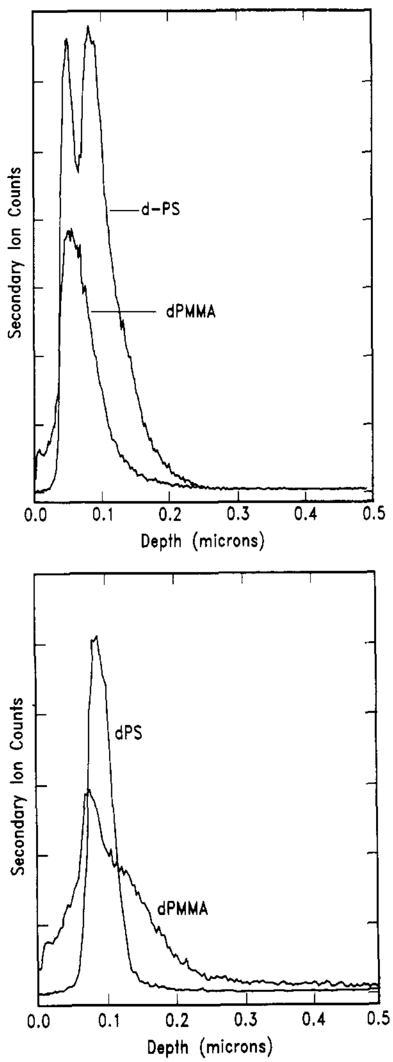

Figure 4. Deuterium depth profiles under the fracture surfaces for both diblocks taken with a Σ value of 0.3 chains/nm^2. The multiple lamellae are evident in the dPS profile on the PPO fracture surface.

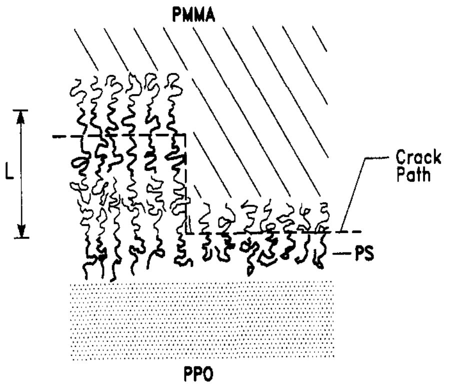

Figure 5. Diagram showing the organization of the diblock at the interface and the fracture plane for $\Sigma > L/2$.

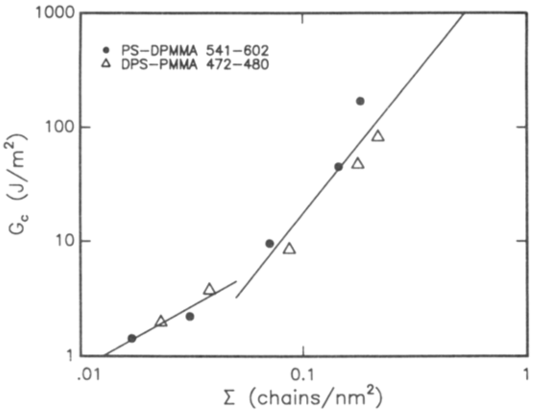

Figure 6. Variation of G_c with Σ for both copolymers showing the linear dependence at low Σ and a higher power when Σ is large enough to cause crazing.

G_c, was not the very asymmetric configuration used by Char but a slightly asymmetric one where the thickness of the PMMA sheet was twice that of the PPO sheet. This result stresses the fact that a good understanding of the effect of ratio of mode I to mode II is really needed if one wants to extract real material parameters from fracture tests of bimaterial interfaces.

Discussion

Our results can be interpreted in the light of the recent models and experimental observations on asymmetric polymer interfaces.[11,13,15–17,29] At low Σ, the value of fracture toughness is extremely low, corresponding to a regime where very little or no crazing is present. In this regime, it has been found that the block copolymer chains break in the region of the joint between blocks for the PS/PVP system, where a range of Σ values were studied, and the PMMA/PPO, and PMMA/PS systems, where only one Σ value was used. Our results confirm this finding. Furthermore, G_c appears to increase linearly with Σ, consistent with a regime where G_c is not controlled by crazing. At higher Σ, G_c increases sharply, a clear signature of the onset of the main plastic deformation mechanisms. In our system, PPO is known to form deformation zones while the PMMA deforms by crazing. Optical observations clearly showed the presence of a characteristic PMMA craze at the interface so that it is reasonable to think that the stability of the craze in the PMMA will control G_c. As was recently proposed by Brown, G_c is expected to vary with Σ^2 in this regime.[13] While we have too few data points here to reconfirm this hypothesis, G_c does indeed vary more rapidly with Σ than linearly as is particularly evident in the log–log plot of Figure 6.

The SIMS results are here quite different from the FRES results reported by Creton et al. on the PS/PVP system.[11,28,30] They found a clear transition in the locus of fracture of the copolymer from the area of the joint between the two blocks to a point within the PS block when Σ increased above a critical value of around 0.04 chains/nm^2. As the PS block forms an unstretched brush within the PS homopolymer, the latter failure was called brush failure. In the PMMA/PPO system studied here, we do not observe any change in the locus of fracture as long as Σ remains below the value corresponding to a layer thickness of $L/2$. The transition from joint to brush failure was associated in the PS/PVP system with the onset of fracture by crazing as the two effects did occur at the same level of Σ. However, our results here show that failure by crazing can also occur where the reinforcing copolymer chains break in the joint area. To understand this difference between the two systems, one needs to introduce the concept of an effective strand. As shown schematically in Figure 7, the interface can be broken down into two regions: the interface proper, which is the joint area, and the brush between the block and the homopolymer. These two regions can be thought of as two links in a chain so that failure will occur in the weakest link. In the first region, the areal density of effective strands is the areal density of block copolymer chains Σ, while in the second region there will be two regimes. At low Σ/Σ_{sat}, where Σ_{sat} is the areal density at saturation, the areal density of effective strands, Σ_{eff}, will depend on the degree of polymerization of the copolymer, N (assuming high molecular weight homopolymer), and if $N \gg N_c$ will be greater than Σ. At highest Σ/Σ_{sat}, the amount of interpenetration between the block and the homopolymer decreases with increasing coverage and is dependent on N and the interaction parameter χ between the block and the homopolymer. As pointed out in the analysis done by Creton et al.,[11] the relation between the amount of interpenetration and the number of effective strands is mainly controlled by N_e, so for high coverage and N not very much greater than N_e, Σ_{eff} in the brush region can be significantly lower than Σ and become the weak link in the interface. Hence this brush transition is expected to occur over a fairly restricted range of values of N/N_e between perhaps 2 and 6 and at a value of Σ/Σ_{sat} that increases with increasing N/N_e. Coming back to our experimental situation, while in the PS/PVP system, fracture occurs in the PS(N_c=180), in our system, it occurs in the PMMA(N_e=90) rather than in the PS–PPO mixture as the former has the lower entanglement density.[17] For a ratio of N/N_c = 4–5, Σ_{eff} in the PS brush–PS homopolymer case starts to be significantly lower than Σ when Σ becomes larger than ~0.04 chains/nm^2; this transition would not happen until a higher Σ for the PMMA brush–PMMA homopolymer case as the lower value of N_e and hence N would cause Σ_{sat} to be higher. In fact, the value of N/N_e is rather higher in the PMMA/PPO system than the value used in the PS/PVP system, so one would expect to either see the brush transition in our experimental system at a higher level of Σ than 0.04 chains/nm^2 or not see it at all. In fact, we saw no brush transition. This difference in properties between different polymers is due to the fact that N_e and the width of the interface between homopolymer and copolymer are not closely related quantities so that while the thermodynamic parameters that control the width of the brush area are well understood,[31] the same cannot be said for N_e, though progress is being made in this area.[32]

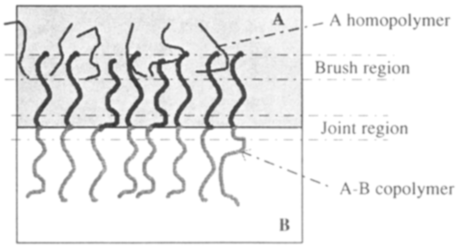

Figure 7. Diagram showing the joint and brush failure regions.

When the layer thickness is further increased from $L/2$, G_c goes through a clear maximum and then decreases toward a constant value. Such a behavior has already been observed by Brown using PS–PMMA copolymers between PS and PMMA homopolymers[29] and by Washiyama et al. in the PS/PVP system. A very thorough analysis of the PS–PVP case showed that when the block copolymer is capable of forming multiple lamellae at the interface, these lamellae are swollen with a low molecular weight fraction of the homopolymer and become the weaker part of the interface so that the locus of fracture moves from the brush region to the PS lamella.[28] The case in the current work, however, is slightly different as the creation of a pure block copolymer lamella implies the existence of an unmixed PS region which is not present in the homopolymers. SIMS results clearly show that when multiple lamellae are formed, the locus of failure shifts from the joint area to the center of the PS lamella which is closer to the PMMA homopolymer, as illustrated in Figure 5. This result can be interpreted in light of the effective strand arguments that have just been made. PS has a larger N_e than either PMMA or PPO, so a fully developed PS lamella (two brushes on end) should be expected to become the weakest link in the interface. Homopolymer is not expected to be present in this lamella; there is no PS homopolymer in the system and the PPO homopolymer, with a T_g higher than the joining temperature would be unlikely to get into the PS lamella.

The maximum in G_c occurs at a coverage, ~0.2 chains/nm^2, significantly greater than that corresponding to a layer thickness of $L/2$ in a regime where, from the SIMS results, some small amount of failure in PS lamellae is already occurring. As the coverage is increased beyond 0.2 chains/nm^2, G_c decreases rapidly as Σ is increased. In the simplest model, one might expect G_c to just decrease linearly with the proportion of the interface that is covered by multiple lamellae. Clearly, the decrease is much more rapid than this expectation and so the multiple lamellar patches may be operating as weak regions in the crack tip craze which fail and cause extra stress concentration in the single-layer patches, thereby initiating their failure. The fact that the maximum in G_c occurs at a Σ where a small number of multilayer patches have already formed could be explained by the suggestion that a small number of such patches toughens rather than weakens the interface because their failure causes a crack tip diversion from its normal plane at the copolymer joints.

The peak in toughness observed here is rather reminiscent of effects that have been seen in adhesive joints. As the layer thickness of a toughened epoxy adhesive between steel plates is increased, the toughness has been shown to show a maximum.[33] However, this maximum is typically at layer thickness of ~1 mm, ~5 orders of magnitude thicker than the copolymer layers used in this work. The peak in the toughness shown by the epoxy systems is explained by plastic zone size and constraint effects that, considering the different sizes involved, can have no relevance to the work presented here.

It is instructive to compare our results with those of Washiyama et al. for PS–PVP copolymers. The maximum G_c for a saturated PS brush before any formation of multiple lamellae in the PS–PVP system is plotted vs N_{PS} in Figure 8 together with our results in the regime where the measured toughness is controlled by the strength of the PS lamella (after the maximum in G_c). Our results fall very well within the results for the PS brush and suggest a sigmoidal curve with an inflection point around $N = 550$ rather than a curve with a monotonically increasing slope as it was suggested by Creton et al.[11] or as would be predicted by de Gennes' model.[15] It is interesting at this point to make a comparison with the fracture toughness of monodisperse PS homopolymer.[34] G_c increases rapidly with N when N becomes larger than $2N_e$ and goes through an inflexction point around $N = 700$ to become a constant value around N = 1000–1500. The reported maximum values for PS are of the order of 400–1000 J/m^2, which is a factor of 3–8 larger than the value reported for the high molecular weight PS–PVP. This difference stresses the fact that, because the stretching of the chains at the interface causes a lower degree of interpenetration than that between random coils, the fracture toughness of the homopolymers may never be achieved by using block copolymers as coupling agents. However, from the arguments given above, it follows that if N_e of the homopolymers is low enough, a very significant interface toughness, not very different from that between homopolymers, may be obtained.

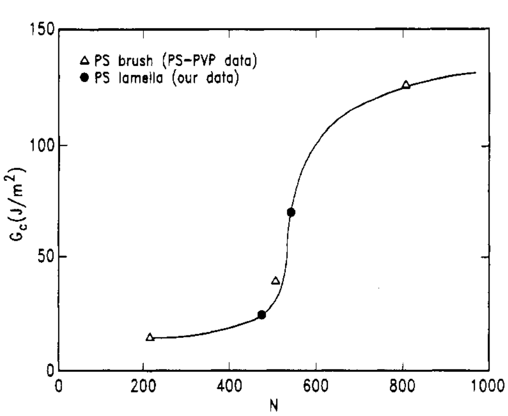

Figure 8. Comparison of the G_c values at multilayer coverage for the PS–PMMA diblock where failure occurs through the PS lamellae with the G_c maximum observed in the PS–PVP system where failure occurs in the brush.[12]

Conclusions

When block copolymers of PS–PMMA were added to an interface between PMMA and PPO, the measured fracture toughness increased by 2 orders of magnitude. The dependence of G_c on the areal density of block copolymer suggested that, at low Σ, the interface failed by fracture of the block copolymer chains near their junction point without any significant amount of plastic deformation, while at higher Σ, the interface failed by forming a wide craze, the maximum thickness of which was controlled by the fracture of the block copolymer chains in the joint area. SIMS analysis of the fracture surfaces revealed that the block copolymer was well organized at the time of fracture and that when the surface coverage was below the value corresponding to $L/2$, the block copolymer fractured in the middle. When Σ was larger than the value corresponding to $L/2$ and a lamella of pure block copolymer was formed at the interface, the locus of fracture shifted to the center of the PS lamella. No fracture in the brush between the block copolymer and the homopolymer was observed, in contrast with the observations made on the PS–PVP system. The difference between the two systems was explained in terms of the difference in M_e between the PS and the PMMA which allows a PMMA brush, at equal interpenetration distance, to be stronger than a PS brush. This fact was confirmed by the very sharp maximum observed in G_c when Σ was increased above the value corresponding to a layer thickness of $L/2$ and the weaker PS lamella controlled the craze failure.

In conclusion, one should bear in mind when designing a blend containing a block copolymer as a reinforcing agent that a low M_e of the mixture of the block copolymer with the homopolymer will allow effective use of low molecular weight block copolymers. Such copolymers have the double advantage of permitting the existence of high values of Σ at the interface without saturation and greatly accelerating the kinetics of the diffusion, which is required for the segregation of the block copolymer chains at the interface between the immiscible components of the blend.

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