The Block Length Effect of Polystyrene-*block*-Poly(methyl methacrylate) on the Interfacial Adhesion between Polystyrene–Poly(methyl methacrylate) and between Polystyrene/Phenoxy

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ABSTRACT: The effect of the poly(methyl methacrylate) (PMMA) block length of polystyrene(PS)–poly(methyl methacrylate) diblock copolymer on the interfacial adhesion between PS/PMMA and between PS/phenoxy has been investigated. When the block copolymer with the PMMA block length of $6.6 \, \mathrm{kg \, mol^{-1}}$ is reinforced at the interfaces, the fracture behavior follows the pure chain pull-out mechanism, and the estimated monomer friction coefficient, f_{mono}, are 1.69×10^{-11} and $3.42 \times 10^{-11} \, \mathrm{N/monomer}$ for PS/PMMA and PS/phenoxy, respectively. The higher value of f_{mono} in PS/phenoxy arises from the specific interaction between the PMMA block chain and phenoxy homopolymer. When the block copolymer with the PMMA block length greater than $10.9 \, \mathrm{kg \, mol^{-1}}$ is added to the interfaces, the fracture behavior of both PS/PMMA and PS/phenoxy follows the craze formation followed by the chain scission, indicating that the entanglement molecular weight of PMMA lies in between $6.6 \, \mathrm{kg \, mol^{-1}}$ and $10.9 \, \mathrm{kg \, mol^{-1}}$.
KEY WORDS Diblock Copolymer / Block Length / Interfacial Adhesion / Fracture Mechanism / Entanglement Molecular Weight /

Most polymer pairs form immiscible blends due to the low entropy gain upon mixing, which may lead to phase separation. For immiscible polymer blends, coarse phase separation and poor adhesion between phases often become the limiting factors in all applications. Thus, there have been many attempts to reduce the interfacial tension and to improve the interfacial adhesion between two phases. For example, it has been reported that the use of block copolymers can control the interfacial properties such as interfacial tension and adhesion, resulting in improved mechanical properties.[1-5] However, the role of block copolymers as an interfacial agent may show different behaviors depending upon the structure of block copolymers. The block copolymers having molecular weight shorter than its entanglement molecular weight may not give an appreciable interfacial adhesion although the addition of block copolymers always reduces the interfacial tension.

Recently, an asymmetric double cantilever beam method has been used for measuring the fracture toughness of interface between immiscible polymers.[6-14] These studies have examined the effect of the addition of block copolymers on the fracture toughness of interfaces between immiscible homopolymers as a function of the molecular weight of each block and the areal density of the block copolymer chains. However, most studies have focused on athermal systems, *i.e.*, A–B block copolymer in A and B homopolymer blends. On the other hand, if A–B block copolymers are added in the interface between A and C homopolymers in which the B block is miscible with C homopolymer, the reinforcing effect of A–B block copolymer on A/C interface might be different from the effect on A/B interface.

In this study, we synthesized polystyrene–poly(methyl methacrylate) (PS-*block*-PMMA) diblock copolymers with different block lengths, and the block copolymers

were reinforced at the interfaces between PS/PMMA and between PS/phenoxy. Here the PS/PMMA pair with the block copolymer is chosen as a model system of A/B/A-*block*-B, and the PS/phenoxy pair with the block copolymer is chosen as a model system of A/C/A-*block*-B, where C (phenoxy) homopolymer is miscible with B (PMMA) block.[15] The fracture toughnesses of interfaces between PS and PMMA and between PS and phenoxy have been examined as a function of block length and of areal density of the copolymer chains, and discussed in terms of the specific interaction between the block and homopolymer.

EXPERIMENTAL

Materials and Characterization

PS-*block*-PMMA copolymers used in this study were synthesized by the sequential anionic polymerization of styrene and methyl methacrylate using *sec*-butyllithium as an initiator. All the monomers and reagents were purified by following the standard method described in the literature.[16] The detailed polymerization procedures were described elsewhere.[17] Table I lists characteristics of block copolymers synthesized in our laboratory. Commercially available PS, PMMA, and phenoxy were obtained from the companies and their reported molecular weights were listed in Table II.

Sample Preparation and Adhesion Test

The PS, PMMA, and phenoxy were compression molded into sheets ($70 \, \mathrm{mm} \times 50 \, \mathrm{mm} \times 2.4 \, \mathrm{mm}$) at $160°\mathrm{C}$. A thin film of PS-*block*-PMMA copolymer was spin-coated on PMMA or phenoxy sheet from a toluene solution, and the sheet was dried at $80°\mathrm{C}$ for 4 hours under vacuum. The PS sheet was brought into contact with the PMMA or phenoxy sheet coated with the block copolymer and then annealed at $160°\mathrm{C}$ for 2 hours under a slight pressure to confirm contact between the two

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Table I. Characteristics of block copolymers used in this study

Block copolymers	PS block[a] kg mol^{-1}	PMMA block[b] kg mol^{-1}	Polydispersity
I	63.6	6.6	1.08
II	63.6	10.9	1.06
III	63.6	26.6	1.08
IV	45.6	54.8	1.07

[a] Determined by GPC. [b] Determined by ^{1}H NMR.

Table II. Characteristics of homopolymers used in this study

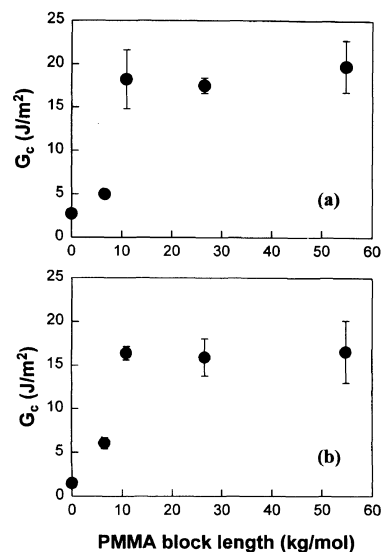| Polymers	Molecular weight kg mol^{-1}	Source
Polystyrene	230	Polyscience
Poly(methyl methacrylate)	74	Lucky
Phenoxy	80	Union Carbide

Figure 1. Fracture toughness of interface between (a) PS/PMMA and between (b) PS/phenoxy reinforced with PS–PMMA block copolymers as a function of the PMMA block length. Film thickness of the block copolymer is *ca.* 45 nm.

sheets. The film thicknesses of block copolymers were measured by ellipsometry on the copolymer films that were spin-coated on silicon wafers under the same spinning conditions which were used for preparing the copolymer film in the PS/PMMA or PS/phenoxy sandwiches. The PS side of annealed sample was fixed to a slide glass to drive the crack along the interface. The fracture test was performed by inserting a single-edged razor blade at the interface and the crack was allowed to propagate for 24 hours before measuring the crack length. The fracture energy was then calculated using the equation proposed by Kanninen.[18] The areal density, Σ, was calculated using the relation: $\Sigma = \rho t N_A / M$, where ρ is the density of the block copolymer, t is the film thickness of the copolymer, N_A is Avogadro's number, and M is the molecular weight of the copolymer. This relation is valid when one diblock copolymer contributes only one joint across the interface due to the well-organized structure at the interface. We assume here the organization of the block copolymer at the interace, although it is not clear that the block copolymers used in our experiment organize so well that one block copolymer molecule stitches the interface only one time.

RESULTS AND DISCUSSION

The block copolymers used in this study were designed to observe the effect of PMMA block length on the fracture toughness at the interface. In order to achieve the objective, we prepared several diblock copolymers with each having different PMMA block lengths, while the PS block lengths are long enough to exceed the entanglement molecular weight of PS in order to exclude the effect of PS block lengths.[19] Table I lists the block lengths of PS and PMMA in the diblock copolymers used in this study.

The fracture energies, G_c, of the PS/PMMA and PS/phenoxy interface reinforced with block copolymers are plotted against the molecular weight of PMMA block, as shown in Figure 1. When the block copolymer having the PMMA block length of 6.6 kg mol^{-1} is reinforced at the interface between PS/PMMA and between PS/phe-

noxy, the fracture toughness is not improved remarkably, whereas the addition of block copolymers with longer PMMA blocks significantly improves the fracture toughness. Figure 1 also shows that an increase in the fracture toughness of interface with the length of PMMA block levels off when the diblock copolymers having molecular weights higher than 10.9 kg mol^{-1} are reinforced in both PS/PMMA and PS/phenoxy interfaces. Therefore there exists a critical molecular weight below which the block copolymer does not effectively reinforce the interface between two homopolymers. It is well known that the block molecular weight at which the transition from low to high fracture toughness takes place is remarkably close to the entanglement molecular weight, M_e. Thus our experimental results show that the M_e of PMMA lies in between 6.6 and 10.9 kg mol^{-1}. This value seems to be well consistent with others (9 kg mol^{-1}).[20]

Figure 2 shows the fracture toughness of the PS/PMMA and PS/phenoxy interface reinforced by a block copolymer with the PMMA block of 6.6 kg mol^{-1} when plotted against film thickness corresponding to the amount of block copolymer added. The PMMA block length is not long enough to entangle with PMMA homopolymer or with phenoxy. In both cases, as the amount of the block copolymer increases, the fracture energy increases slightly and then levels off at constant value. The level-off behavior of G_c may be interpreted as the saturation of interface with block copolymer. Another possible explanation for a slight increase of fracture energy with the addition of block copolymers is the molecular weight dependence of mutual penetration between PMMA block chains and PMMA homopolymer chains. Shorter block lengths may be less effective at increasing the interfacial adhesion, since the penetration of block copolymers into homopolymer phases becomes shallower as the molecular weight of blocks decreases.[21]

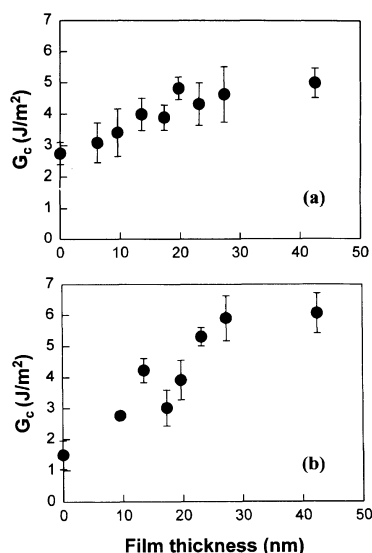When the fracture energy of PS/PMMA (Figure 2(a))

Figure 2. Fracture toughness of interface between (a) PS/PMMA and between (b) PS/phenoxy reinforced with a PS–PMMA block copolymer as a function of film thickness. Molecular weight of the PMMA block is 6.6 kg mol^{-1}.

Figure 3. Fracture toughness of interface on (a) PS/PMMA and on (b) PS/phenoxy reinforced with a PS–PMMA block copolymer as a function of film thickness. Molecular weight of the PMMA block is 10.9 kg mol^{-1}.

is compared with that of PS/phenoxy (Figure 2(b)), the PS/phenoxy has higher value of saturation than the PS/PMMA. This may be explained by considering the specific interaction between PMMA block and phenoxy homopolymer. The specific interaction may induce stretching the PMMA block at the interface into phenoxy phase. As a result, the areal density of the block copolymer at saturation becomes greater in the PS/phenoxy interface than in the PS/PMMA. In other words, the amount of block copolymer at the saturation of interface is larger in the PS/phenoxy than in the PS/PMMA.

The G_c of the PS/PMMA and the PS/phenoxy interfaces reinforced by a block copolymer with the PMMA block of 10.9 kg mol^{-1} is plotted against film thickness in Figure 3. As mentioned above, the PMMA block length of 10.9 kg mol^{-1} is long enough to entangle with either PMMA homopolymer or phenoxy. Therefore, we may expect a significant increase of fracture energy. Experimental results show that the fracture energy increases 10—15 times larger when the block copolymer is reinforced at the interfaces between both PS/PMMA and PS/phenoxy. The amounts of saturation are, however, the same for both pairs, not likely the case when the block copolymer with a shorter PMMA block is added. Figure 3 also shows that the fracture energy significantly decreases rather than levels off above the saturation. As the amount of block copolymers added increases to a degree of saturation of interface, the block copolymers become in dry brush regime. In this case, less penetration of homopolymers into block copolymer brush results in less entanglement between homopolymer chains and block copolymer chains. As a result, the adhesion strength drops significantly. This phenomenon is also observed in another case.[8]

Recently, Creton et al.[6] and Washiyama et al.[7–9] observed the fracture behavior of PS/poly(vinyl pyridine)(PVP) and (PS/PPO)/PVP interface reinforced with PS-block-PVP diblock copolymer and described the
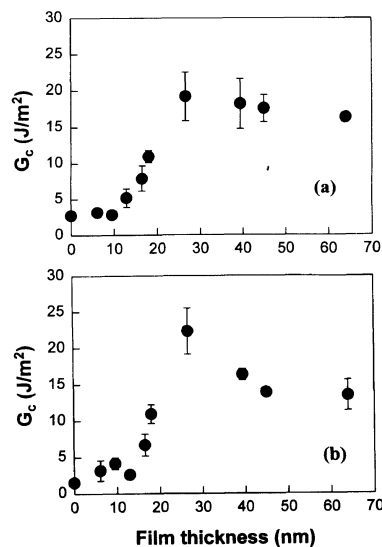
fracture mechanism in terms of the PVP block length, N_{PVP}, and areal density of block copolymer at the interface, Σ. According to their proposed failure mechanism map, the interface fails by crazing followed by chain scission when N_{PVP} and Σ are large, while fracture takes place by chain scission of block at the junction point when N_{PVP} is large and Σ is small. On the other hand, for block copolymers with at least one short block, chain pull-out is the primary mechanism for the interface fracture when Σ is small. They also suggested that the upper limit of N_{PVP} above which chain scission occurs rather than pull-out is approximately equal to entanglement molecular weight. If we apply their explanations to our system, the block copolymer with the PMMA block length of 6.6 kg mol^{-1} follows the fracture mechanism of simple chain pull-out, whereas the block copolymers with the PMMA block length higher than 10.9 kg mol^{-1} follows the chain scission mechanism.

Assuming that no other extra energy dissipation except the chain pull-out takes place during fracture and that the one-sided block chain pulls out (in our case, only the PMMA block pulls out from the PMMA side or from the phenoxy side; the PS block stays anchored), Xu et al.[22] proposed the following equation:

$$\Delta G_c = f_{mono} N_{block}^2 \Sigma l_0 / 2$$

where ΔG_c is the fracture energy difference between the interfaces with block copolymer and without block copolymer, f_{mono} is the static monomer coefficient, N_{block} is the block length (in our case, N_{block} should be N_{PMMA}), and l_0 is the monomer length ($2.3 \times 10^{-10} \text{ m}$ for MMA). This equation allows us to evaluate f_{mono} from the slope of the plot of ΔG_c versus $N_{PMMA}^2 \Sigma$. Figure 4 shows plots of ΔG_c versus $N_{PMMA}^2 \Sigma$ when the PS/PMMA and the PS/phenoxy are reinforced with the block copolymer with the PMMA block length of 6.6 kg mol^{-1}. As discussed above, we may assume that the block copolymer with the PMMA block of 6.6 kg mol^{-1} follows the pull-out mechanism. Thus, we obtained the value of f_{mono} as
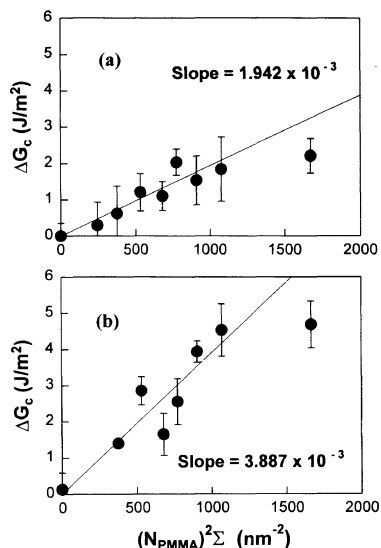
Figure 4. Plot of ΔG_c versus $(N_{PMMA})^2 \Sigma$ for (a) PS/PMMA and for (b) PS/phenoxy interfaces reinforced with a block copolymer with the PMMA block length of $6.6\,kg\,mol^{-1}$.
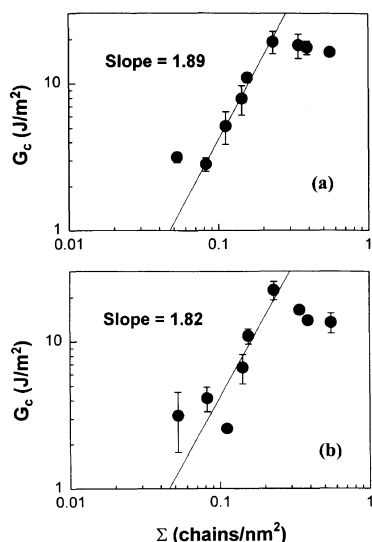

Figure 5. Log–log plot of G_c versus areal density for (a) PS/PMMA and for (b) PS/phenoxy interfaces reinforced with a block copolymer with the PMMA block length of $10.9\,kg\,mol^{-1}$.

1.69×10^{-11} and $3.42 \times 10^{-11}\,N/monomer$ for PS/PMMA and PS/phenoxy, respectively, by fitting the equation to the plots of ΔG_c versus $N_{PMMA}^2 \Sigma$. The reason that the PS/phenoxy has a higher value of f_{mono} than the PS/PMMA may be explained by considering that there exists a specific interaction between the PMMA block and phenoxy homopolymer while there exists neither a specific interaction nor molecular entanglements between the PMMA block and PMMA homopolymer chains.

Figure 5 shows the fracture energy G_c plotted against the areal density Σ of the block copolymer when the block copolymer with the PMMA block length of 10.9 $kg\,mol^{-1}$ is reinforced to the PS/PMMA interface or to the PS/phenoxy interface. It has been reported that the G_c increases with Σ^2 in the regime of craze formation.[23] This means that the slope of the plot of $\log G_c$ versus

$\log \Sigma$ must be equal to 2 if the fracture mechanism follows the craze formation. Therefore, the slopes of Figure 5 indicates that the fracture behavior nearly follows the craze formation followed by the craze breakdown for both PS/PMMA and PS/phenoxy. The craze formation is very closely related to molecular entanglements. Thus an indirect evidence of the craze formation from Figure 5 tells us that the block length of $10.6\,kg\,mol^{-1}$ is sufficient for molecular entanglements between the PMMA block and PMMA (or phenoxy) homopolymer. Therefore, it may be concluded that the M_e of PMMA lies in between 7 and $11\,kg\,mol^{-1}$, because two block copolymers with different PMMA block lengths show different fracture behaviors.

CONCLUSIONS

The fracture toughness of the PS/PMMA and PS/phenoxy has been examined as a function of the PMMA block length when the block copolymer is reinforced at the interfaces. The PS blocks in block copolymers were long enough to exceed its entanglement molecular weight which leads to exclude the effect of PS block lengths. When the block copolymer with the PMMA block length of $6.6\,kg\,mol^{-1}$ was reinforced at the interfaces between PS/PMMA or between PS/phenoxy, the fracture behavior follows the pure chain pull-out mechanism, and the estimated monomer friction coefficient f_{mono} are 1.69×10^{-11} and $3.42 \times 10^{-11}\,N/monomer$ for PS/PMMA and for PS/phenoxy respectively. The higher value of f_{mono} in PS/phenoxy seems to arise from the specific interaction between the PMMA block chain and the phenoxy homopolymer. When the block copolymer with the PMMA block length greater than $10.9\,kg\,mol^{-1}$ was added to the interfaces, the fracture behavior of both PS/PMMA and PS/phenoxy follows the craze formation followed by the chain scission of block copolymers at the interface, indicating that the block length is sufficient for molecular entanglements between the PMMA block and homopolymers.

REFERENCES

1. R. Fayt, R. Jerome, and Ph. Teyssie, *Polym. Eng. Sci.*, **27**, 328 (1987).
2. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 775 (1987).
3. W. H. Jo, H. C. Kim, and D. H. Baik, *Macromolecules*, **24**, 2231 (1991).
4. H. C. Kim, K. H. Nam, and W. H. Jo, *Polymer*, **34**, 4043 (1993).
5. H. C. Kim and W. H. Jo, *Polym. Eng. Sci.*, **35**, 648 (1995).
6. C. Creton, E. J. Kramer, C. Y. Hui, and H. R. Brown, *Macromolecules*, **25**, 3075 (1992).
7. J. Washiyama, E. J. Kramer, and C. Y. Hui, *Macromolecules*, **26**, 2928 (1993).
8. J. Washiyama, C. Creton, E. J. Kramer, F. Xiao, and C. Y. Hui, *Macromolecules*, **26**, 6011 (1993).
9. J. Washiyama, E. J. Kramer, C. Creton, and C. Y. Hui, *Macromolecules*, **27**, 2019 (1994).
10. H. R. Brown, *J. Mater. Sci.*, **25**, 2791 (1990).

11. H. R. Brown, *Macromolecules*, **22**, 2859 (1989).
12. H. R. Brown, K. Char, V. R. Deline, and P. F. Green, *Macromolecules*, **26**, 4155 (1993).
13. K. Char, H. R. Brown, and V. R. Deline, *Macromolecules*, **26**, 4164 (1993).
14. H. R. Brown, K. Char, and V. R. Deline, *Macromolecules*, **23**, 3383 (1990).
15. J. S. Chiou and D. R. Paul, *J. Appl. Polym. Sci.*, **42**, 279 (1991).
16. M. Morton and L. J. Fetters, *Rubber Chem. Tech.*, **48**, 359 (1975).
17. D. Freyss, M. Leng, and P. Rempp, *Bull. Soc. Chim. Fr.*, 221 (1964).
18. M. F. Kanninen, *Int. J. Frac.*, **9**, 83 (1973).
19. S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **2**, 109 (1970).
20. T. Masuda, K. Kitagawa, and S. Onogi, *Polym. J.*, **1**, 418 (1970).
21. K. R. Shull and E. J. Kramer, *Macromolecules*, **23**, 4769 (1990).
22. D. B. Xu, C. Y. Hui, E. J. Kramer, and C. Creton, *Mech. Mater.*, **11**. 257 (1991).
23. H. R. Brown, *Macromolecules*, **24**, 2752 (1991).