

# Improvement of Adhesion Between Polyaniline and Ion-Assisted-Reaction-Treated Polypropylene

Cheol-Su Lee,<sup>1,2</sup> Sung Han,<sup>3</sup> Young-Whoan Beag,<sup>3</sup> Jin-Soo Joo,<sup>1</sup> Seok-Keun Koh<sup>2,3</sup>

<sup>1</sup>Department of Physics, Korea University, Seoul 136-701, South Korea

<sup>2</sup>Thin Film Technology Research Center, Korea Institute of Science and Technology, Seoul 130-650, South Korea

<sup>3</sup>P&I Corporation, Seoul 131-221, South Korea

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**ABSTRACT:** A nonwetable polypropylene (PP) surface was modified by an ion-assisted reaction (IAR) to improve its adhesion with a conjugated polymer, polyaniline (PAN). Hydrogen ions with energies ranging from 0.6 to 1 keV were irradiated on the PP surface in an oxygen gas environment. Ion doses were in the range  $5 \times 10^{14}$  to  $1 \times 10^{17}$  ions/cm<sup>2</sup>. The lowest static wetting angle of the irradiated PP without blowing oxygen gas was about 60°, but that of IAR-treated PP was less than 10°; the surface free energy of the modified PP was larger than 64 dyne/cm, and adhesion between PAN and PP passed the Scotch tape test. The main contribution to

this improvement was the high concentration of hydrophilic groups on PP. Surface chemistry was investigated by X-ray photoelectron spectroscopy, and hydrophilic functional groups such as C—O, C=O, (C=O)—O were not washed with water. Surface morphology was observed with atomic force microscopy, and surface roughness changed from 8.30 to 20.8 nm after the treatment. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 258–265, 2003

**Key words:** conjugated polymers; poly(propylene) (PP); adhesion

## INTRODUCTION

Since the discovery of conjugated polymer in early 1970s, various types of studies have been carried out for applications such as rechargeable batteries,<sup>1</sup> electrolytic capacitors,<sup>2</sup> electrochromic smart windows,<sup>3</sup> electromagnetic shielding,<sup>4</sup> fibers,<sup>5</sup> flexible LEDs,<sup>6</sup> nanomaterials,<sup>7</sup> quantum wires,<sup>8</sup> thin film transistors,<sup>9</sup> sensors,<sup>10</sup> biomedical instruments,<sup>11</sup> and so on.

Among the various types of conjugated polymers, polyacetylene, polyaniline (PAN), polypyrrole, polythiophene, polyphenylenesulfide, and polyphenylenevinylene have been studied intensively because of their light weights, easy manufacturing processes, easily controlled electrical conductivity by doping, mass production, and so on, but adhesion to polyolefin insulators such as polyethylene, polypropylene (PP), and polystyrene has not been satisfactory in industrial applications because of low wettability and nonreactivity.

To enhance the adhesion between two materials, various types of surface modifications have been studied to make the substrate surface hydrophilic. The physical methods of the modification of polymers have been investigated with plasma treatment,<sup>12,13</sup> ion-beam mixing,<sup>14</sup> corona discharge,<sup>15</sup> ultraviolet-ozone treatment,<sup>16</sup> laser treatment,<sup>17</sup> X-ray irradiation,

e-beam treatment, heat treatment, metallization, sputtering, and other methods. Chemical methods such as direct chemical reaction,<sup>18</sup> surface grafting,<sup>19</sup> and so on have also been tried. Because these methods use high energies, the substrate gets damaged, and it is difficult to get not only satisfactory adhesion but also reproducibility and controllability in industrial applications. To avoid these phenomena, in this study the ion energy was lowered in the surface modification. To reduce molecular damage by ion-beam bombardment of the polymer chain, low-energy hydrogen ions having light weights and deep penetration depths were used instead of argon ions, as used in a previous study.<sup>20</sup> The mechanism of hydrophilic group formation on the surface of a polymer substrate by an ion-assisted reaction (IAR) was already reported previously with a two-step model.<sup>20</sup>

In this work, the relation between adhesion properties and the surface free energy of IAR-treated polymers with a hydrogen ion beam was investigated. Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) data showed the correlations among the polar force (PF), dispersion force (DF), roughness, and the hydrophilic groups.

## EXPERIMENTAL

PAN as a conjugated polymer was used because it has high electrical conductivity and is more stable in air compared to other conjugated polymers.<sup>21,22</sup>

The commercial PP used in this experiment had a water wetting angle of 93°. PP was cut to a size of 0.5

Correspondence to: C. S. Lee (gocharles@kist.re.kr).

$\times 15 \times 50 \text{ mm}^3$ . A cold, hollow, cathode-type ion source was used for the IAR treatment because it could generate reactive gas ions such as hydrogen and oxygen.

Hydrogen ions were difficult to generate in the cold, hollow, cathode ion source because of a low scattering yield and a high ionization energy. A mixture of hydrogen and argon ion gas was used to get the initial discharge. The addition of hydrogen gas and the reduction of argon gas was used to obtain a high concentration of hydrogen ion beams from this initial discharge. The optimum quantity of hydrogen gas and argon gas was 4 and 1.25 standard cubic centimeters per minute (sccm), respectively.

The ion energy was varied from 0.6 to 1 keV. The oxygen gas blown on the surface of PP was controlled from 0 to 8 sccm by a mass flow controller, and the ion dose was varied from  $5 \times 10^{14}$  to  $1 \times 10^{17}$  ions/cm<sup>2</sup>. The base pressure inside chamber was  $2.5 \times 10^{-5}$  Torr, and the working pressure was about  $1.5 \times 10^{-4}$  Torr during the IAR treatment. The surface of PP was thus modified by controlling the ion-beam energy, amount of blown oxygen gas, and ion dose.

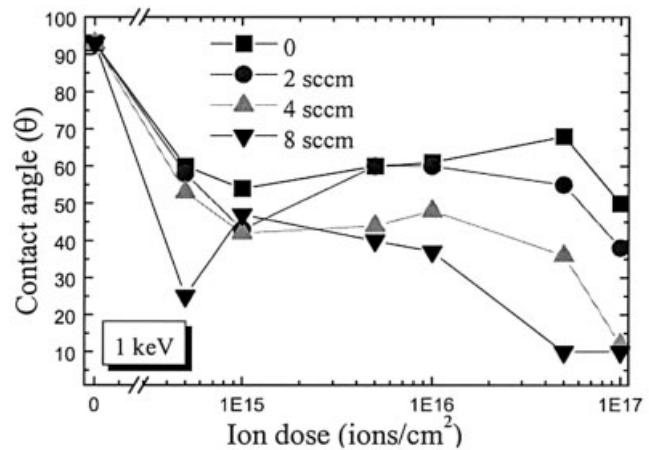
The wetting angle of IAR-treated PP was measured with a contact anglemeter (Tantec-CAM Micro). After the IAR treatment of the PP, each set was kept in deionized water and air. The average values of the static wetting angles of the modified PP to water and formamide were calculated after cleaning with dry N<sub>2</sub> gas. The variation of wetting angle against time elapse showed different trends in two different conditions. The surface free energy of PP was calculated by the well-known Young's formula:

$$\cos \theta \gamma_{lv} = \gamma_{sv} - \gamma_{sl} - \pi_e$$

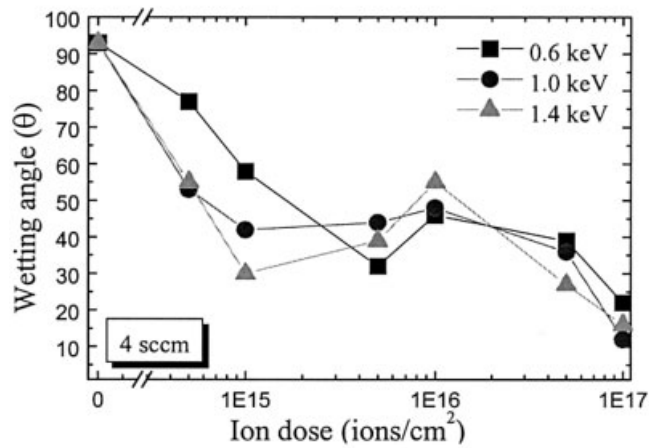
where  $\gamma_{lv}$ ,  $\gamma_{sv}$ , and  $\gamma_{sl}$  are the free energies of the liquid and solid against their saturated vapor and that of the interface between liquid and solid, respectively, and  $\pi_e$  is the equilibrium pressure of the adsorbed vapor of the liquid on the solid.

For comparison of the surface roughness of the IAR-treated and untreated PP, AFM images were obtained with PSI Autoprobe-M5. XPS measurement was carried out to analyze the newly formed chemical bonds on the IAR-treated PP surface.

To study the improvement of adhesion on the surface of the treated PP, we dipped the IAR-treated PP into the PAN solution. After drying the sample at room temperature, we made the crosscut experiment for these dried PAN into  $1 \times 1 \text{ mm}^2$  with a total matrix area of  $10 \times 10 \text{ mm}^2$ . The 3-M Scotch tape test was performed. The results were observed with an optical microscope, and PP showed improved adhesion with the PAN under all conditions. To get the electrical conductivity of PAN, we doped the conjugated poly-



(a)



(b)

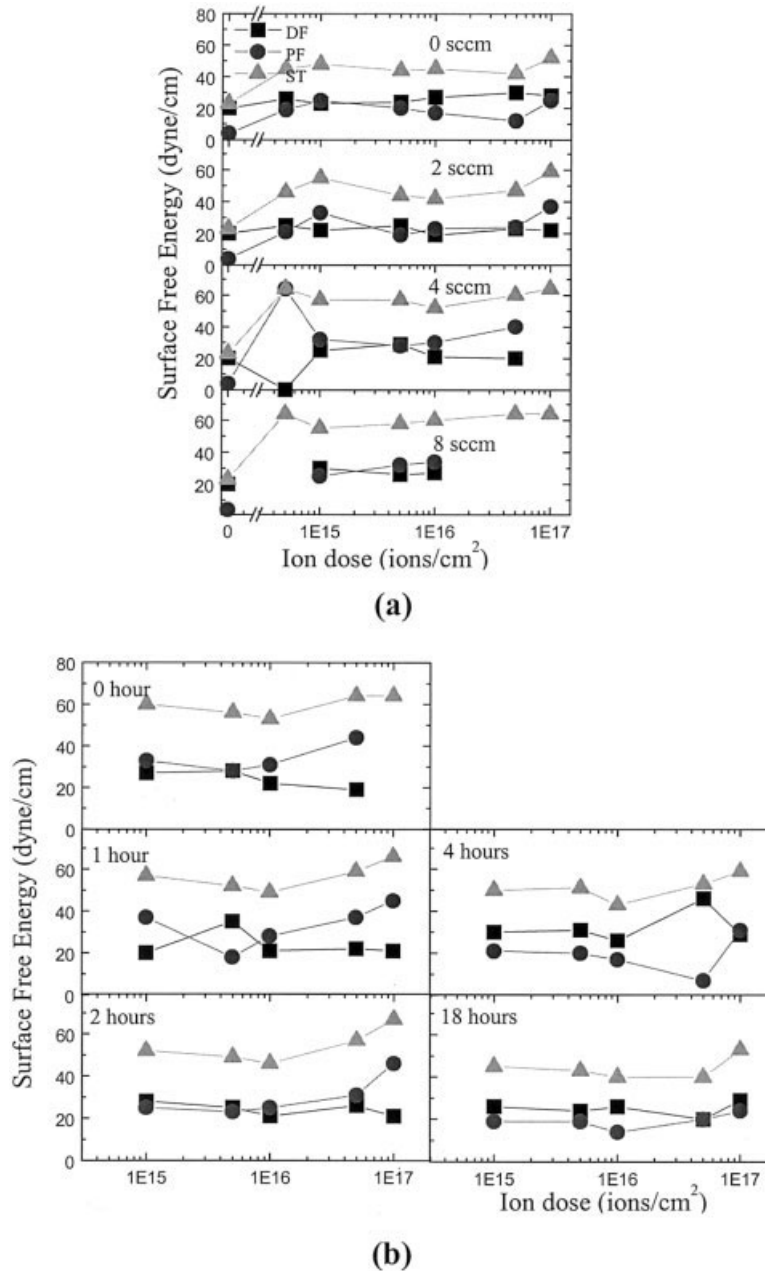
**Figure 1** Variation in the wetting angles of IAR-treated PP under different conditions: (a) change of oxygen gas flow at a fixed ion energy of 1 keV and (b) change of ion energy at a fixed oxygen gas flow.

mer by HCl. Also, the 3-M Scotch tape test was performed.

## RESULTS AND DISCUSSION

The variation of wetting angles with ion dose of untreated and IAR-treated PP are shown in Figure 1. The PAN could not coat well on the hydrophobic PP surface. The wetting angle of untreated PP was 93°. When the ion beam of the hydrogen and argon mixture gas was irradiated on the PP surface without an oxygen gas environment, the wetting angle decreased 50–70° with the increase of ion dose at an ion energy of 1 keV.

In the case of IAR-treated samples by the hydrogen ion beam, the wetting angles decreased with increase of ion dose in a fixed oxygen environment. Also, at a fixed ion dose, the wetting angles were decreased with increasing oxygen gas. The minimum value of the



**Figure 2** Variation in the surface energy of IAR-treated PP under different conditions: (a) change of oxygen gas flow at a fixed ion energy of 1 keV, (b) an ion energy of 1 keV and an oxygen gas flow of 4 sccm in air, and (c) an ion energy of 0.6 keV and an oxygen gas flow of 4 sccm in deionized water.

water wetting angle was less than  $10^\circ$  for the samples treated at 1 keV energy with an oxygen environment of 8 sccm and ion doses of  $5 \times 10^{16}$  and  $1 \times 10^{17}$  ions/cm<sup>2</sup>, as shown in Figure 1(a). The change of wetting angles with the argon ion treatment from  $85^\circ$  to  $22^\circ$  was reported previously.<sup>23</sup> These results showed larger penetration depth for hydrogen ions than for argon ions without any damage to the surface.

At a fixed ion energy, most of the data showed that the wetting angles were inversely proportional to the flow rate of oxygen gas. The results of the IAR-treated PP were similar to those of other IAR-treated poly-

mers.<sup>23,24</sup> Figure 1(a) also shows that the maximum difference in wetting angle for the rate of oxygen blowing rate from 0 to 8 sccm was about  $60^\circ$  at an ion dose of  $5 \times 10^{16}$  ions/cm<sup>2</sup> and an ion energy of 1 keV. As also shown in Figure 1(b), the maximum difference of wetting angle was about  $30^\circ$  for ion energies from 0.6 to 1.4 keV at an ion dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup> and a fixed blowing oxygen gas rate of 4 sccm. This showed that the wetting angle was more sensitive to the oxygen flow rate than the ion energy.

Figure 2 shows the variation in surface energies calculated by Young's formula with ion dose. The

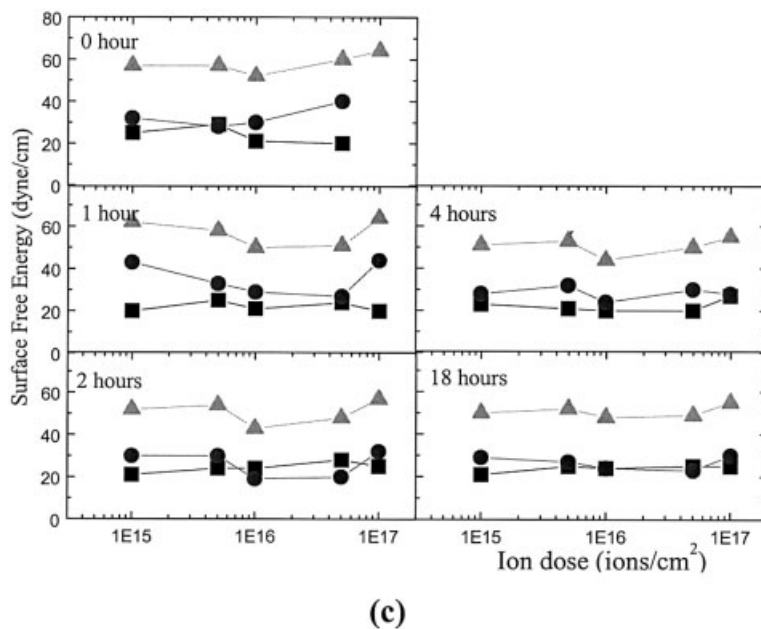


Figure 2 (Continued from the previous page)

surface tension, generally called surface free energy, involves DFs and PFs.

As shown in Figure 2(a), the surface free energy of untreated sample was 23 dyne/cm, which increased to a maximum value of 64 dyne/cm for the IAR-treated samples at an ion energy of 1 keV, an ion dose of  $5 \times 10^{14}$  ions/cm<sup>2</sup>, and an oxygen flow rate of 4 sccm. We can infer that the maximum surface free energy would be greater than 64 dyne/cm because the wetting angle of water was less than 10° in some conditions, which was beyond the measuring limitations of contact anglogrometer. As shown in Figure 2, the surface free energy data without PFs and DFs meant that the surface free energy was greater than 64 dyne/cm because the wetting angle was less than 10°. When the mixture ions were irradiated on the surface of PP without an oxygen gas environment, the surface free energy increased from 23 to 42 dyne/cm. However, for IAR-treated samples, it increased from 23 to 64 dyne/cm. In these two cases, the DFs were not so much changed, and the surface free energy depends on the trend of PFs, as shown in Figure 2(a).

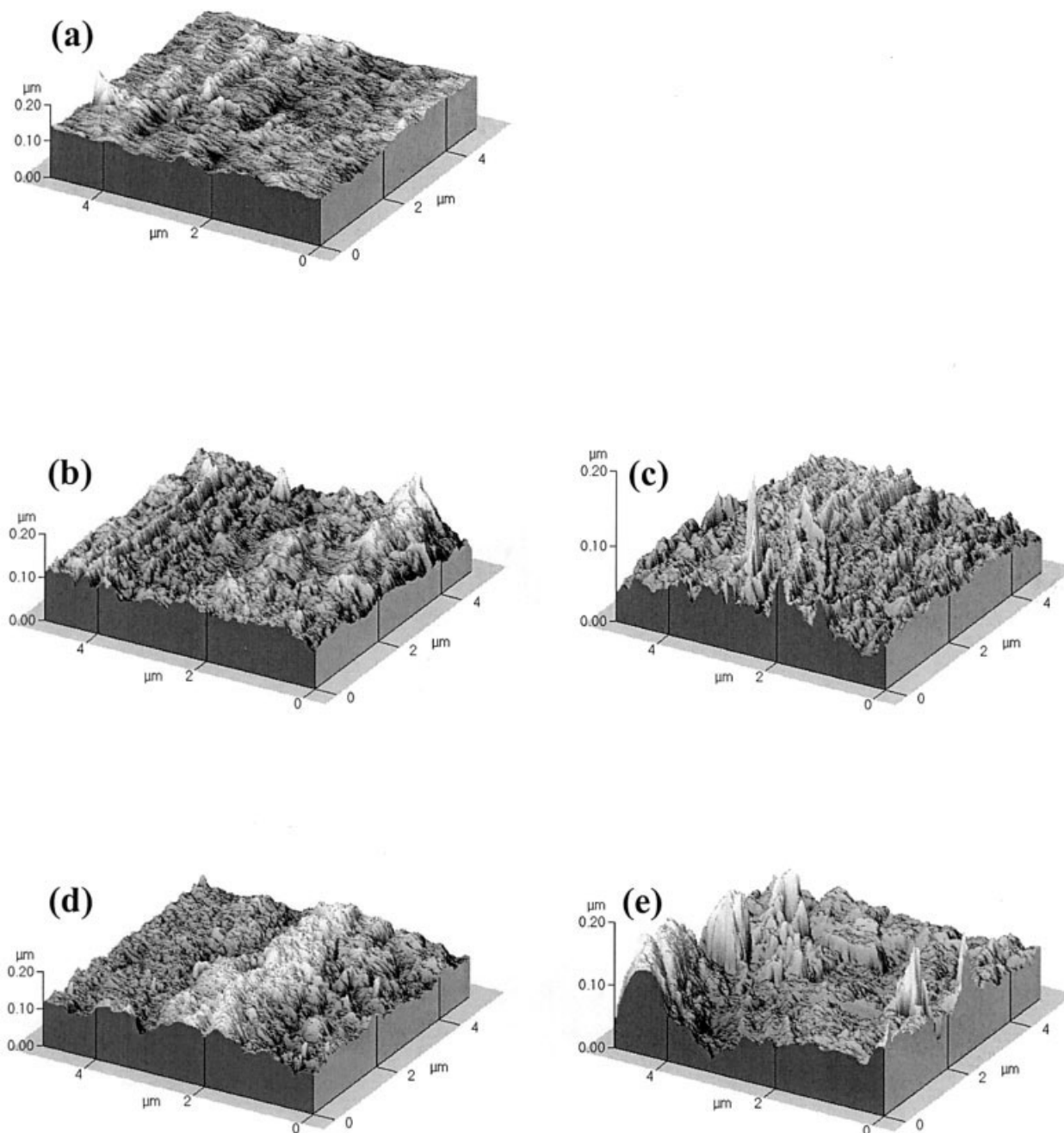
All these results of surface energies depended on the wetting angle. Figure 2(b,c) shows the variation in surface free energy of IAR-treated PP, which was kept in air and in deionized water. The maximum change in the surface free energy of IAR-treated PP that was kept in air was 24 dyne/cm, and that in deionized water was 10 dyne/cm. The data for the IAR-treated sample showed that PFs were larger than DFs. Although the result of the sample kept in deionized water for 18 h showed larger PFs than DFs, the sample kept in air showed smaller PFs than DFs. It is clear that the hydrophilic groups on the surface of the sample

kept in air rotated into the bulk of PP, and those kept in water rotated to the outer surface of the PP because of dipole interaction between the hydrophilic groups and deionized water. As shown in Figure 2(b,c), the surface energies rarely changed after washing, which means that the hydrophilic groups formed by IAR were not washable.

The reported water wetting angle of untreated PP is about 100°, and the surface free energy is about 23 dyne/cm.<sup>25,26</sup> The minimum wetting angle of plasma-treated PP was reported to be about 45°, and the maximum surface free energy is about 50 dyne/cm.<sup>27,28</sup> In the case of surface oxyfluorinated PP, the minimum wetting angle of water is 41°, and the maximum surface free energy is about 55 dyne/cm.<sup>29</sup>

Thus, the IAR-treated PP surface showed superior values of wetting angle and surface free energy than those previously reported. When conventional method such as plasma and ultraviolet–ozone for surface modification are used, energetic ions could break the main chain into small lengths, and the hydrophilic groups easily dissolve after washing.

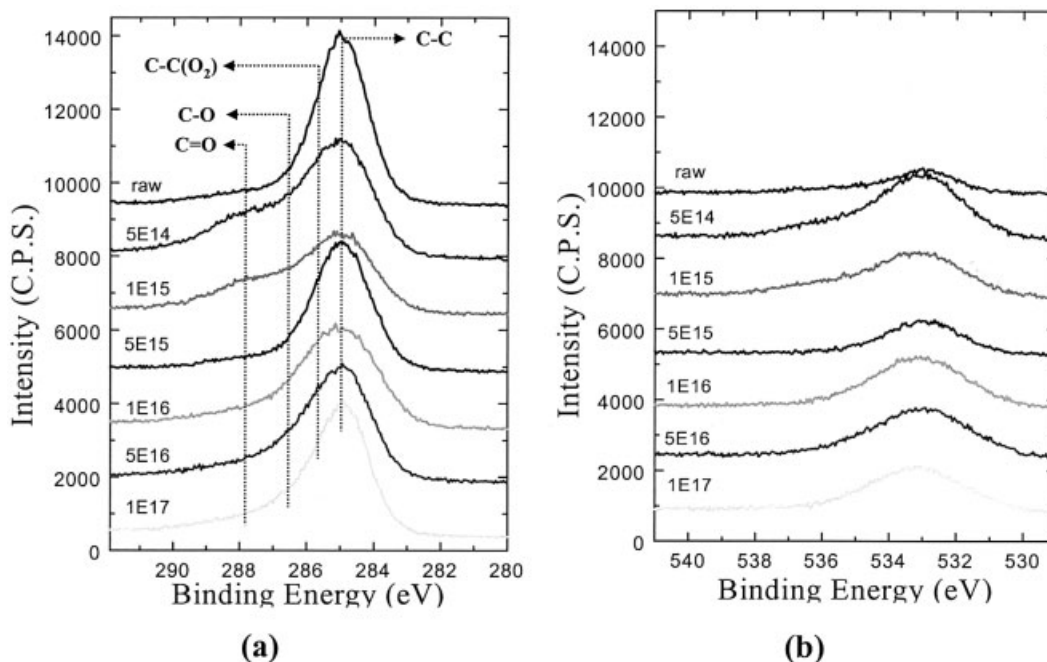
Figure 3 shows AFM images of the untreated and IAR-treated PP samples. The root mean square (RMS) value of the untreated sample was 8.30 nm, and that of IAR-treated PP was 20.8 nm at an ion energy of 1 keV, an ion dose of  $1 \times 10^{17}$  ions/cm<sup>2</sup>, and an oxygen flow rate of 4 sccm. This meant that the IAR treatment induced a small change in surface roughness and did not damage the bulk properties of PP. The change in roughness by IAR treatment contributed to the DFs, but this was a small contribution to the surface free energy, as shown in Figure 2.



**Figure 3** AFM images of IAR-treated PP under different conditions: (a) untreated PP, RMS = 8.30 nm, 1 keV ion-beam energy, 4 sccm oxygen gas, and an ion dose of (b)  $1 \times 10^{15}$  ions/cm<sup>2</sup>, RMS = 14.3 nm; (c)  $1 \times 10^{16}$  ions/cm<sup>2</sup>, RMS = 13.8 nm; and (d)  $1 \times 10^{17}$  ions/cm<sup>2</sup>, RMS = 20.8 nm, and (e) 1.4 keV ion-beam energy, oxygen flow = 4 sccm, and ion dose =  $1 \times 10^{15}$  ions/cm<sup>2</sup>, RMS = 20.7 nm.

To investigate the change in the chemical states on the PP surface by IAR treatment, we performed XPS analysis. Figure 4 shows the XPS data for the untreated and IAR-treated PP samples. XPS data showed that a new unwashable chemical bond was formed on the unstable surface, which was induced by the ion-beam irradiation in ambient oxygen gas. The new chemical bond containing oxygen showed hydrophilic properties. These new chemical covalent bonds containing hydrophilic groups were explained by a two-

step model in our previous article.<sup>20</sup> The possible hydrophilic groups and the binding energies of the C1s orbital were C—C (O<sub>2</sub>) (~285.7 eV), C—O— (286.6 eV), —O—C—O— (287.9 eV), —C=O (287.9 eV), —O—C=O (290.0 eV), —O—C—O—O— (290.4 eV), and so on. The binding energy of the C1s orbital at the chemical bond —C—C— was 285.0 eV.<sup>30,31</sup> At an ion dose of  $5 \times 10^{14}$  and  $1 \times 10^{15}$  ions/cm<sup>2</sup>, the peak of C1s binding energy showed a remarkable increase in the chemical bond C=O. The large shoulder of the



**Figure 4** (a) C1s and (b) O1s core-level binding energy from the XPS data of IAR-treated PP under conditions of 1 keV ion-beam energy, 4 sccm oxygen gas, and an ion dose from  $5 \times 10^{14}$  to  $1 \times 10^{17}$  ions/cm<sup>2</sup>.

C1s spectrum to a high binding energy decreased and the full width of half maximum became wide with an increase in ion dose. Even though the relative rate of the C1s and O1s areas was not in accord with the rate of the number of carbons and that of oxygen, it can be said that the oxygen bonding increased.

The rate of the O1s area to the C1s area of IAR-treated PP at an ion dose of  $5 \times 10^{14}$  ions/cm<sup>2</sup> increased 48%, and that at an ion dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup> increased 33% compared to that of the untreated sample. The wetting angle of IAR-treated PP at an ion dose of  $1 \times 10^{17}$  ions/cm<sup>2</sup> was less than that of the sample at an ion dose of  $5 \times 10^{16}$  ions/cm<sup>2</sup>. However, the area of O1s of IAR-treated PP at an ion dose of  $1 \times 10^{17}$  ions/cm<sup>2</sup> was less than that of the sample at a dose of  $5 \times 10^{16}$  ions/cm<sup>2</sup>. These new hydrophilic groups mainly contributed to PFs. The surface free energy of the IAR-treated PP resulted from the combination of the high quantity of chemical-bond-containing oxygen-related PFs and the low-surface-roughness-change-related DFs.

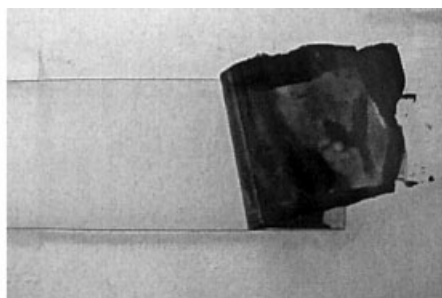
Figure 5 shows the results of the adhesion test between PAN and PP by 3-M Scotch tape. The PAN, which was not easily coated on the untreated sample, was detached completely from the surface of PP, as shown in Figure 5(a), whereas IAR-treated PP showed improved adhesion. This was because of the absence of hydrophilic groups on the surface of the untreated sample. Only a weak van der Waals force exists between PAN and PP.

The samples were treated by IAR with an ion energy of 1 keV at an oxygen flow rate of 8 sccm and at

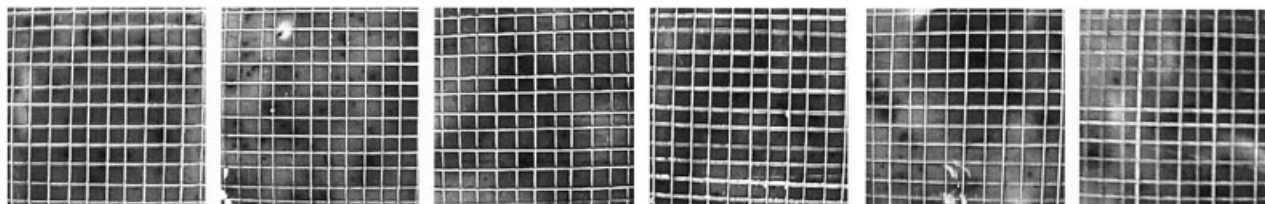
an ion dose of  $5 \times 10^{14}$  to  $1 \times 10^{17}$  ions/cm<sup>2</sup>; the PP samples were dipped into the PAN solution, and the Scotch tape test was partially and perfectly passed. Large improvements in adhesion between PAN and PP were observed under all conditions. This undoped PAN is called polyaniline emeraldine base (PAN-EB). The minimum surface free energy of IAR-treated PP was 55 dyne/cm, but the PAN-EB films were not detached from PP.

After the Scotch tape test between PP and PAN-EB, the PAN-EB was doped by HCl (0.1 mol), called polyaniline emeraldine salt (PAN-ES). To reduce the contact resistance of gold wire, the direct current conductivity of the sample was measured by the four-wire contact method. In this method, current flows through outer two wires, and the voltage is measured across the inner two wires. To measure the conductivity, the PAN-ES sample was cut to a size of  $1 \times 8$  mm, and gold wire was attached to the surface of PAN-ES with carbon paste. The electrical conductivity of PAN-ES as measured by this technique was 5.3 S/cm at room temperature.

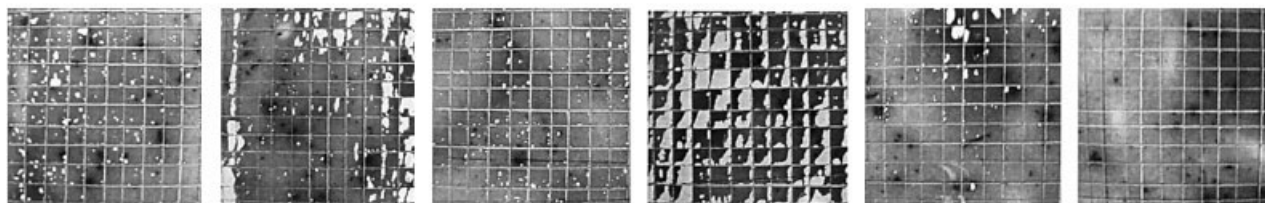
The PAN-ES on IAR-treated PP at an ion dose of  $1 \times 10^{17}$  ions/cm<sup>2</sup> showed excellent adhesion properties. The surface free energy of this PP was 64 dyne/cm. However, there was some detachment in other conditions, especially at ion dose of  $1 \times 10^{16}$  ions/cm<sup>2</sup>: half of the area of the PAN-ES on PP was detached. After HCl proton doping, the trend of detachment of PAN on PP was not exactly in accord with the IAR treatment conditions of PP. This phenomenon is being investigated further to explain the detachment of



(a)



(b)



(c)

**Figure 5** 3-M Scotch tape test of PAN on (a) raw PP, (b) IAR-treated PP under conditions of 1 keV ion-beam energy, 8 sccm oxygen gas, and an ion dose from  $5 \times 10^{14}$  to  $1 \times 10^{17}$  ions/cm<sup>2</sup> PAN-EB, and (c) PAN-ES.

PAN-EB from the IAR-treated PP surface by HCl proton doping.

### CONCLUSIONS

Excellent adhesion was attained between PAN and IAR-treated PP. The main contribution to the adhesion was the increased surface free energy resulting from nonwashable hydrophilic groups, such as C—O, C=O, and (C=O)—O, that formed on the surface of PP by IAR treatment. The PFs related to hydrophobic group formation contributed more greatly to the surface free energy than DFs related to surface roughness. The surface roughness produced by the IAR also contributed to the adhesion but not so much. IAR treat-

ment can contribute to industrial applications on the attachment of conjugated polymers on high-insulator polyolefin polymers.

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