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Polymer/Polymer Interface Adhesion by In Situ Compatibilization

Ho Youn Kim^a and Yongsok Seo^{a*}^a *Intellectual Textile System Research Center (ITRC) and RIAM School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul, Korea*

Abstract

We studied enhanced interfacial adhesion between a flexible amorphous polymer (polystyrene, PS) and a semi-crystalline polymer (a polyamide, Ny6). The surface modification of PS to provide functional groups reacting with the functional groups of Ny6 was carried out with ion-beam and/or plasma treatment. These surface modifications were found to significantly alter the interfacial adhesion strength between PS and Ny6. Though the fracture toughness was varied depending on the process, its overall behavior was quite similar with one another; the fracture toughness increased with increasing bonding temperature and bonding time, passed through a peak, and then decreased with further increase of the bonding time or temperature.

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1. Introduction

Recent reports from our laboratory have dealt with the interfacial adhesion between incompatible polymer pairs (Seo 2006, Seo 2004, Kim 2003, Kim2001, Seo 2006, Seo 2007, Kim 2011). These studies are intended, in part, to contribute to a general understanding of fracture mechanisms occurring at the interface between incompatible polymer pairs, so prevalent in polymer blends or composite systems for lamination or coating. Among the systems considered so far are a semicrystalline-semicrystalline polymer pair (Seo 2006, Seo 2007,), a flexible

* Corresponding author. Tel.: 822-880-9085; fax: 822-885-9671
E-mail address: ysseo@snu.ac.kr

semicrystalline-rodlike polymer pair¹ and an amorphous-semicrystalline polymer pair (Seo 2007, Kim 2011). In addition to the compatibilizer effect on the adhesion between polymer pairs, we have reported the effect of the surface functionalization on the interfacial adhesion which could exclude the compatibilizer's diffusion problem to the interface (Kim2001, Seo 2006).

To provide a further support of our conclusions, we have carried out more experiments to investigate the variation of the fracture toughness between an amorphous polymer (polystyrene) and a semicrystalline polymer (Ny6). We employed surface treatments consisting of Ar⁺ ion-beam irradiation and/or RF oxygen plasma treatment to exploit the necessary interfacial adhesion between polystyrene (an amorphous polymer) and nylon 6 (a semicrystalline polymer) (Seo 2007, Kim 2011). Thereafter a fracture mechanism universally applicable to all polymer interfaces was sought for the in situ reactive compatibilization process.

2. 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. The PS strips (2cm x 4cm) were clamped with Ny6 strips (2cm x 4cm) in an airtight mold under slight pressure. The mold was heated in a temperature-controlled furnace between 180 and 220°C. The mold was slowly cooled to room temperature in air. All the samples were stored in a desiccator for 24 hours prior to fracture test.

2.2 Ion-beam Irradiation and Plasma Treatment : The surface modification system consists of a low energy ion-beam irradiation apparatus with a reactive gas feeding system (IBO) and a conventional plasma treatment system. In the oxygen plasma treatment process (OP), a radio frequency (13.56MHz) plasma was generated with an RF power source (RF5S-PF Power Products Inc.), and the plasma power was fixed at 100 W. The gas used in this system was O₂ with a fixed flow rate of 10 cm³/s. In another modification process (IBOP), the ion-beam and plasma processes were applied sequentially in the same reactor; low-energy Ar⁺ ion-beam irradiation was carried out first in the absence of reactive oxygen gas to change the surface morphology, and then, O₂ plasma treatment was done to functionalize the surface. The radio frequency (13.56MHz) plasma was again generated with the RF power source, and the plasma power was fixed at 100 W. The O₂ gas flow rate was the same as that used in the OP process.

2.3 Measurement of the fracture toughness: The fracture toughness was measured using the asymmetric double cantilever beam (ADCB, Figure 1) test because it has been shown to be a reliable test for the fracture toughness of a polymer interface (Seo 2006, Seo 2004, Kim 2003, Kim2001, Seo 2006, Seo 2007, Kim 2011).

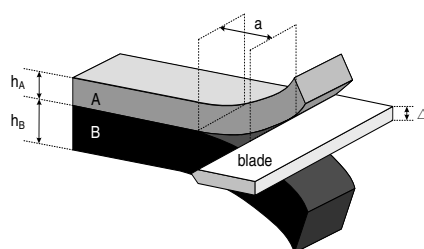


Fig. 1. Schematic diagram of the ADCB test.

To minimize contributions of the second component, all of our samples were made with a thickness ratio h_{PS}/h_{tot} of 0.67 because G_c had a minimum value at a ratio between 0.55 and 0.7 (Seo 2006). In this system, the Young's moduli of PS and Ny6 are 1.5 GPa and 2.05 GPa, respectively. Since the crack length ahead of the blade, a , was less than $10h_{PS}$ for most of our samples, the following equation derived by Boucher et al.¹ based on calculations by Kanninen,⁴ whose assumption was that the finite elasticity of the material ahead of the crack tip required correction factors for small crack lengths, was used:

$$Gc = \frac{3\Delta^2}{8a^4} \frac{E_{PS} h_{PS}^3 E_{Ny6} h_{Ny6}^3}{E_{PS} h_{PS}^3 \alpha_{Ny6}^2 + E_{Ny6} h_{Ny6}^3 \alpha_{PS}^2} \quad (1)$$

where E_i and h_i denote the Young's modulus and the thickness of material i , respectively, and Δ is the thickness of the blade. α_i is the correction factor for material i and is given by

$$\alpha_i = \left(1 + 1.92 \frac{h_i}{a} + 1.22 \left(\frac{h_i}{a} \right)^2 + 0.39 \left(\frac{h_i}{a} \right)^3 \right) / \left(1 + 0.64 \frac{h_i}{a} \right) \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Surface characterization

Fig. 2 shows the surface roughness change of the PS surfaces resulting from the different processes for various duration of treatment time. The surface of neat PS had some large hills, mounds and shallow valleys. The surface roughness increases rapidly with the treatment time but reaches a steady value after long irradiation time. During the ion-beam and/or plasma treatments, the PS surfaces develop many active species. Some C-C or C-H bonds on the surface are broken during the processing which results in the rearrangement of molecular bonds and etching on the surface, and thus changes the surface morphology.⁷ Some of those active species encounter those broken bonds, resulting in the implantation of polar groups onto the surface and changes in the surface chemistry (Seo 2007, Kim 2011). The kinetic energy of the ion bombardment enhances the surface roughness first rather than the smoothing etching action. Reactive oxygen gas (or oxygen plasma in the IBOP process) is then incorporated into the surface. For the complex treatment process (IBOP), initial roughness appears as the result of two consecutive processes (ion-beam irradiation followed by plasma treatment), hence it reaches steady plateau soon (Seo 2007, Kim 2011). The etching pits, which appear at short irradiation times, evolved finer and deeper one with increasing irradiation time as a result of physical bombardment and chemical interaction. Due to the inherent hardness of PS, it does not show much development of very fine needle-like morphology. All processes show similar trend showing very rough surfaces with small mountainous region. Plasma process (OP) or the complex process (IBOP) produce less rough surfaces than that by ion beam process only due to smaller kinetic energy of plasma (Seo 2006, Seo 2004, Kim 2003, Kim2001, Seo 2006, Seo 2007, Kim 2011).

Functional groups generated on the PS surface can be checked by FTIR spectroscopy. New peaks not existing in the neat PS surfaces were observable at 1140, 1270 and 1720 cm^{-1} corresponding to C-O symmetric stretching mode, C-O anti-symmetric stretching mode and C=O stretching mode, respectively. They can be also checked by XPS. The C1s peak of neat PS in the XPS analysis shown in Figure 3(a) is symmetric with a narrow full width at half-maximum (FWHM). In contrast, the C1s peaks of the Ar^+ ion-beam irradiated and O_2 plasma (IBOP) treated PS sample overlap, are reduced in intensity, and are asymmetric because of the oxygen containing groups incorporated into the surface (Figure 3(b)). After more than 5 min of plasma treatment, the O/C atomic ratio, however, reached almost a steady value except IBO case (Figure 4), which can be explained in terms of the carbonization of the PS surface and the re-etching effect: increasing the bombardment of the PS surface can result in not only the cross-linking between polymer chains but also re-etching the functionalized surface (Kim 2011). IBOP (5min) results in the highest O/C ratio while IBO results in the lowest O/C ratio. In the IBOP process, the effect of plasma treatment becomes more significant than the OP process due to increased surface area and radical generation by previous ion-beam irradiation. On the other hand, the oxygen plasma treatment is less efficient to increase the surface area than ion beam irradiation of higher kinetic energy. The change in the roughness during the plasma treatment process(OP) is also small due to its relatively low kinetic energy while the effect of surface functionalization was good because of the electrically high potential which generates bonds with the polymer chains on the surface (Seo 2006, Seo 2004, Kim2001, Kim 2011). The broken bonds on the PS surface and the active oxygen species generated by the collision between Ar^+ ion beam and oxygen gas or by the oxygen plasma encounter with each other, resulting in the implantation of polar groups onto the surface. The formation of this polar oxygen containing groups on the PS surface such as hydroxyl, carbonyl, and carboxyl group contributes to the formation of a hydrophilic surface.

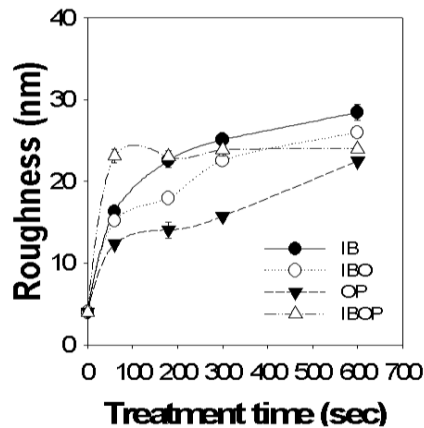


Fig. 2. Surface roughness change with irradiation (Kim 2011).

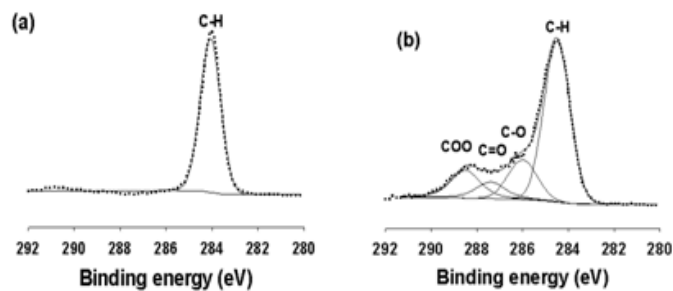


Fig. 3. XPS spectra of (a) neat PS and (b) surface modified PS (IOBP, 5min) (Kim 2011).

3.2 The fracture toughness variation and the fracture mechanism.

The strength of the adhesive joint between the PS and nylon 6 films was found to vary with the treatment time (Figure 4). Up to a bonding time of 30 minutes, the fracture toughness increases very slowly, which indicates that not much reaction occurs at the interface, hence, some induction bonding time is required. For longer bonding times, the fracture toughness passes through a maximum and/or reaches a plateau value depending on the bonding temperature. Regardless of the surface treatment process, the peel strength is severely affected by the changes in the functional groups. Untreated PS shows a very low interfacial strength under 0.1 N/cm, whereas the interfacial strength rapidly increases with the treatment time for all the surface modification processes. This result indicates that the interaction between the functional groups on the PS surface and nylon 6 is the primary reason for the adhesion improvement. The SEM image in Figure 5 of fractured neat PS shows that it contains roughened and rugged surfaces due to strong adhesion at the interface (Seo 2006, Kim 2011). The strength of the adhesive joint between the PS and nylon 6 films was found to vary with the treatment 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 that some induction bonding time is necessary. For longer bonding times, the fracture toughness passes through a maximum and/or reaches a plateau value depending on the bonding temperature. Regardless of the surface treatment process, the peel strength is severely affected by the addition of the functional groups. Untreated PS shows a very low interfacial strength under 0.1 N/cm whereas the interfacial strength rapidly increases with the treatment time for all three different modification processes. This result indicates that the interaction between the functional groups on the PS surface and nylon 6 is the primary reason for the adhesion improvement. The SEM image in Figure 5 of fractured neat PS shows that it contains roughened and rugged surfaces due to strong adhesion at the interface.

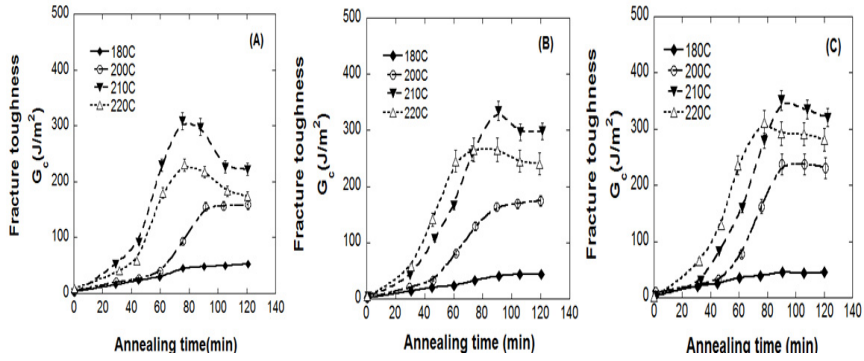


Fig. 4. Fracture toughness of PS / Ny6 interface with bonding time; (A) IBO, (B) OP, (C) IBOP (Kim 2011)

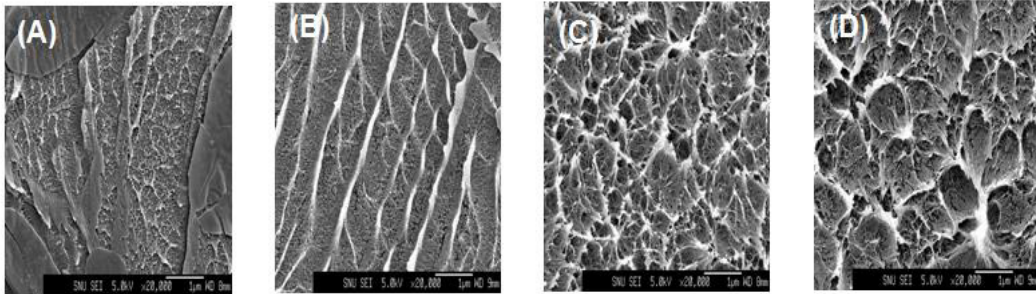


Fig. 5. SEM photographs of the cleaved PS surfaces at the bonding temperature of 210°C for 90 minutes of bonding time (x22000); (a) PS, (b) IBO PS, (c) OP PS, (d) IBOP PS. (Kim 2011).

The temperature dependence is interpreted as follows : 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 (shown in Figure 6 by the arrow).

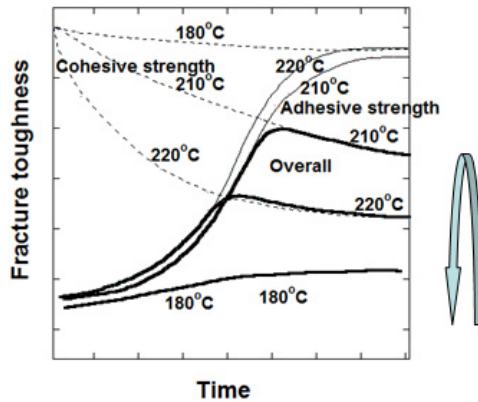


Fig. 6. Schematic representation of the locus of failure of PS(+PSMA)/Ny6 interface. When the adhesive strength (—) is lower than cohesive strength (---), the failure occurs first through the adhesive failure. The arrow indicates the fracture toughness variation with the bonding temperature after sometime (like 120 minutes) (Kim 2011).

The fracture toughness at the same bonding time increases with bonding temperature, reaching its highest value at 210°C, and then decreases with further increase in the temperature. Also a maximum in the fracture toughness at a bonding time of around 90 minutes for all bonding temperatures appears regardless of the surface treatment process. Since the cooling conditions for all the samples were the same, the early increase in the interfacial adhesion with bonding time is mainly due to the increase in the number of intermolecular reactions at the interface. The concentration of grafted copolymers produced at the interface is not sufficient to produce a strong interface. The production rate increased with temperature until 210°C. The fracture toughness showed a clear maximum around 210°C and then decreased at higher bonding temperatures.

4. Conclusions

In this study, we attempted to figure out plausible fracture mechanisms at the polymer-polymer interface by experimentally investigating the effect of in situ reactive compatibilization on the fracture toughness between an amorphous polymer (PS) and a semi-crystalline polymer (Ny6). In general, the behavior of this interface was found to be similar to that of the interface between semi-crystalline polymers. The fracture toughness was found to increase with bonding time, pass through a maximum value, and then reaches a plateau for bonding temperatures higher than 200°C. The fracture toughness also increases with the bonding temperature, with a maximum near 210°C and then decreases at higher bonding temperatures. The variation of the fracture toughness with bonding was similar to that with the bonding time.

Acknowledgements

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