

Reactive Compatibilized Polymer-Polymer Interface : Amorphous and Semi-crystalline Polymer Pair.

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ABSTRACT: We present an investigation of the reinforcement of the interface between a flexible amorphous polymer (polystyrene, PS) and a semi-crystalline polymer (a polyamide, Ny6). Different processes (a reactive ion-beam process(RIB), a plasma surface activation process(PSA), and a combined ion-beam process(CIB)) were used for the surface functionalization. Poly(styrene-co-maleic anhydride) was also used as the compatibilizer. Fracture toughness was measured using the asymmetric double cantilever beam test (ADCB). For bonding temperatures above 190°C, the adhesion strength was found to increase with bonding time, pass through a peak value, and then reach a plateau. The fracture toughness increased with increasing bonding temperature, passed through a peak near 200°C, and then decreased with further increase of the bonding temperature. This behavior was more obvious for an amorphous polymer / semi-crystalline polymer pair than for a pair of semi-crystalline polymers. The variation of the fracture toughness with bonding time and temperature can be plausibly explained in terms of two different failure mechanisms : adhesive failure at the interface for short bonding times and when the bonding temperature is low, and for longer bonding times and at high temperatures, cohesive failure between chains at the interface and the bulk PS due to decreased chain entanglement. CIB process showed better efficiency than the others because of surface area expanding effect by etching process and more effective surface functionalization.

Key words: Reactive Compatibilization, Ion Beam Surface Functionalization, Plasma Modification

1. INTRODUCTION

The interfacial properties and the properties of the component polymers are the strongest influences on the final physical and chemical properties of polymer blends. Since most polymer pairs are thermodynamically immiscible, their interfacial adhesion is quite poor due to poor mutual diffusion of molecules at the interface.¹ To fabricate a useful blend, the addition of a compatibilizer at the interface is normally required.^{1, 2} The addition of a compatibilizer such as a block copolymer is only useful if the compatibilizer is available. If no compatibilizer is available, in situ reactive compatibilization is another approach that can be used to improve the interfacial properties. Compatibilizer produced in situ at the interface can transfer the stress larger than the crazing stress of one of two matrix polymers. A compatibilized polymer blend with high adhesion strength can then be achieved because plastic deformation occurs in the more ductile polymer and the asymmetric craze propagates ahead of the crack.^{3,4} A few studies of semi-crystalline polymer interfaces

have been carried out until very recently. The most heavily investigated system is the interface between polypropylene (PP) and polyamide 6 (Ny6) reinforced by reactive blending.⁵⁻⁸ We verified experimentally that the appearance of a maximum in the fracture toughness is not because of variation of the amount of compatibilizer formed at the interface nor because of functionalized molecular diffusion to the interface.⁶ To obtain these results, we used a surface functionalization method using ion-beam irradiation in an oxygen environment, which produces some reactive functional groups on the PP surface at a relatively shallow depth. The fracture toughness was found to exhibit almost identical behavior: the fracture toughness passes through maxima at 200°C and at the bonding time of 60 min. In this study, we have carried out a further investigation of the fracture toughness of the interface between an amorphous polymer (polystyrene) and a semi-crystalline polymer (Ny6). Poly(styrene-co-maleic anhydride) with a high molecular weight was used in the in situ reactive compatibilization. A fracture mechanism that is universally applicable to polymer interfaces was sought for the in situ reactive compatibilization

process. The effect of surface functionalization methods by varying the functionalization process was also investigated.

1 EXPERIMENTS

2.1 Materials : Materials employed in this study were commercial polyamide (Ny6) and a polystyrene (PS). Polystyrene was supplied by Kumho Petrochemicals (Korea). The weight average molar mass was 2.8×10^5 g/mol and the polydispersity index was 2.4. Ny6 was a Kolon product (KN171), whose weight average molar mass was 8.5×10^4 g/mol and the polydispersity index was 3.5. Commercially available poly(styrene-co-maleic anhydride) (PSMA), added as a compatibilizer, was purchased from Aldrich in pellet form. It contains 7wt% maleic anhydride group. The weight average molar mass was 2.34×10^5 g/mol and the polydispersity index was 2.3. Pellets of all polymers were dried for 24 hours in a vacuum oven at 100°C (Ny6) and 80°C (PS and PSMA). Blending of PS and PSMA (97:3 weight ratio) was done in an internal mixer at 200°C. Samples were made by compression molding at 160°C and 240°C for PS blend and Ny6, respectively. The PS blend strips (2cm x 4cm) were clamped with Ny6 strips (2cm x 4cm) in an airtight molder under slight pressure. The mold was heated in a temperature-controlled furnace between 180 and 220°C. All the samples were stored in a desiccator for 24 hours prior to fracture test.

2.2 Measurement of the fracture toughness : The fracture toughness was measured using the asymmetric double cantilever beam (ADCB) test because it has been shown to be a reliable test for the fracture toughness of a polymer interface.⁹⁻¹⁰

2.3 Surface characterization : Scanning electron microscopy (SEM) observations of the samples were performed on a Hitachi S-2500C. Chemical components on the fractured surfaces were analyzed by XPS. XPS spectrum was recorded by Surface Science 2803-S spectrometer ($h\nu = 1.5$ keV).

3. RESULTS AND DISCUSSION

The chemical reactions occurring at the interfaces of reactively blended polymers are controlled either by the rate of diffusion or by the rate of reaction.^{9,10} The parameters affecting the rates of diffusion and reaction are the temperature and the initial concentration of the functional groups on the polymer surface. Figure 1 shows the variation of the fracture toughness with bonding time. Several facts

are worthy of note. First, the interfacial fracture toughness for each temperature increases with the bonding time. Up to a bonding time of 30 minutes, the fracture toughness increases very slowly, which indicates that not much reaction occurs at the interface, so some induction annealing time is required.^{6,9} For longer bonding times, the fracture toughness passes through a maximum and/or reaches a plateau value depending on the bonding temperature. Second, the fracture toughness at the same bonding time increases with bonding temperature, reaching its highest value at 200°C, and then decreases with further increases in the temperature. Third, there is a clear maximum in the fracture toughness at a bonding time of around 60 minutes for all bonding temperatures. Though further diffusion of PSMA molecules from the deep bulk side to the interface is difficult due to the hindrance, further reaction between the functional groups of PSMA and Ny6 can happen because the PSMA polymer chains are multifunctional.^{1,10}

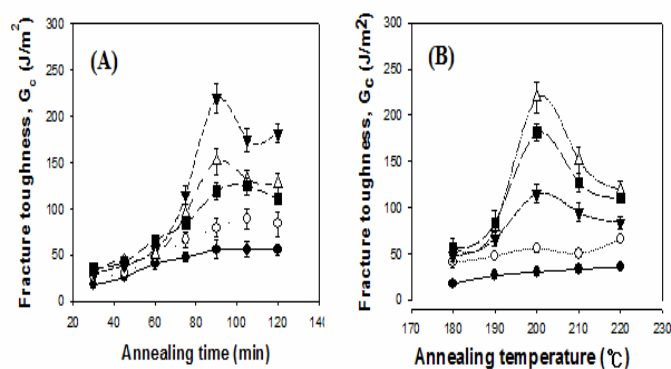


Figure 1. (A) Variation of the fracture toughness of PS(+PSMA)/Ny6 interface with bonding time.¹ Bonding temperatures were (●) 180°C, (○) 190°C, (▼) 200°C, (△) 210°C, and (■) 220°C, respectively. (B) Variation of the fracture toughness between PS(+PSMA) and Ny6 with bonding temperatures. Bonding times were (●) 30 minutes, (○) 60 minutes, (▼) 75 minutes, (△) 90 minutes, and (■) 120 minutes. The lines are guides for the eyes.

Hence the type of grafting depends on temperatures and time. As Char and Lee⁹ explained, the situation may evolve from one graft per SMA chain to several grafts per chain reducing hence greatly the molecular weight of the SMA chain portion (loop or chain end) able to entangle with PS homopolymer. As a result, the molecular weight of the “effective brush” at the interface decreases.¹ As long as the copolymers (or the block copolymers added as a compatibilizer) at the interface have sufficiently high molecular weights to become fully entangled

with the matrix polymers on both sides of the interface, fracture occurs by chain scission when the areal density of the copolymers at the interface is low.^{1,6} If the areal density of a long compatibilizer is above some critical value, the adhesive strength is high enough to withstand the fracture stress. The fracture is then determined by the cohesive strength of the polymers on either side, depending on the states of the individual chains. Thus, the failure at the interface proceeds as a result of adhesive failure or cohesive failure, i.e., failure of the interface proceeds by the mechanism with the lower intrinsic failure energy. In the present study, cohesive failure proceeds only in the PS side because the crazing stress of Ny6 is higher than that of PS, As already mentioned, all the deformation is, thus, in the PS side and the NY6 side acts like a solid wall with functional groups.

When the surface was functionalized by the ion-beam assisted gas reaction to incorporate functional groups, bulk properties of the ion-beam treated polymer does not change remarkably because the modification proceeds at relatively shallow depth from the surface. Low energy ion-beam can penetrate and modify polymer surface less than 70Å deep. The interfacial fracture toughness shows a similar behavior when the PS surface was modified by ion-beam irradiation and/or plasma surface modification process (Figure 2). It increased with bonding time and then reached a plateau for each temperature series. Reactive oxygen gas added system showed higher fracture toughness than only Ar⁺ beam irradiated case. We believe this to be the result of inter-reaction between the surface functional groups (carboxyl groups mostly involved) and the amine end group of Ny6.^{1, 6} As the inter-reaction between activated PS molecules and Ny6 molecules proceeded, the fracture toughness increased. After a critical surface coverage of reacted molecules was attained, further reaction at the interface became scarce due to the consumption of functionalized PP molecules at the interface and less diffusion of the other chains from the bulk side due to the crowdedness at the interface. Hence the interface fracture toughness reaches the plateau value.

Decrease of the fracture toughness with higher temperature was attributed to the fracture mode change at higher temperature. The adhesive interface strength at the interface increased with temperature due to more reaction at the interface while the cohesive strength of PS decreases with the temperature due to less entanglement of PS molecules at the interface with other chains in the bulk.¹ For the ion-beam irradiated PS surface

bonded at high temperature, the adhesive strength at the interface is strong enough to induce the crack propagate into the PS phase. We emphasize a particularly useful aspect of the ion-beam assisted gas reaction route to polymer surface modification. It is quite unique and very efficient to change the polymer surface properties.

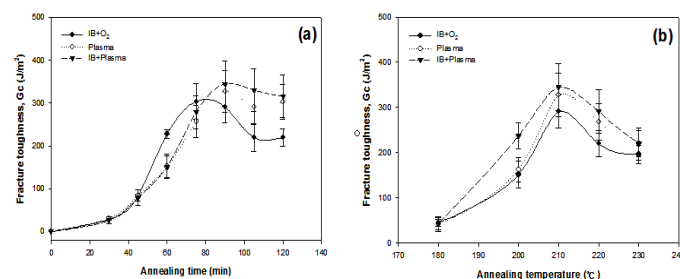


Figure 2 Variation of fracture toughness between surface modified PS and Ny6 with annealing time (at 210°C of annealing temperature)-(a), and with annealing temperature (after 90min of annealing time)-(b)

In the present system, the amine end groups of Ny6 and the maleic anhydride groups of SMA or surface functional groups easily react to form covalent bonds during processing.¹ When a critical surface coverage of interacted molecule is attained, further reactions at the interface become difficult due to the consumption of functional groups at the interface and little diffusion of functionalized groups occurs from the deep bulk side to the interface.^{4,5} The interface is occupied by graft copolymers whose grafting branches entangled with Ny6 molecules on the bulk side. The entropic constraints for functionalized molecules to diffuse to the interface from the deep side are too large to be overcome by a specific energetic driving force from opposing functional groups because the reacted molecules stay at the interface.^{1,8} As we mentioned above, the interfacial adhesion strength is determined by the adhesive strength at the interface and by the cohesive strengths of both polymers. This is summarized in Figure 3. The fracture toughness at first increased with annealing time because of the increased adhesive strength due to interfacial reactions. When the adhesive strength is lower than cohesive strength, the failure occurs first through the adhesive failure. If the cohesive strength becomes lower than the adhesive strength, failure occurs due to failure of cohesion between the molecules at the interface and PS molecules below the interface. If the fracture strength is plotted versus bonding time, whether a maximum appears or not depends on the relative magnitudes of the adhesive strength and the

cohesive strength. After sufficient time, both the adhesive strength and cohesive strength reach steady state values. The temperature dependence shows a similar behavior. As the bonding temperature increases, more reactions occur faster. The adhesive strength increases more rapidly with the reaction time at high temperatures, and the cohesive strength also decreases more rapidly. Depending on the relative values of the adhesive and cohesive strengths, the total adhesion strength varies with the temperature (see the arrow in Figure 3).

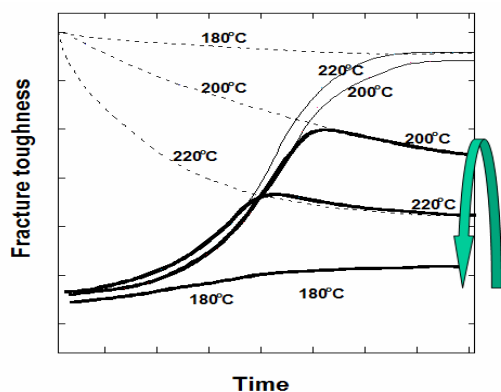


Figure 3. Schematic representation of the locus of failure of PS(+PSMA)/Ny6 interface.¹ Bold lines implicate the overall path of the failure with time at different temperatures. The arrow indicates the fracture toughness variation with the bonding temperature after a long time (120 minutes).

4. CONCLUSIONS

In this study, we attempted to determine plausible fracture mechanisms at the polymer-polymer interface by investigating experimentally the effect of in situ reactive compatibilization on the fracture toughness of the interface between an amorphous polymer (PS) and a semi-crystalline polymer (Ny6) compatibilized with PSMA or by reactive compatibilization. In general, the behavior of this interface was found to be similar to that of the interface between semi-crystalline polymers (PP/Ny6) compatibilized by maleic anhydride grafted polypropylene (MAPP). The variation of the fracture toughness with bonding time and temperature can be plausibly explained in terms of two different failure mechanisms, i.e., adhesive failure at the interface for short bonding times and/or low bonding temperature and the failure of cohesion between the chains at the interface and the bulk of the lower modulus polymer (PS) for long bonding times and/or high temperature due to decreased chain entanglements.

Therefore, there is an optimum bonding times and temperature for the fracture toughness which appears as a maximum in the variation of the fracture toughness with bonding time and temperature. This behavior is more obvious for an amorphous polymer/semi-crystalline polymer pair than for semi-crystalline polymer pairs because of the absence of co-crystallization in the amorphous polymer phase.^{1,6} CIB process showed better efficiency than the others because of surface area expanding effect by etching process and more effective surface functionalization.

ACKNOWLEDGEMENT

This work was supported by KRF (0417-20060134), the SRC/ERC program of MOST/KOSEF (R11 - 2005-065), and KOSEF (R01-2006-000-10062-0)

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