Enhancement of Interfacial Adhesion between Amorphous Polyamide and Polystyrene by *in-Situ* Copolymer Formation at the Interface

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ABSTRACT: The enhancement of interfacial adhesion between immiscible amorphous polyamide and polystyrene (PS) by the addition of thin layers of styrene–maleic anhydride (SMA) random copolymer, used as a reactive compatibilizer, has been investigated. The asymmetric fracture test was employed to measure the fracture toughness of the interface as a function of the SMA amount placed at the interface. The fracture toughness of the interface between amorphous polyamide and bulk SMA remained low at all temperatures and annealing times of our experiment. When a thin layer of SMA was introduced between amorphous polyamide and PS, the fracture toughness was however remarkably increased as the amount of SMA layer and the annealing temperature were increased. This is believed to be due to copolymer formation at the interface due to reaction between the amine end group of the polyamide and the maleic anhydride (MAH) of SMA. A qualitative model is suggested for the combined effect of reaction at the interface and diffusion to obtain a strong interface. On the basis of this model, the experimental results obtained here are successfully divided into two regions: a diffusion-dominant region and a region in which the diffusion and the reaction at the interface are comparable, thus yielding a strong interface.

Introduction

Current multiphase polymer alloys and blends commonly contain more than one pair of immiscible polymers for which each phase is separated by an interface or interphase. The interface between immiscible polymers is normally weak due to low entropy of mixing of long polymer chains. Thus for successful manufacturing of polymer alloys and blends with desired properties, it is necessary to compatibilize the immiscible polymer pairs so that the domains are evenly distributed in the continuous phase and the interfacial adhesion is increased.

In the past decade, many articles reported on the synthesis of the compatibilizer as well as on the method of compatibilization and its effect on final physical properties.[1-4] There are in general two ways of compatibilization. One is to introduce a small amount of preformed block copolymer for which each block is miscible with each homopolymer counterpart: *physical compatibilization*. The other, which has recently been receiving more attention, is *reactive (or chemical) compatibilization*, which uses reactive functionalized polymers and forms *in-situ* copolymers at the polymer interface due to the reaction between the two different functionalized polymers during processing. In contrast to physical compatibilization, the latter method is particularly effective when one of the immiscible polymer pairs contains the crystalline phase and has economic merit in that it is not necessary to synthesize the block copolymers separately before blending.

The compatibilization of immiscible polymers is known to play a key role in enhancing final polymer properties such as impact strength and tensile strength. Detailed understanding of the enhancement of interfacial adhesion resulting from compatibilization is one of the important issues in the research of advanced polymer materials. Recently, Brown and co-workers investigated the effect of polystyrene (PS)–poly(methyl methacrylate) (PMMA) diblock copolymer on adhesion between PS/PMMA[5] as well as between poly(phenylene oxide) (PPO)/PMMA.[6] They have also shown that the different interfacial fracture behavior between PS/PMMA and PPO/PMMA for the same PS-*b*-PMMA block copolymer is closely related to the distribution of the diblock copolymer at the interface, as evidenced by dynamic secondary ion mass spectroscopy (SIMS). Creton and co-workers[7] obtained similar results for PS–poly(2-vinylpyridine) (PVP) diblock copolymer between immiscible PS/PVP interfaces, and they also proposed a micromechanical model on the interfacial fracture behavior. In the case of reactive compatibilization, no detailed information has yet been reported about the enhancement of interfacial adhesion.

In our study, we examined the effect of a reactive compatibilizer on the macroscopic interfacial fracture toughness. The reactive compatibilizer we have chosen is styrene–maleic anhydride (SMA) copolymer for which a maleic anhydride (MAH) functional group is known to react easily with an amine end group of a polyamide. The reaction between SMA and a polyamide to form a copolymer is schematically shown in Scheme 1. The formation of the copolymer is well known and verified.[8] The reactive compatibilizer SMA was placed between immiscible amorphous polyamide and PS with controlled amount. The interfacial adhesion between amorphous polyamide and PS was found to be very weak (<5 J/m^2). The reason we decided to use amorphous polyamide instead of normal semicrystalline polyamide was to minimize the residual stress developing at the interface when crystalline polymer having a widely different thermal expansion coefficient was used.

Experimental Section

The materials used in this study are described as follows: amorphous polyamide is Trogamide-T from Dynamic Nobel Co. PS is HC-2 from Hannam Chemical Co. with M_n = 126 000 and M_w = 300 000, and SMA is Dylark 232 from Arco Chemical Co. with M_n = 100 000 and M_w = 200 000 containing ~8 wt % of MAH. To obtain an ideal planar interface, sheets of polymers (64 mm × 50 mm × 3 mm) were compression molded well above their glass transition temperatures. The reactive compatibilizer SMA dissolved in toluene was spun onto the amorphous

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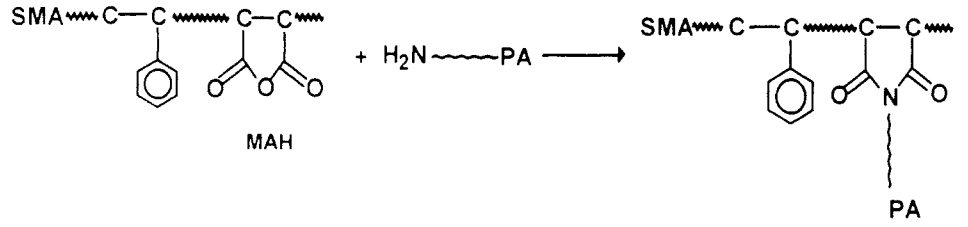
Scheme 1



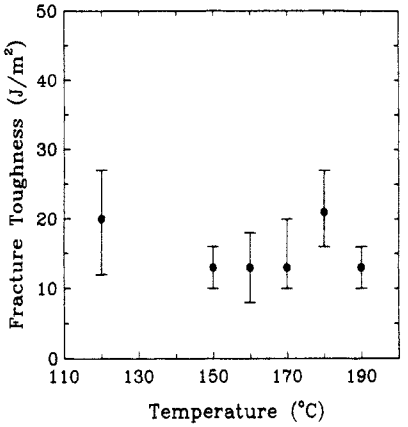


Figure 1. Fracture toughness between amorphous polyamide and bulk SMA as a function of annealing temperature. Annealing time is 1 h.

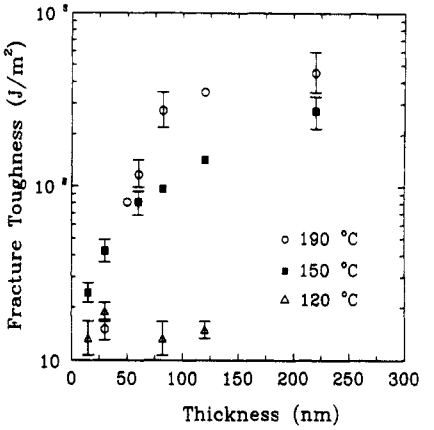


Figure 2. Fracture toughness of amorphous polyamide and PS interface as a function of SMA layer thickness for different annealing temperatures. Annealing time is 1 h.

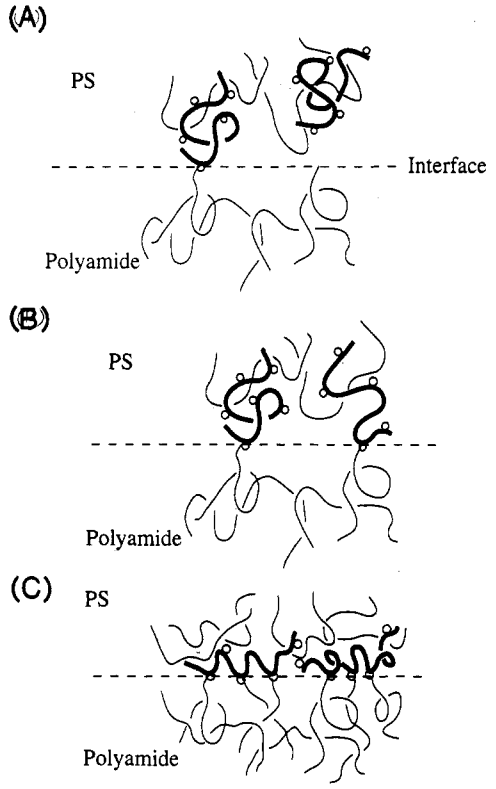
polyamide sheet. The amount of compatibilizer was varied by changing the concentration of the solution and the rotation speed of a spin coater. After the PS sheet was placed on top of the solvent-free polyamide sheet supporting the SMA layer, samples for the fracture test were prepared by annealing the joint of the sheets at different temperatures for 1 h. Also as a limiting case of excess amount of compatibilizer, a joint between amorphous polyamide and bulk SMA sheet was prepared at the same temperature and annealing conditions as for the amorphous polyamide and PS joints. The annealed samples were cut into fracture test specimens, and the interfacial fracture toughness was measured by an asymmetric fracture test for which a lower crazing stress material such as PS was glued to the rigid substrate so that the crack was driven to propagate along the interface. Details of the asymmetric test were described elsewhere.[9]

Results and Discussion

As shown in Figure 1, the fracture toughness of the interface between amorphous polyamide and SMA remains low at all temperatures of our experiment. Even when an extra SMA layer is introduced between the amorphous polyamide and the SMA by spin coating, the fracture toughness does not increase. When the SMA layer is placed between amorphous polyamide and PS, the interfacial fracture toughness is however remarkably increased as shown in Figure 2. The fracture toughness increases as the amount of SMA layer and annealing temperature are increased. The enhancement of the interfacial adhesion becomes significant at temperatures above 150 °C, which is above the glass transition temperature of the amorphous polyamide (145 °C). When the annealing temperature is further increased to 190 °C, the interfacial fracture toughness value increases and finally reaches the approximate cohesive failure energy value of pure PS. The data from Figure 2 imply that both amine-containing polyamide and MAH-containing PS move around the interface to form *in-situ* copolymers, which cause the interfacial fracture toughness to increase. Previously, Brown and co-workers[6] showed that a small amount of PS–PMMA diblock copolymers, which is somewhat related to half the long spacing of the symmetric diblock copolymer, was required to reach the saturation value of the fracture toughness of PPO/PMMA. In contrast to their study, the fracture toughness for our cases in which reactive compatibilizers are employed is increased much more gradually as the amount of SMA at the interface increases. This difference can be explained by two arguments. One is that SMA is a random copolymer. In their study, Brown and co-workers[5] demonstrated that PS–PMMA random copolymer was less effective than the block copolymer in increasing interfacial adhesion. SMA might have an effect on the increase of interfacial adhesion similar to that of random PS–PMMA copolymers. The other is the effect of diffusion. In the case of physical compatibilization, most of the block copolymers initially placed at the interface, if the amount is small, thermodynamically prefer to stay at the interface and each block then relaxes into the relevant homopolymer side during annealing. In the case of reactive compatibilization however, SMA at the interface continues to diffuse into PS due to the finite miscibility between PS and SMA. However, only the SMA chains that have reacted with the amine end groups of the polyamide can contribute to the interfacial adhesion. Some of the SMA does not react directly with the polyamide during the residence of SMA at the interface, and the unreacted SMA chains as a result are ineffective in interfacial adhesion. This could partly explain the slow increase in the fracture toughness of the polyamide/PS interface by the addition of SMA.

It is interesting to note the combined effect of diffusion and reaction at the interface on the macroscopic fracture toughness since the SMA layer is both reacting with the polyamide at the interface and diffusing constantly at the elevated temperatures. Diffusion and reaction are the two competing driving forces for the enhancement of interfacial adhesion by SMA. Fast diffusion reduces the concentration of functional groups at the interface, and the SMA chains that diffuse far away from the interface will have little chance to react with the counterpart reactive polyamide across the narrow immiscible interface. If reaction occurs at any part of the SMA chains, the

Scheme 2[a]



[a] Thick solid lines represent SMA molecules; open circles represent MAH functional groups.

copolymer thus formed can stay near the interface due to thermodynamic reasons for compatibilization. The parameters that affect the rates of diffusion and reaction are temperature and initial concentration of the functional groups. An increase in temperature will increase both the diffusion coefficient and the reaction rate. The initial amount of compatibilizer, on the other hand, only affects the reaction rate. The relative importance of diffusion over reaction at the interface thus varies as a function of annealing temperature and initial amount of reactive compatibilizer. From previous works on physical compatibilization it is known that thorough entanglement of the copolymer with bulk homopolymer and a higher areal density of the copolymer at the interface combine to yield a high fracture toughness.[5-7] By combining all the considerations mentioned above and the experimental data obtained, we propose a qualitative model predicting molecular conformation of the reactive SMA compatibilizers at the interface and its effect on the fracture toughness as follows:

Case A: If diffusion of SMA chains into bulk PS side is more dominant than reaction at the interface, most of the SMA chains will diffuse away from the interface, little copolymer will be formed, and the reaction site will also be presumed to be limited to the end of the SMA molecules. A schematic of the resulting molecular conformation of SMA is shown in Scheme 2A. The fracture toughness in this case is low because the areal density of the copolymer is low although the molecular entanglement is sufficient.

Case B: When diffusion is almost comparable to reaction at the interface, there will be large amount of copolymers formed at the interface and at the same time the copolymers thus formed maintain enough entanglement with homopolymers as shown in Scheme 2B. This type of conformation yields a strong interface.

Case C: If too much reaction occurs before diffusion, as shown in Scheme 2C, the reaction sites will be almost

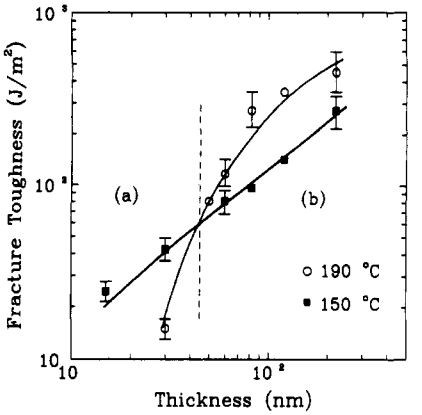


Figure 3. log–log plot of fracture toughness between amorphous polyamide and PS showing two different regions: diffusion-dominant region (a) and comparable reaction and diffusion region (b).

evenly distributed along one SMA chain. Many copolymers are thus formed at the interface but the entanglement of SMA with PS is insufficient and the fracture toughness remains low.

With this model in mind, we are now able to separate the fracture toughness data in Figure 2 obtained for two different temperatures of 150 and 190 °C into two regions, as shown in Figure 3. Figure 3 is a log–log plot of fracture toughness against the initial amount (thickness) of SMA layer between PS and amorphous polyamide. Since the initial thickness of the SMA layer, as mentioned before, only affects the probability of reaction at the interface to form copolymers, the abscissa in Figure 3 means increasing reaction at the interface when the thickness of the SMA layer is increased. In region a the fracture toughness for 190 °C is lower than that for 150 °C at the same initial thickness of the SMA layer. The trend shown in region a is reversed in region b as the thickness of the SMA layer is increased. These results imply that when the initial amount of SMA at the interface is small, the SMA chains are more likely to diffuse away from the interface as the annealing temperature is increased from 150 to 190 °C. The 190 °C data for region a are thus relevant to case A where diffusion is dominant. The higher 190 °C fracture data in region b imply that this region belongs to case B where there is enough reaction at the interface comparable to diffusion into bulk PS as the initial thickness of the SMA layer is increased.

To confirm this trend further, we selected two fixed SMA layers with thicknesses of 30 and 82 nm and measured the fracture toughness by varying the annealing temperatures as shown in Figure 4. In Figure 4, 30 nm was chosen from region a and 82 nm was from region b of Figure 3. For the 30-nm specimen, the fracture toughness reached its maximum at 150 °C and decreased at higher temperatures. In this region the amount of initial SMA is rather small and reaction at the interface becomes small compared to diffusion when the annealing temperature is over 150 °C. Temperatures higher than 150 °C seem to increase the difference between diffusion and reaction at the interface. In contrast, for the specimen containing the 82-nm-thick SMA layer, the fracture toughness kept increasing as the annealing temperature was increased. For the 82-nm specimen the increased amount of initial SMA makes the two driving forces almost comparable.

This model also suggests that the interface between amorphous polyamide and bulk SMA seems to pertain to either case A or case C from such a low fracture toughness value as seen in Figure 1. Inoue[10] demonstrated in his

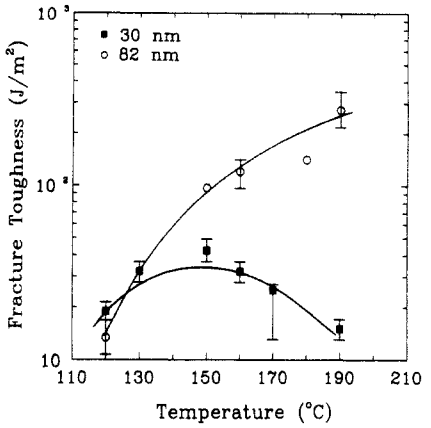


Figure 4. Variation of fracture toughness between amorphous polyamide and PS with annealing temperature at two different SMA thicknesses, 30 and 82 nm.

ellipsometry experiment that the interfacial thickness between thin layers of amorphous polyamide and (SAN + SMA) mixtures increased with time at high annealing temperatures. We think that his data verify the interfacial chemical reaction between SMA and amorphous polyamide, and the interface between amorphous polyamide and bulk SMA might consequently belong to case C. More detailed work on this polyamide and PS interface will be reported soon.

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