Macromolecules **2002,** *35,* 1267−1275

Enhancement of Interfacial Adhesion between Polypropylene and Nylon 6: Effect of Surface Functionalization by Low-Energy Ion-Beam Irradiation

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Received May 11, 2001

ABSTRACT: The effect of surface functionalization on the interfacial adhesion between two immiscible semicrystalline polymers, polypropylene (PP) and a polyamide (nylon 6, Ny6)), was investigated. The surface of PP was functionalized by a low-energy ion-beam-assisted gas reaction. Surface functional groups containing carboxyl and carbonyl groups created remarkably different interactions at the interface. Fracture toughness was measured using an asymmetric double cantilever beam test (ADCB). The calculated fracture toughness was significantly increased for the functionalized PP case. The system with reactive oxygen gas added showed a higher fracture toughness than the case with only argon-ion-beam irradiation because of more reactions and/or interactions between the functionalized PP surface and Ny6. Analysis on the locus of failure by using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) revealed that the fracture toughness between PP and Ny6 was influenced not only by the bonding temperature but also by the bonding time at constant bonding temperature. The fracture toughness increased after some induction time of annealing; then, it reached a plateau value. The fracture toughness increased with the bonding temperature, showed a maximum at 200 °C, and then decreased at a higher temperature of 210 °C. This behavior is different from other reported results. The present system is more or less like a chain tethered to a solid surface. The failure was caused by the weaker of the adhesive strength or the cohesive strength. The effect of bonding temperature is attributed to the cohesive failure in the PP phase. The adhesive strength increased with the bonding temperature while the cohesive strength decreased with the bonding temperature because of less entanglement of reacted chains with the other chains in the bulk. The dependence of the fracture toughness on the bonding time was explained in terms of this fracture mechanism.

Introduction

Interfacial adhesion plays a very important role in the mechanical properties of polymer blends.[1,2] Interfacial phenomena, such as interactions, wetting, and reactions between polymers, are very important in polymer processing, and these are complex functions of the chain architecture, the reaction rate, the diffusion coefficients of polymers, the annealing time, the temperature, etc.[3,4] The final physical or chemical properties of polymer blends and alloys depend mostly on the interfacial properties as well as the properties of both component polymers. Since most polymer pairs are thermodynamically immiscible, not enough interdiffusion of molecules exists to create entanglements on both sides of the interface.[5−7] Thus, the interfacial fracture strength between them is very weak.[1,7] A prevalent way of diminishing the incompatibility at a polymer/polymer interface is the addition of a copolymer (often a diblock copolymer). [8−10] Each block of the diblock copolymer is miscible with one of two homopolymers. Sometimes, random copolymers can be more effective than diblock copolymers, because they make multiple “excursions” across the interface.[9,11] In the case of diblock copolymers, the interfacial adhesion strength is a function of the areal density and the chain length of the diblock copolymer.[12]

Another method to improve the interfacial properties and to control the morphologies of polymer blends is reactive (or chemical) compatibilization.[5,13−22] Reactive functionalized polymers form in situ block or graft copolymers at the interface during the blend preparation. It is an attractive alternative to costly block copolymer synthesis. Though such interfacial agents have been used for a long time, the analysis is not simple and unambiguous because experimental measurements of the reaction rates and the diffusion of functional groups to the interface are quite difficult.[10] Also, the complex flow conditions in mixers and extruders make it even more difficult.[13,16]

For polymer blends, the failure mechanism at the polymer/polymer interface depends on the homopolymer pairs. In glassy amorphous polymers, the stress is mainly transferred by entanglements so that the fracture toughness of the interface is negligible until the chains on both sides of the interface are mutually entangled.[12] In systematic studies, Kramer and coworkers[12,18,20] and Boucher et al.[11,21] observed that, in the case of a diblock copolymer where the full length of a block is entangled with its respective homopolymer, the fracture toughness is a function of the areal density of the copolymer chains. The fracture mechanism changes from the chain scission to the crazing depending on the areal density number.[12,18] If failure of the interface occurs by simple chain scission or chain pullout without any extensive plastic deformation, the fracture toughness of the interface is a linear function of the areal density of connecting chains while it scales with the

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10.1021/ma0108259 CCC: $22.00

square of the areal density if the applied stress at the interface is sufficient to activate the bulk plastic deformation mechanism.[12,21]

For a semicrystalline polymer interface, Boucher et al.[11,21] have argued that the mechanism of reinforcement is similar to that observed for glassy polymers. They investigated the reinforcement of the interface between polypropylene (PP) and nylon 6 (Ny6) associated with the incorporation of a small amount of maleic anhydride functionalized PP (mPP), which reacts with the NH_2 group of the Ny6 to form a copolymer in situ. They insisted that the general structure of the plastic deformation zone in the PP was able to transfer some stress laterally in a way similar to that in a craze in glassy polymers.[21] At a reaction temperature above 220 °C, the interfacial fracture toughness was found to be 4 times higher than that for lower reaction temperatures. They attributed this reinforcing effect to the presence of the β-form of PP at the interface and to the subsequent formation of a much larger plastic zone than when the α-form was present at the crack tip. Obviously motivated by Boucher et al.'s work, Cho and Li[22] also investigated the interfacial reinforcement between polypropylene and amorphous polyamide by using in situ reactive compatibilization. They tried to obtain more details about the effect of the crystalline morphology on the interfacial adhesion. Their results were in line with Boucher et al.'s in that the interfacial property of amorphous and semicrystalline polymer pairs in a reactive system was influenced by the crystalline morphology.[21,22] Maleic anhydride grafted polypropylene was used in both studies for the in situ reactive compatibilization. It was melt blended in pure PP at a predetermined weight ratio. After sheets or plaques were formed, they were put into contact with a Ny6 sheet under slight pressure at the molding temperature. For the in situ formation of a copolymer, the functionalized PP has to diffuse to the interface. Thus, the in situ formation of the block copolymer seems to be controlled by the diffusion of functionalized PP molecules and takes a long time to reach the saturation value. This long bonding time can induce some problems in the experimental reproducibility and analysis of the data.

In this research, we investigated the fracture toughness of the interfaces between semicrystalline polymers of polypropylene and nylon 6. For compatibilization at the interface, we used surface functionalization by ion-beam irradiation. We used the surface functionalization method because it is still controversial whether the interfacial kinetics at the reactive interface is controlled by the reaction rate or by the diffusion of molecules to the interface.[23−29] It has been generally accepted that the chemical reaction is controlled by diffusion because of the small translational diffusivity of macromolecules.[25] Simple theoretical analyses of polymer−polymer interfacial reactions (irreversible reactions between end-functionalized polymers at a planar interface) have been done by Fredrickson[23] and O'Shaughnessy and Sawhney[24] independently. According to the theoretical results, the reaction rate constant at the interface depends on the diffusion coefficients, the radius of gyration, the degree of polymerization, and the surface area. However, the rate-determining step is still controversial. Fredrickson and Milner[28] showed that the local reaction proceeded quickly, before the depletion of the reactants at the interface changed it to the diffusion-controlled reaction. O'Shaughnessy and co-workers[26,27] showed that the interface was saturated with functionalized polymers and that the kinetics was controlled by the reaction rate rather than by the diffusion of molecules to the interface. More recently, Macosko et al.[29] experimentally showed that in situ copolymer formation was limited by the reaction rate rather than by the diffusion of reactive chains through the bulk. They monitored the extent of the reactions between the model end-functional polymers at a polystyrene/poly(methyl methacrylate) interface. The measured growth of the interfacial excess with time for different molecular weights could not be well described with theories based on diffusion-controlled interfacial reactions.

Recently we reported that the low-energy ion-beam irradiation method was very effective in modifying the polymer (high-density polyethylene) surface properties.[30] Since the surface functionalization by low-energy ion-beam irradiation is limited to a very shallow surface region, diffusion problems will not be significant. Thus, we investigated the effect of surface functionalization on the interfacial adhesion between two immiscible semicrystalline polymers (polypropylene (PP) and polyamide (Ny6)). The experiments were carried out using Ar^+-ion-beam irradiation under an O_2 environment and involved the introduction of functional groups via chemical reactions with the reactive gas (O_2) at the outer surface of the polypropylene. Most of the functional groups remained in the shallow surface layer (less than 70 Å) of polypropylene. The energy of the ion beam used to modify the polypropylene surface was maintained at less than 1 keV to minimize chain scission or cross-linking of the irradiated PP. After polypropylene surface modification, the modified PP was bonded with nylon 6 to test the effect of the incorporated functional groups on the interfacial toughness between those two polymers. This case is similar to the polymer−solid interfaces with end-tethered polymer chains but is different in that the surface molecules' functional groups can react with chain end groups on the other side. The feasibility of the ion-beam modification process, which depends mainly on the class of the functional groups, the rate of functional group incorporation, and the chemical and the physical properties of modified polymers, and its effect on the interfacial strength between PP and Ny6 are our main concerns. One objective of this work was to explore the variation of the fracture mode with bonding temperature and bonding time.

Experimental Section

Materials. Materials employed in this study were a commercial polyamide (nylon 6) and a polypropylene. Polypropylene was supplied by Honam Petrochemicals (Korea). The weight-average molecular weight, M_w, was 5×10^4 g/mol, and the polydispersity index was 5.95. PP was supplied in powder form without additives such as antioxidants. Nylon 6 was a Kolon product (KN171). The weight-average molecular weight, M_w, was 8.5×10^4 g/mol, and the polydispersity index was 3.5. The pellets (or powder) of Ny6 and PP were dried in a vacuum oven at 100 °C for 24 h. Samples were then made by compression-molding at 180 and 240 °C for PP and Ny6, respectively, with predetermined dimensions. Argon and oxygen gases of 99.99% purity were used.

Ion-Beam Irradiation. The ion-beam-assisted reaction system was composed of a conventional ion-beam system, a reactive gas feeding system, and a stand for the polymer samples or a powder-mixing bowl (Figure 1). The working pressure in the reaction chamber was kept under 10^{-4} Torr. The Ar^+ ion beam was generated from a 5 cm cold, hollow cathode ion source, and its potential energy was maintained

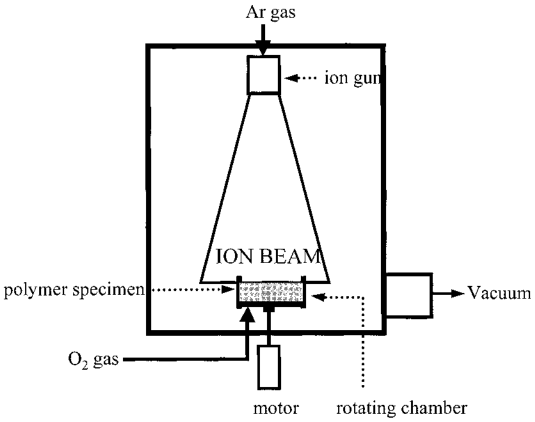

Figure 1. Schematic diagram of the ion-beam irradiation reactor.

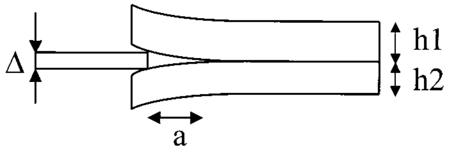

Figure 2. Schematic diagram of ADCB test.

at less than 1 keV. The currents of ions were controlled by the discharge voltage and the ion-beam potential. The discharge current was 0.4 A, and the ion fluence was varied between 1.6×10^{18} and 1.3×10^{20} ions/cm^2. The ion fluence was measured by using a Faraday cup placed slightly above the polymer. The flow rate of Ar gas, which was ionized to Ar^+ by an ion source, was fixed at 2 sccm. Reactive O_2 gas was constantly injected from the bottom of the chamber. The flow rate of the O_2 gas was 3 sccm, which was controlled by a mass flow controller (MassFlo 9121).

Dried PP strips were put in an ion-beam chamber, which was evacuated to less than 10^{-4} Torr. The strips were covered with a circular Faraday cup to protect them from the ion beam before irradiation. Ar gas was injected into an ion gun, and the current density for the appropriate treatment was set by adjusting the discharge voltage and the ion-beam potential. After the ion gun had reached a stable condition and the current density had reached a steady value, the ion-beam irradiation was started. O_2 gas was injected from the bottom of the chamber. After a predetermined period, gas injection was terminated. Then, the irradiated PP strips (2 cm × 4 cm) were clamped with Ny6 strips (2 cm × 4 cm) in an airtight mold under slight pressure. The mold was heated in a temperature-controlled furnace between 180 and 220 °C. The mold was cooled to room temperature in air. All the samples were stored in a desiccator for 24 h prior to fracture testing.

Measurement of Fracture Toughness. The fracture toughness was measured using an asymmetric double cantilever beam (ADCB) test because it has been shown to be a reliable test for the fracture toughness of a polymer interface.[31,32] Details of this test are shown in Figure 2; a blade of thickness Δ was inserted at the interface between PP and Ny6 and was pushed into the sample. Although the materials were semicrystalline, the PP side remained transparent enough at the experimental thickness to allow a video camera to be used to measure the crack length. An image of the region ahead of the blade was recorded after an hour when there was no further increase in the crack length.

Boucher et al.[21] reported that the ADCB test yielded reliable values of the energy of adhesion, Gc, if two precautions were taken. First, the samples had to be asymmetric because the different mechanical properties of the two polymers might induce various modes of fracture. They also noted that varying the ratio of thickness changed the amount of the K_{II} mode in the fracture process[21,33] and that if the fracture tended to deviate into the more ductile material, the measured energy release rate could increase significantly, leading to substantial errors in the evaluation of Gc.[34] To minimize contributions of the second component, all of our samples were made with a thickness ratio h_{PP}/h_{tot} of 0.67 because Gc had a minimum value at a ratio between 0.55 and 0.7.[11] In this system, the Young's moduli of PP and Ny6 are 1.1 and 2.05 MPa, respectively. Because of the lower modulus, the crack would propagate in the PP side if the interfacial stength is strong enough to endure the stress.[11] Also, the critical energy release rate had to be calculated in the proper limit. Since the crack length ahead of the blade, a, was less than $10h_{Ny6}$ for most of our samples, the following equation derived by Boucher et al.[21] based on calculations by Kanninen,[34] whose assumption was that the finite elasticity of the material ahead of the crack tip required correction factors for small crack lengths, was used:

$$\mathrm{Gc} = \frac{3\Delta^2}{8a^4} \frac{E_{PP}h_{PP}{}^3 E_{Ny6}h_{Ny6}{}^3}{E_{PP}h_{PP}{}^3\alpha_{Ny6}{}^2 + E_{Ny6}h_{Ny6}{}^3\alpha_{PP}{}^2} \tag{1}$$

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

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

Surface Characterization. The chemical components on the surfaces of the ion-beam-treated PP and Ny6 were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectrum was recorded using a Surface Science 2803-S spectrometer ($h\nu = 1.5$ keV). A basic pressure of 2×10^{-10} Torr was maintained during the analysis. The energy resolution was 0.48 eV. The XPS spectra were referenced to the main component of the C 1s peak of PP at a binding energy of 284.6 eV. The irradiation treatment generally resulted in a small shift of all peaks (up to ca. 0.6 eV) toward higher binding energies, implying an increased conductivity for the modified surfaces. The overlapping peaks were resolved by using a peak synthesis method based on Gaussian peaks.

Scanning electron microscopy (SEM) observations of the samples were performed on a Hitachi S-2500C. Fractured surfaces were coated with gold in an SPI sputter coater. The morphology was determined using an accelerating voltage of 15 keV.

Results and Discussion

Characterization of Ion-Beam-Treated Polypropylene Surface. Surface modification of polypropylene using an Ar^+ ion beam was carried out in an active O_2 environment. In our previous study[30] it was observed that the ion-beam-irradiated high-density polyethylene surface was covered with oxygen-containing functional groups without severe degradation of the bulk polymer. Since the modification proceeds within a relatively shallow depth beneath the surface, the bulk properties of the ion-beam-treated polymer do not change remarkably. To investigate the depth of incorporation of oxygen into the polymer, we performed a dynamic XPS characterization. Figure 3 shows the O/C atomic ratio as a function of the etching time (or depth from surface). The etching rate was calibrated to 30 Å/min for SiO_2 by using a 3 keV Ar^+ ion beam. The modified surfaces were saturated up to ca. 20% with oxygen. The oxygen content decayed exponentially. The depth of modification with Ar^+ ions was about 70 Å, which was less than the radius of gyration of PP (calculated R_g of PP is about 100 Å).[35,36] The reaction proceeding below the surface

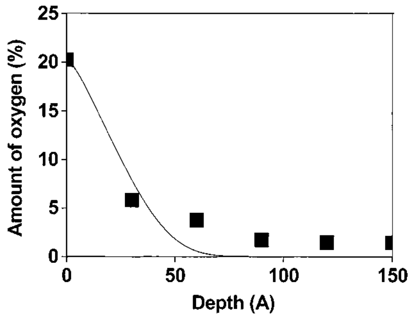

Figure 3. Ar^+ ion-beam penetration depth into the polypropylene at the treatment time of 1 min. The line is theoretically calculated by using binary collision Monte Carlo simulation code, TRIM.[35]

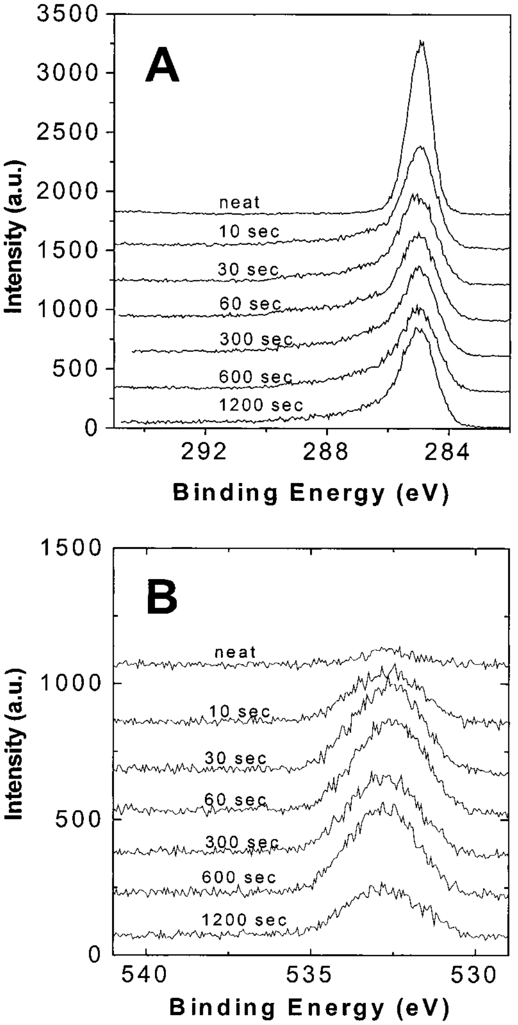

Figure 4. (a) C 1s XPS spectra of polypropylene with various treatment times. (b) O 1s XPS spectra of polypropylene with various treatment times.

is ascribed to surface roughening during the ion-beam irradiation.[30,37]

Figure 4 shows the characteristic modification of the C 1s and O 1s peaks for untreated and ion-beam irradiated samples. The peak synthesis and the assignment of components were performed according to data in the literature.[38,39] The C 1s peak for untreated PP is symmetrical, and its full width at half-maximum is narrow, 1.54 eV. On the other hand, the C 1s peak of ion-beam-irradiated PP is asymmetrical because of the carbon oxidation and can be decomposed into one main peak and three small peaks by using a Gaussian peak-fitting code. The C 1s peak of the untreated sample shows the location of the C–C peak to be at 284.6 eV. In the case of the irradiated PP, the binding energy of the carbon peak is slightly shifted to higher energy (285 eV), as we mentioned above. Three other peaks appear. The one at 286.5 eV is assigned to the C–O peak, the second at 288.2 eV is assigned to the C=O peak, and the third at 289 eV is assigned to the O=C–O peak. The energies of these new peaks in the treated sample indicates that the surface of PP was sufficiently activated by Ar^+ ion irradiation to react with oxygen molecules, which produced covalent bonds between the carbon atoms and the oxygen atoms. This fact can be corroborated by the O 1s peak. Figure 4b shows the C=O peak at 532 eV and the C–O peak at 533.6 eV. The intensity of C–C bond or C–H bond decreased while that of the carbon–oxygen bond increased with increasing irradiation. The O/C atomic ratio increased with the irradiation time, rapidly reached almost a plateau value, and then slowly decreased. In the conventional ion-irradiation process, ion irradiation of a polymer by reactive or inactive gases skews the C 1s peak at a binding energy of 284.6 eV to a higher energy between 285 and 289 eV, but with a decreased peak height, which means the main chemical bonds on the polymer surface have become carbon–carbon bonds.[38] The variations of the functional group intensity with irradiation time are displayed in Figure 5. The number of C–O bonds in the irradiated PP is higher than the number of C=O bonds, and the ratio of the former to the latter varies with irradiation time in the range between 2.2 and 5.3. It is clear that the decrease in the functional group concentration for a long irradiation is due to the functional group disappearing faster than it is being generated during irradiation, which is attributed to a degradation of the functional groups and movement of the functional groups to the bulk side. Though not shown here due to the space limit, FT-IR spectroscopy shows that the ion-beam-irradiated PP surface has new peaks at 1140, 1270, and 1740 cm^{-1}, which correspond to the C–O symmetric stretching mode and the C–O antisymmetric stretching mode and the C=O stretching mode, respectively. These peaks prove that surface functionalization of PP occurred.

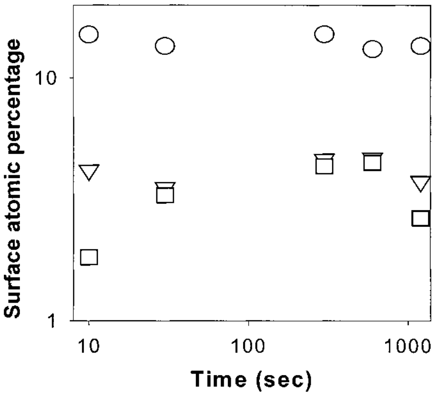

Figure 5. Variation of C–O (○), C=O (▽), and O–C=O (□) functional group contents at the surface of PP with increasing irradiation time.

Fracture Toughness with Bonding Time and Temperature. The fracture toughness vs the annealing time is plotted in Figure 6. Some facts are worthy of note. First, the introduction of surface functional groups onto the PP chains resulted in a substantial improve-

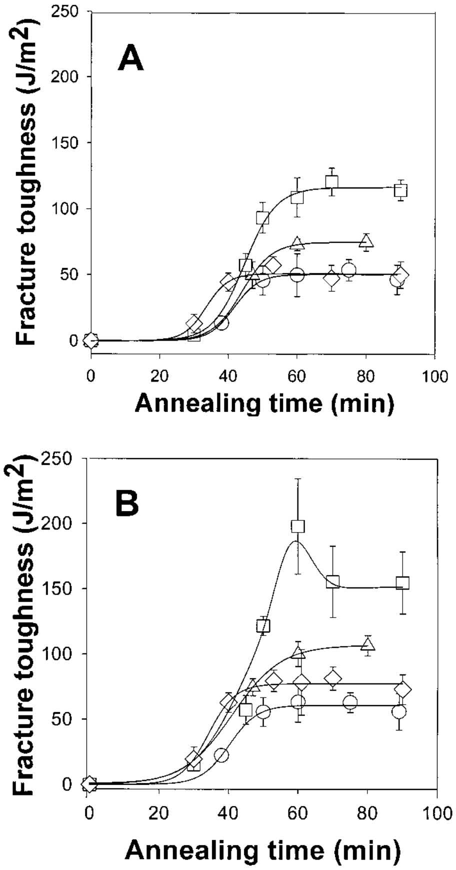

Figure 6. Variation of fracture toughness of IBPP/Ny6 with bonding time. (A) PP surface was irradiated with Ar^+ ion beam only. (B) PP surface was irradiated with Ar^+ ion beam under O_2 environment. Annealing temperatures are (○) 180, (△) 190, (□) 200, and (◇) 210 °C. The lines are guides for the eyes.

ment in the fracture energy for the PP and Ny6 interface. For example, the interface strength of the O_2-functionalized PP−Ny6 interface for a bonding temperature of 200 °C reaches 155 J/m^2. The interfacial fracture toughness for each temperature series increased with bonding time and then reached a plateau. Second, a system with reactive oxygen gas added shows a higher fracture toughness than a system that had only been treated with an Ar^+ beam. Third, the fracture toughness has its highest value at a temperature of 200 °C and then decreases with increasing temperature. Fourth, the fracture toughness increased after some induction time of annealing because of the wetting process between the two polymers.[40,41] Fifth, the fracture toughness obviously shows a maximum for a bonding time of around 60 min for the case of a 200 °C bonding temperature though it is less obvious in other cases.

For a usual reactive compatibilization system, such a PP/PA system with mPP added, the amine end groups of polyamide and maleic anhydride grafted polypropylene easily react to form covalent bonds during processing.[21,22] As mentioned in the Introduction, it has been accepted that the chemical reaction occurring at the interface of reactive blending for polymers is controlled by diffusion, a consequence of the small translational diffusivity of macromolecules.[25] However, recent studies go against this opinion; i.e., the interface is saturated with functionalized polymers and is in a reaction-controlling regime.[26−29] Actually, either process, diffusion or reaction, could govern the interfacial reaction kinetics, especially in the initial stage of adhesion. The parameters affecting the rates of diffusion and reaction are the temperature and the initial concentration of the functional groups. An elevated temperature will increase both rates. For a precise interpretation, we need to know the effects of the annealing temperature and the initial concentration. The former is taken into consideration in this work, but the latter cannot be because we cannot precisely control the amount of functional groups on the polymer surface. Thus, only the effect of bonding temperature is examined in this study, but it provides some clue to the interreaction at the interface.

As the intermolecular reaction between activated PP molecules and PA molecules proceeds, the fracture toughness increases. When a critical surface coverage of interacted molecules is attained, further reaction at the interface becomes rare due to the consumption of functionalized groups at the interface and little diffusion of functionalized groups from the deeper bulk side to the interface.[17,41] As we noticed, however, the functionalization depth was less than the radius of gyration of a PP molecule.[36] Therefore, it is reasonable to assume that diffusion of the functionalized molecules to the interface does not affect the interface reaction; hence, the interface fracture toughness reaches a plateau. This is different from another interpretation for the reactive blending system in which mPP molecules are dispersed in PP rather than concentrated at the interface.[21,22] For a Ny6/(PP + mPP) adhesive joint, Cho and Li reported that the number of copolymers formed in situ at the interface increased with bonding time at a constant bonding temperature.[22] On the basis of the assumption that the chemical reactions occurring at the interface for reactive blending are being controlled by diffusion, they concluded that the critical areal densities of copolymers at the interface increase with bonding temperature and then reach a saturation point where the reactions do not occur near the interface due to the steric hindrance caused by high areal densities. In our case, a large portion of the modified surface molecules stay at the interface though some functionalized molecules may exist slightly below the interface due to the penetration of the ion beam. However, still the penetration depth is within the radius of gyration of the PP molecules. This is evident in the XPS measurement.

Since the cooling conditions for each series were the same, the early enhancement of interfacial adhesion with bonding time was mainly due to an increase in the number of intermolecular reactions at the interface. Boucher et al.[11,21] observed that the energy of adhesion for mPP/Ny6 scaled linearly with the amount of copolymer in the regions of simple chain pullout or chain scission whereas it increased with the square of the density when one of the polymers crazes during separation. Regardless of the conditions for forming the samples, they obtained an exponent of 2.03 ± 0.18 for the fracture toughness vs the areal density of copolymers. If we accept Boucher et al.'s argument, a higher fracture toughness implies that a crack will propagate in the bulk material on the lower yield stress (PP side).[11] Details are discussed again later.

Figure 7 shows the fracture toughness as a function of the bonding temperature. It shows a maximum at 200 °C and then decreases. At 200 °C, the energy of adhesion is saturated after 60 min near 110 J/m^2 for an Ar^+-activated PP/Ny6 interface and 155 J/m^2 for an O_2-

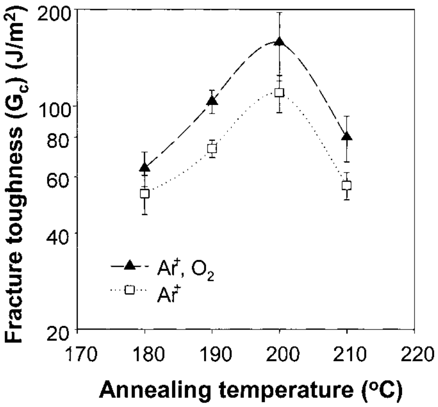

Figure 7. Variation of fracture toughness between IBPP and Ny6 with annealing temperatures at two different irradiation conditions (after 90 min of annealing time): (□) only Ar$^+$ ion beam irradiated and (▲) Ar$^+$ ion beam irradiated under O$_2$ environment.

functionalized PP/Ny6 interface. Raising the temperature to 210 °C accelerated the rate of the fracture toughness increase but decreased the saturation value. A low bonding temperature of 180 °C leads to an interfacial toughness of about 60 J/m^2 for an Ar$^+$-activated PP/Ny6 interface and 80 J/m^2 for an O$_2$-functionalized PP/Ny6 interface after annealing time of 60 min. The interaction or reaction occurring at the interface is possibly a chemical reaction forming a covalent bond between irradiated PP and Ny6. This interaction is not a physical one because it increases with temperature until 200 °C. Most physical interactions decrease with the system temperature. Another reason for a chemical reaction is the time-dependent behavior and the activation energy. This is discussed later. If the interaction is solely physical, no time dependence of the fracture toughness should exist at a constant bonding temperature. The growth rate increases with temperature due to faster reactions. The interface gains most of the adhesion strength more rapidly with higher bonding temperature. From this behavior, we exclude the possibility of diffusion control for the ion-beam-irradiated samples that were in a solid state before bonding. Cho and Li also observed a maximum in the saturation interfacial fracture toughness at around 170 °C, which they ascribed to a different morphology around this temperature due to the different melt behaviors of PP and mPP. However, their models cannot plausibly explain our results. PP molecules are in the melt state at all bonding temperatures in this study. Thus, neither PP crystallinity nor Ny6 melt strength would have any influence.

Fracture Mechanisms. The strength of interfacial adhesion is determined by the adhesive strength at the interface and by the cohesive strength of both polymers, which depends on the state of individual chains. Depending on the intrinsic failure energy of the interface, failure prefers the weaker of the two. The locus of failure was analyzed by using microscopic examination and XPS analysis. Figure 8 shows SEM micrographs of the fractured surface on the PP side for a series of typical specimens bonded at 200 °C. Parts b and c of Figure 8 are SEM micrographs of the fracture surface on the PP side for the ion-beam-irradiated specimen without/with an O$_2$ environment. When only an ion beam without an O$_2$ atmosphere was used, PP molecules and Ny6 molecules interacted less than the case with an O$_2$ gas because fewer functional groups on the PP surface, which resulted in a lower fracture toughness and a less rugged fracture surface. However, interactions due to functional groups appended after exposure to the atmosphere are still enough to build up some stress at the tip of the crack during crack propagation. Since the yield stress of polypropylene is much lower than that of polyamide, the crack tends to propagate in the bulk of the material with the lower yield stress, i.e., polypropylene, when the interface is strong.[11] Cleaved PP surfaces irradiated under an O$_2$ atmosphere are rougher and more rugged, which implies more crack propagation in PP side. Since the PP used in this study has a molecular weight much higher than the critical value for effective chain entanglements, complete cohesive failure is observed in the case of the ion-beam-irradiated specimen.

Time dependence of the fracture toughness substantiated the interaction between the functional groups as the chemical one. Another definite evidence for the chemical interaction can be provided from the activation energy value. In a very recent study, Oyama and Inoue experimentally demonstrated that pseudo-first-order kinetics fits well the data of coupling reaction between functionalized polymer chains at immiscible polymer−polymer interfaces over the whole time scale.[42] They proposed a new reaction model, in which coupling reaction is viewed as involving the formation of a two-dimensional monolayer on the interface surface by copolymers formed in situ. This scheme is ideally suited to our system.[43] Using the relationship with the fracture toughness,[21] the areal density of copolymers formed in situ at the interface, Σ, was calculated. Since the cohesive strength comes into play in late period at the high reaction temperature, we selected the reaction time less than 45 min from the starting moment of the reaction after induction period. The values of saturation areal density of copolymer, Σ^*, was set as Σ value at the latest time. Plotting the calculated $\ln(\Sigma^* - \Sigma)$ vs time showed a reasonable relationship although data points were a little bit scattered later due to the deviation in the fracture toughness. However, it was much better than the second-order plot ($1/(\Sigma^* - \Sigma)$ vs time). According to Oyama and Inoue's model, this implies that the overall coupling kinetics is reaction controlled.[42] From the reaction rate constant values obtained by using the first-order reaction kinetics, the activation energy was calculated. Despite the scattering of Σ values in late period, the reaction rate constant vs $1/T$ gives a good linear relationship (Figure 9). The calculated activation energy was 97.8 kJ/mol. As Oyama and Inoue explained, this is another important information to judge whether interreaction kinetics are controlled by reaction or diffusion; the diffusion-controlled mechanics has a low activation energy of <30 kJ/mol because it involves a physical process, whereas the reaction-controlled mechanism has a higher activation energy because it involves a chemical process.[42] Therefore, the calculated activation energy of 97.8 kJ/mol from the reaction strongly suggests that the coupling kinetics are reaction-controlled.

The schematic bonding dynamics at low and high temperatures are shown in Figure 10. Molecules having functional groups for the reaction at the interface are found to have a strong tendency to move to the interface, resulting in a large concentration gradient near the interface.[41] At low temperature, the number of the

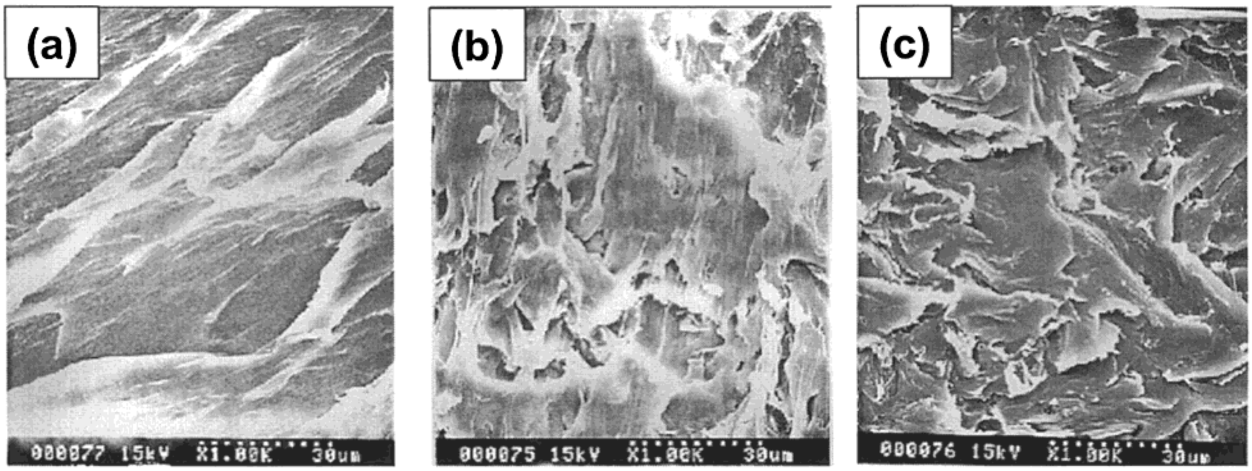

Figure 8. Photographs of the cleaved PP surface after bonding with Ny6 for 1 h at 200 °C: (a) untreated, (b) Ar^+ ion beam irradiated, and (c) Ar^+ ion beam irradiated under O_2 environment.

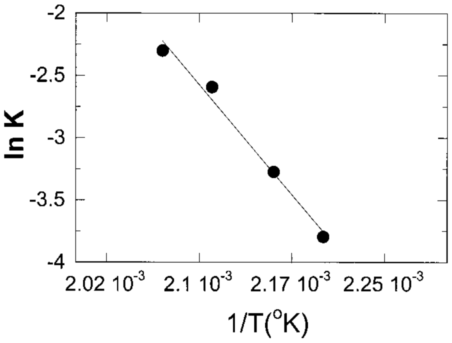

Figure 9. Plot of ln *K* vs 1/*T* (K) where *K* is the first-order reaction rate constant.

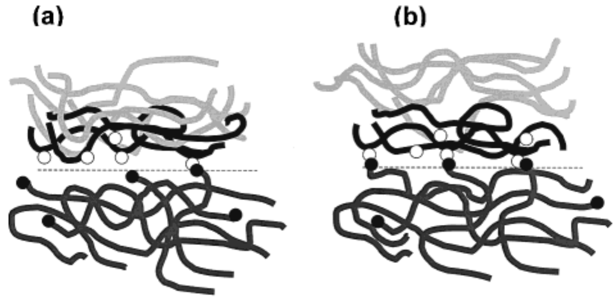

Figure 10. Schematic representation of interfacial chain restructuring with reaction at the interface: (a) low temperature; (b) high temperature. Black lines are functionalized PP chains. Light gray lines are pure PP chains, and dark gray lines are Ny6 chains. Empty and filled circles represent the functional groups on the PP molecules and Ny6 molecules (amine groups). At low temperature, the number of the reacted molecules is small. The functionalized chain keeps its entanglement with other PP chains. At higher bonding temperatures, more reptations and reactions occur for functionalized molecules, but fewer entanglements with other chains occur due to functionalized chains occupying the interface and other chains moving to the low-energy bulk side. The adhesion strength increases with temperature due to more reaction at the interface while the cohesive strength decreases with temperature due to fewer entanglements with other bulk chains. Therefore, an optimum temperature exists for the maximum interface strength.

reacted molecules is small. The functionalized chain keeps its entanglement with other PP chains. Once a functionalized PP molecule reacts with Ny6 molecules at the surface, the whole PP chain forms a branched or tethered chain. Increasing the temperature increases the interreaction and hence the adhesion strength. At higher bonding temperatures, more reptations and reactions occur for functionalized molecules, but fewer entanglements with other chains occur because functionalized chains are still occupying the interface and other chains are moving to the low-energy bulk side. Since the restructuring time of a branched or tethered chain is much longer than that in the bulk,[40] other chains should penetrate into the surface molecules to form entangled chains. However, the interface is already crowded with the functionalized and reacted molecules, and the high energy at the interface hinders the movement of other chains to the interface. The faster the reaction occurs, the faster the movement of other chains from the interface proceeds, and fewer chains move to the interface. The time dependence of adhesion can be compared to the reptation time of pristine PP chains, which is on the order of 0.1 s.[44] This is several orders of magnitude smaller than the corresponding time scales of the bonding time. The cohesive strength then decreases with temperature due to fewer entanglements with other bulk chains. Therefore, an optimum temperature exists for the maximum interface strength.

Now we explain the reason for the appearance of maximum fracture strength at 200 °C. XPS analyses of the cleaved surfaces are shown in Figure 11. On the PP side, the shape of the C 1s peak in the spectrum is almost that of the pure PP surface (Figure 11a) while the intensity of the incorporated oxygen has rapidly decreased for samples irradiated under an active O_2 environment (Figure 11b). The disappearance of oxygen functionalities is due to a transfer of PP chains onto the surface of the Ny6 phase. SEM photographs (Figure 8) clearly show that the crack propagates into the PP phase because of a very strong interaction at the interface, thus leading to the disappearance of oxygen moieties. The increased intensity of the C 1s spectrum and the decreased intensity of the O 1s spectrum in the Ny6 phase (Figure 11c,d) are definitely due to the coverage by PP molecules. Table 1 lists the elemental compositions of the fractured PP and Ny6 surfaces as measured by XPS. The key elemental difference between PP and Ny6 is the presence of nitrogen in Ny6. In all of the tested fractured joints, we found no nitrogen on the PP side. The amount of nitrogen on the Ny6 side decreased at first with the bonding time, implying the presence of PP on this side, and then increased later. The amount of oxygen does not vary noticeably after

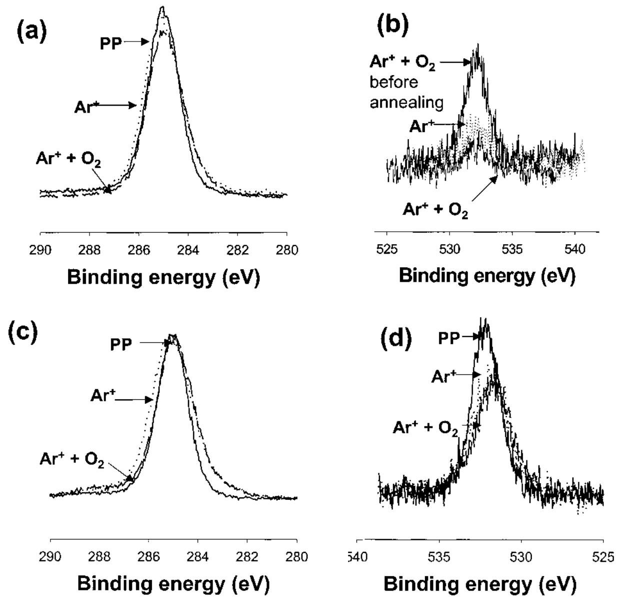

Figure 11. (a) C 1s and (b) O 1s XPS spectra of the cleaved PP surface after annealing for 1 h at 200 °C with Ny6. Lines are for untreated PP (—), Ar^+-irradiated PP (· · ·), and Ar^+-irradiated PP under O_2 environment (— — —). (c) C 1s and (d) O 1s spectra of the cleaved Ny6 surface after annealing for 1 h at 200 °C with PP. Lines are for Ny6 surface bonded with untreated PP (—), Ar^+-irradiated PP (· · ·), and Ar^+-irradiated PP under O_2 environment (— — —).

Table 1. Elemental Compositions of Fractured PP ($Ar^+ + O_2$) and Ny6 Surfaces Measured by XPS (Bonding Temperature 200 °C)

	PP	Ny6	
annealing time, min	% O	% N	% O
30	5.4	7.2	11.6
60	3.7	3.9	7.1
90	5	5.9	8.6

Table 2. Elemental Compositions of Fractured PP ($Ar^+ + O_2$) and Ny6 Surfaces Measured by XPS (Bonding Time 1 h)

	PP	Ny6	
annealing time, °C	% O	% N	% O
180	6.1	5.7	7.8
190	5.1	5.2	7.6
200	3.7	3.9	7.1
210	7.2	5.3	9.8

90 min. Again, initial decrease is obviously attributed to an increased interaction with long bonding time. Later time dependence is related to the movement of other PP chains. The other PP chains move away from the highly energetic interface, so a long bonding time provides more relaxation time for other chains to have fewer entanglements with the molecules at the interface, as well as more reaction time for the functionalized chains (Figure 10). Thus, the cohesive strength becomes weaker, and fewer chains transferred to the Ny6 side. Therefore, we can conclude that the fracture toughness at first increased with annealing time because of increased adhesive strength due to interfacial reactions, passed a peak, and then decreased to a plateau value because of a critical surface coverage by interacted molecules and reduced cohesive strength.

Table 2 shows the XPS spectra for the fractured joints bonded for an hour at different temperatures. The amount of oxygen on the PP side decreased until 200 °C because more PP chains transferred to the Ny6 side and then increased at 210 °C because fewer PP chains transferred. Recent experimental work by Lee and Wool[41] shed light on the similar adhesion behavior between an adsorbed chain (carboxylated butadiene) and a substrate (Al_2O_3 having amine groups on its surface). They ascertained that the two intrinsic failure energies are not independent of each other at equilibrium since the gain in the intrinsic adhesion strength is related to the enthalpic adsorption energy of the chain, and the decrease in the intrinsic cohesive failure energy is related to the entropy loss of an adsorbed chain collapsing to an attractive surface.[41] In our case, the entropic loss of a reacted PP chain at equilibrium can be related to a decrease in intrinsic cohesive failure. Thus, an optimum bonding temperature exists, which is the consequence of increased adhesion strength at the interface due to the rapid reaction with the bonding temperature and reduced cohesive strength due to fewer entanglements with the PP molecules in the sublayer (Figure 10).

Conclusions

In this study, it was experimentally demonstrated that an ion-beam-assisted gas reaction is a very efficient technique for changing the polymer surface properties by incorporating functional groups. Since the modification proceeds in a relatively shallow depth from the surface, the bulk properties of the ion-beam-treated polymer do not change remarkably. A low-energy ion beam can penetrate and modify a polymer surface to depths of less than 70 Å. The number of functional groups reached a saturation value soon. They slowly disappear from the surface because of slower generation rate than sputtering rate and movement of the functionalized chains to the low-energy bulk side.

The interfacial fracture toughness between semicrystalline polyamide and semicrystalline polypropylene was substantially enhanced. Systems with reactive oxygen gas added showed higher fracture toughness than a system treated only with Ar^+ irradiation. We believe this to be the result of an interreaction between the PP surface functional groups (mostly carboxyl groups) and the amine end groups of Ny6.[30] The coupling reaction follows the pseudo-first-order kinetics more reasonably than the second-order kinetics. This indicates that the coupling process is reaction-controlled.[42] A large activation energy value (97.8 kJ/mol) for the reaction is strongly in favor of this coupling reaction kinetics.

For an ion-beam-irradiated PP surface bonded at high temperature, the adhesive strength at the interface is strong enough to induce crack propagation into the PP phase. XPS results corroborate these explanations. The decrease in the fracture toughness with higher temperature is attributed to a change in the fracture mode at higher temperature. The adhesive strength at the interface increases with temperature due to more reactions at the interface while the cohesive strength of PP decreases with temperature due to fewer entanglements of PP molecules at the interface with other chains in the bulk. This result is different from other studies[11,21,22] in which diffusion of functionalized molecules (mPP) to the interface and the experimental temperature range pose problems for proper interpretation. Our system is more like a tethered chain problem with reactions occurring at the interface.[41]

The fracture toughness increased with bonding time and then reached a plateau for each temperature series.

As the interreaction between activated PP molecules and PA molecules proceeds, the fracture toughness increases. After a critical surface coverage by reacted molecules, further reaction at the interface becomes rare due to the consumption of functional groups at the interface and less diffusion of the other chains from the bulk side due to the crowded condition at the interface. On the other hand, a long bonding time provides more relaxation time for other chains to escape from the high-energy interface; hence, the cohesive strength becomes weaker after a long bonding time. Therefore, the interface fracture toughness reaches a plateau. The appearance of a maximum at 200 °C is attributed to this change.

Acknowledgment. This work was supported by KIST (2E16982) and KRCFST (2N22850).

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(43) In Oyama and Inoue's paper,[42] four assumptions were made in order to explain the mechanism of the coupling reaction: (1) a flat interface, (2) the copolymers formed by the reaction stay at the interface, (3) the coupling reaction proceeds two-dimensionally on the interface plains, and (4) a monolayer-like quantity develops at the interface. Since we used plate specimens, the first assumption is automatically satisfied. Also, the surface functionalization occurs at random position on the surface molecules. After the first coupling reaction, the chain becomes a graft copolymer of star shape. Its motion changes from the reptation of a linear chain to a star-arm-like retraction motion. The time scale of the arm retraction motion is known to be very long. Hence, it stays at the interface. The third assumption means the interfacial thickness should be small. This is naturally satisfied due to the shallow functionalization. The fourth assumption means there is a limiting value to the copolymer density required to saturate the surface. Long time behavior of the fracture toughness reaching the plateau grants this assumption.

(44) This was calculated by using the equation $T_r = R_{||}^2/(3\pi^2 D)$, where $R_{||}$ and D are the end-to-end distance and the self-diffusion coefficient.[41] $R_{||}$ was calculated using the relationship with M_w (Zirkel, A.; Urban, V.; Richter, D.; Fetters, L. J.; Huang, J. S.; Kampmann, R.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 6148). D value in the literature[11] was used after recalculation at different temperatures.

MA0108259