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The effect of copolymer mixtures on the interfacial adhesion between slabs of PS and PMMA was investigated as a function of composition, time and temperature using the asymmetric double cantilever beam (ADCB) method. The nature of the interface was further probed using atomic force microscopy (AFM) and dynamic secondary ion mass spectroscopy (D-SIMS). The results show that mixtures of graft and block copolymers are much more effective than pure block copolymers in enhancing the interfacial adhesion. The most effective mixture consisted of a block copolymer of molecular weight 70K and a copolymer with two PS grafts of molecular weight 30K. This mixture yielded an interfacial fracture toughness of $G_c = 127.5$ J/m^2 as compared with $G_c = 38.2$ J/m^2 and $G_c = 3.5$ J/m^2 for the pure block and graft copolymer, respectively.

G_c at the PS/PMMA interface reinforced only with block copolymer was maximal after an annealing temperature of 150°C for 1 hr. It decreased by an order of magnitude when the temperature was increased to 180°C or the joining time was increased from 1 to 10 hours. G_c at the interface reinforced with a graft/diblock copolymer mixture was also maximum at an annealing temperature of 150°C but it decreased only by a factor of 2 with increasing joining time or temperature. Dynamic Secondary Ion Mass Spectroscopy (DSIMS) data show that this effect may be due to decrease in the diffusion of the copolymer from the interface when the mixture is present, i.e, the diblock copolymer is trapped within the graft copolymer.

INTRODUCTION

In recent years there has been much activity, both theoretical and experimental in the study of polymer interfaces. In particular, a chief concern is maximizing adhesion at the polymer-polymer interface, due to its importance in coating and reinforcement applications. It has been known for some time that the presence of a suitable block copolymer can greatly improve the mechanical properties of an immiscible polymer blend [1 – 7]. Diblock copolymers, composed of blocks corresponding to the two immiscible polymers, but joined chemically, are frequently used to reduce the interfacial tension. Reduction of the interfacial tension does not necessarily imply increasing the adhesion. In order to increase the adhesion, Creton *et al.* [8] have shown that entanglements are also necessary between the respective blocks and the homopolymers. Furthermore, if the diblock copolymer is long, the chemical potential of micelle formation is frequently lower than that of localization at the interface. Hence there is competition between localization and micellization. This reduces the efficiency of the copolymer to affect the interfacial properties.

Cho *et al.* [9], Guo *et al.* [10] and Gersappe *et al.* [11] have reported that graft copolymers can also be used to enhance interfacial properties. In the case of graft copolymers the density of grafts was shown to affect the interfacial properties significantly. Adhesion was maximal for a moderate number of grafts, *i.e.*, when the spacing between grafts was roughly equal to R_g (radius of gyration) of the graft. This enabled both grafts and backbone to entangle across the interface. If the grafting density was higher, then entanglement across the interface was reduced for both backbone and grafts.

On the other hand, as the number of grafts increased the chemical potential of micellization also increased and more copolymer tended to localize at the interface between the homopolymers [10]. Since the large amount of grafting induced stretching of the backbone and legs, the increase in volume fraction of grafts of the interface reduced adhesion.

Recently Balazs and coworkers [12] have shown theoretically that improvements in compatibility can be achieved by using different copolymer mixtures as compatibilizing agents. This prediction was experimentally verified by Kim *et al.* [13]. Lyatskaya and Balazs showed that the mixture was more effective at the lowering interfacial tension than the pure components. The adhesion was increased because the block copolymer reduced the effective grafting density, while increasing the ability of the copolymer to entangle. Hence, the interfacial adhesion was governed by the architecture of the blend of graft and block copolymer at PS/PMMA interfaces [13].

In this paper, we study the dependence on annealing time and temperature of G_c for the pure components and the graft/diblock copolymer mixture. We use the asymmetric double cantilever beam (ADCB) to test G_c and secondary ion mass spectroscopy (SIMS) to measure the profile of copolymer at the interface.

EXPERIMENTS

Materials

Polystyrene (PS) and polymethyl methylacrylate (PMMA) were purchased from Aldrich Chemicals with molecular weights (M_W) of 280,000 and 120,000, respectively. These homopolymers were used as bulk materials for the Asymmetric Double Cantilever Beam (ADCB) test. See Figure 1.
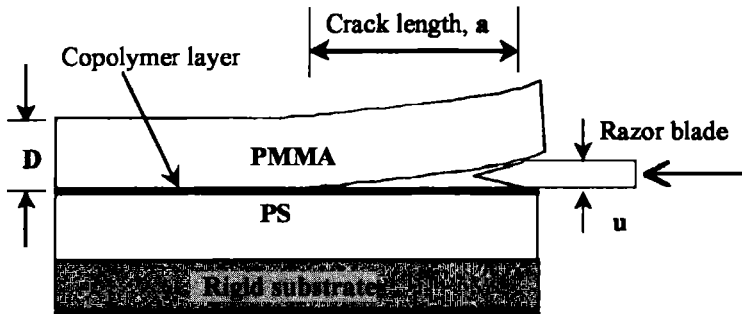

FIGURE 1   Geometry of the ADCB device

These graft copolymers were supplied by Exxon Research & Engineering Company. The total molecular weight of the graft copolymers was fixed as 150,000. The number of grafts per chain and the M_w of the backbone are listed in Table 1. The 3 different types of block copolymers were purchased from Polymer Sources, Inc., and their molecular weights and architecture of graft copolymer type are listed in Table 1.

Asymmetric Double Cantilever Beam (ADCB) Test

The polymers (PS and PMMA) were compression-molded in a hot press into rectangular plates of dimension $5 \times 1.0 \times 0.2$ (cm) using a chrome-plated mould.

The thin layer of copolymers (graft, block, or mixture) was formed by spin-coating from toluene solution. The block or graft copolymers as an interfacial layer, PS-b-PMMA, PS-g-PMMA, and mixtures (50/50, wt.%) of PS-b-PMMA and PS-g-PMMA dissolved in toluene, were spun onto PMMA sheet at 2500 rpm for 30 seconds. Both layers of polymers were then combined in the hot press under 3 metric ton (2000 psi) pressure for between 1 hour and up to 10 hours at 150°C (in the case of temperature dependence, a temperature between 120°C and 180°C was used). The samples were allowed to cool in the mould for 1 hour until reaching room temperature. The thickness of the copolymer films was measured by ellipsometry on silicon wafers with the same

TABLE 1   Architecture of graft and block copolymers

- Graft Copolymers (PS-g-PMMA)

15K PS, $(M_w)_{Total} = 150K$

| 1 graft (10% PS) | 3 grafts (28% PS) | 5 grafts (48% PS) |

30.4K PS, $(M_w)_{Total} = 150K$

| 1 graft (20% PS) | 2.3 grafts (47% PS) | 3.2 grafts (65% PS) |

- Block Copolymers (PS-b-PMMA)

PS-b-PMMA (46.9K-b-39.6K : 40K)
PS-b-PMMA (72.6K-b-70.9K : 70K)
PS-b-PMMA (101K-b-165.8K : 100K)

spinning conditions and concentration used for the adhesion test samples. No significant difference was found between the different ways of picking up the films and the directly spin-coated samples. The joined samples were fractured at room temperature using an asymmetric double cantilever beam (ADCB) device which was used to measure the interfacial fracture toughness (G_c, adhesion) between PS and PMMA, as shown in Figure 2. The PS side of the sample was adhered to an aluminum substrate with an epoxy adhesive (5 minute Epoxy, Devcon Corp.). A wedge, which was a single-edged razor blade, was inserted in between the combined layers and driven by a step micro-motor under computer control to control the speed of the insertion. The crack length ahead of the wedge was measured using an optical microscope and ruler to an accuracy of 0.05mm. At least 6 values of crack length were obtained, and the means of these values were used to calculate the adhesion. The speed of the motor we used in this test was 100 μm/second.

When the layer is attached to a rigid substrate, the crack length can be converted to interfacial adhesion (fracture toughness, G_c) by using the following Equation [16].

$$G_c = \frac{3u^2}{8a^4} \frac{ED^3}{(1 + 0.64(D/a))^4} (J/m^2)$$

where E and D are the Young's modulus and thickness of the top, unattached layer (the PMMA), a is the crack length and u is the wedge

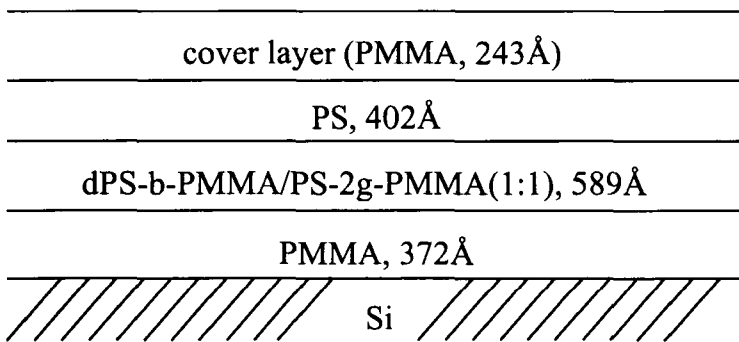| cover layer (PMMA, 243Å) |
| PS, 402Å |
| dPS-b-PMMA/PS-2g-PMMA(1:1), 589Å |
| PMMA, 372Å |
| Si |

FIGURE 2   The structure of trilayer sample for SIMS test.

thickness. Kanninen [14] has developed this model for a single
cantilever beam on an elastic foundation. The equation involves the
assumption that all of the energy is dissipated in a very small region
ahead of the crack tip. It was also assumed that released energy comes
only from the bending of the beam. For this reason, it was necessary
that the blade be inserted slowly enough so that the crack length
achieved its equilibrium value. The G_c value which was then calculated
measures the amount of energy with which the interface was held
together.

Dynamic Secondary Ion Mass Spectroscopy Measurement

To determine the interfacial segregation and diffusion between graft
and block copolymer mixtures, we used dynamic secondary ion mass
spectrometry (DSIMS, Atomika 3000-30) to probe the composition.

A trilayer sample was prepared as follows: PMMA homopolymer
($M_W = 120,000$) was spin-cast from toluene solution directly onto an
HF-etched Si wafer. The layer thickness was 372Å. A layer of the
copolymer mixture (dPS-b-PMMA/PS-2g-PMMA; 50/50, wt.%),
589Å thick, was spin-cast on glass and then floated from deionized
water onto the PMMA. A third layer of PS, 402Å thick, was spin-cast
onto a glass slide and floated on top of the copolymer layer. The
schematic of the trilayer sample is shown in Figure 2. Details of the
SIMS techniques can be found elsewhere [15, 16]. The film was
annealed in a vacuum (10^{-4} torr) at 150°C for 48 hours. The sample
was then covered with a layer of PMMA, 243Å thick, by floating onto
the layer of PS.

RESULTS AND DISCUSSION

The plot of interfacial adhesion (or interfacial fracture toughness, G_c)
vs. the number of grafts for the copolymer mixture (50/50, wt.%) of
short graft chains (15K PS) and block copolymers of different M_W is
shown in Figure 3. Fracture toughness, G_c, was similar for the mix-
tures of graft copolymer and the diblock of $M_W = 70K$ and 100K. G_c
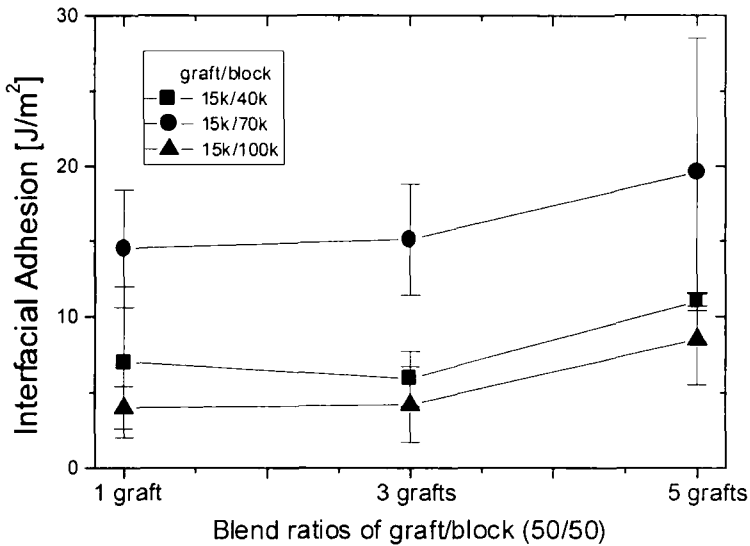was markedly enhanced for all grafts when the diblock M_W was 70K.

FIGURE 3   Interfacial adhesion of copolymer mixture (50/50, wt.%) of graft (2 grafts of 15k PS) and block copolymers of different M_w as a function of the number of grafts.

In Figure 4, we plot the G_c between PS and PMMA *versus* the number of grafts for a copolymer mixture (50/50, wt.%) di-block copolymers and long (30K) graft copolymers. The adhesion of copolymer mixture for 40K and 100K block copolymer with the graft copolymers having 30K grafts of PS was similar to that of the block copolymer mixtures with short (15K) grafted chains for 1 and 3 grafts. The G_c showed a pronounced maximum for the copolymer mixture with 2 of grafts (30K) and block copolymer (70K-b-70K). The interfacial G_c of the 50/50 wt.% graft block copolymer mixture increased from 20 to 130 ± 32 J/m². This narrow window where the mixture is effective is in agreement with the predictions of Balazs *et al.* [12] which show that the maximum effect occurs only when the graft and block co-polymer interfacial activities are evenly matched. This means that the architecture of the copolymer mixture is the determining factor in the adhesion at the interface. As shown in our prior study [13], the morphology of the fracture surface measured by AFM shows stick-slip behavior reflecting strong adhesion and cohesive failure.

   Balazs showed that the effect is a result of a segregation of short blocks from the grafts and long blocks from the diblock copolymers to
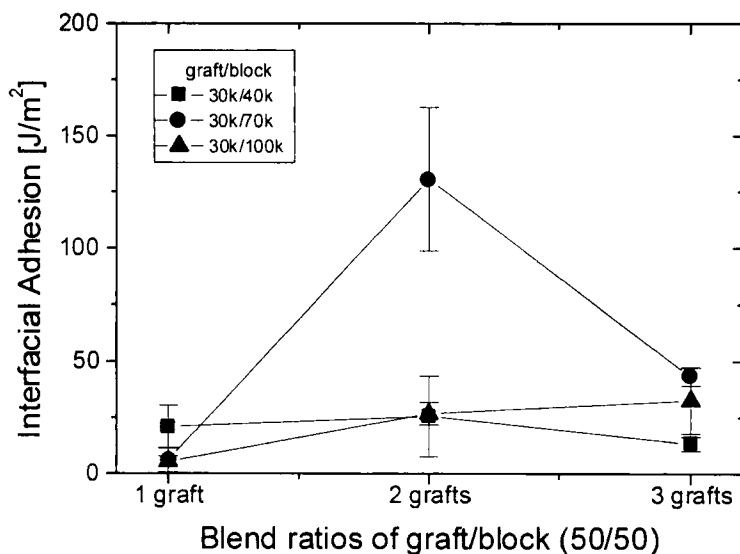
FIGURE 4   Interfacial adhesion of copolymer mixture (50/50, wt.%) of graft (2 grafts of 30k PS) and block copolymers of different M_w as a function of the number of graft.

the interfacial layer [17]. The grafted layer formed by chains of two different lengths can be viewed as two sublayers: an "inner" layer (closer to the interface), where the ends of the short chains are localized, and an "outer" layer (farther from the interface), where the ends of the long chains are localized. The equilibrium amount of each copolymer at the interface can roughly be estimated as a balance between the chemical potentials of the species in the bulk and in the individual sublayers. In this way, chains do not compete for space at the interface and the interfacial layer is more crowded than in the case of either of the pure components. Consequently, the interfacial tension is lower than that for the limiting cases of the pure components as predicted by Lyatskaya and Balazs [12].

   The adhesion between copolymer mixture (2 grafts of 30K PS) with 70K block copolymer, compared with pure block (70K-b-70K) copolymer as a function of annealing time at PS/PMMA is shown in Figure 5. The figure shows that the adhesion for the pure block copolymer decreases by almost an order of magnitude, from 25 J/m^2 to 2.9 J/m^2. This result is consistent with the previous data of Brown and coworkers [6].
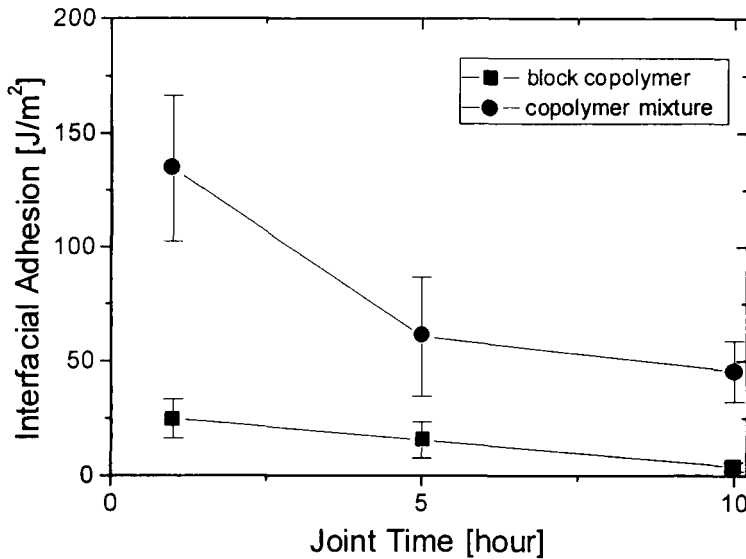
FIGURE 5   The adhesion between copolymer mixture (2 grafts of 30k PS) with 70k block copolymer, pure block (70k-b-70k) copolymer as a function of annealing time at PS/PMMA interface.

Figure 6 shows DSIMS data for a bilayer sample consisting of PS and 10% diblock copolymer trilayer sample when the diblock was spin-cast at the interface in a manner similar to the DCB measurement. In the figure, we show the dPS volume fraction (curve D). The O_2 volume fraction (curve O) corresponds to the PMMA. The solid line fraction is the unannealed data. Both samples were annealed for 24 hours at 170°C. From the figure we can see that there is no diblock copolymer diffusion into the PMMA layer, but significant diffusion of the block copolymer occurs in the dPS layer. In the bilayer sample we see that the copolymer segregates to both the PS/PMMA interface and the air interface. Shull et al. [18] showed that the copolymer at the air interface was in micelle form. In the trilayer sample the block copolymer diffuses into the PS layer and a peak at the free surface forms again, corresponding to micelle formation.

The adhesion of the block/graft mixture also decreased but only by a factor of three or from 134.4 J/m^2 to 45.5 J/m^2 over a period of ten hours. This indicates that micelle formation and diffusion of the copolymers is severely hindered in the mixture. The adhesion between
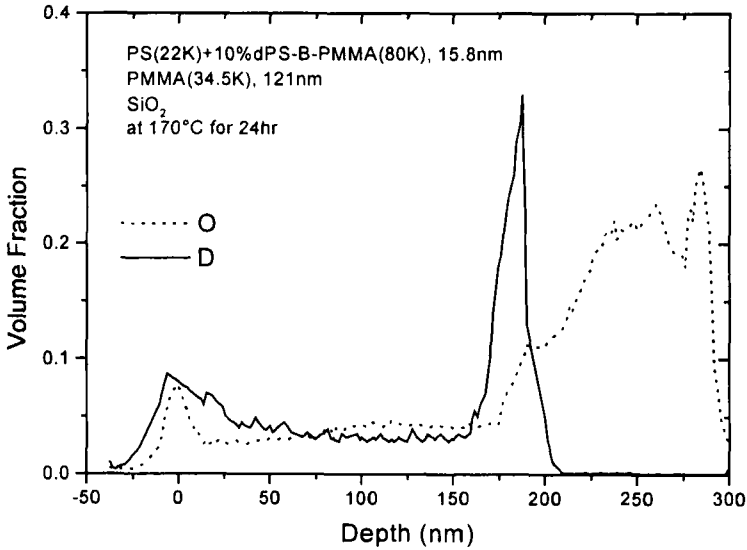
FIGURE 6   DSIMS data for a bilayer sample consisting of PS and 10% diblock copolymer.

the copolymer mixture (2 grafts of 30K PS) with 70K block co-polymer, pure block (70K-b-70K) copolymer, and pure graft (2 grafts of 30K PS) copolymer as a function of annealing temperature is shown in Figure 7. The adhesion of the pure graft copolymer remains low at all temperatures studied. However, the adhesion of the block copolymers increased with temperature in the temperature range between 140°C and 150°C, and then finally decreased to 6.6 J/m² at a high temperature over 180°C. The increase at 150°C is probably due to the time required to melt the thick PS and PMMA slabs. Proper melting is required in order to allow the copolymer to entangle across the interfaces. The adhesion of the copolymer mixture reaches a maximum at 150°C and decreases gradually until it finally reaches 81.2 ± 12 J/m² at a temperature of 180°C. This difference between the adhesion of the pure block copolymer and the copolymer mixture is again consistent with the assumption that the diffusion is decreased when the block and graft copolymers are mixed. Since the chains of block copolymer easily diffuse into the bulk at high temperature, the adhesion of block copolymer is low only at high temperature, while the adhesion of the copolymer mixture keeps the adhesion high due to
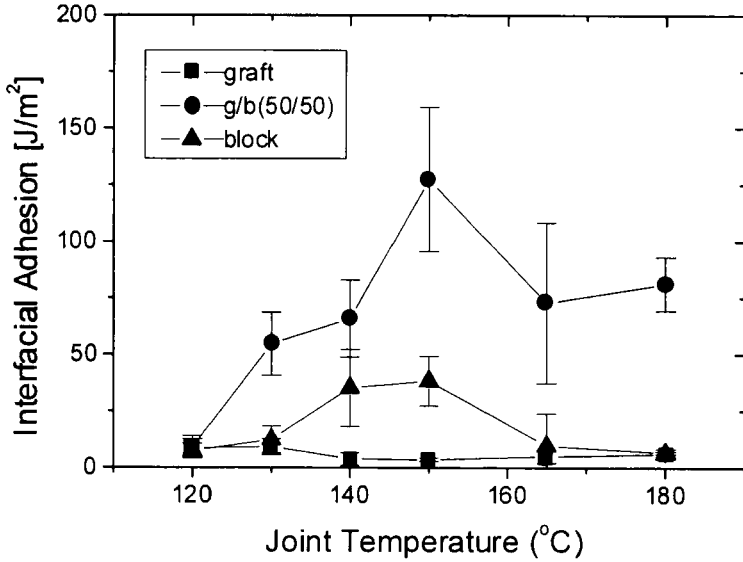
FIGURE 7   The adhesion between copolymer mixture (2 grafts of 30k PS) with 70k block copolymer, pure block (70k-b-70k) copolymer, and pure graft (2 grafts of 30k PS) copolymer as a function of annealing temperature at PS/PMMA interface.
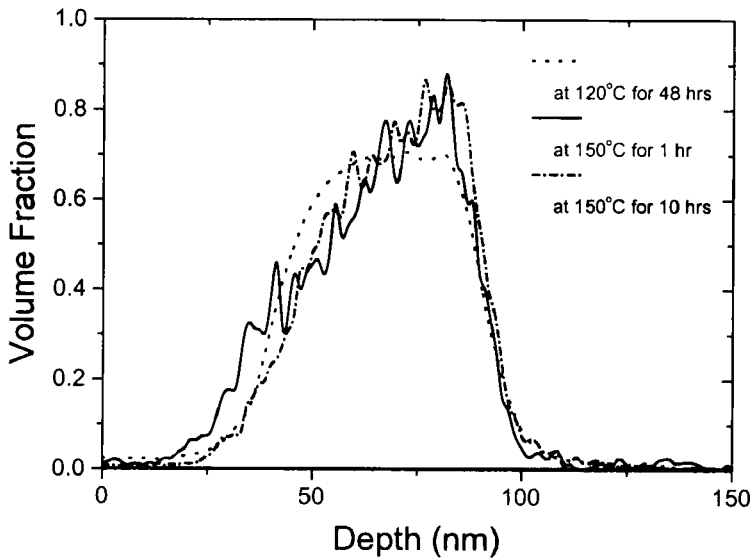

FIGURE 8   SIMS depth profile for copolymer mixture at 120°C and 150°C for 48 hours, 1 hour and 10 hours annealing, respectively.

the chains of the copolymer mixture being localized at interface at the high temperature.

In Figure 8 we show the DSIMS spectra of the diblock copolymer in the bilayer sample. From the figure we see that the copolymer has diffused away from the interface after annealing for 48 hours at 120°C. No change in the concentration profile is seen, between 1 hour and 10 hours at 150°C. This indicates that equilibrium has been reached.

CONCLUSIONS

We have shown that mixtures of graft and block copolymer are much more effective than pure block copolymers in enhancing the interfacial adhesion of poly(styrene) and PMMA. The mixtures are less expensive than the pure block copolymer and they are far less sensitive to the conditions of joint formation. The experimental data show that the fracture toughness of the joint varies only by a factor of 3 as the joining time is changed by an order of magnitude and the temperature is varied between 120°C and 180°C. DSIMS data show that this is consistent with decreased diffusion and micellization of the copolymer from the interface where the graft copolymer is present. The most effective mixture consists of a block copolymer of molecular weight 70K and a copolymer with two PS grafts of molecular weight 30K. This mixture yielded an interfacial fracture toughness of $G_c = 127.5 \text{ J/m}^2$ as compared with $G_c = 38.2 \text{ J/m}^2$ and $G_c = 3.5 \text{ J/m}^2$ for the pure block and graft copolymer, respectively. Our results highlight the importance of molecular architecture in controlling the interfacial activity of macro-molecules.

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