Macromolecules **1998,** *31,* 7091−7094

Notes

Effect of Styrene−Maleic Anhydride Copolymers on Adhesion between Amorphous Polyamide and Polystyrene

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Received November 25, 1996
Revised Manuscript Received June 9, 1998

Introduction

When interfacial adhesion between immiscible polymers is increased by the addition of polymers containing reactive groups, the amount of copolymers formed in situ at the interface is usually influenced by molecular parameters such as activation energy for reaction between reaction pairs and diffusion kinetics of polymers.[1−6] Material properties of polymers also have significant effect on the adhesion behavior of a polymer interface. It is reported that bulk material properties have a close relationship with the mechanism of toughening immiscible polymer interfaces reinforced with preformed block copolymers.[2,7−9]

We previously reported[1] that the interfacial adhesion between immiscible amorphous polyamide (aPA) and polystyrene (PS) was varied by the addition of different amounts (<300 nm) of styrene−maleic anhydride (SMA) random copolymer (Dylark 232), used as a reactive compatibilizer. When the SMA was initially placed at the interface and annealed subsequently at a fixed temperature, it significantly improved the fracture toughness in comparison with the low fracture toughness of the aPA/SMA interface. We at that time put an emphasis on the relationship between the conformational behavior of reacted copolymers and the resulting interfacial adhesion strength.

In the case where the reactive polymer employed is a random copolymer the resulting structure (block, graft, or cross-link) of the copolymer formed at the interface could also be influenced by parameters such as the amount of reactive groups per chain, arrangement of the reactive groups along the chain, and annealing temperature and time. A similar argument about the conformational behavior of the reacted copolymers has been reported in the study of reactive reinforcement of PS/poly(2-vinylpyridine) (PVP) by sulfonated PS.[5,6] It was reported that there exists an optimum sulfonation of PS to increase the interfacial adhesion between PS and PVP, which could be explained by the conformational behavior of the resulting copolymer.

In this paper, we would like to show that another aspect of reactive compatibilizers, namely material properties, should also be considered to understand the role of the reactive compatibilizer in enhancing the interfacial adhesion. Some literature[10,11] already mentioned that the introduction of functional groups into a homopolymer could sometimes alter the bulk material properties of the homopolymer. Since SMA, the reactive compatibilizer used in our previous study, contains 8 wt % of maleic anhydride (MAH) functional groups, it is expected that the material properties of SMA are somewhat different from those of the PS homopolymer although the two polymers are compatible to some extent. In the present study, the effect on material properties due to the change of SMA content near the interface as well as in PS phase on the interfacial adhesion was investigated to understand the different adhesion behaviors of aPA/PS and aPA/SMA reinforced with SMA reactive compatibilizer.

Experimental Section

A series of mixtures of SMA and PS (5, 10, and 20 wt % of SMA) were prepared by a Brabender single screw extruder. aPA, PS, and SMA/PS mixtures were then compression molded into sheets with a thickness of 3 mm for the adhesion test. aPA sheets spun with a SMA layer of thickness varying from 400 to 1500 nm were joined with PS at different temperatures for different joining times ranging from 20 min to 4 h. Compression-molded sheets of SMA/PS mixtures were also joined with aPA sheets spun with SMA of 220 nm thickness for a join time of 1 h at two different temperatures: 150 and 190 °C. The reason we place an SMA layer on top of an aPA plate instead of an PS plate is that the casting solvent toluene significantly swells the PS sheet and the reactive SMA polymer is usually buried deep inside the PS sheet. In this case, no detectable interfacial fracture toughness was observed for annealing conditions at low temperature and for a short period of annealing. In contrast, toluene used in this study did not swell the aPA plate; toluene is the nonsolvent for aPS. There is also the possibility that some prebonding between SMA and aPA might occur when an SMA layer is first spun on an aPA. We, however, noted that such an effect is minimal in our system. The interfacial fracture toughness of the joined samples was measured by the asymmetric fracture test.[12] The detailed procedure of the adhesion test was described in our previous work.[1]

To measure the craze stress of substrate materials, known as one of the important material properties in determining the interfacial strength of immiscible polymers,[2,7−9] PS, SMA, and PS/SMA mixtures were compression molded into specimens for a three-point beam-bending test for which a cross head speed of 0.05 mm/min was applied. Details of the three point beam bending test were given elsewhere.[8]

Results and Discussion

Figure 1 shows the fracture toughness as a function of SMA interlayer thickness for samples annealed for 1 h at two different temperatures: 150 and 190 °C. We note that the fracture data obtained at two different temperatures can be classified into three regions of SMA thickness: regions I, II, and III. We have already reported regions I and II in our previous study[1] showing

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S0024-9297(96)01723-8 CCC: $15.00

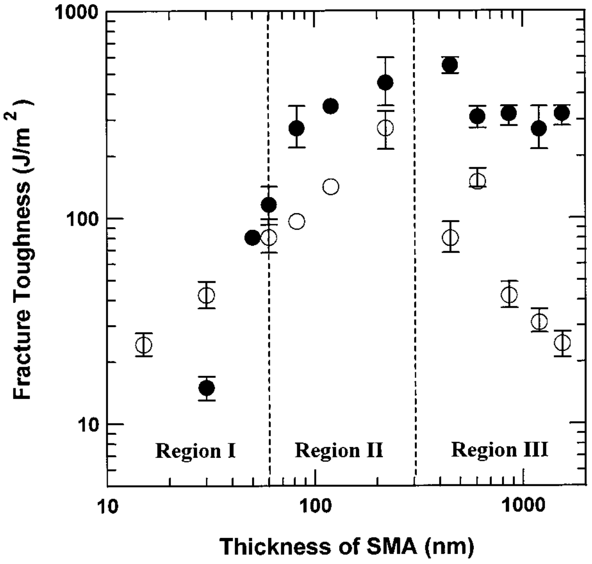

Figure 1. log−log plot of the fracture toughness between amorphous polyamide and PS as a function of SMA thickness, showing three different regions for two different annealing temperatures: 150 °C (○) and 190 °C (●).

that there is a crossover due to the relative importance of the reaction at the interface over the diffusion of SMA into the PS phase for the two annealing temperatures. When the SMA thickness is increased from 400 nm up to 1500 nm in the region III and the samples are joined at 150 °C for 1 h, the fracture toughness rapidly decreases from 250 to about 20 J/m^2, which is close to the fracture toughness value between aPA and bulk SMA. On the other hand, when the join condition is changed to 190 °C for 1 h the fracture toughness remains at a high value of approximately 300 J/m^2, almost independent of SMA thickness in region III.

Since the drastic reduction of the fracture toughness for samples in region III annealed at 150 °C for 1 h was quite surprising, we further studied the effect of annealing time on fracture toughness while the annealing temperature was fixed at 150 °C. Figure 2a shows the change of fracture toughness as a function of annealing time for samples with SMA thicknesses of 830 and 1500 nm, both in region III. As the annealing time is increased up to 4 h the fracture toughness increases up to about 200 J/m^2, which is enough to enable one to observe crazing near the interface.

Figure 2b shows the replotting of the fracture toughness as a function of square root of annealing time for the same data given in Figure 2a. The reason we do this type of plotting is that it is well-known that the fracture toughness increases as a square root of annealing time for crack healing or welding experiments.[13] The significant deviation from linearity in Figure 2b implies that the diffusion of a thick SMA layer into the PS phase is not the important issue to interpret our data and some other factors should be considered. It should also be reminded from our previous study[1] that the fracture toughness between aPA and bulk SMA remains at a low value of about 20 J/m^2 irrespective of annealing time and temperature. Our present study in region III is that thick layers of SMA are initially placed between aPA and PS and annealed at two different temperatures, yielding quite different fracture behaviors. The difference between aPA/bulk SMA and the present study in region III is that the interdiffusion between the PS phase and the initial SMA layer is possible, while there is no such diffusion driving force in the case of bulk SMA used.

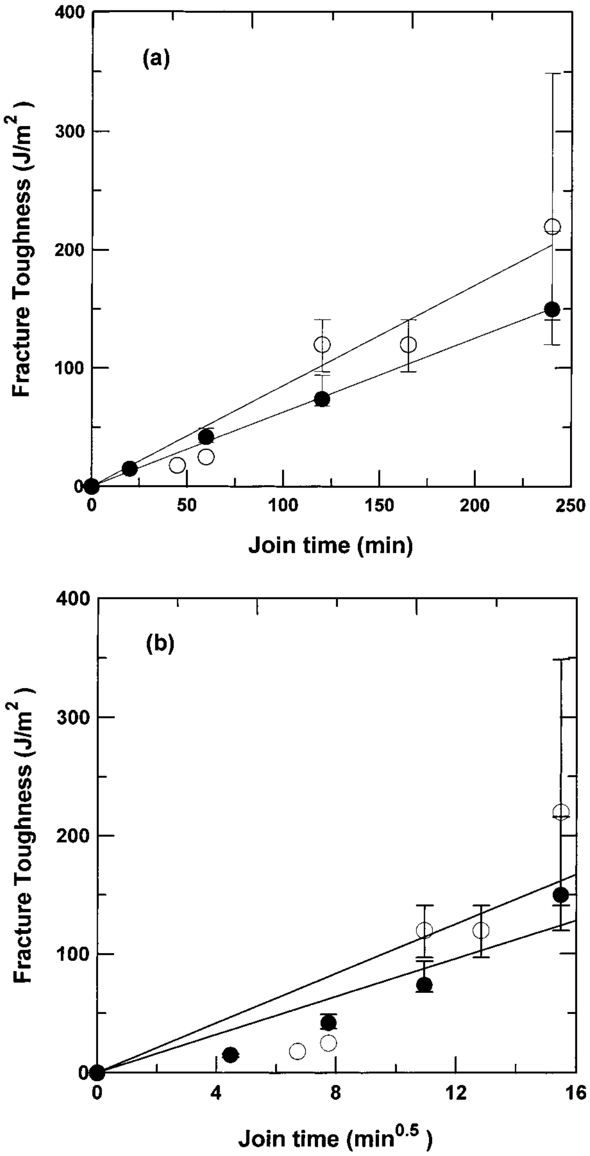

Figure 2. Variation of the fracture toughness between amorphous polyamide and PS with (a) annealing time and (b) square root of annealing time at two different SMA layer thicknesses: 830 nm (●) and 1500 nm (○). The annealing temperature is 150 °C. Solid lines are the fitted line passing through the origin.

Several investigators studying in the area of adhesives[10] have inferred the existence of a weak boundary layer between bulk materials depending on the adhesive thickness. Particularly, it is interesting to note in Robertson's experiment[14] that the opening mode fracture toughness between two plates of PMMA (cleavage fracture energy is 140 J/m^2) containing a weak PS interlayer in the middle (cleavage fracture energy is 0.6 J/m^2) corresponded to the bulk PMMA value when the thickness of the PS interlayer was smaller than 1 μm. As the interlayer became thicker than 1 μm, the fracture toughness dropped to a value about 15% of the bulk PMMA value. This result suggests one possible explanation to our experimental results. When an aPA/PS sample with a thick SMA interlayer ($\sim$1 μm of thickness) is joined at 150 °C for 1 h, there still exists undiffused pure SMA layer left. If the fracture toughness of SMA is lower than that of PS, cracks then pass through the remaining SMA layer resulting in a low fracture toughness. When join time is further increased at 150 °C, as given in Figure 2, or join temperature is elevated to a higher temperature, for example, 190 °C as given in Figure 1, the pure SMA layer either completely disappears from the mix with bulk PS or becomes thinner than the critical thickness, thus increasing the fracture toughness between aPA and PS.

When the fracture mechanism of bulk materials is mainly due to crazing, micromechanical parameters of crazing such as craze stress, maximum fibril draw ratio, craze thickness and craze fibril stability are known to control the fracture behavior of the polymer and the bulk properties such as fracture toughness.[15,16] We measured the craze stresses of PS and SMA/PS mixtures using a three-point beam-bending test. The measured craze stress of PS was 43 ± 5 MPa, a value similar to that obtained by other investigators,[8] and those of SMA/PS mixtures with 5 and 10 wt % SMA were 53 ± 3 MPa. A higher craze stress requires a larger amount of effective chain areal density for fracture by crazing, which is responsible for a strong interface.[2,7−9] This is also to say that if the effective areal (or crossing) density at the interface remains constant while craze stress is increased, the fracture toughness decreases as a result.

Measurement of the craze stress of pure SMA was not possible with the three-point beam-bending test since stable crazes could not be achieved. The fact that the area of mirror zone on the fractured SMA surface is quite small suggests that the craze fibril stability of SMA, which is closely related to the fracture toughness,[16] is much lower than that of PS. It is, however, necessary to conduct a fragility test[16] to obtain the detailed information on the craze fibril stability of SMA. On the other hand, Kim and co-workers[11] reported that the stress intensity factor of SMA, measured by a single edge notched test, decreased rapidly as the MAH content in SMA was increased. This observation gives indirect evidence for the possibility of large changes in material properties of PS by adding a small amount of MAH.

To further investigate the effect of the bulk material property, the PS sheet in the joined aPA/PS was replaced with SMA/PS mixtures containing different amounts of SMA. SMA layers of 220 nm thickness showing the maximum interfacial adhesion after joining at 150 °C for 1 h (Figure 1) were inserted between aPA and the SMA/PS mixture sheets. As noted in Figure 3, the fracture toughness between the aPA and SMA/PS mixture joined at 150 °C for 1 h drops quite rapidly as the amount of SMA in the SMA/PS mixture is increased. When the amount of SMA in the mixture is 20 wt %, the fracture toughness reaches a value close to that of aPA/bulk SMA (~20 J/m^2). This verifies that the difference in bulk material properties between PS and SMA causes different adhesion behavior of aPA/bulk SMA and aPA/PS depending on the amount of SMA at the interface.

Another interesting thing to note in Figure 3 is that, when aPA/(SMA/PS mixture) with a 220 nm thick SMA interlayer was joined at 190 °C for 1 h, the fracture toughness dropped rapidly as the amount of SMA in the SMA/PS mixture was increased up to 10 wt % and then remained at a relatively high toughness value of ~100 J/m^2. This implies that even though different bulk material property was shown to have an effect on the fracture toughness, different joining conditions such as annealing temperature and time also have effects on the amount and the structure of the copolymer formed in-situ at the interface.[1] Annealing either at a higher temperature or for an extended time increases the effective crossing density at the interface and consequently the fracture toughness.

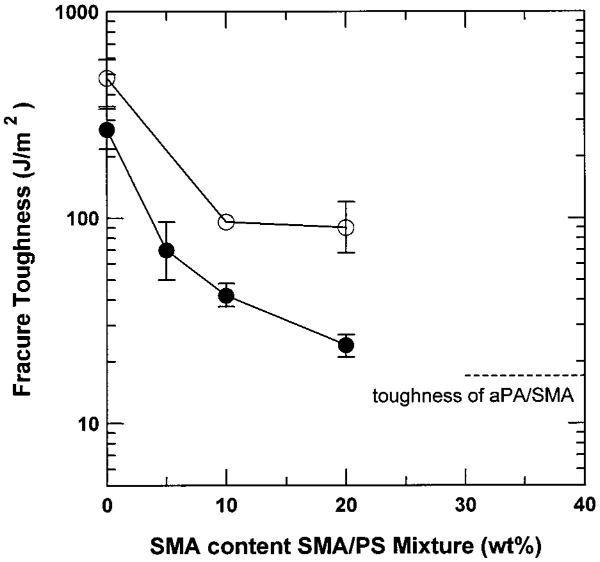

Figure 3. Variation of the fracture toughness between amorphous polyamide and PS with SMA content in the SMA/PS mixture at two different annealing temperatures: 150 °C (●) and 190 °C (○).

We believe that in our system of aPA/PS with an SMA interlayer the conformational behavior (amount of produced copolymer and type of in situ copolymer structure such as block, graft, and comb) of copolymer formed at the interface and the bulk material property are both important in interpreting our experimental fracture data depending on the amount of SMA layer and the annealing condition. This argument can be partially supported by the data given in Figure 2a. When aPA/PS was joined at 150 °C for 1 h the fracture toughness value was higher for a sample with an SMA layer of 830 nm. When the samples are annealed for 4 h, the fracture toughness value is, however, higher for a sample with a 1500 nm thick SMA layer. This means that there is still undiffused bulk SMA layer left for the sample with a thicker SMA layer after annealing for 1 h and thus the remaining SMA layer with high craze stress and/or low fibril stability decreases the fracture toughness. When samples are annealed for 4 h, the undiffused bulk SMA layer finally disappears by diffusion into PS, and since the residence time for SMA chains in contact with aPA is longer for a thicker SMA layer, there is the possibility of forming a larger amount of copolymer at the interface, thus increasing the fracture toughness due to the increase of the effective crossing density.

Conclusion

It is shown in present and previous[1] studies that the material properties such as craze stresses of SMA different from those of PS as well as the conformational behavior of copolymer formed at the interface have an effect on the adhesion behavior of the aPA/PS interface reinforced with SMA or aPA/SMA interface.

Reactive groups in reactive polymer are usually introduced to increase the probability of reaction at the immiscible interface. The reactive polymers having more than one reactive group per chain can thus provide *multiple stitches* to the interface, which is closely related to the macroscopic fracture toughness of the interface.[17] In the case of SMA used as a reactive compatibilizer for aPA/PS, the introduction of maleic anhydride (MAH) groups, however, alters the material properties near the interface significantly, which has an adverse effect on the enhancement of interfacial adhesion between aPA/PS as well as between aPA/SMA. This implies that there exists an optimum content of MAH in SMA that is balanced by the conformational behavior of the copolymer formed at the interface and the variation of material properties of SMA.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (KOSEF) under Grant 94-0520-02-3.

References and Notes

(1) Lee, Y.; Char, K. *Macromolecules* **1994**, *27*, 2603.
(2) Kramer, E. J.; Norton, L. J.; Dai, C.-A.; Sha, Y.; Hui, C.-Y. *Faraday Discuss.* **1994**, *98*, 31.
(3) Norton, L. J.; Smigolova, V.; Pralle, M. U.; Hubenko, A.; Dai, K. H.; Kramer, E. J.; Hahn, S.; Berglund, C.; Dekoven, B. *Macromolecules* **1995**, *28*, 1999.
(4) Boucher, E.; Folkers, J. P.; Hervet, H.; Leger, L.; Creton, C. *Macromolecules* **1996**, *29*, 774.
(5) Beck Tan, N. C.; Tai, S.-K.; Briber, R. M. *Macromolecules* **1996**, *29*, 4969.
(6) Beck Tan, N. C.; Tai, S.-K.; Briber, R. M. *Polymer* **1996**, *37*, 3509.
(7) Brown, H. R. *Macromolecules* **1991**, *24*, 2757.
(8) Creton, C.; Kramer, E. J.; Hui, C.-Y.; Brown, H. R. *Macromolecules* **1992**, *25*, 3075.
(9) Washiyama, J.; Kramer, E. J.; Creton, C.; Hui, C.-Y. *Macromolecules* **1993**, *26*, 2928.
(10) Wu, S. *Polymer Interfaces and Adhesion*; Marcel Dekker Inc.: New York, 1982.
(11) Kim, H.; Keskula, H.; Paul, D. R. *Polymer* **1991**, *32*, 2372.
(12) Brown, H. R. *J. Mater. Sci.* **1990**, *25*, 2791.
(13) Kausch, H. H. *Polymer Fracture*; Springer-Verlag: Berlin, 1987.
(14) Robertson, R. E. *J. Adhesion* **1975**, *7*, 121.
(15) Kramer, E. J. *Adv. Polym. Sci.* **1983**, *52*, 1.
(16) Kramer, E. J.; Berger, L. L. *Adv. Polym. Sci.* **1990**, *91*, 1.
(17) Lee, Y.; Sim, C.; Char, K. Submitted to Macromolecules.

MA961723Z