Effect of ABC Triblock Copolymers with an Elastomeric Midblock on the Adhesion between Immiscible Polymers

Hugh R. Brown*

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

Udo Krappe and Reimund Stadler

Institut fuer Organische Chemie der Johannes Gutenberg-Universitaet Mainz,
J. J. Becher Weg 18-20, D-55099, Mainz, Germany

Received September 12, 1995; Revised Manuscript Received March 28, 1996[⊗]

ABSTRACT: The effect of polystyrene-*block*-poly(1,2-butadiene)-*block*-poly(methyl methacrylate) triblock copolymers (SBM) and their hydrogenated analogs polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-poly(methyl methacrylate) (SEBM) on the fracture toughness of the interface between immiscible polymers has been studied by using an asymmetric double cantilever beam fracture test. The fracture energy G_I has been investigated as a function of the copolymer interfacial areal density Σ and elastomer content as well as the temperature at which the samples were fractured. No reinforcement of the interface was found for a wide range of Σ for all investigated triblock systems at room temperature. In fact, for a range of Σ values the triblock was found to weaken, rather than strengthen, the interface. In addition, it was found that mixing just 25% of triblock into polystyrene-*block*-poly(methyl methacrylate) diblock copolymer was sufficient to remove the interfacial toughening effect of the diblock. The triblock copolymers were found to toughen, rather than weaken, the interface when the sample was fractured at a temperature below the glass transition temperature of the elastomer. These results are in agreement with a model that is based on the assumption that it is impossible to transfer enough stress across a plane glass−rubber interface to initiate crazing in the glassy polymers.

1. Introduction

The effect of block copolymers as coupling agents between polymers has been a matter of great interest for several years. Many studies have shown the effectiveness of such systems as emulsifiers[1−8] and have demonstrated that they are able to increase the interface toughness between immiscible polymers.[9−17] To separate the effect of emulsification by reducing the interface tension from the ability of block copolymers to increase the interfacial adhesion, a test geometry has been developed where thin flat layers of block copolymers are confined between sheets of (homo)polymers.[18] This asymmetric dual cantilever beam test is suitable for measuring the fracture toughness of flat (reinforced) single interfaces between polymers as well as for polymer−nonpolymer pairs as demonstrated in many studies.[13,19,20] It is possible to quantify with this method the effect of areal chain density, degree of polymerization, and composition of the block copolymers on the fracture toughness of interfaces. A detailed description of this method can be found elsewhere.[11,13]

The micromechanical processes at interfaces between glassy polymers reinforced with block copolymers are fairly well understood. Nonetheless, there is little data available on the failure process in systems where at least one phase is rubbery. Our recent synthesis of block copolymers, where the midblock B is an elastomer,[21] offers an interesting new system to study the effect of these macromolecules on the compatibilization of polymers.[22] The basic idea behind using the triblocks was their mutual ability to form a thin continuous elastic B-layer between two immiscible glassy polymers by ordering at the interface. This rubbery layer may be able to compensate for the mismatch of the thermal expansion coefficients of the glassy polymers during processing. Furthermore, it might be possible that the presence of an elastomer similar to that used in commercially toughened systems would lead to formation of multiple crazing. The formation of a large number of crazes round a crack tip is one of the mechanisms by which commercial elastomeric toughened blends dissipate energy. Both effects would improve the mechanical properties of the blend system. Extensive studies of the fracture processes along interfaces have demonstrated that a good adhesion between different polymers is only possible when the system is able to transfer stress effectively across the interface. This stress transfer is not sufficient to produce tough materials. To dissipate large amounts of energy in glassy polymer composites, it is necessary to form a wide crazed zone around the crack tip.[23] If this type of failure process takes place at the weakest interface, the local stress has to be large enough to start the plastic deformation process before the chains break.[15,24] Therefore, in the case of an interface reinforced with diblock copolymer, two conditions have to be present. First, the two blocks of the diblock system have to entangle with their two (homo)polymers to prevent a failure by a chain pullout mechanism. The other necessary condition is that there have to be enough mechanically effective crossing points across the interface to generate enough stress in a certain area to start the plastic deformation process. The block copolymer chains have to resist this stress without breaking.

The main focus of this paper is to study the effects of triblock copolymers with an elastic midblock on the interface toughness of immiscible polymers under conditions similar to the investigations made with glassy diblock copolymers and compare the results. Our investigation was carried out with polystyrene-*block*-poly(1,2-butadiene)-*block*-poly(methyl methacrylate) (SBM) and polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-poly(methyl methacrylate) (SEBM) triblock copolymers with a total molecular weight of ∼200 000

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

S0024-9297(95)01377-5 CCC: $12.00

Table 1. Characteristics of the Polymers Used

(a) Block Copolymers

polymer	$10^{-3}M_n$[a]	M_w/M_n[b]	w_{PS}	$w_{PB/PEB}$	w_{PMMA}
		PS-*b*-PB-*b*-PMMA			
SBM6	225	1.11	0.45	0.06	0.49
SBM17	238	1.10	0.48	0.17	0.35
SBM43	208	1.09	0.27	0.43	0.30
		PS-*b*-PEB-*b*-PMMA			
SEBM17	240	1.13	0.48	0.17	0.35
SEBM39	248	1.15	0.24	0.39	0.37
		PS-*b*-PMMA			
SM280[c]	280	1.1	0.50		0.50

(b) Bulk Polymers

polymer	$10^{-3}M_n$	M_w/M_n	obtained from
PPO[d]	55	2.4	General Electric (646-111)
PMMA	120	2	Du Pont (Elvacite 2010)
PSAN15[e]	76	2.1	Dow Chemical
PSAN25[e]	103	2	Dow Chemical

[a] Determined by membrane osmometry (toluene, 25 °C). [b] GPC calibrated with PS. [c] Polystyrene-*block*-poly(methyl methacrylate) diblock copolymer. [d] Poly(phenylene oxide). [e] Poly(styrene-*co*-acrylonitrile) with 15 and 25% acrylonitrile content.

Table 2. Thicknesses and Joining Conditions of the Samples

polymer pairs	layer thickness (mm)	temp[a] (°C)	joining temp[b]
PPO/PMMA	1.60/3.07	250/160	185
PPO/PSAN(15, 25)	1.60/3.20	250/150	175

[a] Temperature of the compression molding process of the homopolymer sheets. [b] Temperature of the joining process of the "polymer sandwich".

g/mol. The weight ratio of the two glassy end blocks was held nearly constant while the weight fraction of the elastomer blocks was varied between 6 and 39%. The chain length of the elastomer blocks was always well above the entanglement molecular weight of a comparable pure 1,2-polybutadiene or poly(ethylene-*co*-butylene). The neat triblock systems show interesting new morphologies which are governed by the relatively weak incompatibility between the end blocks PS and PMMA compared with the strong incompatibility to the midblock polybutadiene or poly(ethylene-*co*-butylene).[21] This feature will influence the behavior of the triblock copolymers as compatibilizers at interfaces. The pairs of immiscible polymers have been chosen with respect to their different compatibility to the end blocks to study the behavior of these triblock systems at interfaces.

2. Experimental Techniques

Materials. Nearly monodisperse SBM triblock copolymers could be obtained by sequential anionic polymerization techniques in tetrahydrofuran with *sec*-butyllithium as initiator. Via selective reduction with diimine, the polybutadiene block (90% 1,2 content, 10% 1,4 content) was converted into poly(butylene-*co*-ethylene) without significant broadening of the molecular weight distribution of the SEBM's. Details of the polymerization and the reduction procedure can be found elsewhere.[25] The SBM and SEBM will be designated by a number which denotes the weight percent of the elastomer in the block systems. For example, SEBM6 describes a triblock copolymer with 6% elastomeric midblock poly(ethylene-*co*-butylene). The detailed characteristics of the triblock systems as well as the homopolymers are shown in Table 1.

Fracture Tests. Sheets (50 mm × 64 mm) of the homopolymers were obtained by compression molding. To drive the crack along the interface, the thickness of the PPO sheet was chosen to be about half that of the PMMA or SAN. This thickness ratio was used in previous work[27] but no attempt was made to optimize it. The thickness of the polymer sheets and the conditions of the compression molding are summarized in Table 2.

Solutions of the block copolymers in toluene were spun directly onto the homopolymer sheets. For the system PPO/PMMA, the spinning process was performed on the PMMA sheet. For the system PPO/PSAN, the PSAN plates were used for the spinning process. After drying the block copolymer covered samples overnight at 60 °C under vacuum, the second sheet was placed on top and the sheets were joined in a press at the desired temperature for 2 h, using just enough pressure to facilitate wetting. The samples were slowly cooled over a period of 2 h to suppress the formation of thermal stress at the interface due to the different thermal expansion coefficients of the two polymers in the sandwich. Furthermore, tests were made where the block copolymer solutions were spun onto glass slides and floated on deionized water. The films were picked up so that either the air surface or the water surface of the block copolymer film came into contact with the homopolymer sheet. The samples were first dried for several hours in air at room temperature followed by further drying under the same conditions as the spin-coated samples. This was done to investigate the difference in the fracture process because of possible ordering while spinning the block copolymer solutions. No significant difference was found between the different ways of picking up the films or the directly spin-coated samples. The thickness of the block copolymer films was measured by ellipsometry on silicon wafers with the same spinning conditions and concentrations used for the fracture tests samples. Copolymer refractive index was obtained by ellipsometry on thick films and then used to obtain the thickness of thin films. On occasion, this thickness was converted to molecular areal density Σ by assuming a density obtained by adding the volumes of the different components of the triblock copolymer.

The polymer sandwiches were cut into 8 mm wide strips by using a diamond saw and dried at 50 °C under vacuum overnight. At least six samples could be used in the asymmetric dual cantilever beam test to calculate the fracture toughness. A wedge (a single-edged razor blade) was pushed into the interface until the crack was clearly moving. The length of the crack ahead of the shoulder of the wedge was measured 10 min and 24 h after the insertion using an optical microscope with a micrometer table to an accuracy of 0.1 mm. With the assumption that most of the fracture energy released during the fracture process is dissipated in a small region around the crack tip and no energy is stored in front of the crack tip, the critical crack extension energy G_I can be calculated by standard relationships.[11]

Some fracture tests were performed between −45 and −60 °C. For these tests, the polymer strips, in which the razor blade was inserted 48 h before, were cooled down with dry ice

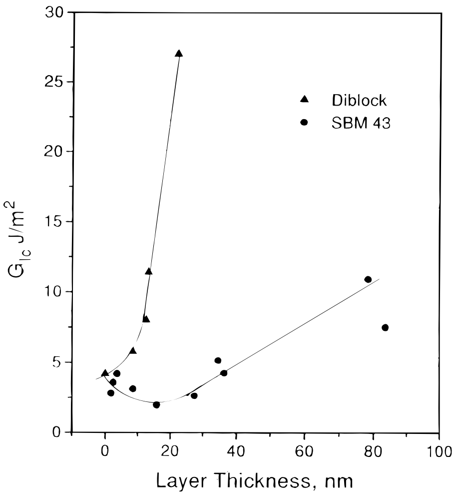

Figure 1. Variation of interface toughness with copolymer layer thickness comparing the SBM43 triblock with previously published results on a polystyrene−PMMA diblock of similar molecular weight.

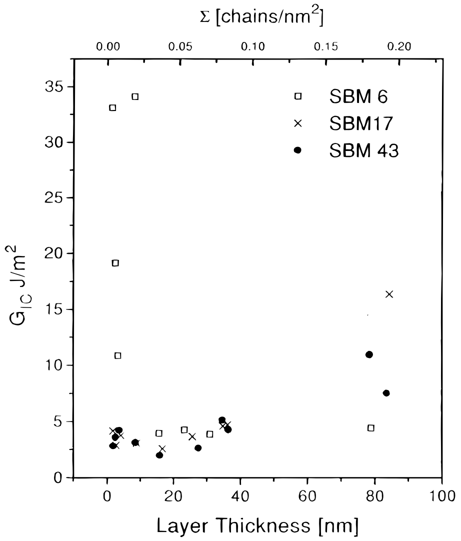

Figure 2. Variation of interface toughness with copolymer layer thickness for the three butadiene-containing triblock copolymers, SBM6, SBM17, and SBM43.

in PS boxes and then the crack was propagated further. After 10 min with the sample still cool, the crack tip was marked. The distance between the razor blade and the mark was measured after reheating the polymers to room temperature.

3. Experimental Results

3.1. The System PPO/PMMA. The well-understood behavior of PS-*b*-PMMA copolymers as coupling agents at PPO/PMMA interfaces was the reason this system was chosen for first investigations with the ABC triblock copolymers.[13,27] A negative Flory interaction parameter χ between PS and PPO drives the PS block of the SBM or SEBM copolymer into the PPO homopolymer. This strong force causes the stretching of the PS block away from the interface and the formation of a "wet brush" situation.[7,28] For the chosen test conditions, this behavior is valid even when the temperature of the joining process (185 °C) is far below the T_g of the PPO homopolymer (~216 °C). The miscibility of PS and PPO reduces the T_g in the contact zone, and this plasticization permits the interdiffusion of PS into the PPO.[13,28] The highest temperature the industrial PMMA could resist without decomposition was 185 °C. Figure 1 compares the fracture energy of an interface in the presence of the 43% elastomer nonhydrogenated triblock copolymer as a function of initial layer thickness with equivalent results obtained using a diblock. It should be pointed out that the initial layer thickness (which is often much less than the radius of gyration of the copolymer molecule) obtained by spinning the copolymer solution onto polymer plates or silicon wafers is not equivalent with the thickness of the interface after the joining process. Figure 2 gives the results obtained with the three different nonhydrogenated triblock copolymers.

An important reference point for the fracture energy is the value for a PPO/PMMA interface without block copolymer. We found that the cooling conditions after joining the polymer plates have a strong effect on the fracture behavior of the PPO/PMMA interfaces with little or no diblock but little effect when the diblock layer was 10 nm in thickness or more. Therefore, a great effort was made to standardize the test. After joining the polymer plates in a press for the desired time, every sample was slowly cooled to room temperature over a period of 2 h. Compared with former investigations,[27] a relatively high value of 15 (±6) J/m^2 for the fracture energy of the "neat" PPO/PMMA interface resulted despite the fact that PPO and PMMA are highly immiscible (Flory interaction parameter $\chi_{PPO/PMMA} \sim 0.5^7$). This result is probably caused by the use of an unoptimized ratio of the thicknesses of the PPO and PMMA sheets. It is known that very small changes of the mode mixity can cause large changes in measured G when they permit the initiation of crazes ahead of the crack tip.[26] In our case, this high value of fracture toughness of the neat PPO/PMMA interface is probably an artifact caused by such crazes.

All the triblock systems used in this investigation showed similar behavior. The presence of the triblock polymer was found to decrease, rather than increase, the toughness of the interface. Initially, the interface toughness decreased rapidly with triblock concentration and then, after the fracture toughness reached a minimum, G_I increased slowly. The fracture energy even for the thickest copolymer layers, 80 nm, was not much above the value of the neat interface. This result strongly contrasts with the behavior of PS-*b*-PMMA copolymers (comparable in molecular weight) at the interface where the fracture energy increases rapidly with the amount of diblock copolymer and levels off at much higher values.[11,13] Striking is the fact that in the region where the diblock copolymer induced toughness reaches its highest value (near the point where the interface is saturated with block copolymer), the triblock systems run through their minimum. It seems reasonable to assume, especially for the triblock system with only 6% of elastomer, that there is no great difference in the shape of the molecule at the interface compared with an equivalent diblock system and, therefore, the interface is also near its saturation point when the fracture toughness reaches its minimum. When the elastomer content is increased in the triblock systems (SBM17 and 43), the minimum is slightly shifted to smaller Σ values.

The hydrogenated triblock copolymers (Figure 3) behave similarly to their nonhydrogenated analogs. The minimum of the fracture toughness is shifted to lower Σ values by the hydrogenation. For the hydrogenated systems as well as for the nonhydrogenated systems, the initial decrease of the fracture energy is very rapid.

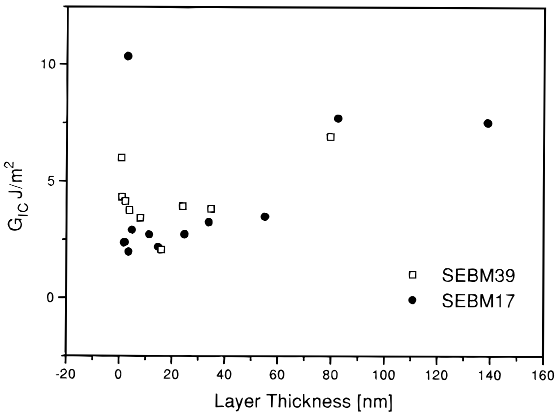

Figure 3. Variation of interface toughness with copolymer layer thickness for the two hydrogenated triblock copolymers, SEBM17 and SEBM39.

In the case of SEBM17, a layer thickness of only 3.6 nm decreases the fracture toughness of the PPO/PMMA system to about 2 J/m^2, which is similar to the value previously observed[27] for the bare interface using quenched samples. For a hypothetical lamellar structure of the system at the interface, the thickness of the rubber layer would be of the order of 1 nm. Undoubtedly the elastomer is not able to form a continuous layer under these conditions. In contrast, a continuous elastomer layer could possibly occur at the interface for diblock thicknesses of 20 nm, which is near the minimum of the fracture toughness in all investigated triblock copolymers. However, one should note that in blends with similar homopolymers, the elastomer layer never really becomes continuous but forms a "raspberry morphology".[22] Systems with a larger elastomer block should reach the point where they form a continuous rubber layer at a smaller initial layer thickness of the block copolymer. The systems SBM17 and SBM43 indeed show a shift of the minimum in fracture toughness toward lower Σ values. Similar considerations would explain why hydrogenated systems also decrease their minimum in the fracture toughness compared to their nonhydrogenated analogs. Hydrogenation of the SBM copolymers leads to an increase of the incompatibility of the end blocks to the elastomer midblock. Therefore, the SEBM systems are able to form a continuous elastomer layer at a lower layer thickness because of the increasing tendency to phase separate. For the different copolymers, the minimum in fracture toughness does not appear at the same amount of elastomer present at the interface. A possible explanation for this observation is based on the different morphologies the neat triblock copolymer shows as bulk material.[21] In all cases, the PS and PMMA form lamellae; however, the elastomer morphology varies between the different systems. SBM43 and SEBM39 form a completely lamellar morphology, SBM17 and SEBM17 assemble into a morphology with elastomer cylinders located at a lamellar PS/PMMA interface, and in SBM6 the polybutadiene forms spheres at the PS/PMMA interface. The strong forces which lead to these different morphologies will also affect the behavior of the triblock systems at the interface. There is not enough information available currently for a further discussion of this point.

All investigated triblock systems have a remarkable effect on the interface toughness at small layer thicknesses. A 30 nm layer of SBM6 with only 6% of elastomer reduces the fracture toughness to a value of 5 J/m^2. By assuming that this system forms a lamellar structure, one estimates that the elastomer layer thickness would be on the order of 2 nm. A 30 nm layer for a PS/PMMA diblock system leads to a 14 times higher fracture toughness of 70 J/m^2 measured under the same conditions. An explanation of this weakening effect could be based on a possible organization of the triblock copolymer during the spinning process. Even though the spinning process is very rapid, the elastomer may be able to form a layer or islands at the air–polymer surface because the elastomer has the lowest surface energy of the three diblock components. This elastomer layer could then prevent the mixing of one end block in each of the bulk polymers. To test this hypothesis, experiments were performed where the triblock was first spun onto a glass slide and then floated onto deionized water. Afterward the thin triblock film was picked up both possible ways: either with the "air" side or with the "water" side on the PMMA plate. One might have expected more driving force for organization when the air (elastomer) side was on the PMMA as the PS would be sucked into the PPO by the $-\nu_e\chi$, thereby destroying the organization. However, no difference in the fracture toughness was obtained between the two cases. Of course, this test is not a proof that organization of the triblock is not the reason for the poor adhesion. But, together with the fact that glassy diblock systems do not show a microphase separation when spin coated from a dilute solution, it seems unlikely that organization is the reason for the lack of adhesion.

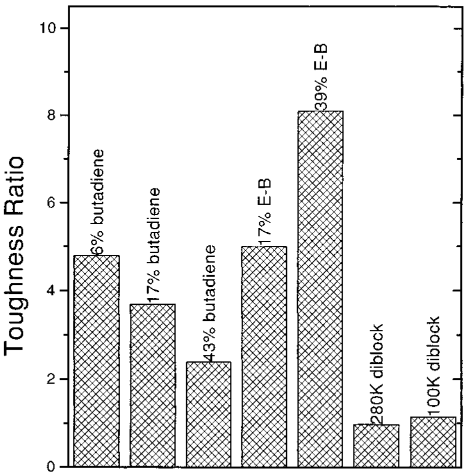

Figure 4. Ratio of the toughness at room temperature to the toughness measured at −60 °C for triblocks and diblocks.

To investigate if the physical state of the center block, elastomer not glass, is the reason for weakening the interface, the fracture toughness test was performed at a temperature below the glass transition temperature of the elastomer. An increase in the fracture toughness can be expected if this presumption is correct. The glass transition temperatures (T_g) of the 1,2-polybutadiene and the poly(ethylene-*co*-butylene) in the triblock systems are −11 and −21 °C, respectively, obtained by dynamic mechanical measurements (at a frequency of 10 Hz). Fracture tests were made as described in the Experimental Section at low temperatures somewhere between −45 and −60 °C. The fracture toughness for the PPO/PMMA system reinforced with the hydrogenated and nonhydrogenated triblock copolymers increased by a factor between 4 and 6 when fractured at low temperatures, as shown in Figure 4. This increase only occurred for layer thicknesses between 1 and 45 nm. Thicker layers of the triblock copolymers showed

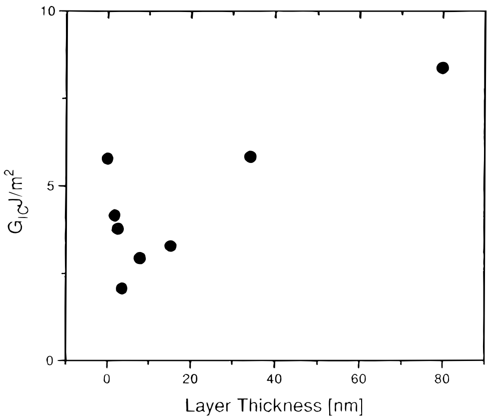

Figure 5. Variation of the interface toughness with triblock layer thickness when the SEBM17 copolymer was placed between PPO and PSAN25.

no difference in the fracture energy between samples fractured at room temperature and those fractured at low temperature. Control experiments with diblock copolymers at the PPO/PMMA interface showed only a slight increase of the fracture toughness in the range of 5−20%. This result clearly indicated that the elastomeric state of the center block is the main reason for the low toughness of interfaces with the triblock copolymers. It is worth noting that, even when the samples with the triblock copolymers were fractured at temperatures below the glass transition of the elastomer, they never reached the fracture toughness which could be obtained with S/M diblock systems. However, the test temperature was never very far below the elastomer T_g, and it was clear from the dynamic mechanical measurements that the glass transition temperature loss extended down to −60 °C.

3.2. The System PPO/PSAN. This system is governed by two strong driving forces. PPO and PS have a favorable enthalpy of mixing as mentioned above. Also a miscibility window exists for a range of AN contents in the PSAN copolymer between PMMA and PSAN. This window is approximately between 9 and 30% AN content.[29] The ternary system PPO, PSAN, and SBM or SEBM represents one of a few examples for an A′/ABC/C′ system where favorable enthalpic interactions between the end blocks and both bulk polymers drive the block system to organize at the interface. The elastomer in the triblock systems is again not miscible with the other components and therefore tends to phase separate. The test conditions were chosen to be similar to those used in the PPO/PMMA system except that the joining process was performed at a temperature of 175 °C. The fracture toughness of the neat systems PSAN15/PPO and PSAN25/PPO were found to be 10 (±3) and 9 (±2) J/m^2, respectively. These low values obtain even when the samples are cooled very slowly.

Figure 5 shows the fracture energy dissipated per unit area of the crack at the interface of PPO/PSAN as a function of layer thickness and areal density of the triblock copolymer SEBM17. The behavior of the system PPO/PSAN25 is very similar to the one observed in the PPO/PMMA system, only the "starting point" (the neat system) is at a much lower value. A sharp drop of the fracture toughness for thin layers of copolymer is followed by a broad minimum between 4 and ∼30 nm. For a layer thickness greater than 40 nm, the fracture toughness becomes a little greater than the toughness of the neat PPO/PSAN25 system. The behavior when the homopolymer is changed to the low-acrylonitrile PSAN15 is similar but the minimum is not so clearly defined. For both PSAN/PPO systems, the value of the minimum in fracture toughness is similar to that in the PPO/PMMA system.

4. Discussion

A Model for the Failure Process at a Thin Elastomer Layer at Glassy Interfaces. The experimental results clearly prove that the existence of an elastomer layer confined at the interface is the main reason for the low adhesion when the SBM and SEBM triblock systems are used as compatibilizers. As pointed out above, crazing is necessary to dissipate large amounts of energy and provide high toughness in glassy polymers. If there is no elastomer center block, an interface reinforced with block copolymer is toughened by crazing when several conditions are present. The two blocks of the diblock copolymer have to entangle with their respective polymers, and the number of mechanically effective joints per unit area have to be large enough to initiate the formation of a craze zone before the chains of the block copolymer break. Kramer and co-workers[15,24] gave an equation for this criterion

$$\Sigma f_s > \sigma_c \tag{1}$$

where f_s is the force to break a single C−C bond of the polymer backbone and σ_c is the crazing stress of the polymer with the least craze resistance. It is assumed here that the end blocks are of molecular weight considerably above M_e. One might expect f_s to be similar in glassy or elastomeric systems and so we need to consider why this simple criterion is no longer applicable in the presence of an elastomeric layer.

There is a necessary condition to form a craze at a crack tip that has not yet been considered. Craze initiation is believed to occur by a meniscus instability process that itself occurs within a yield zone (an active zone) in front of a crack tip.[30,31] This yield zone blunts the crack tip and averages out the stress singularity that would occur at a crack tip in a purely elastic system. The initial strain within the yield zone may be small. It is only after the occurrence of the interface convolution process to form the fibrils that the strain becomes high enough to sense entanglement (or the lack of it). It would seem likely that the length of this yield zone has to be on the order of at least two fibril diameters for the meniscus instability process to occur. At an interface between two different polymers, the yield zone is expected to occur at least partly within the mixed layer of material. In the case of a PPO/PMMA interface reinforced with diblock copolymer, the mixed layer has to sustain a stress a little above a glassy polymer yield stress because of the constraint, say 100 MPa, in a zone of length 30 nm[31] to start the crazing. The opening of this zone would be about 2 nm, which could exist easily within the mixed layer. The formation of this zone could only lead to the formation of a stable craze if the fibrils, as they form and the strain increases, are stabilized by sufficiently entangled coupling chains, as described by Kramer's criterion. If the mixed layer at the interface contains elastomeric material, then it is liable to pull apart at stresses well below a glassy yield stress. Hence a yield zone cannot form at the interface and the crazing process cannot start. Highly loaded elastomer chains from the triblock would remain spanning the crack but they are not able to average the stress in the manner of a yield zone. Hence these load-

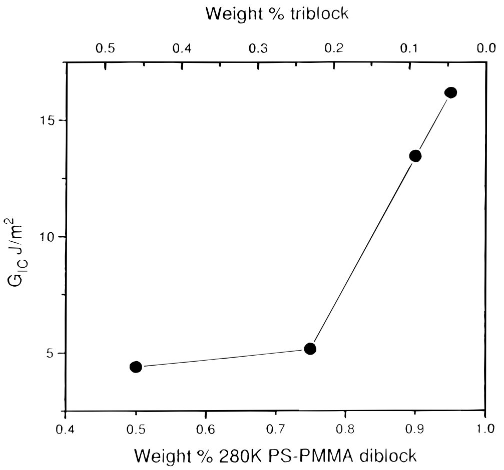

Figure 6. Effect of mixing SEBM17 with PS/PMMA diblock of similar molecular weight at a constant layer thickness of 36 nm between bulk PPO and PMMA.

bearing chains at the crack tip would break successively, and the major part of the energy to propagate the crack would be the energy to break these chains. An indication of the validity of the mechanism proposed here, namely pullout of the mixed layer followed by chain scission, is the great time dependence of the fracture toughness in all investigated systems. After initiating propagation of a crack by pushing a wedge into an interface reinforced with diblock copolymer, the crack was nearly stationary only a few minutes after the movement of the wedge was stopped. In the triblock systems, on the other hand, the crack tip continued moving a long time after the insertion of the wedge. In some systems, the crack was still moving 48 h after the insertion of the wedge, which suggests the existence of a process where polymer chains disentangle very slowly followed by scission of the highly loaded chains. It will be demonstrated below that only little energy is necessary to propagate the crack for the kind of failure process suggested here.

Note that it is not a necessary condition in the model proposed here that the elastomer layer be continuous. Even small amounts of elastomer confined at the interface are able to suppress crazing. To obtain more information about the amount of elastomer required to weaken the interface, experiments were performed where mixtures of di- and triblock copolymer were placed at the interface. Figure 6 shows the effect of mixing a 280K PS/PMMA diblock with the triblock system SEBM 17. The initial layer thickness of the mixture was held constant at ~36 nm. With up to 75% diblock copolymer content, the fracture toughness is in the range of the pure triblock at ~5 J/m^2. The amount of elastomer in this mixture is below 5% and so corresponds to layer thicknesses of less than 2 nm. When the portion of the diblock is increased to 90%, a slight increase in fracture toughness is noticeable. But even at 95% diblock content, where the amount of elastomer is below 1%, the fracture toughness of the system is still far below the value of the pure diblock copolymer (~75 J/m^2) at this layer thickness. Optical microscopy shows the formation of crazing for a diblock content greater than 75%. From the values of the fracture toughness, it must be assumed that the crazing zone around the craze tip is small or discontinuous.

The model suggested here of the failure process of a thin elastic layer at a glassy interface invites a comparison with the classic Lake–Thomas theory[32] of elastomer failure. This theory describes in a simple manner the threshold fracture toughness G_{I0} of a cross-linked elastomer network. G_{I0} is the lower bound on the fracture energy of a material when all time-dependent dissipative processes are minimized. It is assumed that to break a polymer strand with n main chain bonds (defined as between cross-link points), an energy of nU is necessary. U is the dissociation energy of a main chain bond. To break Σ equal polymer strands crossing the fracture plane of unit area the threshold fracture energy is

$$G_{I0} = \Sigma n U \tag{2}$$

The situation where the distance between cross-links (or in our equivalent, the length of the elastomer chain) is greater than the distance between entanglements is not entirely clear. However, the relevant number of main chain bonds is probably the number between entanglements. Typical experimental methods to obtain G_{I0} are tear strength measurements on highly swollen networks at high temperatures using low crack velocities. These experimental conditions are chosen because they minimize the bulk viscoelastic dissipation in the highly strained material around the crack tip. Another way to minimize this dissipation is to use a very thin layer of elastomer between more rigid materials so that the volume of highly strained elastomeric material is very small. Hence the failure of the elastomer chains in the triblock systems confined at the interface considered here might be expected to follow the Lake–Thomas predictions. Even for the triblock system with the lowest elastomer content, the molecular weight of the elastomer chains is far above their entanglement molecular weight (M_e). For a typical layer thickness of 35 nm, Σ is ~0.075×10^{18} chains/m^2, all of which shall be assumed to cross the interface just once. This assumption is most likely for the region in front of the crack tip where the (temporary) elastomer entanglements are already pulled out of the glassy matrix. For a dissociation energy[33] of 5.75×10^{-19} J and an M_e of 3000 g/mol,[34] a fracture energy of ~6 J/m^2 is predicted. This value does not include the energy necessary to disentangle the elastomer chains at the interface, which we assume to be small. This application of the Lake–Thomas theory is doubtless a crude simplification of the real situation, so it is gratifying that the resulting values are similar to those observed experimentally. This model also explains the increase in fracture toughness for higher copolymer areal densities.

Very thick initial triblock layers > 70 nm show neither a big time dependence nor a large change in fracture toughness when fractured below the T_g. It is most probable that a mode change in the fracture process takes place. In thick layers of symmetric diblock copolymers, the formation of a multilayered structure at the interface has been observed.[16,27] The interfacial strength of this lamellar structure was shown to be much weaker than a block copolymer saturated interface because of a change of the failure process within the secondary lamellae. In the PS/PVP system, this change occurred because low molecular weight PS from the PS homopolymer swelled the PS layer and reduced its entanglement density. In the system PMMA/PPO with PS–PMMA copolymer, a PS layer was formed at the interface and failed at low toughness. It is likely that something similar happened here.

As discussed above, interfaces with the triblock copolymers are less tough than those with diblock copolymers even when the fracture process is performed at temperatures below the T_g of the elastomer. The reason might be that initial entanglement density between the highly immiscible center block and the glass is lower than the entanglement in the case where a PS/PMMA diblock is used and the incompatibility of the two polymers is only weak. It might also be because our low-temperature experiments were done at a temperature not very far below the T_g of the elastomer. However, the model suggested here for the craze initiation process does have the interesting implication that a crack tip craze can only form if the mixed layer is capable of forming a sufficiently large yield zone. As the width of a mixed layer varies as $\chi^{-1/2}$, it would seem possible that in very repulsive systems such a zone cannot form and so the interface cannot be significantly toughened by a diblock copolymer.

5. Conclusions

We have found that ABC triblock copolymers with an elastomeric center block are ineffective at toughening the interface between homopolymer miscible with the A and C blocks. In fact, the interface is often weaker in the presence of the triblock than it would be with no copolymer present. This remarkable weakening effect is caused specifically by the elastomeric nature of the center block.

Acknowledgment. We would like to thank Clemens Auschra, Röhm GmbH, Darmstadt, for synthesizing some of the polymers. We have benefited greatly from discussions with E. J. Kramer, T. P. Russell, C. Creton, and L. Leibler.

References and Notes

(1) Teyssié, P.; Fayt, R.; Jérôme, R. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 41.
(2) Fayt, R.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 79.
(3) Fayt, R.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1269.
(4) Fayt, R.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2209.
(5) Fayt, R.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 775.
(6) Adedeji, A.; Jamieson, A. M.; Hudson, S. D. *Macromolecules* **1994**, *27*, 4018.
(7) Auschra, C.; Stadler, R.; Voigt-Martin, I. G. *Polymer* **1993**, *34*, 2081.
(8) Auschra, C.; Stadler, R.; Voigt-Martin, I. G. *Polymer* **1993**, *34*, 2094.
(9) Brown, H. R. *Annu. Rev. Mater. Sci.* **1991**, *21*, 463.
(10) Brown, H. R. *Macromolecules* **1989**, *22*, 2859.
(11) Creton, C.; Kramer, E. J.; Hui, C.-Y.; Brown, H. R. *Macromolecules* **1992**, *25*, 3075.
(12) Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* **1993**, *26*, 4155.
(13) Char, K.; Brown, H. R.; Deline, V. R. *Macromolecules* **1993**, *26*, 4164.
(14) Washiyama, J.; Creton, C.; Kramer, E. J. *Macromolecules* **1992**, *25*, 4751.
(15) Washiyama, J.; Kramer, E. J.; Hui, C. Y. *Macromolecules* **1993**, *26*, 2928.
(16) Washiyama, J.; Creton, C.; Kramer, E. J.; Xiao, F.; Hui, C. Y. *Macromolecules* **1993**, *26*, 6011.
(17) Washiyama, J.; Kramer, E. J.; Creton, C.; Hui, C. Y. *Macromolecules* **1994**, *27*, 2019.
(18) Brown, H. R. *J. Mater. Sci.* **1990**, *25*, 2791.
(19) Xiao, F.; Hui, C.-Y.; Kramer, E. J. *J. Mater. Sci.* **1993**, *28*, 5620.
(20) Smith, J. W.; Kramer, E. J.; Xiao, F.; Hui, C.-Y.; Reichert, W.; Brown, H. R. *J. Mater. Sci.* **1993**, *28*, 4234.
(21) Stadler, R.; Auschra, C.; Beckmann, J.; Krappe, U.; Voigt-Martin, I.; Leibler, L. *Macromolecules* **1995**, *28*, 3080.
(22) Auschra, C.; Stadler, R. *Macromolecules* **1993**, *26*, 6364.
(23) Brown, H. R. *Macromolecules* **1991**, *24*, 2752.
(24) Xu, D.-B.; Hui, C.-Y.; Kramer, E. J.; Creton, C. *Mech. Mater.* **1991**, *11*, 257.
(25) Auschra, C.; Stadler, R. *Polym. Bull.* **1993**, *30*, 257.
(26) Xiao, F.; Hui, C.-Y.; Washiyama, J.; Kramer, E. J. *Macromolecules* **1994**, *27*, 4382.
(27) Creton, C.; Brown, H. R.; Deline, V. R. *Macromolecules* **1994**, *27*, 1774.
(28) Brown, H. R.; Char, K.; Deline, V. R. *Macromolecules* **1990**, *23*, 3383.
(29) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.
(30) Argon, A. S.; Salama, M. M. *Mater. Sci. Eng.* **1976**, *23*, 219.
(31) Kramer, E. J. *Adv. Polym. Sci.* **1983**, *52* (3), 1.
(32) Lake, G. J.; Thomas, A. G. *Proc. R. Soc. London, A* **1967**, *300*, 108.
(33) Bhowmick, A. K. *Rev. Macromol. Chem. Phys.* **1988**, *C28*, 339.
(34) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.

MA9513776