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Effects of a Diblock Copolymer on Adhesion between Immiscible Polymers. 1. PS-PMMA Copolymer between PS and PMMA

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ABSTRACT: Thin layers of polystyrene (PS)-poly(methyl methacrylate) (PMMA) diblock copolymers were placed at the interface between PS and PMMA homopolymers, and the samples were joined at high temperatures. Fracture tests were used to measure the interface toughness, and secondary ion mass spectroscopy (SIMS) was used to examine the organization of the diblock. Diblock copolymers with molecular weights of 84 000 and above gave strong interfaces whose saturation toughness was independent of the copolymer molecular weight. Both kinetic studies and the SIMS results showed that the rate of diblock copolymer organization was a function of the layer thickness. Copolymer layers of thickness greater than about one-fourth of a long period did not organize in a simple way at the interface but gave interfaces with a high toughness. For thin layers that did organize, the toughness was low and the diblock molecules broke near their junction points. Low molecular weight symmetric and asymmetric diblocks were shown to give lower toughnesses than the high molecular weight materials, probably because they were pulled out of the PS homopolymer.

Introduction

The use of polymer blends as a means of combining the advantageous properties of more than one homopolymer is a subject of considerable current interest. However, different homopolymers are normally not miscible as the large size of the molecules ensures that there is very little mixing entropy available. In addition, polymer-polymer interfaces are frequently sufficiently narrow that there is little entanglement between the different species. As entanglement is a prerequisite for strength in polymer systems, interfaces between two immiscible polymers are normally weak.

There is a considerable body of literature on the use of diblock copolymers as additives to improve the properties of polymer blends.[1-9] The diblock copolymers are normally chosen so that each block is miscible with one or the other of the homopolymers, thereby ensuring that the diblock can both reduce the interfacial tension and improve the adhesion between the homopolymers. Both the reduced interfacial tension, which tends to reduce phase size, and the improved interphase adhesion may be expected to improve the mechanical properties of the blend. When a diblock copolymer is melt mixed with homopolymers, it is not clear how much of the diblock is dissolved in the two homopolymer phases, how much exists in the form of micelles, and how much goes to the interfaces. The distribution of the copolymer between the different phases depends on the molecular weights of both the homopolymers and the copolymer, the composition of the copolymer, and the time and temperature of mixing. It is not surprising then that much of the literature on mixtures of a diblock copolymer with homopolymers gives little fundamental information on the role of the block copolymer at the interface and, in particular, its effect on the interfacial adhesion.

One way to gain information on the effects of a block copolymer on the adhesion between immiscible polymers is to take sheets of homopolymers, place a layer of block copolymer of known thickness between them and then heat the system to the joining temperature for a fixed period of time.[10-12] Normally, the joining temperature used is above the glass transition temperatures of all the relevant materials. In this way one constructs a planar interface between the two homopolymers with a known amount of copolymer at the interface. It is possible to then measure the toughness of the interface as a function of the amount and type of the diblock. However care must be used in selecting the correct mechanical tests[12,13] that can drive the crack along the interface. In addition, if partly deuterated diblocks are used, secondary ion mass spectroscopy (SIMS) or forward recoil ion scattering (FRES) can be employed to examine the location and organization of the diblock copolymer at the interface. Some results using these techniques have already been published.[10,12] We have shown that PS-PMMA diblock copolymers can have a profound effect on the toughness of interfaces between PS and PMMA. The effect saturates at a layer thickness of about half a long period (L) of the diblock copolymer. If the same diblock copolymer is placed between PMMA and poly(phenylene oxide) (PPO) where there is a $-ve\ \chi$ (a favorable enthalpy of mixing) between the PS blocks and PPO, the PS block dissolves in PPO and is swollen with respect to a random coil configuration. When a crack is propagated along the interface, the diblock molecules all break near their junction points. Similar toughening effects have been observed in the PS/poly(vinylpyridine) (PVP) system.[12]

In the experiment discussed here the thin layer of diblock copolymer is formed by spin coating from solution. In the spin coating process the solvent loss is very rapid so the initial diblock layer is quite disorganized, meaning that the material has not microphase separated and so the PS and PMMA segments are intimately mixed. When the sandwich of homopolymer sheets and diblock copolymer is heated to the joining temperature, the diblock will slowly organize so that its PS segments dissolve in the PS homopolymer while the diblock PMMA segments dissolve in the PMMA homopolymer. It will be shown that this organization process is not rapid so that many of the samples were disorganized or partially organized. The state of the diblock organization was found to have a

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Table I. Characteristics of the Polymers

polymer	$10^{-3}M_w$	% styrene	M_w/M_n
PS	355		3
PMMA	118		2
P(S-*b*-MMA)	31	47	1.06
	53	50	
	84	50	1.2
	282	54	1.08
	355	44	1.2
	900	63	1.12
	67	86	
	110	7	
P(dS-*b*-MMA)	28	47	1.10
P(S-*b*-dMMA)	289	48	1.07
P(dS-*b*-MMA)	301	56	1.08
P(S-*r*-MMA)	270	70	

profound effect on the interface toughness.

The aim of the current work is to examine, in some detail, the effects of the PS–PMMA diblock at the interface between PS and PMMA homopolymers, thereby gaining an understanding of the effects of diblock molecular weight and organization on the interface toughness. It should be emphasized that such information can only complement the work on mechanical properties of blends, as it gives no information on the ability of the diblock to diffuse to the interfaces or on the phase morphologies caused by the diblock copolymer.

Experimental Techniques

Materials. Most of the PS–PMMA nearly symmetric diblock copolymers used in this study were purchased from Polymer Laboratories. These polymers were prepared by sequential anionic polymerization, and the residual PS prepolymer was removed by successive extractions in cyclohexane. Molecular weights of the diblocks range from 31 000 to 900 000. Some of the copolymers were made so that either the PS block or the PMMA block or both of the blocks were perdeuterated. d-PS-*b*-h-PMMA denotes perdeuteration of the PS block with the PMMA block undeuterated. The molecular weights of the d-PS-*b*-h-PMMA and the h-PS-*b*-d-PMMA copolymers were both about 300 000. The 900 000 molecular weight copolymer was obtained from Professor M. Tirrell and synthesized by Polymer Standards Services. The asymmetric diblock copolymers were obtained from Professor Robert Jérôme and synthesized and characterized in his laboratory. Detailed characteristics of the copolymers are given in Table I. A PS–PMMA random copolymer was purchased from Polysciences. The ratio of PS to PMMA segments was 70:30. It was polydisperse with a weight average molecular weight of 270 000.

The homopolymers used in this study were fairly broad molecular weight distribution materials. The polystyrene was obtained from Dow Chemical Co. (Styron 685) and had an M_w of 355 000. The PMMA was from DuPont (Elvacite 2021) and had an M_w of 118 000. A small amount of narrow molecular weight distribution PS of molecular weight 200 000 was obtained from Polysciences.

Fracture Tests. Sheets (50 mm × 64 mm × 1.7 mm) of the homopolymers were compression molded at 160 °C. For some samples a film of the narrow molecular weight distribution polystyrene with a M_w of 200 000 was spun directly onto the homopolystyrene sheet and the sheet was dried at 70 °C for 12 h; however this was found to make no difference to the fracture results. This check was done to find if the molding process produced a surface, either oxidized or perhaps low molecular weight, that would behave differently from a free surface of nearly monodisperse high molecular weight polystyrene. Similar tests were not done for PMMA, as previous experiments have shown that the fracture normally runs mainly through the polystyrene.[11] The diblock copolymer, dissolved in toluene, was typically spun onto the PMMA sheet which was then dried at 70 °C for at least 3 h to remove residual toluene. For diblock layer thicknesses greater than 15 nm, the diblock copolymer was sometimes initially spun onto a 125-mm × 75-mm glass slide, the sides of the slide were scored with a razor, and then the copolymer film was floated off the slide onto deionized water. The diblock film was then picked up onto a homopolymer sheet, and the specimen was dried in air, first at room temperature and then at 60 °C. Film thicknesses were measured by ellipsometry on copolymer films spun on a silicon wafer under the same conditions of solution concentration and spin speed that were used to make the fracture samples.

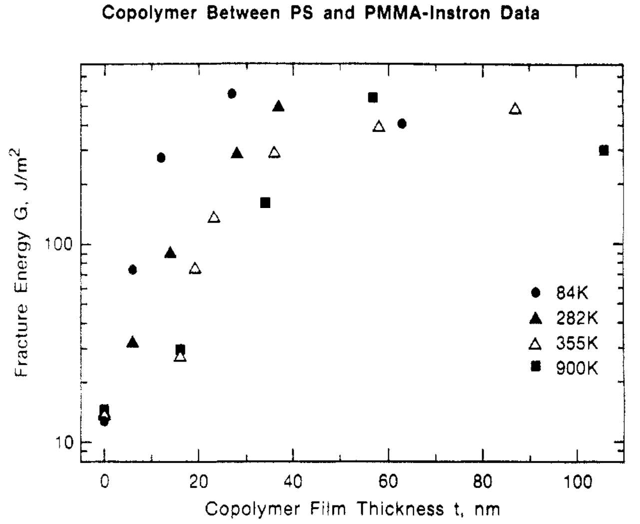

Figure 1. Variation of the interface toughness, G, with the thickness of the diblock copolymer layer, t, for the high molecular weight symmetric copolymers.

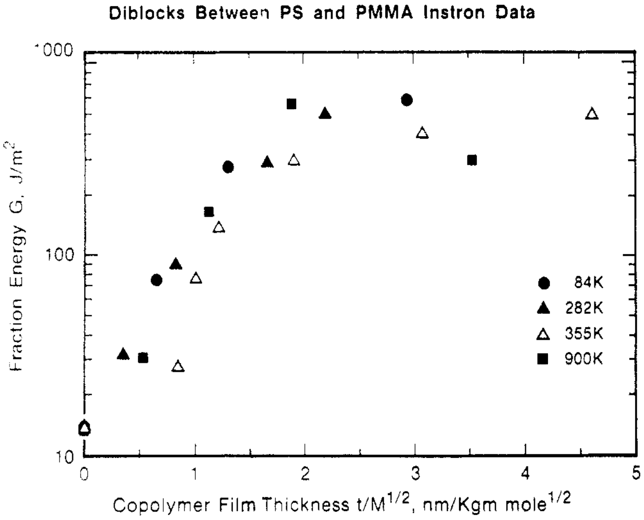

Figure 2. Results of Figure 1 plotted to show the $t/M^{1/2}$ scaling.

The two homopolymer sheets, one now covered by a thin diblock layer, were joined in a press, typically at 150 °C for 2 h. Very little pressure was used, just enough to facilitate wetting of the two sheets. The joined samples were fractured at room temperature using an asymmetric fracture toughness test that drives the crack along the interface.[13] The PS side of the sample was adhered to an aluminum substrate with a cyanoacrylate adhesive; then the crack was propagated, either by inserting a razor blade into the interface or by loading the sample in a mechanical testing (Instron) machine. In the razor test the crack was allowed to propagate slowly for 24 h before measurement. In both tests the crack length was measured using an optical microscope, yielding the fracture toughness of the interface.[13] The difference in crack propagation rate of the two tests has previously been shown to cause the Instron test to give results that are about a factor of 2 larger than those from the razor test.[13] The results shown in Figures 1 and 2 were obtained using the Instron test; all other results were obtained using the razor test. Results obtained from the samples made by the direct spinning of the copolymer onto the PMMA were compared with those from floated specimens. No significant differences were found.

Samples for Dynamic SIMS. Specimens for dynamic SIMS were prepared by two different techniques, producing samples that will be referred to as fracture samples[14] and thin film samples.[15] The fracture samples were prepared as described above for the fracture test; then, after splitting along the interface, 50-nm films of homopolystyrene were floated onto the fracture surfaces to provide a buffer layer for stabilizing the SIMS sputtering transition. The thin film SIMS samples were made as follows: PMMA homopolymer was first spin coated from a 6% solution in chlorobenzene at 3000 rpm onto an optically smooth 1-in. quartz wafer to yield a film approximately 250 mm thick. A thin diblock copolymer film was then spin coated from toluene solution onto a glass slide under conditions to produce the required diblock layer thickness, floated onto water, and then picked up on the coated quartz wafer. The bilayer film was allowed to dry at room temperature and then at 60 °C for 20 min. Finally, a film of PS of approximately 205-nm thickness was spun onto glass, floated onto water, and picked up on the bilayer film. The trilayer film was allowed to dry in air and was then placed in a vacuum oven at 150 °C for 2 h.

SIMS Experiments. The SIMS experiments were done on a Perkin-Elmer 6300 secondary ion mass spectrometer with oxygen primary ion bombardment. Details of the SIMS technique can be found elsewhere.[16–18] In our experiment, negative secondary ion intensity was monitored as a function of sputtering time. Electron beam charge neutralization was used to compensate for the positive charge deposited on the samples by the primary ion beam. The raw data were converted to secondary ion intensity vs depth using standard samples which enabled us to calculate the sputtering rates for both PS and PMMA. For the thin film samples we used the sputtering rates for the two homopolymers to the inferface, though, in reality, the sputtering rate probably changed smoothly through the interface. The PS and PMMA profiles at the interface of the thin film samples were constructed by the superposition of the results using the d-PS-*b*-h-PMMA sample with those from the h-PS-*b*-d-PMMA sample. This superposition required a precise knowledge of the position of the interface. The interface was marked by monitoring mass numbers 26 (CN) and 35 (Cl), both of which showed interface peaks caused by interface contamination. The instrument is very sensitive to both CN and Cl, so these peaks corresponded to very little material. The source of the Cl was probably the chlorobenzene solvent.

Experimental Results

High Molecular Weight Diblocks—Mechanical Results. Preliminary results for the toughness of the interface as a function of the original thickness of the diblock copolymer layer were presented in a previous publication.[10] It should be emphasized that, in all this work, the original layer thickness (normally just called the layer thickness) is a measure of the amount of diblock copolymer present and does not refer to the width of the copolymer layer in the joint. These layer thicknesses are often considerably less that the radius of gyration of the copolymer molecules, and when the joint is made by heating the polymers, the copolymer molecules doubtless expand to more like an equilibrium conformation. Four symmetric diblocks of molecular weight between 84K and 900K were used. The interfacial toughness was found to increase rapidly with the amount of diblock present and then saturate at a layer thickness approximately equal to half the long period, L, of the diblock copolymer. This behavior is shown in Figure 1. The long period of these diblock copolymers increases with molecular weight M as M^{α} where α is in the range 0.5–0.6.[19] As the saturation toughness was found to vary little with diblock molecular weight, it is evident that the data from the four diblock copolymers will approximately superimpose when toughness is plotted against $t/M^{0.5}$. This scaling can be seen in Figure 2. Although the data seem to show that G depends on $t/M^{0.5}$, it is worth noting that there is considerable scatter in the fracture data; therefore this scaling should be treated with caution. It is perhaps more reasonable to consider Figure 2 as suggesting that the toughness is a function of the fractional saturation of the interface by the diblock copolymer.

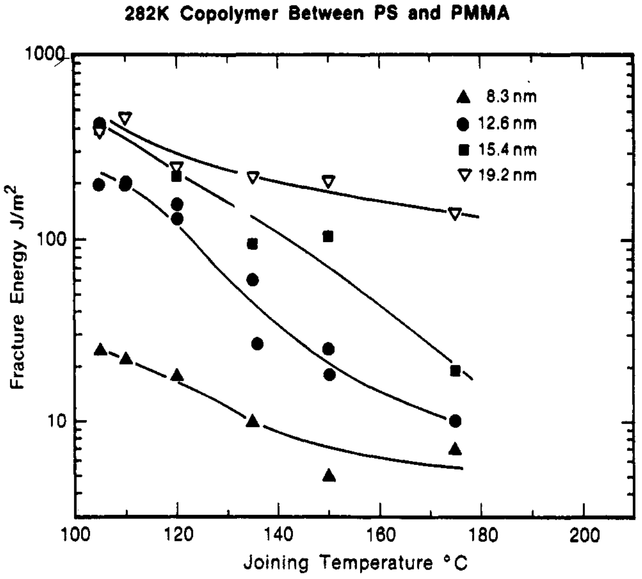

Figure 3. Variation of interface toughness with joining temperature for four thicknesses of the 282K diblock. All joints were made for 30 min.

Information on the nature of the organization or diffusion processes that occur at an interface can be obtained by examining the effect of joining time and temperature on the joint toughness. Such experiments have been performed with two of the high molecular weight diblock copolymers, the 900K polymer and the 282K polymer.

Samples were made with a 44-nm layer (~$L/2$) of the 900K polymer using a wide range of joining temperatures, from 115 to 150 °C, and joining times, from 10 min to 2 h. No significant changes in the joint toughness were obtained. Samples were then made with just 16 nm of 900K copolymer. A joint made at 150 °C for 2 h was found to be weak, $G = 16$ J/m^2, as previously observed, but a 110 °C, 10 min joint was much stronger with a toughness of 150 J/m^2. This observation of joint toughness decreasing with increasing joining temperature was sufficiently surprising that the experiment was repeated by joining new samples at 110 °C for 10 min, retaining half of each sample for mechanical testing and returning the other half to the mold to reheat to 150 °C for 2 h. The toughness obtained after the low temperature join was 70 J/m^2, and it dropped to 11 J/m^2 after reheating. The difference of a factor of 2 between the toughnesses of the samples that were both nominally made at 110 °C for 10 min was probably caused by the temperature being so close to the T_g of PMMA that small uncontrolled temperature variations could have a big effect on the mobility of the material.

The results presented above show that, at least for the 900K copolymer, the form of joining time/temperature effects on the joint toughness was influenced by the thickness of the copolymer layer. As we had very little of the 900K copolymer, this coupling of the joining time/temperature with the layer thickness was examined in more detail using the 282K copolymer. Figure 3 shows the variation of joint toughness with joining temperature (all joints were made for 30 min) for four thicknesses of the copolymer layer. The long period of this polymer is 73 nm,[19] so all these thickness are well below an expected saturation thickness of about $L/2$. In all cases the

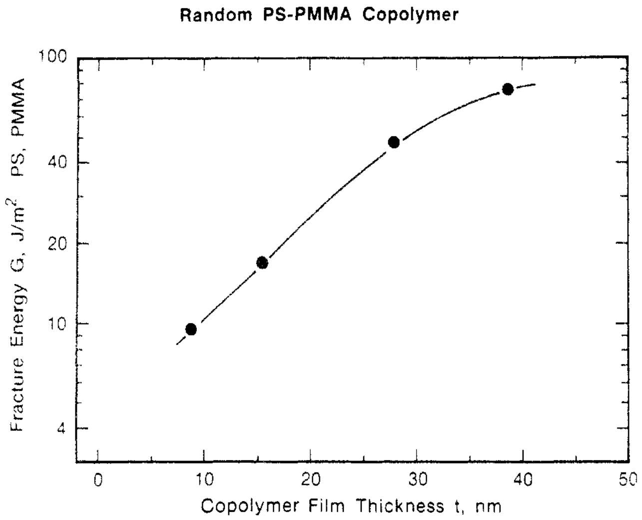

Figure 4. Dependence of interface toughness on interface thickness for the PS–PMMA random copolymer.

toughness decreased with increasing joining temperature but this decrease was much more pronounced for the intermediate layer thicknesses (12 and 15 nm) than for thicknesses of either 8 or 19 nm. Evidently, the decrease in toughness with increasing joining temperature occurred for both copolymer molecular weights but there was a layer thickness for which this decrease was maximized.

Although the main aim of this work was to study the effects of PS–PMMA diblock copolymers at the interface between PS and PMMA, for comparison purposes we did examine the joint toughness using one PS–PMMA random copolymer. Unfortunately, the random copolymer was not directly comparable with the diblocks as it contained 70% PS and had a broad molecular weight distribution. Figure 4 shows the variation of the joint toughness with the thickness of the random copolymer layer. It is clear from these results that the random copolymer was a very effective coupling agent for the interface between the homopolymers. However, it was not as effective a coupling agent as the diblock copolymers in this system.

High Molecular Weight Diblocks—SIMS Results. The degree of organization of the diblocks at the interface was examined with the use of SIMS and the partly deuterated 300K series of diblock copolymers. Both thin film samples and fracture samples were made using 8- and 24-nm layers of the d-PS-*b*-h-PMMA and h-PS-*b*-d-PMMA copolymers. Figure 5 shows deuterium profiles under the fracture surfaces for the 8-nm layer. When the PS half of the diblock copolymer was deuterated, the deuterium was mainly found on the PS fracture surface, and when the PMMA half of the diblock was deuterated, the deuterium was mainly found on the PMMA fracture surface. Hence the diblock copolymer molecules organized in a simple manner at the interface with the PS block mixing with the PS homopolymer and the PMMA block mixing with the PMMA homopolymer. When the joint was fractured, the diblock molecules broke at positions close to the junction point between the two species. Very similar results have already been described[14] for the situation where 24-nm layers of the same diblock copolymers were placed between PMMA and poly(phenylene oxide) (PPO): the diblock molecules again broke near their junction points. A small amount of the diblock copolymer was found on the "wrong" fracture surface suggesting that the diblock molecules do not fracture precisely at their junction points. If the fracture probability distribution along the diblock copolymer chain is assumed to be Gaussian, then it is possible to estimate the distance of

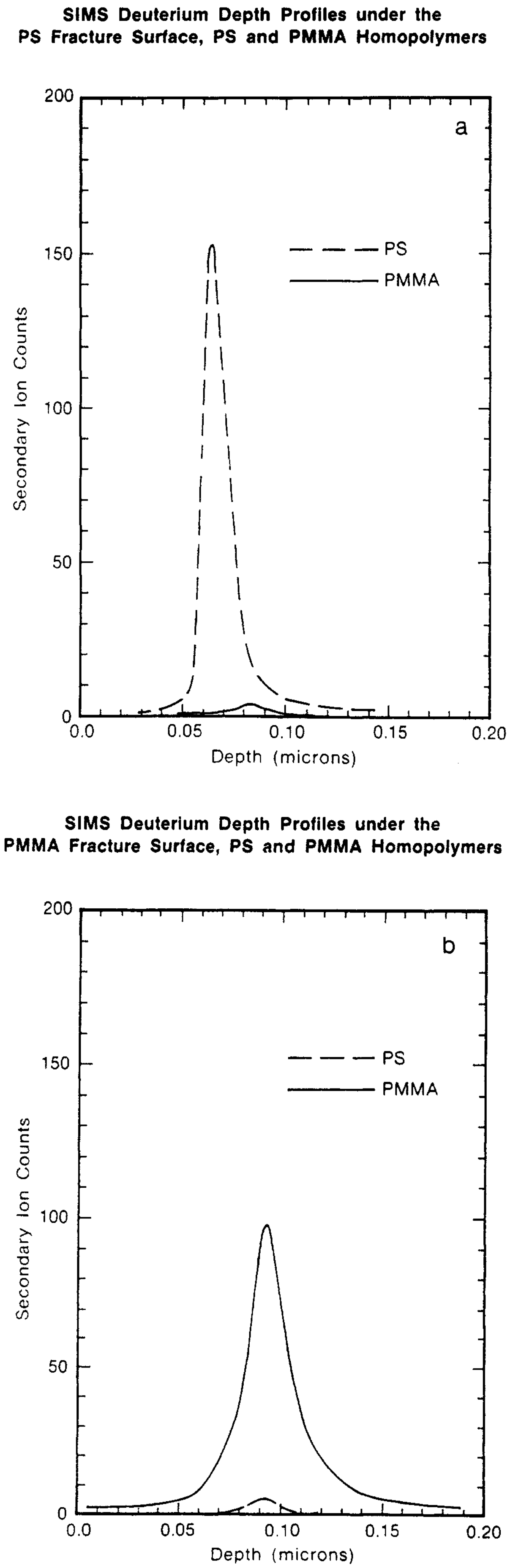

Figure 5. SIMS deuterium depth profiles for the two halves of the copolymers under the fracture surfaces showing that the 300K copolymer molecules broke very near their junction points.

Table II. Breakage Probabilities

homopolymers	layer thickness t, nm	Δ, Da	σ, Da
PPO and PMMA	24	2000 into PMMA	4700
PS and PMMA	8	3300 into PS	7700

the center of this distribution (the mean fracture position) from the junction point, Δ, and the standard deviation, σ, of the distribution from the amounts of diblock copolymer on the wrong sides. When Δ and σ are small with respect to the copolymer chain length, then the fractions of copolymer on the wrong sides (I_1, I_2) are given for the two sides by

$$I_1(\Delta,\sigma) = \int_{\Delta}^{\infty} (y - \Delta) \frac{\exp(-y^2/2\sigma^2)}{\sqrt{2\pi}\sigma}\, dy$$

$$I_2(\Delta,\sigma) = \int_{-\Delta}^{\infty} (y + \Delta) \frac{\exp(-y^2/2\sigma^2)}{\sqrt{2\pi}\sigma}\, dy$$

where σ and Δ are given as fractions of the half-length of the (symmetric) diblock copolymer molecules. Values of Δ and σ, shown in Table II, were obtained from the experimental results with the use of published tables of the relevant integrals.[20] The values of Δ and σ obtained previously for the same copolymers between PMMA and PPO are also given for comparison.

The SIMS profiles from the fractured samples with a 24-nm layer of diblock copolymer gave little information on the copolymer organization and failure. Deuterium was found mainly on the PMMA side for both PS deuterated and PMMA deuterated diblocks with a peak at depths of of 0.1–1 μm below the fracture surfaces. The samples had a high toughness and failed at a G_c of 250 J/m^2, causing a rough fracture surface. This toughness should be compared with values of 30 J/m^2 obtained for the 8-nm layer between PS and PMMA and 26 J/m^2 for a 24-nm layer between PS and PPO. The very high toughness of the 24-nm layer between PS and PMMA caused so much fracture surface deformation and crazing that useful information on diblock organization could not be obtained from this experiment. However it is clear that the failure occurred mainly on the PS side of the interface.

It is possible to examine the organization of the diblock at the interface by SIMS experiments on the thin film samples. As fracture is not involved in this sample design, the interface does not have to be weak but no information can be obtained on the failure process. Figure 6 shows deuterium profiles for the two deuterated diblocks for layer thicknesses of 8 and 24 nm. SIMS depth profiles are the real profiles convoluted by a resolution function. The resolution was approximately 10 nm for etching into PS and rather worse (larger) for etching into PMMA. Figure 6 shows that the 24-nm diblock layer was not at all organized at the interface. The 8-nm layer showed a significant degree of organization, and considering the resolution, it is not possible to tell if the layer is fully organized. It is immediately evident from this figure that the ability of the diblock to organize in a simple manner at the interface decreases as the thickness of the diblock layer increases. We already know from the SIMS results obtained on fractured samples that the 8-nm diblock layer is well organized, so the results of this figure give a graphic demonstration of the effects of SIMS resolution on the observed profiles at the interface. Clearly, SIMS resolution is good enough to show simple diblock organization when it exists. It is evident then, from Figure 6, that the 24-nm diblock layer did not organize in a simple manner at the interface during the 2-h join at 150 °C. It must be emphasized that SIMS has good depth resolution but relatively poor resolution in the film plane. It is not possible to tell from SIMS experiments whether the diblock is completely disorganized at the interface or is organized in a complex structure (such as a set of micelles or an interconnected structure) that would cause the mean PS and PMMA profiles to show great overlap.

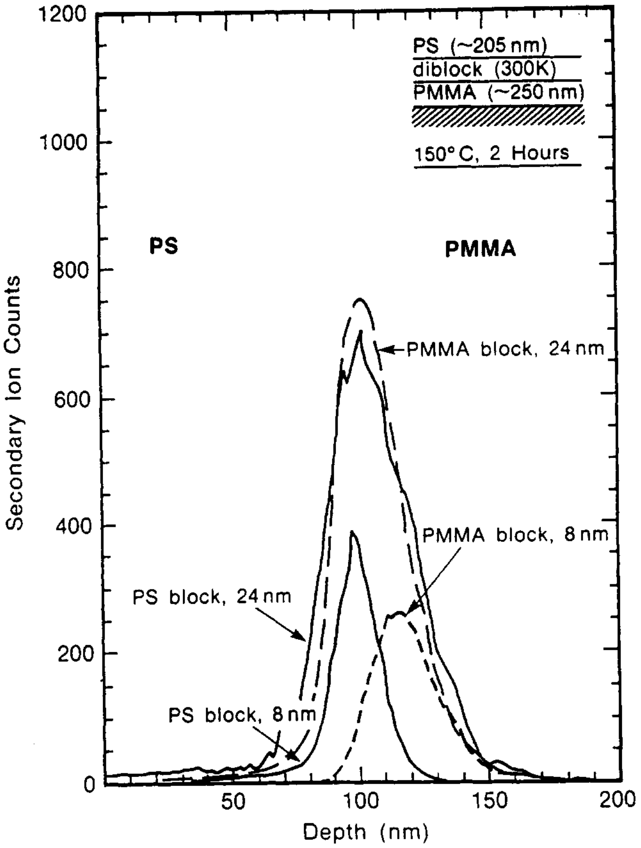

Figure 6. SIMS deuterium depth profiles for two different thicknesses of the 300K diblock showing that the 8-nm layer organized at the interface while a 24-nm layer showed no organization.

In both Figures 5 and 6 the profiles of PS are not identical to those PMMA. It is not clear whether this difference in the profiles comes from instrumental effects caused by the different sputtering properties of the two materials or from an actual difference in the diblock profiles caused by the different molecular weight distributions of the two homopolymers.[8] As the main aim of the SIMS experiments described here was to help understand the mechanical results, it was necessary to use the same homopolymers and joining conditions that were used in the mechanical tests. It was not practical to use a narrow molecular weight distribution homopolymer for the mechanical tests except as a thin film close to the interface, as such tests use large quantities of material.

Low Molecular Weight and Asymmetric Diblocks. Mechanical results for the interfaces joined by the 53K symmetric copolymer using two different joining conditions are shown in Figure 7. Equivalent results for the 31K copolymer are shown in Figure 8. It is clear from these figures that the variation of toughness with layer thickness is different in kind for these low molecular weight diblock copolymers from that obtained with high molecular weight copolymers. For the low molecular weight materials

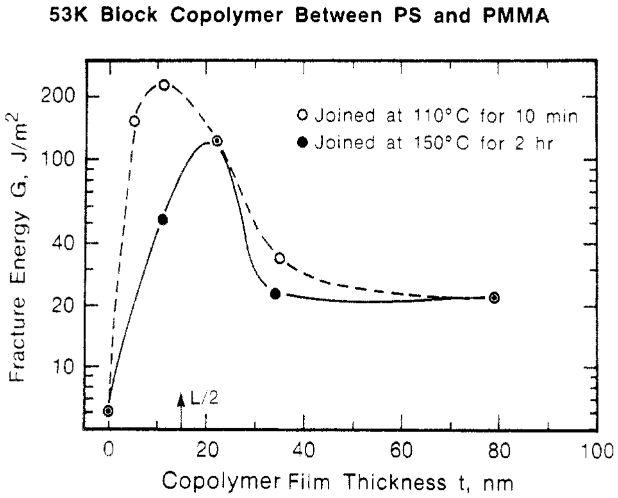

Figure 7. Variation of fracture energy with copolymer film thickness for the 53K copolymer at two different joining conditions.

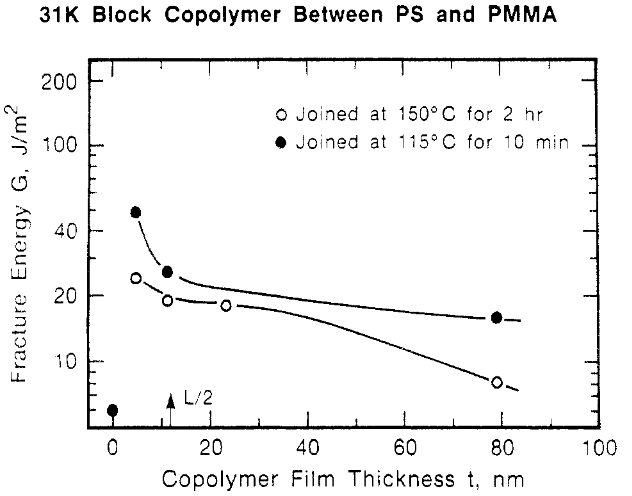

Figure 8. Variation of fracture energy with copolymer film thickness for the 31K copolymer at two different joining conditions.

the toughness goes through a maximum and then drops as the thickness is increased whereas the high molecular weight diblocks showed no such maximum.

The two asymmetric diblocks showed different behaviors again. The results for the high styrene diblock, the 58K–9K PS–PMMA, are shown in Figure 9. Clearly, this material was effective at toughening the interface but required high layer thickness akin to those required by the symmetric 355K diblock. The other asymmetric diblock, the 8K–102K PS–PMMA gave low toughnesses of only about 18 J/m^2 for layer thicknesses between 9 and 90 nm.

We used forward recoil spectroscopy (FRES) to examine the fracture surfaces of samples made with a 24-nm layer of fully deuterated 29K symmetric diblock. This sample was joined for 2 h at 150 °C. The deuterium depth profiles, shown in Figure 10, make it clear that the deuterium, and hence the diblock molecules, all ended up on the PMMA side of the fracture surface. No deuterium could be seen on the PS side; hence the failure must have occurred between the diblock and the PS homopolymer. The deuterium profiles all have a width that is controlled just by the resolution of the experiment and so can give no detailed information on the positioning of the block copolymer at the interface. It is clear however that much of this very low molecular weight diblock material stayed at the interface and did not diffuse deep into the bulk material.

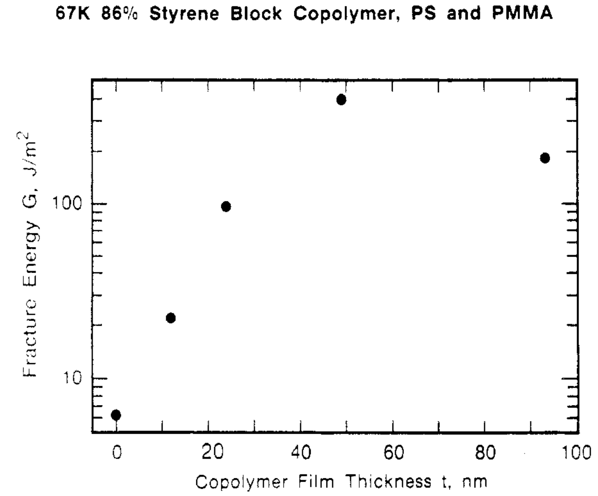

Figure 9. Variation of fracture energy with copolymer film thickness for the high styrene asymmetric block copolymer.

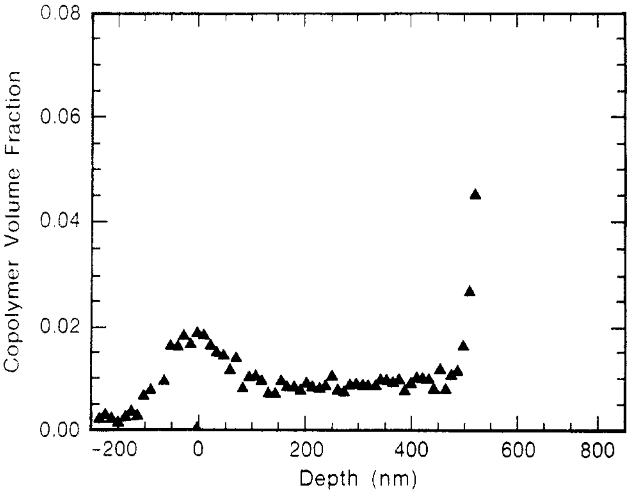

Figure 10. FRES results showing the depth profile of a 30K fully deuterated diblock copolymer on the PPMA side of the fracture. No deuterium was found on the PS side.

Discussion

We shall consider first the results obtained with the symmetric diblocks of molecular weight equal to or greater than 84K. These diblock molecules have a very large effect on the toughness of the interface between PS and PMMA homopolymers. For example, just 23 nm of the 84K diblock increases the interfacial toughness from 6 to 200 J/m^2; clearly, we can consider the diblock as an excellent adhesive.

A strong implication of the small amount of diblock required for high toughness is that, for all these molecular weights, the diblock molecules stay at the interface during the joining process. The SIMS results demonstrate directly that the 300K diblock molecules stay at the interface, as no significant amounts of material could be found deep into the sample. For diblock molecules to escape from the interface, they need to either dissolve in one of the homopolymers and diffuse as separate molecules or diffuse as micelles. The amount of diblock dissolved in the homopolymer must be less than the critical micelle concentration (cmc), and Leibler[8] has shown that the cmc of an A–B diblock dissolved in A should vary as $\exp(-\chi N_B)$ where N_B is the degree of polymerization of the B section of the diblock. For the 84K diblock, χN_B

$\simeq$ 16, so the cmc is probably very small and the loss of diblock molecules by diffusion is likely to be very slow.

The scaling of the toughness with the fractional saturation of the interface was not what we originally expected. We expected that the diblock molecules would organize at the interface with the PS part of the diblock dissolved in the PS homopolymer and the PMMA part dissolved in the PMMA homopolymer. This would give one joint across the interface per diblock molecule, and so, as long as the diblock molecules were long enough to entangle fully with the homopolymers, one would expect the toughness to scale as the number of molecules per unit area, Σ, at the interface and hence as t/M, not $t/M^{1/2}$. In addition, one would expect the saturation toughness to decrease with increasing diblock molecular weight as the saturation value of Σ decreases with molecular weight. Both these expectations are not observed when the diblocks are placed between PS and PMMA homopolymers. However, as shown in the companion paper,[21] both the scaling of the toughness with Σ and the decreasing saturation toughness with increasing diblock molecular weight were found when the same diblocks are placed between PMMA and PPO.

The mechanical and SIMS results presented here are all consistent with two hypotheses. These hypotheses are (1) a disorganized diblock layer will tend to give a strong interface and (2) the degree of diblock organization at the interface for any given joining condition decreases rapidly with increasing diblock layer thickness. There is no direct evidence for hypothesis 1, but the ability of the random copolymer to cause fairly high toughness at the interface carries a strong implication that a disorganized diblock will also cause a high interface toughness. PS and PMMA, though immiscible, are not strongly repulsive at the segment level. The interaction parameter χ between them is small (it is only 0.037),[24] and the interface between the homopolymers is relatively broad with a width (a_I) of about 50 Å.[19] It is likely then that a layer consisting of a random mixture of PS and PMMA, either a disorganized diblock or a random copolymer, could entangle well with both homopolymers, giving high interface toughness. This point is reinforced by some recent theoretical and simulation work on the effects of sequence distribution on the arrangement of a copolymer at a fluid–fluid interface.[22,23] For weak interactions a fully random copolymer can form long loops at an interface. Unlike the situation for hypothesis 1, there is direct evidence for hypothesis 2. This evidence is to be found in the SIMS results shown in Figure 6. Clearly, the 24-nm diblock layer did not organize at the interface in a simple manner in 2 h at 150 °C while the 8-nm layer organized well.

The results obtained on the time/temperature dependence of the interface strength are all consistent with these two hypotheses. The thick layer of 900K diblock probably never developed much organization in any of the tests, but was rapidly coupled to the two homopolymers by homopolymer diffusion. The thin layer of the 900K diblock was still disorganized after the short time/low temperature join but it was coupled to the homopolymers with a number of joints (entanglements) per copolymer molecule, giving a strong interface. This thin diblock layer organized at the interface during the higher temperature/longer time join to give just one joint across the interface per diblock molecule. The interface was then weak.

The results presented in Figure 3 show the dependence of the interface toughness on the joining temperature for the 282K diblock. It is tempting to interpret these data as giving information on the layer thickness dependence of the rate of diblock organization, though there is no direct evidence that loss of diblock from the interface might not be a significant feature. However, as explained earlier, such loss seems unlikely for these high molecular weight diblocks. It is conceivable also that the main effect of changing layer thickness is not to change the rate of organization but to change the equilibrium degree of organization. However there is no obvious reason when a thick layer of a high molecular weight diblock should fail to organize at equilibrium, considering that the diblocks are well microphase segregated in the bulk. Figure 3 shows that the main temperature dependence occurs for the 15- and particularly the 12-nm-thick copolymer layers. Presumably, the 8-nm layer can organize easily and so is organized at the low joining temperature while the 19-nm layer organizes so slowly that it has very little organization at the highest temperature. One can estimate from the WLF equation that the effective time change corresponding to the experimental temperature range 105–175 °C is approximately 7 decades. A change in just over a factor of 2 in diblock layer thickness has a remarkable effect on the rate of diblock organization.

The scaling of the copolymer layer thickness and molecular weight shown in Figure 2 suggests that the fractional saturation of the interface by the diblock may be the important parameter controlling the rate of diblock organization. The saturation toughness for the disorganized layers was typically about 400 J/m^2, a value that was not very different from the toughness of bulk polystyrene. It is likely then that the areal density of entangled strands across the interface between the disorganized diblock layer and the bulk materials was similar to that across any plane in the bulk homopolymer. For an organized layer of the 84K copolymer also, the number of chains per unit interface area, Σ, at saturation is not very different from the areal density of entangled strands in bulk polystyrene; so for this low molecular weight copolymer the toughness of the interface is expected to be fairly independent of diblock organization. To a reasonable approximation the value of Σ at saturation would be expected to vary as $M^{-0.5}$ (assuming that the saturation layer thickness goes as $M^{0.5}$) and, as G has been shown[25] to vary as Σ^2, the saturation toughness for an organized layer should vary as M^{-1}. This expectation is approximately followed when the homopolymers are PPO and PMMA, a system in which thick layers of the diblock are known to organize. The lack of dependence of the saturation toughness on the diblock molecular weight in the PS/PMMA system described here shows that the number of effective joints per unit area is independent of diblock molecular weight for the unorganized layer. It seems reasonable that the driving force for diblock organization might vary with fractional saturation of the interface. However one might still expect that the rate of organization at fixed driving force would depend on the diblock diffusion constant and so decrease with increasing diblock molecular weight. This effect of the change in diffusion constant is not expected to be very large compared with the effect of fractional saturation of the interface. The diffusion constant can be expected to vary as M^{-2}, so in changing from the 282K to the 900K copolymer, where one can be confident that the diblock did not organize, the diffusion constant would change only by about a factor of 10. This is a very small factor when compared with the estimate given above for the apparent change in the rate of diblock organization when the layer thickness changes by a factor of 2.

It is interesting to speculate on the mechanism by which the diblock layer thickness might change its rate of organization. One can imagine that initially the homopolymers would diffuse into the disorganized diblock layer and set up a kind of potential gradient to encourage the diblock organization. The strength of this gradient will of course decrease with increasing diblock layer thickness, so the rate of organization would also decrease with increasing diblock layer thickness.

The results in Table II on the positions of the break points for the 300K diblock copolymer chains show that the chains broke very near the junction between the blocks. It is instructive to compare these diblock chain breakage positions obtained here with the diblock between PS and PMMA homopolymers with the previously published results obtained with the diblock between PPO and PMMA homopolymers. The width of the distribution in fracture positions is greater for the PS/PMMA system than for the PPO/PMMA system. Also, the mean fracture position is on the PS side of the copolymer for the PS/PMMA system while it is on the PMMA side of the copolymer for the PPO/PMMA system. It is possible that both of these observations are related to the nature of the entanglement of the copolymer on the two sides of the interface. It is likely that entanglements control the rate of force buildup in a chain anchored in a polymer glass. The copolymer chains are anchored at both ends, with the force increasing toward the junction point. Hence, in block copolymer chains, the rates of force buildup in the two blocks are likely to vary inversely with the entanglement molecular weights, M_e, of the two blocks in the relevant homopolymers.[26] A high M_e would thus give a slow force buildup, and hence, as the maximum force in the chain is the chain breakage force, a large length of the copolymer chain would be subjected to a high force. The width of the distribution of breakage positions would, therefore, be expected to increase with increasing M_e on either side of the interface. For the same reason one might expect that the mean fracture position would be in the copolymer block which has the higher M_e with its homopolymer. The value of M_e for PS is 18K,[27] for PMMA is 9K,[27] and for a 50% PS/PPO mixture[28] is estimated to be 6.5K.[29] Hence, one would expect the fracture position to be on the PS side of the copolymer for the PS/PMMA system and the PMMA side for the PPO/PMMA system, as observed. In addition, the decrease in the width of the distribution of fracture positions, σ going from PS/PMMA to PPO/PMMA, is consistent with the decrease in M_e values. The spread in fracture positions could also increase with the width of the distribution of copolymer junction points about the interface and so be dependent on the strength of the interactions between the relevant polymers. The PPO/PMMA system has stronger interactions than the PS/PMMA system and so is expected to have a narrow distribution of copolymer junction points.

The low molecular weight symmetric diblocks, the 31K and 54K copolymers, gave joints of significantly lower toughness than those formed with the higher molecular weight copolymers. This reduced toughness is not surprising, as the molecular weights of the PS parts of the copolymers, at 15K and 25K, were not large with respect to M_e. As M_e for PMMA is significantly lower than that for PS, one would expect that it would be the PS part of the copolymer that pulls out from the homopolymer. This expectation was clearly confirmed by the FRES results from the 29K polymer. We found that, in a sample with layer thickness of about L, the failure was all by a pull-out mechanism with all the copolymer pulled out of the PS homopolymer. The pull-out process and the related process of brush failure has been studied in detail in the PS/PVP system[12] using both low molecular weight and asymmetric copolymers. PVP blocks of molecular weight less than M_e were found to pull out of the PVP homopolymer in agreement with the results presented here.

Both low molecular weight symmetric copolymers showed a very evident peak in toughness at a copolymer layer thickness of about half a long period. The precise position of this peak varied with joining conditions. Samples made using the short time and low temperature joining conditions gave peaks at lower layer thicknesses. It should be emphasized that the relevant layer thicknesses are fairly small and we had no check on the actual amount of polymer deposited on the PMMA, so precise values of these small layer thicknesses could not be obtained. In addition it seems likely that a certain amount of these low molecular weight diblocks will dissolve into the homopolymers and be lost from the interface during the joining process. Such copolymer loss may be the explanation for the effect of joining condition on peak position.

A number of possible explanations can be suggested for the existence of this toughness peak. One explanation is related to the fact that copolymers have been shown to form multilayers at homopolymer interfaces.[30] It is very unlikely that a multilayer would form with a PS homopolymer to PMMA copolymer interface, though the existence of such an interface, which would be very weak, would be consistent with our mechanical and FRES results. A block copolymer layer of thickness between $L/2$ and $3L/2$ would be much more likely to form patches of thickness $L/2$ and patches of thickness $3L/2$ similar to the situation observed when a thin layer is spread on a silicon wafer.[17] It is also possible that the PS internal copolymer layer in the multilayer situation is weak, as observed in the PS/PVP system.[31] However if the failure had been along an internal copolymer layer, then deuterium in the FRES results on the 29K copolymer would have been found on both fracture surfaces. In reality deuterium was found only on the PS fracture surface, so this multilayer explanation for the peak in toughness is unlikely to be correct. An alternative explanation for the peak is that, at saturation, there is little mixing and hence entanglement between the PS part of the copolymer and the PS homopolymer, as the latter is of significantly higher molecular weight, so the copolymer "brush" is essentially dry. At less than saturation quantities of copolymer, as the copolymer chains do not collapse, they must mix well and entangle with the homopolymer. This explanation implies that the entanglement between copolymer and homopolymer chains decreases as the quantity of copolymer at the interface is increased toward saturation. One might expect then that the peak in toughness will occur at a thickness of less than $L/2$.

The two asymmetric copolymers gave remarkably different results. The low styrene material was ineffective as a coupling agent at the interface, whereas the high styrene material gave strong interfaces when it was used at large layer thicknesses. It would appear that the low styrene material, if it was at the interface, was pulled out very easily from the homopolystyrene. Excess copolymer doubtless formed micelles in the PMMA, as the copolymer was PMMA rich. The requirement of large quantities of the high styrene copolymer for high toughness suggests that this copolymer either did not organize at the interface or most of it formed into micelles in the polystyrene. If the material did organize, then it is surprising that the 8K PMMA part of the copolymer was long enough to form significant entanglement with the PMMA homopolymer. This entanglement could exist because the PS part of the diblock, being the larger part, would control the amount of diblock at the interface and hence ensure that the PMMA part would always be dilute (a "wet brush"), so mixing well with the homopolymer.

The random copolymer was found to be a remarkably effective coupling agent, giving maximum toughnesses of nearly 100 J/m^2. As discussed earlier, this copolymer probably formed loops in both the homopolymers and hence could form more than one effective joint per molecule. The effectiveness of the random copolymer is important because it demonstrates that a range of copolymer architectures could possibly be used to make effective coupling agents. Also, it is worth noting that random copolymers are much cheaper than block copolymers.

Conclusions

PS–PMMA diblock copolymer can work as very effective coupling agents between PS and PMMA homopolymers. With symmetric diblocks the maximum interface toughness obtainable is independent of the diblock molecular weight as long as the molecular weight is at least 80K. The amount of diblock required to reach this maximum toughness equals approximately half the long period of the neat diblock polymer and so increases with the diblock molecular weight. There exists, therefore, an optimum diblock molecular weight in the sense that, for molecular weights greater than 80K, the amount of diblock required to give a maximum toughness increases with diblock molecular weight whereas, for molecular weights less than 80K, less toughness is obtainable.

Both the mechanical results and the direct SIMS experiments have shown that the diblock copolymer between PS and PMMA frequently does not organize in a simple manner at the interface. The rate of organization was found to decrease rapidly with the thickness of the diblock layer; so, with the high molecular weight copolymers, layer thicknesses greater than $L/4$ probably never organized in the time scale of the experiment. It must also be emphasized that we could not distinguish a genuinely disorganized diblock layer from one that had organized into a complex micellar or interconnected structure. The diblock layers that did not show simple organization tended to give interfaces with a high toughness.

When the high molecular weight diblock did organize at the interface, then the interface fracture caused the diblock molecules to break very close to the junction between the two blocks. The actual distribution of breakage positions was consistent with that expected from entanglement coupling.

Low molecular weight symmetric diblocks showed a peak in toughness with increasing layer thickness at a layer thickness of about $L/2$. This peak was probably related to poor mixing between the PS chains of the diblock and the PS homopolymer, presumably the "dry brush" situation.

A random copolymer was shown to be remarkably effective as a coupling agent between homopolymers, probably because it could form a number of effective joints per molecule.

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