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Enhancement of interfacial adhesion between polystyrene and styrene maleic anhydride random copolymer via reactive reinforcement

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The effects of amine-terminated polystyrene (ω-amino-PS) of various molecular weights on the interfacial adhesion strength between polystyrene and styrene maleic anhydride (SMA) random copolymer have been investigated. The adhesive joint is composed of SMA and a blend of PS and ω-amino-PS, in which the ω-amino-PS acts as a reactive compatibilizer. Here, the amine end-group of ω-amino-PS in the PS/ω-amino-PS blend is known to react with the anhydride group of SMA and form an end-grafted copolymer, which acts as an interlinking molecule across an interface and improves the interfacial adhesion strength. The fracture toughness of the interface was measured using a modified double-cantilever beam fracture test. The enhancement of fracture toughness of the interface was evaluated as a function of molecular weight and content of ω-amino-PS, i.e. interlinking chain length and area density of interlinking molecules. The fracture toughness was found to increase with the amount of ω-amino-PS and then decreased or saturated at a certain content depending on the molecular weight of ω-amino-PS. When the molecular weight of ω-amino-PS was 26 000 (26 k), which is just above the entanglement molecular weight, there was an optimum content in reinforcing the interfaces due to the weak mechanical strength of 26 k ω-amino-PS. However, when the molecular weight was far above the entanglement molecular weight, i.e. 67 k and 127 k, the fracture toughness levelled off as the content of ω-amino-PS increased. At the same concentration of amine groups, 127 k ω-amino-PS showed the highest fracture toughness. © 1997 Elsevier Science Ltd.

(Keywords: adhesion; interface; reactive reinforcement)

INTRODUCTION

Interfacial adhesion between polymers plays an important role in the mechanical properties of multiphase polymer alloys. However, the mechanical strength of the interfaces between immiscible polymers is very weak because of little chain entanglement between the polymers due to the low mixing entropy available.

Many studies have been performed on the use of reactive interfacial agents to improve the interfacial properties and control the morphologies of immiscible polymer blends. The reactive interfacial agent has specific functional groups, and it can generate *in situ* formation of block or graft copolymers at the interface during the blend preparation through the reaction of functional groups incorporated onto the blend components[1,2]. The reactive compatibilization method has been proved to be effective for controlling morphology in a variety of blend systems[3–6]. However, research on the detailed understanding of the enhancement of interfacial properties resulting from reactive compatibilization is very limited[7–9].

Recently, several studies have been reported on the reinforcement of polymer interfaces with reactive compatibilizer[10–12]. Lee and Char[10] have shown that the interfacial adhesion between immiscible amorphous polyamide and polystyrene (PS) was enhanced by the addition of thin layers of styrene–maleic anhydride (SMA) random copolymer. It was believed to be due to copolymer formation at the interface through the reaction between the amine end-group of the polyamide and the anhydride group of SMA. They have explained the remarkable increase in fracture toughness of the interface over a certain interfacial region in which the diffusion and the reaction are comparable. Briber and co-workers[11] have observed the effect of sulfonated polystyrene on the adhesion between the immiscible PS and poly(2-vinylpyridine) interface through varying the

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concentration of sulfonic acids of sulfonated polystyrene. They found the optimum concentration in reinforcing the interface between the two immiscible polymers. Kramer and co-workers[12] have reported on an elegant set of experiments on the reinforcement of the polymer interface between PS and epoxy resin using end-functionalized PS of various molecular weights which can be end-grafted into epoxy networks during curing. They studied the effects of interlinking chain length and grafting density on the fracture toughness of the PS/epoxy interface. It was shown that the toughest interfaces were obtained with an intermediate length of grafted chains, $N = 838$, when the chains were well entangled and the grafted brush was dense enough to cause energy dissipation through craze formation. Although they elucidated the correlation between the chain length of interlinking molecules and the fracture toughness of the polymer interface, the chain length they observed was not the actual length because the chain migrated into the epoxy network during curing. In addition, the end-functionalized PS was end-grafted before preparing the PS/epoxy interface, contrary to the case of the common reactive compatibilization method. Although the effect of molecular weight and the concentration of reactive compatibilizer on the interfacial adhesion strength has been somewhat verified by them, a more precise understanding is needed.

In this study, we performed a model experimental study to examine the correlation between the microscopic interfacial structure and the interfacial adhesion strength using well-characterized end-functionalized reactive compatibilizer. Primary amine-terminated PS (ω-amino-PS) of various molecular weights was synthesized anionically. The PS/SMA interface was reinforced using ω-amino-PS, in which the terminal amine group can react with the anhydride group of SMA as the reactive compatibilizer. The enhancement of interfacial adhesion strength as a function of molecular weight and content of ω-amino-PS was determined using the modified double-cantilever beam (DCB) fracture test. Then, the effects of the chain length and the areal density of the interlinking chain on the fracture toughness of PSA/SMA interface were studied.

EXPERIMENTAL

Materials

As reactive compatibilizers, ω-amino-PS with different molecular weights was synthesized by anionic polymerization[13]. The end-functionalization of PS was proceeded by terminating a living polystyryl anion with 1-[4-[*N*,*N*-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene. The end-functionalized PSs were characterized by size-exclusion chromatography and proton n.m.r. spectroscopy. The incorporation of the primary amine functionality was completed after the hydrolysis of the silyl protecting groups. The characteristics of the amine-terminated PS are given in *Table 1*. The PS used in this study was a commercial moulding grade, obtained from the Dongbu Chemical Co., and has a weight-average molecular weight of 260 000 g mol^{-1} ($M_w/M_n = 2.4$). SMA copolymer was supplied by the Daelim Industrial Co., and has a weight-average molecular weight of 100 000 g mol^{-1}. The SMA has 15 wt% maleic anhydride content, which is not miscible with PS[14]. The PS and SMA were dried under vacuum at room temperature for 24 h before use.

Table 1 Characteristics of the amine-terminated PS

ω-Amino-PS	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	Functionality (%)
26K	26 100	1.01	100
67k	67 600	1.02	89.3
127k	127 100	1.01	46.2

Fracture toughness measurement

PS and SMA were compression moulded into sheets of 2 mm thickness using a hot press. The moulding temperatures were 160 and 200°C, respectively. To obtain a smooth glossy moulding surface, a polished Ferrotype plate was used as the moulding plate. The moulded sheets were stored in a vacuum oven before use in order to prevent contamination. PS and ω-amine-PS were dissolved in chloroform and cast onto a glass slide, and followed by drying at room temperature. Then, the blend film was removed and dried under vacuum for 24 h. The thickness of the final blend film was around 40 μm. The blend film was inserted between PS and SMA sheets. The sandwich sheets were joined in a hot press at 150°C for 2 h. Light pressure was exerted on the sheets to promote good contact between the surfaces. The joined specimens were allowed to cool slowly in the moulds and then cut into strips of 5 mm in width using a diamond saw. The specimens were dried under vacuum for a minimum of 10 h at 60°C before fracture testing.

The adhesive joint specimens were fractured at room temperature using a modified DCB fracture test to measure the critical strain energy release rate, G_{IC}. The crack was propagated by inserting a razor blade into the PS/SMA interface. The crack was allowed to propagate slowly for 24 h before measurement. The crack length was measured using a travelling microscope. Details of the modified DCB fracture test are described elsewhere[15–17].

To study the failure mode, the fracture surfaces were examined using optical microscopy and solvent treatment. In all experiments, matching sides of the fractured specimens were examined with the optical microscope in a reflection mode. For solvent treatment, cyclohexane was used because it is a good solvent for PS and a non-solvent for SMA. The fractured samples were stirred in cyclohexane for a given period then removed from the cyclohexane and dried. The solvent-treated fracture surfaces were examined with the optical microscope in a reflection mode.

RESULTS AND DISCUSSION

Interfacial adhesion according to the content of ω-amino-PS

In this study, ω-amino-PS was chosen as the reactive compatibilizer in the PS/SMA system. The amine end-group in ω-amino-PS reacts with the anhydride group in SMA and forms an imide bond at the PS/SMA interface. This imide bond bridges two polymers and improves the interfacial adhesion strength. A schematic diagram of *in situ* copolymer formation at the interface is shown in *Figure 1*.

Fracture toughness results for the PS/SMA interface as a function of the content of 26k ω-amino-PS are presented in *Figure 2*. Its molecular weight is 26 100 g mol^{-1}, which is larger than the corresponding entanglement molecular weight for PS (~18 000 g mol^{-1})[18]. The fracture toughness was found to increase with the amount of

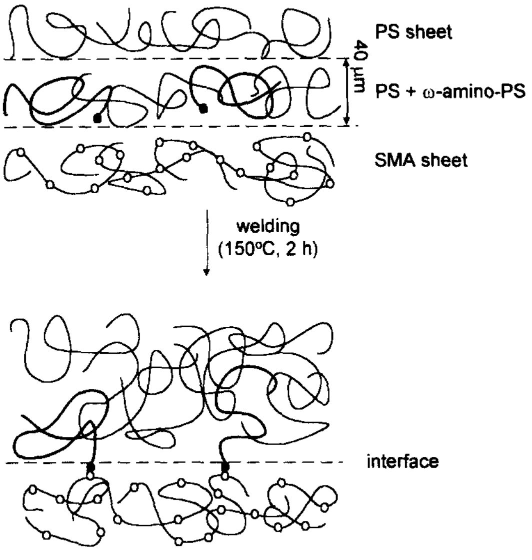

Figure 1 Schematic diagram of *in situ* copolymer formation at the (PS + ω-amino-PS)/SMA interface (●, amine group of ω-amino-PS; ○, anhydride group of SMA)

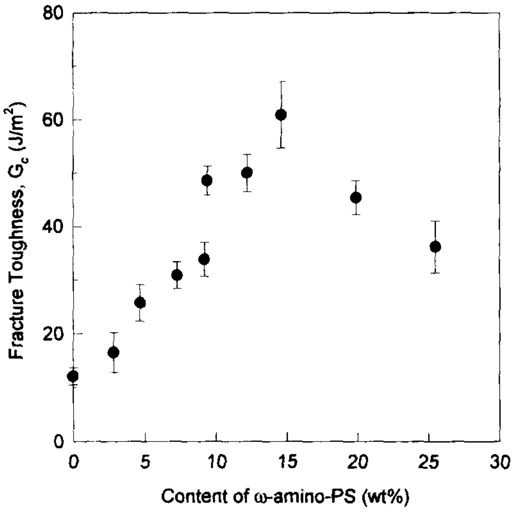

Figure 2 Interfacial fracture toughness as a function of the content of 26 k ω-amino-PS

ω-amino-PS. However, there was a rapid decline in fracture toughness above ~15 wt%. This is an unexpected result. The data in *Figure 2* are divided into two regimes, i.e. increasing toughness below the optimum content and post-optimum toughness above the optimum content. These different trends in fracture toughness as a function of the content of ω-amino-PS can be explained as follows.

In the increasing toughness regime, the fracture toughness increased almost linearly with increasing amounts of ω-amino-PS. This implies that the *in situ* formation of interlinking copolymer due to the reaction between ω-amino-PS and SMA will cause the interfacial fracture toughness to increase. Since the anhydride groups of SMA are greatly in excess compared to the amine groups of ω-amino-PS, any amine group making contact with the PS/SMA interface will be end-grafted into the SMA surface. Therefore, the content of ω-amino-PS is proportional to the number of interlinking copolymer molecules. This suggests that the interfacial fracture toughness will increase with an increasing number of interlinking chains or grafting density. This is well in accordance with the results of Kramer *et al.*[12].

However, the effect of chain length is not consistent with their results. They reported that end-grafted PS chains with lengths of over $N = 688$ were effective in reinforcing the PS/epoxy interface, where N is the degree of polymerization of PS. According to their results, the maximum interfacial fracture toughnesses in the cases of $N = 412$ and 535, which are larger than in our case ($N = 251$), were just 11 and 16 J m^{-2}, respectively. However, these values are quite low compared to our maximum value, around 60 J m^{-2}. In our study, the PS chain of molecular weight 26 000 g mol^{-1} ($N = 251$) is very effective at reinforcing the interface compared to the interfacial fracture toughness without ω-amino-PS, although the chain length is much shorter than the PS chain length they used.

This inconsistency may be explained by the difference in preparing the interface. Kramer *et al.* deposited the end-functionalized PS on the B-stage cured epoxy surface by spin coating followed by curing before making the PS/epoxy interface. During the curing stage, the end-functionalized chains were end-grafted into epoxy network. The interface was then formed by joining a PS sheet and a cured epoxy sheet, covered by end-functionalized PS film, at 160°C for 2 h under contact pressure to allow the tails of the grafted PS chains to entangle with the PS sheet. In their experiment, as they mentioned, the end-functionalized PS could penetrate the epoxy surface during the grafting procedure before joining the two sheets, resulting in shorter tails available for stress transfer through entanglement with the PS homopolymer chains.

As the length of end-grafted chains available to entangle with PS homopolymer chains was shortened by this effect, their results could not be directly compared to our results. In contrast to their experiment, we used a different procedure for the preparation of the interface. We prepared a thin blend film of about 40 μm by casting a blend solution of ω-amino-PS and PS homopolymer. The interfaces were then prepared by inserting a cast blend film between PS and SMA sheets followed by joining the sandwich sheets in a hot press at 150°C for 2 h. One can consider two interfaces, i.e. the interface between the blend film and the PS homopolymer sheet and the interface between the blend film and the SMA sheet, as shown in *Figure 1*. The interface between the blend film and the PS homopolymer sheet disappeared due to interdiffusion of the respective PS chains because the calculated mean diffusion distance $(Dt)^{1/2}$ of the PS homopolymer during the joining process was 227 nm, which is much larger than the radius of gyration of the relevant PS. Also, the diffusion length is much smaller than the thickness of the blend film (~40 μm), so the PS/SMA interface is not likely to be affected by PS chains in the PS homopolymer sheet.

In the blend film, the ω-amino-PS chains were already entangled with PS homopolymer chains before the preparation of the interface. At the PS/SMA interface, the amine groups in the pre-entangled ω-amino-PS could react with the anhydride groups in SMA during heating. Thus, the shortening in the length of the reactive PS chain which occurred in the case of Kramer *et al.* may not occur in this experiment. Since the molecular weight of the end-grafted PS chain (26 000 g mol^{-1}) is larger than the corresponding entanglement molecular weight of PS (~18 000 g mol^{-1}), it can sustain stress transfer across the interface, resulting in enhancement of interfacial fracture toughness as can be seen in *Figure 2*. The fact that the fracture toughness increases as the content of reactive compatibilizer, i.e. the areal density of interlinking chains, increases is well in accordance with other results reported[11,12]. The concept that the interfacial fracture toughness is related to the number of interlinking chains crossing a given interface has been verified by many investigators using a block copolymer as a compatibilizer[19–21]. Therefore, the enhancement of interfacial fracture toughness in this regime is mainly due to the increase in the number of interlinking chains available for stress transfer across the interface.

However, above 15 wt% of ω-amino-PS the interfacial fracture toughness decreased rapidly. This result is quite unexpected and is inconsistent with the above-mentioned concept. In this model experimental study, the property change of the material near the interface due to the increased amount of lower molecular weight ω-amino-PS may cause the decline in fracture toughness. In other words, as the content of ω-amino-PS in blend film increases, the mechanical strength of the blend film is weakened due to the lower molecular weight fraction because the molecular weight of ω-amino-PS is much lower than that of the PS homopolymer. According to Robertson's data[22], the fracture toughness of 26 k ω-amino-PS is approximately 1 J m^{-2}, which is very low compared to that of high molar mass PS.

Kramer *et al.*[23] have predicted the fracture toughness of a diluted entanglement network in a glassy polymer, which is applicable to our system, through continuum and discrete modelling of craze failure at a crack tip. In their study, they used the diluted entanglement network, i.e. dilution of high molecular weight polymer with chains of the same polymer which are too short to entangle. In this experiment, our system is also PS homopolymer diluted with lower molecular weight ω-amino-PS, which is very similar to theirs. They reported the deleterious effect by addition of a relatively small volume fraction of low molecular weight polymer, i.e. the fracture toughness approaches zero when the volume fraction of low molecular weight polymer is about 0.56 even for the highest molecular weight case ($\bar{M}_n$ = 1 000 000 g mol^{-1}). Therefore, the decline of fracture toughness shown in *Figure 2* is believed to be mainly due to the dilution effect by the weak mechanical properties of ω-amino-PS itself. As a result, the crack initiated by the razor blade may propagate into the PS side instead of propagating along the interface between the PS/SMA interface which is now stronger than PS. This was also supported by fractographs of the fracture surface of the PS/SMA joint taken with an optical microscope. The fractograph results verifying the locus of failure are described in a later section.

The results for interfacial fracture toughness as a function of the content of 67 k and 127 k ω-amino-PS are presented in *Figures 3* and *4*, respectively. In these cases, the interfacial fracture toughness increased with the amount of ω-amino-PS and then saturated at a certain content depending on the molecular weight of ω-amino-PS. The fact that the fracture toughness increased with an increasing amount of reactive compatibilizer is well in accordance with other results reported[11,12] and consistent with the concept that the fracture toughness is related to the number of interlinking chains crossing a given interface[19–21]. As shown in *Figures 3* and *4*, the trend of linear increase in fracture toughness with increasing ω-amino-PS content was found to be very similar in each case. However, the values of saturated fracture toughness and the content of ω-amino-PS for saturation of fracture energy are very different from each other. The saturated fracture toughness in the case of 67 k ω-amino-PS was found to be smaller compared to that of the 127 k case. This may be due to the mechanical strength of 67 k ω-amino-PS being less than that of 127 k ω-amino-PS, which is explained earlier.

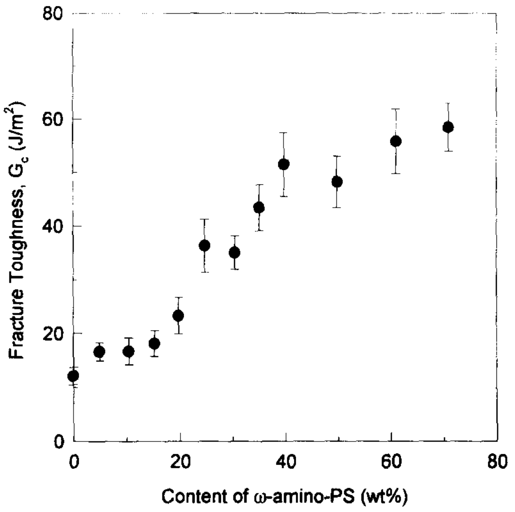

Figure 3 Interfacial fracture toughness as a function of content of 67 k ω-amino-PS

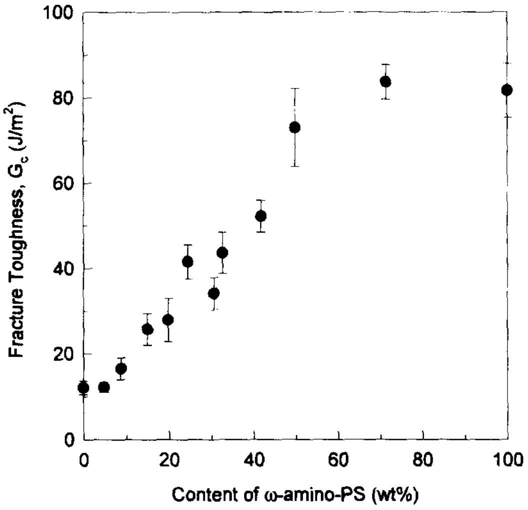

Figure 4 Interfacial fracture toughness as a function of content of 127 k ω-amino-PS

Interfacial adhesion according to the length of interlinking chain

Since the number of interlinking chains is proportional to the concentration of amine groups at the interface, which is directly related to the content and the molecular weight of ω-amino-PS, fracture toughness results are plotted as a function of amine group concentration in *Figure 5* in order to study the correlation between the interfacial adhesion strength and the length of the interlinking chain. As the longer interlinking chain has a higher probability of entanglement with other chains, one would expect the longer chain to show higher interfacial fracture toughness at the same amine group concentration. The 127 k ω-amino-PS showed the highest fracture toughness compared to the others at the same amine concentration as expected. This means that the longer interlinking chain showed a higher interfacial fracture toughness per interlinking chain, which concept has been well established in a model study using a diblock copolymer as the compatibilizer[20].

However, in the case of 26 k ω-amino-PS, the fracture toughness per interlinking chain showed a somewhat higher value than expected, similar to that of the 67 k ω-amino-PS case. This result cannot be explained by the concept established in the model study of diblock copolymer. The interaction between the amine group in ω-amino-PS and the anhydride group in SMA could promote segregation of the ω-amino-PS chains at the PS/SMA interface. However, it should be noted that the entropy loss due to the pinning of molecules by grafting would prevent this segregation. The entropy loss by grafting of ω-amino-PS is highly dependent on the length of the end-grafted chain[12], i.e. the longer chain has more entropy loss in end-grafting. Since these two effects are competing with each other during welding, the molecular weight of ω-amino-PS is a very important factor in determining the degree of segregation of ω-amino-PS to the interface. The difference in diffusion rate of ω-amino-PS with molecular weight should also be considered here because, in this model study, ω-amino-PS was blended with commercial moulding grade PS, for which the number-average molecular weight is 108 000 g mol^{-1}. It is known that the diffusion coefficient (D) is inversely proportional to the square of molecular weight. This indicates that the shorter the chain the faster the diffusion rate.

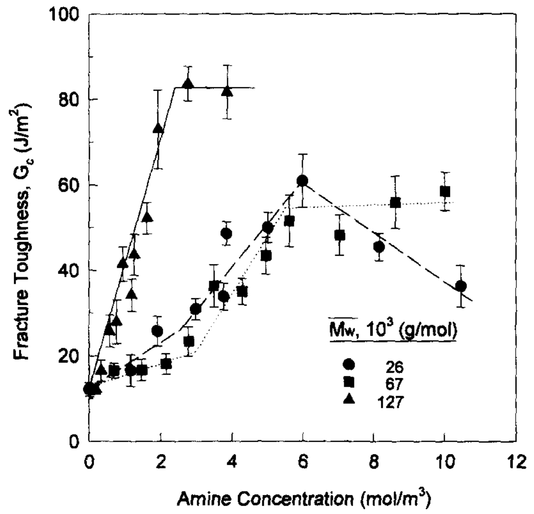

Figure 5 Interfacial fracture toughness as a function of concentration of the amine group (●, 26 k ω-amino-PS; ■, 67 k ω-amino-PS; ▲, 127 k ω-amino-PS)

In the case of 26 k ω-amino-PS, its diffusion rate is much faster than that of the non-functionalized matrix PS and has a lower entropy loss when grafted compared to the high molecular weight ω-amino-PS. Thus, the ω-amino-PS could diffuse into the interface from the bulk and form greater numbers of interlinking chains than expected. The increased number of interlinking chains may account for the higher efficiency of the 26 k ω-amino-PS than expected in reinforcing the interface at low amine group concentrations. It may be thought that the diffusion

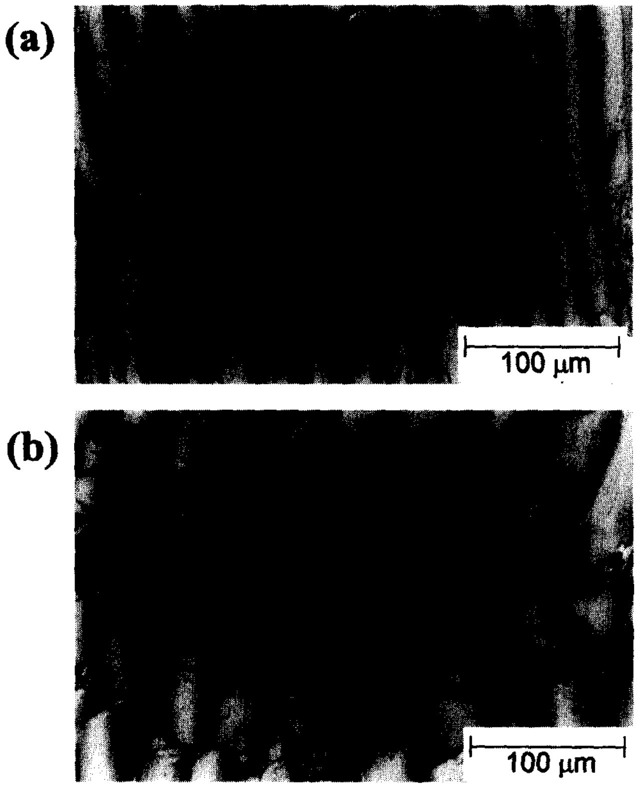

Figure 6 Optical micrographs of the fracture surface of PS side for the PS/SMA joint: (a) 26 k ω-amino-PS 7.26 wt% and (b) 26 k ω-amino-PS 25 wt%

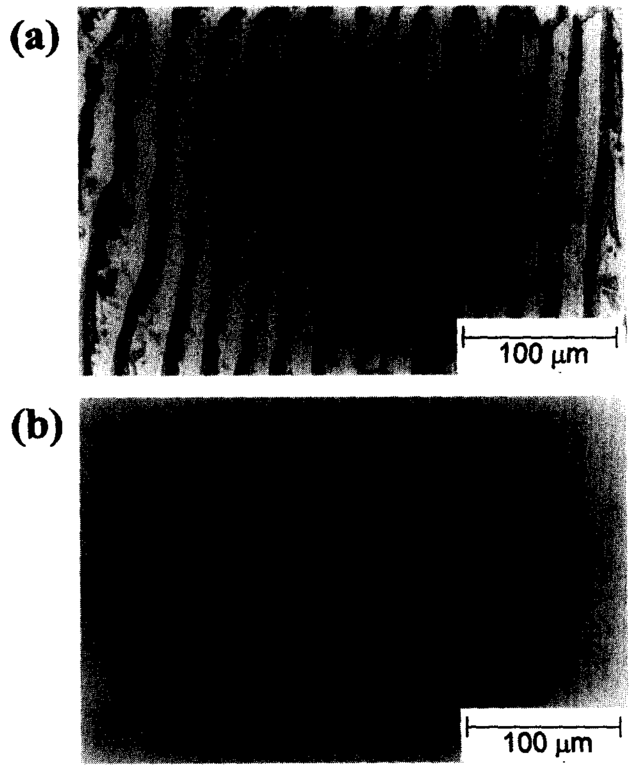

Figure 7 Effect of solvent treatment on the fracture surface of the SMA side of the PS/SMA joint in the case of 26 k ω-amino-PS 7.26 wt%: (a) before solvent treatment; (b) after 30 s of stirring in the solvent

and segregation mechanism is not possible in the cases of 67 k ω-amino-PS and 127 k ω-amino-PS due to their higher molecular weights, comparable to that of non-functionalized PS, and a large entropy loss. So, the 127 k ω-amino-PS showed a higher efficiency in reinforcing the interface than the 67 k ω-amino-PS at the same concentration of amine groups.

Examination of fracture surfaces

To ascertain the locus of failure, the fracture surfaces were examined by optical microscopy in a reflection mode. In all cases, the fracture mechanism was crazing followed by craze failure once the content of ω-amino-PS became high enough to generate a toughness of $\sim$30 J m^{-2} or more. The fractographs are shown in *Figure 6*. The fractograph of the increasing toughness regime of 26 k ω-amino-PS (*Figure 6a*) shows that crazes grew down into the PS from the interface and the crack tended to follow these crazes and then jump back to the interface. Similar fractographs were seen in fracture surfaces in increasing toughness or saturated toughness regimes independent of the molecular weight of ω-amino-PS. The fractograph in the post-optimum regime of 26 k ω-amino-PS (*Figure 6b*) shows quite different features. This reveals the cohesive failure of the weak mechanical property of 26 k ω-amino-PS/PS blend film as described earlier. The matching side of the SMA fracture surface showed the same feature because the crack propagated into the PS.

As the crack propagated nearly into the PS side, some PS remained on the SMA fracture surface. To verify this the SMA fracture surface was treated with cyclohexane, which is a solvent for PS but not for SMA. *Figure 7* shows the micrographs of SMA fracture surface before and after solvent treatment. The roughness of the SMA fracture surface disappeared after treatment with cyclohexane, to give a clean surface. This reveals that the roughness of the SMA fracture surface is due to the residual PS, which is crazed in the fracture process.

CONCLUSION

A model experimental study of the interfacial adhesion strength between PS and SMA using ω-amino-PS with different molecular weights and contents as a reactive compatibilizer was conducted. The addition of ω-amino-PS to the PS/SMA system leads to a large enhancement of interfacial fracture toughness, which implies the formation of end-grafted copolymer at the interface through reaction between the amine group of ω-amino-PS and the anhydride group of SMA.

In the case of 26 k ω-amino-PS, which is just above the entanglement molecular weight, the fracture toughness increased with the amount of ω-amino-PS and then decreased rapidly due to the weak mechanical strength of ω-amino-PS itself. In the cases of 67 k and 127 k ω-amino-PS, which are far above the entanglement molecular weight, the fracture toughness increased with the amount of ω-amino-PS and then levelled off at a certain content. At the same concentration of amine groups, the 127 k ω-amino-PS showed the highest fracture toughness since the longer chain has a higher probability of entanglement with other chains. Finally, ω-amino-PS with a lower molecular weight appeared to be more effective in reactive reinforcement at the same content due to a higher concentration of amine groups per unit volume. However, at the same concentration of amine groups, ω-amino-PS with a higher molecular weight appeared to be more effective due to greater entanglement with other chains for stress transfer across the interface.

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