Multiblock Copolymers in the Compatibilization of Polystyrene and Poly(methyl methacrylate) Blends: Role of Polymer Architecture

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ABSTRACT: An asymmetric double cantilever beam (ADCB) was utilized to determine the ability of a series of styrene and methyl methacrylate copolymers with varying architectures to compatibilize the polystyrene/poly(methyl methacrylate) interface. Diblock, triblock, pentablock, and heptablock multiblock copolymers with similar molecular weights were compared to a random copolymer. When the surface is saturated with copolymer, PS/PMMA interfaces compatibilized with pentablock copolymers [S−M−S−M−S(30) and M−S−M−S−M(30)] were the strongest, followed by triblock [S−M−S(50) and M−S−M(50)] and then diblock [S−M(100)]. The least blocky structures, heptablocks [S−M−S−M-S−M−S(21) and M−S−M−S−M−S(21)] and random, provided the weakest interfaces under similar conditions. The ability of the multiblock copolymers to strengthen the PS/PMMA interfaces was attributed to multiple interface crossings and blocks of monomers that are able to anchor into the homopolymers. The results suggest that block lengths with molecular weight greater than 21 000 are required for adequate anchoring into the PS/PMMA homopolymer phases. Surprisingly, a dependence of the interfacial fracture toughness on copolymer composition was not observed for the multiblock copolymers studied. Both styrene-centered and methyl methacrylate-centered multiblock copolymers gave comparable results even though the compositions of the comparable copolymers differed greatly, as much as 70/30 to 30/70. In addition, increasing block lengths in multiblock copolymers of a given architecture increased interfacial adhesion.

Introduction

Compatibilization of polymer blends continues to be an area of considerable research interest. Rather than develop completely new polymers, which may be time-consuming and expensive, polymer blending offers many advantages. Polymer blends are much more cost-effective, and the properties of the original polymers may be synergistically combined and tuned to a desired product.[1−3] Unfortunately, because of unfavorable thermodynamics (low entropy of mixing), most polymer pairs form an immiscible polymer blend. This incompatibility and the subsequent sharp interfaces between homopolymer phases leads to coarse phase morphology in the system. The resulting two-phase material has poor properties compared to the original components, primarily due to the lack of stress transfer across the sharp interface.[3]

One method to obtain a useful material from an immiscible polymer blend is to compatibilize the blend by the addition of a third component, usually a copolymer that is composed of monomers that are miscible with both phases.[2−18] Copolymer molecules that reside at the biphasic interface in a phase-separated blend can couple the two phases together, which brings about improved morphology (finer dispersion), mechanical properties, phase behavior, and interfacial adhesion in the blend.[2−5] Reinforcement of the interface is primarily accomplished by the copolymer crossing the interface and entangling with both homopolymers forming “stitches”.[6] The result is a coupling of the two phases over which stress can be transferred.

Architecture and sequence distribution of the copolymer are important parameters that impact the solubility of a copolymer and thus the ability of a copolymer to compatibilize a polymer blend. The sequence distribution of a linear copolymer can vary continuously from alternating to random to blocky and will certainly play an important role in the ability of the copolymer to modify a biphasic interface. This is best exemplified by discussing the most probable alignment/arrangement/conformation of the copolymer at the biphasic interface. Both theoretical and experimental studies[19,20] have shown that the diblock copolymer arranges itself across an interface in a cylindrical or dumbbell shape, crossing the interface once. As the copolymer becomes less blocky,[19−23] the copolymer will begin to become more isotropic at the interface, crossing the interface many times. As the copolymer becomes more random and alternating, it will attain a pancake-type structure, covering a substantial area of the interface. However, the number of times these copolymers cross the interface and are able to entangle with the homopolymer is less clear than for blocky structures such as the diblock and multiblock copolymers.

This concept is illustrated in Figure 1, which diagrammatically depicts the possible conformations of several blocky copolymers. If the interface is sharp, diblock copolymer chain will cross the interface only once; however, as the number of blocks increases, the number of interface crossings also increases. For example, a triblock will cross the interface twice, a pentablock has four interfacial crossings, and a heptablock stitches the interface six times. The random copolymer is also believed to cross the interface multiple times although the exact number is not known. It should be emphasized that this picture is a simplistic version of a real interface but emphasizes the point that the microstructure of the copolymer can dramatically affect the configuration of a copolymer at the interface. Additionally, theory[19−24] predicts that the more times a copolymer molecule crosses the interface, the more effective interfacial modifier that copolymer would be. The logic is that there exist more joints or “stitches” sewing the two phases together, which must be broken or pulled out to allow fracture. This creates a stronger interface over which stress can be transferred whether

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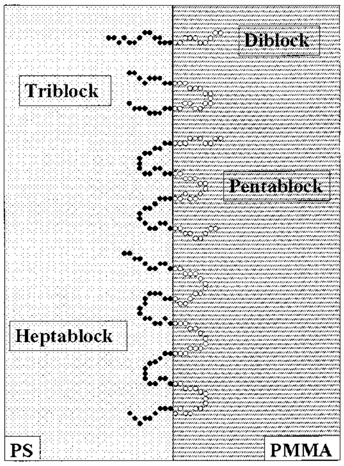

Figure 1. Illustration of the probable alignment of block copolymers at an interface.

the failure mechanism is by chain pullout or chain break.[7,8]

Conceptually, this trend makes sense, but there is very little information on how changing the sequence distribution from diblock to random and alternating will precisely impact the ability of a copolymer to compatibilize an interface. Therefore, while substantial work has been completed on understanding the fundamentals of the mechanism by which copolymers can compatibilize immiscible polymer blends, there is no clear picture of how copolymer architecture and sequence distribution affect the ability of a given copolymer to compatibilize a polymer blend. Different copolymer structures such as diblock,[6,9−14] random,[7,11,12,15,16] multiblock,[4,5,8,17] alternating,[18] and graft[12,17] copolymers have been examined as compatibilizers, but comparison of these results does not provide conclusive insight into the role of copolymer microstructure in the interfacial modification process. This is primarily because other parameters such as copolymer composition, molecular weight, and monomer pair also vary in these studies, and thus separation of sequence distribution effects cannot be definitively achieved.

Thus, to more thoroughly understand the importance of copolymer architecture on its ability to compatibilize an immiscible polymer blend, the interfacial strength of an interface compatibilized by a series of copolymers with varying sequence distribution for given monomer pair has been experimentally determined. The monomer pair chosen for this study was styrene (S) and methyl methacrylate (MMA). This pair was chosen due to the availability of the copolymers with a variety of sequence distributions and the fact that significant data appears in the literature for PS and PMMA homopolymers compatibilized by random,[7,11,16] diblock,[10−12] and graft[12] copolymers. Styrene/methyl methacrylate random, alternating, and diblock copolymers can be readily purchased or synthesized. The multiblock copolymers are more difficult to obtain; however, a method to synthesize triblock, pentablock, and heptablock copolymers of styrene and methyl methacrylate was developed in our lab.[25]

A few theoretical studies have investigated the ability of multiblock copolymers to compatibilize polymer blends. Noolandi predicts that diblock and triblock copolymers will align perpendicular to the interface plane when placed at a biphasic interface, resulting in dumbbell-shaped conformations.[26] Multiblock copolymers such as pentablock and heptablock copolymers lie in the plane of the interface and thus form pancake-shaped conformations. Pancake-shaped conformations require less material to cover a given interfacial area than dumbbell-shaped conformations. Furthermore, multiblock copolymers are less likely than diblock copolymers to form micelles or mesophases. Supporting this theory, Kramer and co-workers found that the critical concentration where micelle formation began was higher for triblock copolymers than that for diblock copolymers.[27] Poly[(2-vinylpyridine)-*b*-styrene-*b*-(2-vinylpyridine)] triblock copolymer had a larger critical micelle concentration than that of a similar molecular weight PS−PVP diblock copolymer. Noolandi speculated that “multiblock copolymers should be effective as polymeric surfactants, provided that the blocks are large enough to form loops which extend well beyond the original homopolymer interface, and to enable physical entanglements or chemical linkages to form with homopolymers”.[26]

Monte Carlo computer simulation has also been used to theoretically evaluate the ability of multiblock copolymers to compatibilize. Balazs demonstrated that, provided blocks are long enough to form entanglements with the homopolymers, the number of effective crossings at the interface or “stitches” that a copolymer is capable of achieving determines the improvement of interfacial adhesion.[24] Failure at such an interface can occur by either chain pull out or chain scission.[6−8,16] Either way, the greater the number of blocks or more interface crossings that a multiblock copolymer possess result in either more blocks being pulled out or more “stitches” that need to be cut. Also using Monte Carlo methods, Dadmun found that blocky type copolymers were more effective at expanding at the interface into the homopolymer phases than random copolymers.[19−22] Therefore, theoretical evidence suggests that blocky or multiblock copolymers should be very effective interfacial modifiers in the compatibilization of polymer blends.

Experimentally, multiblock copolymers have been shown to be very effective interfacial modifiers. Poly(2-vinylpyridine-*b*-styrene-*b*-2-vinylpyridine) triblock copolymers reinforced the interface between polystyrene (PS) and poly(2-vinylpyridine) (PVP) better than poly(PS-*b*-PVP) diblock copolymers at thick copolymer layers.[8] PS/PVP interfaces were also reinforced by multiblock copolymers composed of blocks of PS and poly(4-hydroxystyrene), PS(OH).[17] The poly[PS(OH)-*b*-PS-*b*-PS(OH)] triblock was compared to the poly[PS-*b*-PS(OH)-*b*-PS-*b*-PS(OH)-*b*-PS] pentablock. This pentablock copolymer was found to be a more effective interfacial modifier than the triblock copolymer. Other multiblock copolymers composed of styrene and butadiene monomer blocks efficiently compatibilized blends of polystyrene and polypropylene.[4,5] In these studies, the triblock and pentablock copolymers provided a finer dispersion of the minor phase and better mechanical properties than either diblock or heptablock copolymers.

A common method for measuring the ability of copolymers to strengthen an interface is to measure the interfacial adhesion by an asymmetric double cantilever beam (ADCB) test.[6−17,28−30] This test geometry determines the interfacial fracture toughness (G_c) of a crack propagating at the interface between two homopolymers.[6] The procedure entails driving a razor blade at the interface between two homopolymer layers and measuring the length of the resulting crack.

Table 1. Molecular Weight and Composition of Multiblock Copolymers Synthesized

polymer/copolymer	M_w	M_n	M_w/M_n	% Sty	% MMA
PMMA50	53 500	45 100	1.19	0	100
PMMA30	32 100	29 000	1.10	0	100
PMMA21	24 500	21 300	1.15	0	100
PS50	69 800	50 000	1.40	100	0
PS30	36 800	28 700	1.28	100	0
PS21	23 600	20 700	1.14	100	0
S−M100	201 500	169 300	1.19	46	54
S−M−S50	153 000	96 700	1.58	69	31
S−M−S30	115 000	76 700	1.50	68	32
S−M−S21	92 800	62 600	1.48	68	32
M−S−M50	170 000	111 100	1.53	33	67
M−S−M30	120 300	80 400	1.50	32	68
M−S−M21	65 000	49 600	1.31	34	66
M−S−M−S−M30	159 000	105 000	1.51	41	59
M−S−M−S−M21	127 000	83 800	1.52	41	59
S−M−S−M−S30	175 000	115 100	1.52	60	40
S−M−S−M−S21	126 500	82 300	1.54	62	38
S−M−S−M−S−M-S21	151 000	98 200	1.54	57	43
M−S−M−S−M−S−M21	155 000	98 100	1.58	45	55
random(S0.7−MMA0.3)	162 000	99 300	1.63	70	30
homopolymer PS	230 000	140 000	1.64	100	0
homopolymer PMMA	100 000	62 500	1.60	0	100

The results of an ADCB study are presented here in which the strength of an interface between PS and PMMA homopolymers that are reinforced with a thin layer of copolymer is measured. Random, diblock, triblock, pentablock, and heptablock copolymers of styrene/methyl methacrylate were all used to reinforce PS/PMMA strips and analyzed by ADCB at varying copolymer thickness (20−300 nm layers). The multiblock copolymers, which all have approximate molecular weights of 150 000, were also compared to diblock and random copolymers with similar molecular weights. In addition, triblock copolymers with different block lengths (30 000 and 21 000) and a pentablock copolymer with block lengths of 21 000 were also analyzed to evaluate the effect of block length on the ability of multiblock copolymers to compatibilize a biphasic interface.

Experimental Section

1. Homopolymers. Polystyrene (PS) was purchased from Aldrich ($M_w = 230\,000$; $M_n = 140\,000$). Atactic poly(methyl methacrylate) (PMMA) was purchased from Polysciences, Inc. ($M_w = 100\,000$; $M_n = 62\,500$). Both homopolymers were heated at 150 °C under vacuum for 48 h to remove any remaining solvent or other impurities.

2. Copolymers. The poly(styrene$_{93.5K}$-*b*-methyl methacrylate$_{108K}$) diblock was purchased from Polymer Source, Inc., while the poly(styrene$_{0.7}$-*ran*-methyl methacrylate$_{0.3}$) random copolymer was synthesized via free radical techniques. Multiblock copolymers were synthesized by utilizing ATRP (atom transfer radical polymerization) techniques as previously reported.[25] A difunctional initiator (phenoxybenzene-4,4′-disulfonyl chloride) was used in the presence of a copper halide/2,2′-bipyridine complex to sequentially polymerize alternating blocks of styrene and methyl methacrylate. This method was used to prepare both styrene and MMA-centered triblock copolymers consisting of differing block lengths. Some of the triblocks were then extended further to synthesize pentablock copolymers, which in turn were used to synthesize heptablock copolymers.

Copolymer composition was determined by ^{1}H NMR, and molecular weight data were obtained by gel permeation chromatography (GPC). These values can be found in Table 1. Degrees of polymerizations for the multiblocks' initial blocks were found by GPC. However, due to increasing polydispersity, the degrees of polymerization of the remaining blocks were obtained from the NMR composition data, which can be viewed in Table 2 for all block copolymers. It is important to note that, due to the sequential nature of this synthetic procedure, it is expected that the multiblock copolymers will exhibit narrow composition distributions, a parameter that is also known to be important in the interfacial modification process by copolymers.[23,31]

3. ADCB Sample Preparation. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) homopolymers were compression molded and then cut into strips that were 1 cm wide, 6.5 cm long, and either 0.20 cm thick for the PMMA layer or 0.23 cm thick for the PS layer. This difference in thickness is required to help minimize craze formation and help maintain the crack propagating at the interface.[10,28,29] If both layers were the same thickness, the crack may swerve into the more compliant material, in this case, PS. This would cause the formation of crazes, which would inflate the measured fracture toughness. The thickness ratio used in this study ($h_{PS}/h_{PMMA} = 1.15$) was found by Winey,[16] and later a similar value (1.2) was found by Brown[11] to be the optimal thickness ratio for a PS/PMMA system in ADCB experiments.

Copolymer layers ranging from 20 to 300 nm were spin-coated from a copolymer solution (toluene) onto a glass slide at 2500 rpm for 30 s. The thickness of the copolymer film was controlled by the concentration of the solution, which varied from 0.7 to 5.3 wt %. The correlation between film thickness and solution concentration was accomplished by spin-coating similar solutions onto silicon wafers and determining the thickness of these films with a nulling ellipsometer. In addition, the areal chain density, Σ, was calculated for each copolymer thickness by eq 1 using the polymer density (ρ), Avogadro's number (N_A), and the molecular weight.

$$\Sigma = \text{thickness}\cdot\rho\cdot N_A/(\text{molecular weight}) \tag{1}$$

The copolymer film was floated off the glass slide into a water bath and captured by the PS homopolymer strip. The samples were dried at 80 °C for at least 2 h and then dried at the same temperature under vacuum for 24 h. A PMMA strip was placed on top of the copolymer layer, resulting in a three-layer sandwich (PS/copolymer/PMMA). This trilayer sample was annealed for 2 h at 150 °C under slight pressure. For copolymers composed of styrene and methyl methacrylate, this

Table 2. Block Structure of Multiblock Copolymers Utilized in This Study

block copolymer type	block copolymer symbol	block degree of polymerization
diblock	S−M(100)	935−1050
triblock (MMA centered)	S−M−S(50)	483−451−483
triblock (MMA centered)	S−M−S(30)	296−290−296
triblock (MMA centered)	S−M−S(21)	218−213−218
triblock (Sty centered)	M−S−M(50)	485−481−485
triblock (Sty centered)	M−S−M(30)	305−276−305
triblock (Sty centered)	M−S−M(21)	201−199−201
pentablock (MMA centered)	M−S−M−S−M(30)	298−296−290−296−298
pentablock (MMA centered)	M−S−M−S−M(21)	219−218−213−218−219
pentablock (Sty centered)	S−M−S−M−S(30)	301−305−276−305−301
pentablock (Sty centered)	S−M−S−M−S(21)	216−201−199−201−216
heptablock (MMA centered)	S−M−S−M−S−M−S(21)	197−219−218−213−218−219−197
heptablock (Sty centered)	M−S−M−S−M−S−M(21)	200−216−201−199−201−216−200

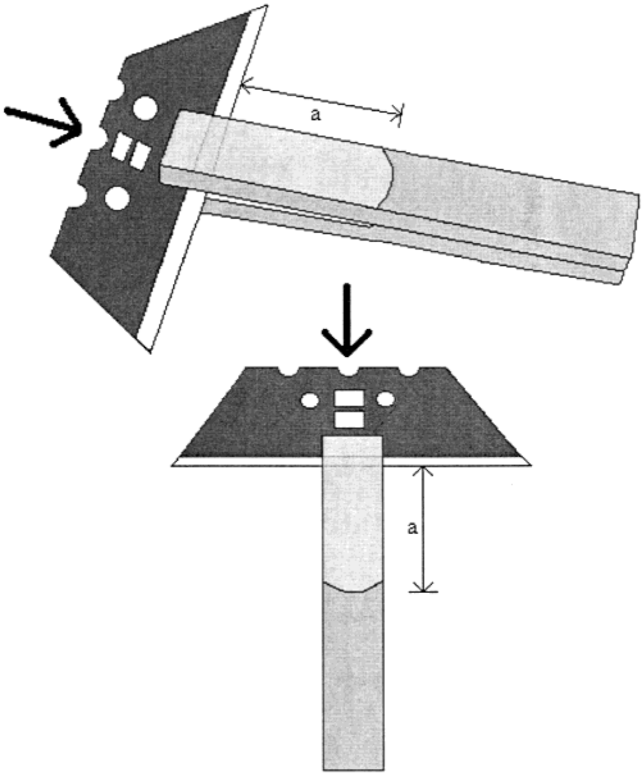

Figure 2. Illustration depicting the asymmetric double cantilever beam test.

annealing time has been shown to be insufficient to achieve thermodynamic equilibrium.[16] However, this annealing time and temperature were used in order to be consistent with similar ADCB studies of styrene/methyl methacrylate copolymers given in the literature.[7,10−12,16,31] Also, increasing the annealing time from 2 to 18 h was reported by Brown to give little variation in fracture toughness.[28] The final ADCB samples were then stored in a desiccator until testing by ADCB.

4. Fracture Toughness Measurement. The fracture toughness was measured by asymmetric double cantilever beam (ADCB). Details concerning this experiment can be found in the literature.[6−17,28−30] A diagram of a sample being tested can be seen in Figure 2. In short, a razor blade was inserted at the interface and driven in at a speed of 0.20 mm/min. Pictures were captured on a computer every minute using a video camera, and crack lengths were measured from the razor blade to the crack tips. The value found for the crack length, a, was then utilized in eq 2 to calculate the fracture toughness (G_c).

$$G_c = \frac{3\Delta^2 E_1 h_1^3 E_2 h_2^3}{8a^4} \frac{E_1 h_1^3 C_2^2 + E_2 h_2^3 C_1^2}{[E_1 h_1^3 C_2^3 + E_2 h_2^3 C_1^3]^2} \qquad (2)$$

where $C_1 = 1 + 0.64h_1/a$ and $C_2 = 1 + 0.64h_2/a$. In eq 2, Δ is the thickness of the razor blade, h_1 and h_2 are the thickness of the homopolymer layers, and E_1 and E_2 are Young's moduli of the homopolymers which were found by a three-point flexural test (ASTM D790).[32] For each interface examined, 7−12 samples were tested.

Results and Discussion

A. Copolymer Architecture. Results from the ADCB experiments are given as plots of interfacial fracture toughness, G_c, as a function of the copolymer layer thickness and Σ, areal chain density. These plots for PMMA-centered multiblock copolymers are given in Figure 3, while those for PS-centered multiblock copolymers are shown in Figure 4. In these plots, 0 nm on the x-axis represents no copolymer present at the interface. This resulting weak interface reveals a measured fracture toughness of 3.4 J/m^2. After placing copolymer layers at the interface, increases in the fracture toughness are observed for all copolymers.

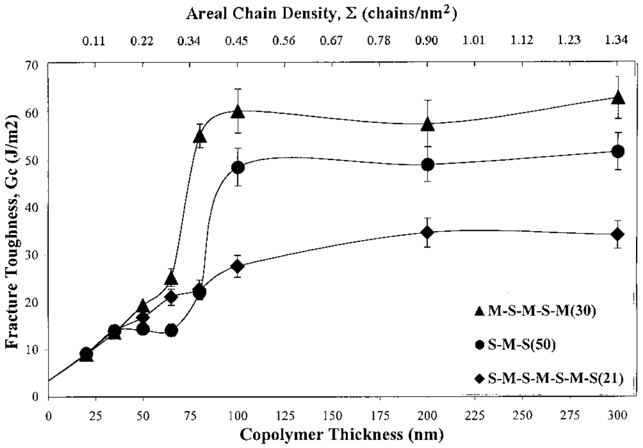

Figure 3. Fracture toughness, G_c, of PS/PMMA interfaces reinforced with MMA-centered multiblock copolymers [S−M−S(50), M−S−M−S−M(30), S−M−S−M−S−M−S(21)] plotted as a function of copolymer layer thickness and areal chain density, Σ.

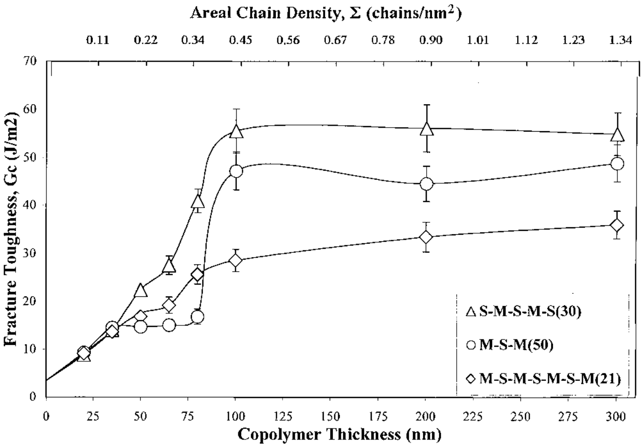

Figure 4. Fracture toughness, G_c, of PS/PMMA interfaces reinforced with styrene-centered multiblock copolymers [M−S−M(50), S−M−S−M−S(30), M−S−M−S−M−S−M(21)] plotted as a function of copolymer layer thickness and areal chain density, Σ.

Upon examination of Figure 3 (or Figure 4), three different regions of behavior are observed. The first region occurs when the copolymer thickness is between 0 and 35 nm, the second from 35 to 100 nm, and the third when the copolymer layer is thicker than 100 nm. In the first initial region, very little difference in the interfacial strengths of the various multiblock copolymers is observed. This trend makes sense, as in this regime the PS/PMMA interface is lightly covered with interfacial modifier and any improvement in the fracture toughness is due to the presence of any interfacial modifier that can interact with both phases. However, in the second, transition regime, the fracture toughness does begin to differ with copolymer architecture. For instance, the interfacial fracture toughness of the M−S−M−S−M(30) pentablock and the S−M−S−M-S−M−S(21) heptablock increase consistently with copolymer thickness. Conversely, the S−M−S(50) triblock copolymer reveals a plateau that occurs from 35 to 65 nm.

Relating this behavior to a physical picture of the interface is not as trivial in this regime as in the initial regime, but comparable triblocks in a PS/PVP system revealed similar trends.[8] In the transition region, the M−S−M−S−M(30) pentablock yielded the highest measured G_c's of all of the copolymer structures examined. The S−M−S−M−S−M−S(21) heptablock gave the next highest fracture toughness in this region, followed by the S−M−S(50) triblock.

The third and final region (thickness >100 nm) will be referred to as the saturated region and is marked by little changes in G_c with increasing copolymer thickness. This region correlates to the physical condition where the copolymer has saturated the interface between the two homopolymer layers and may form its own third layer between the two homopolymers, and the addition of further copolymer provides little improvement of the fracture toughness of the interface. Optimum strengthening for all multiblock copolymers is observed in this region, presumably due to the interaction of the copolymers with both homopolymer phases. In this region, the strongest interfaces are found for those modified with the M−S−M−S−M(30) pentablock copolymer, followed by the S−M−S(50) triblock copolymer which, in turn, yielded higher fracture toughness values than the S−M−S−M−S−M−S(21) heptablock copolymer.

The copolymer thickness where the interface is saturated (or covered) with copolymer can be estimated by simple volume arguments. The surface area of the interface is known from the dimensions of the original sample. Assuming that the copolymer chain occupies an area on the surface that is the cross section of a sphere, the total area covered by the copolymer can be estimated from the dimensions of the polymer coil and the number of moles of copolymer present at the interface. The saturation areal chain density is then found when the area of the interface equals the area covered by the applied copolymer. To complete this calculation, a radius of gyration of the copolymer must be assumed, and this value is taken to be approximately 110 Å. This value is estimated from the R_g of 150 000 MW PS[33] (120 Å) and PMMA[34] (100 Å) as determined from light scattering. This volume estimation results in eq 3

$$T_{\text{sat}} = \frac{M_w}{\pi R_g^{\,2} N_A \rho} \qquad (3)$$

where T_{sat} is the saturation thickness, M_w is the copolymer molecular weight, R_g is the radius of gyration of the copolymer (≈110 Å), N_A is Avogadro's number, and ρ is the copolymer density. For a copolymer with a molecular weight of 150 000 g/mol, full coverage is calculated to begin at a thickness of approximately 60 nm, which agrees well with the experimental evidence that shows a transition to the saturated regime in 35−100 nm.

Before further discussion of these three regimes and their relationship to the structure of the copolymers, it is interesting to note the similarities between the curves in Figures 3 and 4. The shapes and fracture toughness values are nearly identical for each type of multiblock copolymer in both plots. Essentially, little to no difference is observed between the styrene-centered and the methyl methacrylate-centered multiblocks. This occurs *despite* the fact that the compositions of the styrene-centered copolymers are very different than the composition of the methyl methacrylate-centered copolymers with the same architecture. For example, the two heptablock copolymers have the smallest composition difference with the M−S−M−S−M−S−M(21) at 45% styrene while the S−M−S−M−S−M−S(21) is 57% styrene, yet these two copolymers demonstrate similar strengthening abilities. Similarly, S−M−S−M−S(30) is composed of 60% styrene, M−S−M−S−M(30) is made up of 41% styrene, and M−S−M(50) has a composition that is 33% styrene, while S−M−S(50) is 69% styrene. Yet, each of these copolymer pairs give comparable G_c vs copolymer thickness curves. This demonstrates that the ability to improve interfacial adhesion for multiblock copolymers is less sensitive to the copolymer composition than random copolymers. Russell and co-workers determined a significant dependence of interfacial fracture toughness on copolymer composition for random MMA/S copolymers and found that the optimal fracture toughness was found when the random copolymer contains 68% styrene.[7] This composition dependence was related to the symmetry of the distribution of the copolymers between the two homopolymer phases, with the strongest interface correlating to a symmetric broadening of the interface by the random copolymer. A similar study on the multiblock copolymers is currently underway in our laboratory.

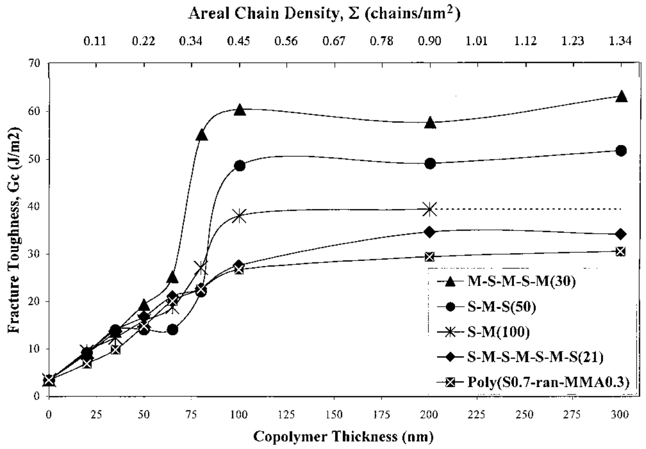

Figure 5. Fracture toughness, G_c, of PS/PMMA interfaces reinforced with diblock [S−M(100)], poly($S_{0.7}$-*ran*-$MMA_{0.3}$), S−M−S(50), M−S−M−S−M(30), S−M−S−M−S−M−S(21)] plotted as a function of copolymer layer thickness and areal chain density, Σ.

To more completely correlate our results to those reported previously, the interfacial strengthening of the multiblock copolymers are also compared to that of random and diblock copolymers in Figure 5, where only the MMA-centered multiblocks from Figure 3 are included. Note that the composition of the random copolymer is similar to that found by Russell and co-workers to be optimal. In the initial region, the S−M(100) diblock exhibits similar results to the other blocky copolymers; however, the random copolymer displays slightly lower interfacial fracture toughness values than those of the blocky copolymers. It appears that blocky copolymers are slightly better than random copolymers for interfacial modification when the surface is lightly covered, although there is not much difference between the various blocky copolymers. Through the transition region, the fracture toughness of the samples with the diblock and random copolymers both consistently increase with compatibilizer layer thickness. It is of particular interest that the diblock copolymer does not form the plateau, which was observed with the triblocks.

It appears that the plateau phenomenon is only observed for the triblock copolymer at the block molecular weights studied. Upon reaching the saturation region, the diblock and random copolymer flatten out similarly to the other structures examined.

The observed initial, transition, and saturated regions can be correlated to known mechanisms of failure/fracture of polymeric interfaces. Previous researchers have correlated the type of interfacial failure to the lengths of each block and the number of chains at the interface (areal chain density, Σ) for diblock and triblock copolymers.[6,8,13,14] Copolymers with blocks longer than the critical entanglement molecular weights of the homopolymers and low areal chain densities have been shown to fail by chain scission. During chain scission, copolymer chains break upon fracturing of the interface. This mechanism of failure should occur in our initial region (0−35 nm) for copolymers with blocks greater than the critical molecular weight. As Σ is increased, the type of fracture mechanism transitions from chain scission to crazing.[6,8,13,14] During crazing, crazes are formed in one of the homopolymers followed by copolymer failure. A signature of crazing is an abrupt increase in the fracture energy, primarily due to the large amount of material that undergoes plastic deformation in a craze.[35] Inspection of the data, therefore, suggests that crazing begins in the transition region for copolymers S−M−S(50), M−S−M(50), M−S−M−S−M(30), S−M−S−M−S(30), and S−M(100) and occurs throughout the saturated region (100−300 nm). Copolymers with block lengths below the critical entanglement molecular weight and low areal chain densities are known to fail by chain pull-out. Shorter block lengths are not long enough to adequately anchor into the homopolymer phases and simply pull out upon fracturing of the interface.[6,8,13,14] For copolymer with short block lengths, failure occurs in our initial region (0−35 nm) by chain pullout. At higher areal chain densities, the mechanism of failure again transitions from pullout to crazing of one of the homopolymers followed by copolymer chains disentangling or breaking.[6,13−15] Once again, crazing should begin in the transition region and occur throughout the saturated region.

Correlation of this interpretation to our data suggests that little differences in the ability of various copolymer structures to strengthen a biphasic interface are found when only chain pullout or chain scission occurs for the PS/PMMA, as the data show very little difference between the various copolymers in the initial region. Larger differences, however, are observed when crazing is the failure mechanism in the saturated regime.

In the saturated regime, the illustration shown in Figure 1 is no longer adequate to describe the interface, because the increased copolymer content at the interface leads to crowding of the copolymer chains at the interface and eventually the formation of a separate copolymer layer. At this point, a separate copolymer layer forms (estimated to occur at ~60 nm), and the copolymer layer has two interfaces: one between the copolymer and the PS homopolymer and the other at the copolymer/PMMA homopolymer junction. The strength of this saturated system will thus depend on the interactions of the copolymer with *both* homopolymers at both interfaces. Nonetheless, the argument that the multiblock copolymer chains that cross the interface(s) the most times and entangles with the homopolymer will be the most effective interfacial strengthener is still valid; however, it must interact equally with *both* homopolymer phases (i.e., at both interfaces). This situation is illustrated in Figure 6. It should be emphasized that the interfaces in Figures 1 and 6 are drawn as sharp for clarity. The interface is undoubtedly broader than this; however, this does not influence the essential physics of the mechanism described above: the copolymer must take excursions into the homopolymer, form loops, and entangle with the copolymer and homopolymer layers.

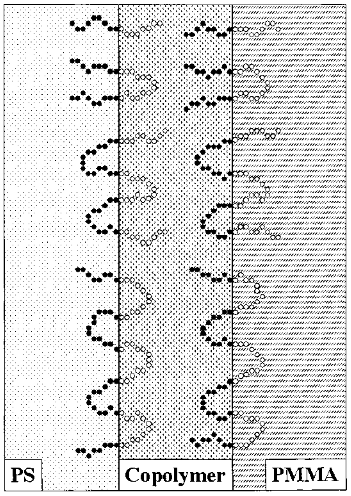

Figure 6. Illustration of possible of block copolymer alignment at a PS/PMMA saturated interface.

Dai and Kramer have found that, for PVP−PS−PVP triblocks within this separate copolymer layer, microstructure such as lamellae may form.[11] Because of a smaller χ value associated with the styrene/methyl methacrylate system ($\chi = 0.030$)[36] and the compositions of the multiblock copolymers used in this study (volume fractions are approximately 2:1), it is not expected that these S/MMA multiblock copolymers would microphase separate and form similar morphology. In fact, initial SEM analysis indicates that the multiblock copolymers in the bulk do not microphase separate into ordered phases upon annealing for 2 h. Apparently, the styrene/methyl methacrylate multiblock copolymers strengthen the interface by a different process than that of the PS/PVP triblock as proposed by Kramer.

A comparison of the ADCB results in Figure 5 to the copolymer alignment illustrations in Figures 1 and 6 reveals some interesting trends. The diblock copolymer, with one interface crossing per chain, has an interfacial fracture toughness value of approximately 40 J/m^2 in the saturated region. As the number of blocks is increased to three, the triblocks exhibit G_c's close to 50 J/m^2. This trend is repeated when we further increase the number of blocks and interfacial crossing for the pentablock copolymer, which displays a fracture toughness of around 60 J/m^2. Pentablocks demonstrate the highest measured interfacial fracture toughness and thus are the most effective compatibilizer used in this study.

However, a further increase in the number of blocks to seven results in a decrease in interfacial fracture toughness relative to the pentablock as the G_c's for heptablocks in the saturated region are found to be approximately 35 J/m^2. The random copolymer proves to be the least effective compatibilizer with a fracture toughness of 30 J/m^2. Table 3 summarizes these results. Therefore, for the copolymers with similar molecular

Table 3. Summary of Fracture Toughness of Saturated Interfaces

copolymer	no. of blocks	block MW	G_c(satd), J/m^2
pentablock	5	30 000	~60
triblock	3	50 000	~50
diblock	2	100 000	~40
heptablock	7	21 000	~35
random	NA	NA	~30

weights, the final order in the saturated region is pentablock > triblock > diblock > heptablock > random with the most effective interfacial modifier listed first.

One surprising outcome is that the heptablocks are the least effective compatibilizer of the multiblock copolymers even though they have the greatest number of blocks and, thus presumably, interface crossings. A possible explanation for our results may be a result of the lower block molecular weight of the heptablocks used in our study. As can be seen in Table 3, each block of the heptablock is approximately 21 000, which may not be long enough to effectively anchor into the homopolymer phases and reinforce the interface.

This phenomenon of a "critical block length" for entanglement of the blocks within a compatibilizer with the homopolymers is similar to the critical entanglement molecular weight of a homopolymer as the critical entanglement molecular weight of a homopolymer is defined as the molecular weight above which entanglements affect the dynamics and flow properties of a polymer. Interestingly, the critical entanglement molecular weights for PS and PMMA are 31 000 and 27 500 g/mol, respectively,[37] and therefore, the critical block length of the PS/PMMA multiblocks is in the vicinity of the critical entanglement molecular weight of the homopolymers. Unfortunately, an exact "critical block length" cannot be definitively identified from these studies; however, the data suggest that it is between 30 000 and 21 000. One final interesting note is that the surfaces that are modified with the heptablock copolymers give similar results (curves and fracture toughness values) to those of the random copolymer. This would seem to indicate that both copolymers modify the interface in a similar manner and further support the concept that the heptablock copolymer interacts with the homopolymer phases in a different way than the other multiblock copolymers.

B. Effect of Block Molecular Weight for a Given Architecture. To further investigate the effect of block length on the compatibilization of phase-separated blends by multiblock copolymers, the ability of triblock copolymers to strengthen the biphasic interface as a function of block lengths was also investigated. The ADCB results from MMA-centered triblocks with three different block molecular weights are given in Figure 7. S−M−S(30) triblock has block lengths of 30 000 while the S−M−S(21) triblock has 21 000 block molecular weights and are compared to the triblock with 50 000 block molecular weight, S−M−S(50), presented earlier. It is interesting that the S−M−S(21) triblock curve and fracture toughness values are more similar to the heptablock (S−M−S−M−S−M−S(21)) than the other triblocks [S−M−S(50) and S−M−S(30)], which show a plateau from 35 to 65 nm and dramatic increase in G_c when the copolymer layer increases from 65 to 100 nm. Figure 8 provides further evidence of the importance of block length as it compares the interfacial strengths of interfaces that are modified by the methyl methacrylate-centered pentablock copolymers M−S−M−S−M(30) and M−S−M−S−M(21). Again, for these compatibilizers, the multiblock copolymer with block molecular weights that are below 30 000 exhibit a G_c vs thickness curve that resembles those found for the heptablock and random copolymer. This resemblance is exemplified in Figure 9, which shows the G_c of the surfaces that are modified with the triblock, pentablock, and heptablock copolymers that have block lengths of approximately 21 000 as well as that of the interface that is compatibilized with the random copolymer. Each of these curves shows a steady increase in fracture toughness as the copolymer layer thickness increase up to about 100 nm where it saturates to a constant value that increases with overall copolymer molecular weight.

This similarity between various copolymer structures provides further evidence that a critical parameter in determining the ability of a copolymer to compatibilize a biphasic interface is the block molecular weight. In the results presented here, the copolymers that have block lengths that are 30 000 or larger are the most effective interfacial strengtheners, suggesting that this molecular weight is an upper limit to the "critical block length" for effective entanglement of the blocks with the homopolymer phase. For multiblock copolymers with blocks whose molecular weights are at least 30 000, there is at least a doubling (and often a tripling) in the fracture toughness of the interface as the copolymer

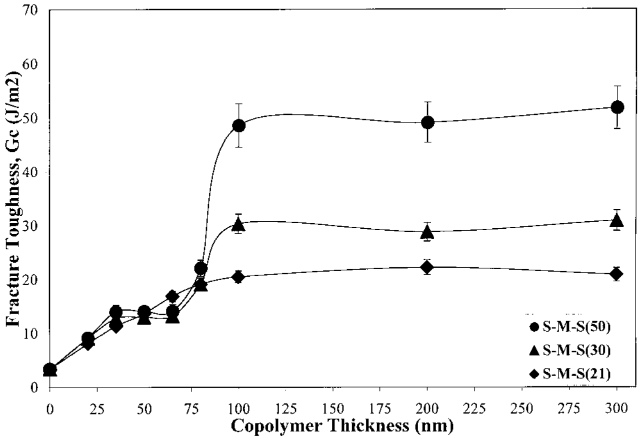

Figure 7. Fracture toughness, G_c, of PS/PMMA interfaces reinforced with triblock copolymers with varying block lengths [S−M−S(50), S−M−S(30), S−M−S(21)] plotted as a function of copolymer layer thickness.

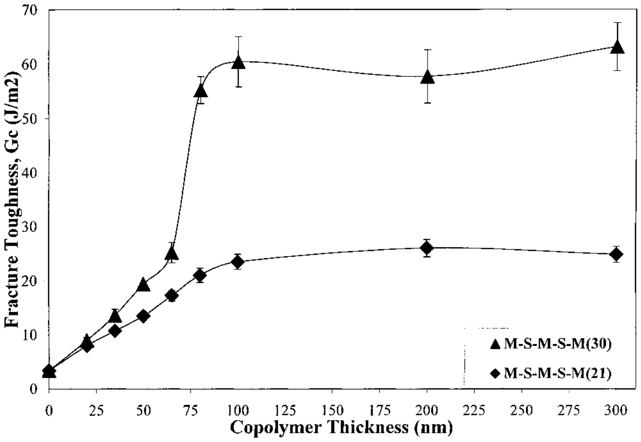

Figure 8. Fracture toughness, G_c, of PS/PMMA interfaces reinforced with pentablock copolymers [M−S−M−S−M(30), M−S−M−S−M(21)] plotted as a function of copolymer layer thickness.

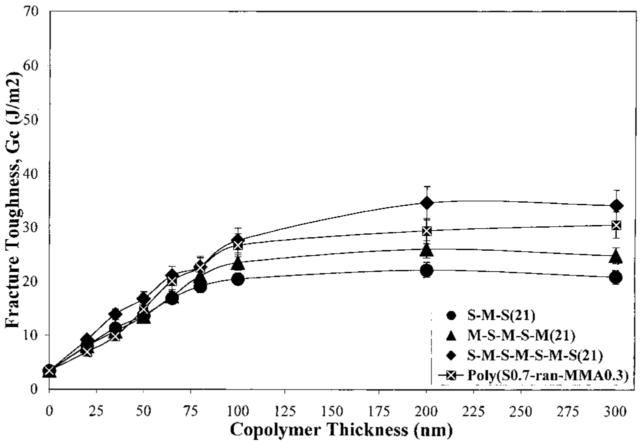

Figure 9. Fracture toughness, G_c, of PS/PMMA interfaces reinforced with multiblock copolymers with 21 000 block lengths [S−M−S(21), M−S−M−S−M(21), S−M−S−M−S−M−S(21)] and poly($S_{0.7}$-*ran*-$MMA_{0.3}$) plotted as a function of copolymer layer thickness.

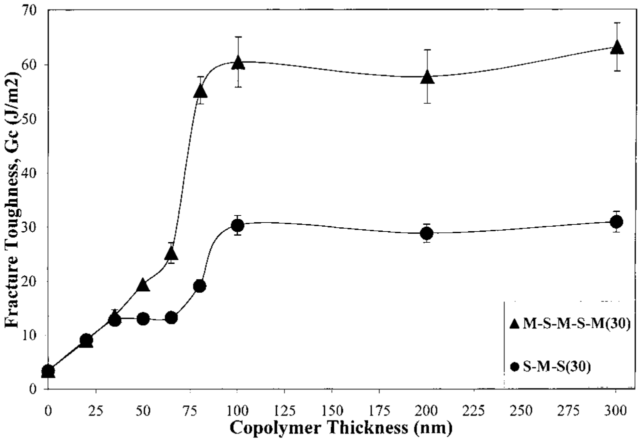

Figure 10. Fracture toughness, G_c, of PS/PMMA interfaces reinforced with multiblock copolymers with 30 000 block lengths [S−M−S(30) and M−S−M−S−M(30)] plotted as a function of copolymer layer thickness.

thickness goes from 65 to 100 nm and the interface is saturated. For multiblock copolymers with blocks whose molecular weights are below this threshold value, the increase with thickness is significantly more modest.

Finally, comparing the multiblocks copolymers with the block molecular weights of 30 000 provides further evidence of the interplay between copolymer architecture and block molecular weight. Figure 10 shows the G_c vs copolymer thickness for the multiblocks with 30 000 block molecular weight, S−M−S(30) and M−S−M−S−M(30). As expected, increasing the number of blocks also increases the molecular weight, which, in turn, increases the interfacial fracture toughness. However, the influence of the copolymer architecture is also apparent. In Figure 10, a large increase in the interfacial adhesion going from triblock to pentablock copolymer is observed, unlike the data shown in Figure 9 where this increase is slight. These results further confirm that block molecular weights must be above a minimum value to effectively anchor in the homopolymer phases and strengthen the interface. For the styrene and methyl methacrylate system, multiblock copolymer with block molecular weights greater than 21 000 are required to obtain the strongest interfacial adhesions in polymer blends, while blocks that are at least 30 000 molecular weight appear to sufficiently anchor into the homopolymer phases to provide optimum interfacial modification.

Conclusions

It has been demonstrated that copolymer architecture plays a crucial role in the ability of a copolymer to improve the interfacial adhesion in polymer blends. Optimum strengthening was observed with maximum number of blocks that are longer than a critical block length, similar to the critical entanglement molecular weights of the parent homopolymers. S−M−S−M−S(30) and M−S−M−S−M(30) pentablock copolymers gave the highest interfacial fracture toughness, followed by S−M−S(50) and M−S−M(50) triblocks. Strengthening of the PS/PMMA interfaces by these multiblock copolymers was attributed to multiple interface crossings. Failure of the heptablock copolymers to give relatively strong interfaces was ascribed to the block lengths of these structures that are insufficient to entangle with and anchor in the homopolymer. Unlike data using random copolymers as interfacial modifiers, dependence of the fracture toughness on the copolymer composition was not observed for the multiblock copolymers studied. Styrene-centered and methyl methacrylate-centered multiblock copolymers of each type (triblock, pentablock, or heptablock) demonstrated similar results.

Besides architecture, block length in multiblock copolymers also played a pivotal role during interfacial modification. Increasing lengths of blocks in multiblock copolymers increased interfacial adhesion. In addition, it was found that molecular weights of the blocks must be long enough to obtain significant anchoring in the homopolymers. Blocks of 21 000 g/mol were not sufficiently long enough to accomplish this feat; however, blocks of 30 000 appeared to be adequate.

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