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Adhesion improvement of epoxy resin/polyethylene joints by plasma treatment of polyethylene

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Low density polyethylene (LDPE) and high density polyethylene (HDPE) were plasma-treated with N_2 and O_2 plasma. The wettability and polar component of surface free energy of plasma-treated polyethylene were investigated by contact angle measurement. The concentration of functional groups formed by plasma treatment such as hydroxyl and carbonyl groups was measured using attenuated total reflection Fourier transform infrared spectroscopy (ATR *FT*i.r.). The concentration of polar functional group increased rapidly with 5–10 s of plasma treating time and then very slowly after that. The adhesion strength of epoxy resin/plasma-treated polyethylene joints was examined by a 90° peel test. The increase of the adhesion strength was similar to that of concentration of polar functional groups. The higher adhesion strength of epoxy resin/plasma-treated HDPE joints was observed than that of epoxy resin/plasma-treated LDPE joints since HDPE deformed more during the peel tests and had more polar functional groups on the surface. © 1997 Elsevier Science Ltd

(Keywords: polyethylene; surface treatment; plasma)

INTRODUCTION

Polyethylene (PE) has been widely used since it has many good properties such as high chemical resistance, high impact strength, and flexibility with low cost[1]. However, nonpolar property of PE limits the applications in composites and coatings owing to the lack of adhesion. Plasma treatment has been applied to modify the polymer surface to improve the adhesion strength to other materials without affecting the bulk properties: polymer surface can be cross-linked to reinforce the weak boundary layer[3,4]; polymer surface can be etched to form a rough surface inducing mechanical interlocking[5,6]; the mobility of polymer chain can be improved by chain scission to facilitate interdiffusion; and the wettability of polymer surface can be improved by introducing the polymer functional groups[7].

In this study, PE surface was plasma-treated and the effects of polar functional groups formed by plasma treatment on adhesion were studied. Plasma treatment time was adjusted to avoid the effect of etching. The chemical composition and concentration of functional groups depending on the gas and the plasma treatment time were quantitatively examined by ESCA and ATR *FT*i.r. and their effects on the wettability and adhesion strength between epoxy resin and plasma-treated PE were investigated.

EXPERIMENTAL

Materials

Low density polyethylene (LDPE, Hanyang Chemical Co. 722) and high density polyethylene (HDPE, Daehan Yuwha F500M) chips were placed between two stainless steel plates covered with poly(ethylene terephthalate) using silicone rubber spacer and then compression-moulded to form sheets at 120°C for 2 min under 40 atm and at 140°C for 2 min under 40 atm, respectively. Diglycidyl ether of bisphenol A (DGEBA) epoxy resin (YD128, epoxy equivalent weight $= 180\,\mathrm{g\,eq^{-1}}$) manufactured by Kukdo Chemicals (Korea) was used. Triethylene tetramine (TETA) from Kukdo Chemicals (Korea) was used as a crosslinking agent. Purity of oxygen and nitrogen gases was 99.999%.

Plasma treatment of polyethylene sheets

Polyethylene sheets of dimension of 5 cm × 7 cm were treated with oxygen and nitrogen plasma using a home-made plasma generator operating at 13.56 MHz. The flow rate was 30 standard cubic centimetres per minute (sccm), the pressure was 0.3–0.9 torr and power was 50 W. Plasma treated polyethylene sheets were taken out under argon atmosphere and stored in a vacuum desiccator.

Surface free energies

The surface free energies of plasma treated polyethylene were determined by measuring the contact angles at a room temperature with a contact angle gonimeter (CA-A, Kyowa Surface Science, Tokyo, Japan). The

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Figure 1 SEMs of plasma-treated LDPE: (A) untreated, (B) treated with O_2 plasma for 1 min, (C) treated with O_2 plasma for 5 min, (D) treated with N_2 plasma for 5 min, and (E) treated with N_2 plasma for 10 min

Table 1 X.p.s. analysis of O_2 plasma-treated LDPE

Functional group (%)		Binding energy (eV)	Treatment time (s)					
			0	5	10	30	60	120
C_{1s}	$-CH_2-$	284.6	100	80.5	80.8	88.0	80.8	85.0
	$-C-OH$	286.2	–	14.7	13.4	8.1	13.5	10.6
	$-C=O$	287.5	–	2.7	3.8	2.5	4.0	2.5
	$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-O-$	288.6	–	2.1	2.0	1.4	1.8	2.0
O/C (%)		533.6(O_{1s})	0.2	8.7	9.2	8.5	9.9	9.4

Table 2 X.p.s. analysis of N_2 plasma-treated LDPE

Functional group (%)		Binding energy (eV)	Treatment time (s)					
			0	5	10	30	120	300
C_{1s}	$-CH_2-$	284.6	100	79.9	83.2	82.6	79.0	87.0
	$-C-OH$	286.2	–	14.1	10.5	11.0	15.3	7.2
	$-C=O$	287.5	–	4.3	4.0	4.5	4.1	3.5
	$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-O-$	288.6	–	1.8	2.3	1.8	1.6	2.3
O/C (%)		533.6(O_{1s})	0.2	10.0	11.7	9.4	8.7	9.1
N/C (%)		402.5(N_{1s})	0.1	2.2	2.9	3.5	3.0	0.5

following simultaneous equations[13,14] were solved to obtain dispersive (γ_s^d) and polar (γ_s^p) components of surface free energies of plasma-treated polyethylene from the contact angle using two test liquids, water (1) and formamide (2)

$$(1+\cos\theta_1)\gamma_1 = 2[(\gamma_1^d\gamma_s^d)^{0.5} + (\gamma_1^p\gamma_s^p)^{0.5}] \qquad (1)$$

$$(1+\cos\theta_2)\gamma_2 = 2[(\gamma_2^d\gamma_s^d)^{0.5} + (\gamma_2^p\gamma_s^p)^{0.5}] \qquad (2)$$

The surface free energy γ, the dispersive component γ^d and the polar component γ^p values used in these calculations were 72.2, 22.0 and 50.2 mJ m^{-2} for water, and 58.3, 32.3 and 26.0 mJ m^{-2} for formamide, respectively, as reported in the literature[15].

X-ray photoelectron spectroscopy (X.p.s.)

The surface atomic composition of plasma-treated polyethylene were analysed with a Perkin–Elmer Phi-5400 X-ray photoelectron spectrometer using a Mg K_α X-ray source (1253.6 eV, 350 W). The take-off angle between the analyser and the sample surface was 90°. C_{1s} peaks were deconvoluted to examine the concentration of the functional groups introduced by plasma treatments.

Attenuated total reflection Fourier transform infrared spectroscopy ATR FT *i.r.*

ATR *FT*i.r. spectra of plasma treated polyethylene were obtained to measure the concentrations of the functional groups introduced by plasma treatment using a Perkin–Elmer 1800 *FT*i.r. spectrometer. Polyethylene films 0.2 mm thick were attached on both sides of 30° trapezoid germanium crystal and clamped after inserting silicone rubber on the polyethylene films. In an ATR *FT*i.r. scan, the ATR *FT*i.r. spectrum of germanium crystal was used as a background to avoid the effects of the contaminants in germanium crystal and the optics. The concentrations of the functional groups such as hydroxyl, ketone and carboxylic acid were calculated from the following equations[12]

$$C_v = (A/40)/(\epsilon t) \qquad (3)$$

$$C_a = C_v t = (A/40)/\epsilon \qquad (4)$$

where C_v in the concentration of functional group per unit volume in mol cm^{-3}, C_a is the concentration of functional group per unit area in mol cm^{-2}, A is the absorbance of functional group, ϵ is the molar extinction coefficient of functional group in cm^2 mol^{-1} and t is the thickness of functional group layer in cm. ATR *FT*i.r. spectrum of plasma-treated polyethylene was subtracted by that of untreated polyethylene to obtain the absorbance of functional group. Molar extinction coefficients of hydroxyl and carbonyl groups were measured from the Bouga–Lambert–Beer law using isopropyl alcohol and methyl ethyl ketone, respectively as a model compound. The calculated molar extinction coefficients of hydroxyl and carbonyl groups were 81 and 820 cm^2 mol^{-1}, respectively.

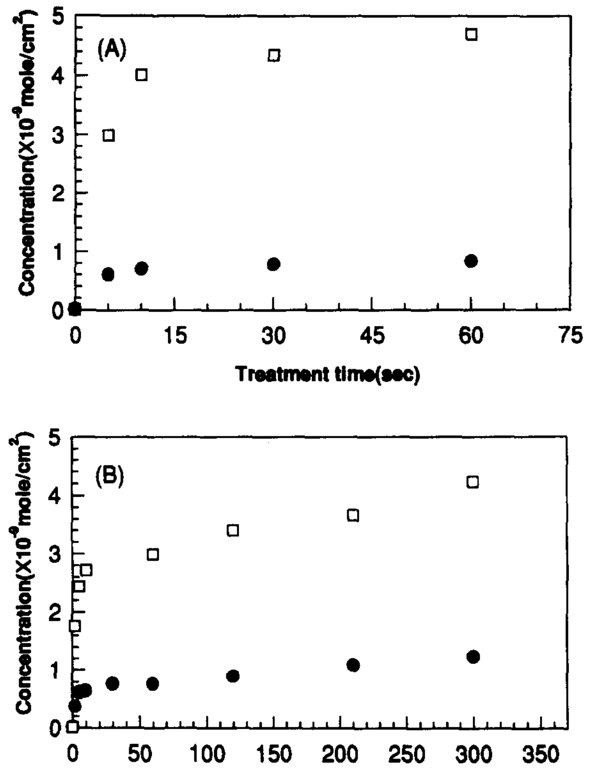

Figure 3 Concentrations of functional groups with increasing the plasma treating time: (A) O_2 plasma: □ hydroxyl group and ● carbonyl group and (B) N_2 plasma: □ hydroxyl group and ● carbonyl group

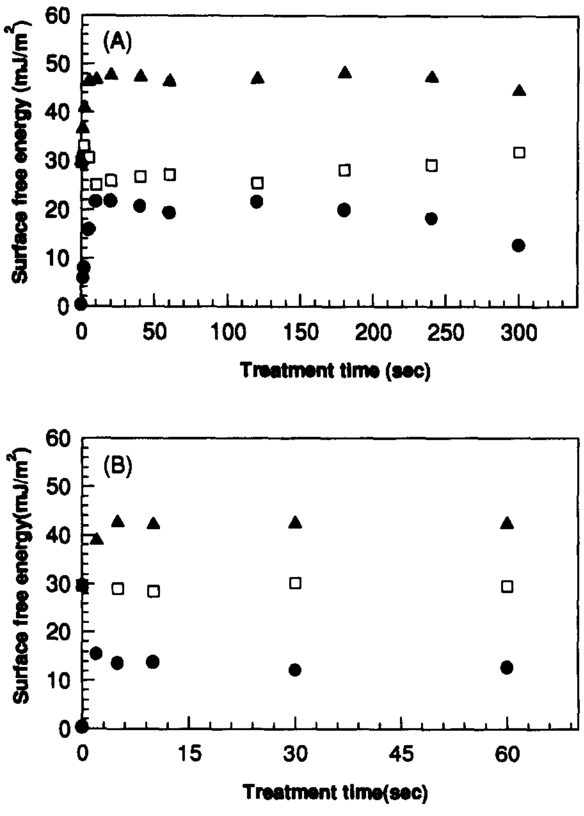

Figure 2 Surface free energies of plasma-treated LDPE with increasing the plasma treating time: (A) O_2 plasma: ▲ surface free energy (γ), □ dispersive component (γ^d) and polar component (γ^p) and (B) N_2 plasma: ▲ surface free energy (γ), □ dispersive component (γ^d) and ● polar component (γ^p)

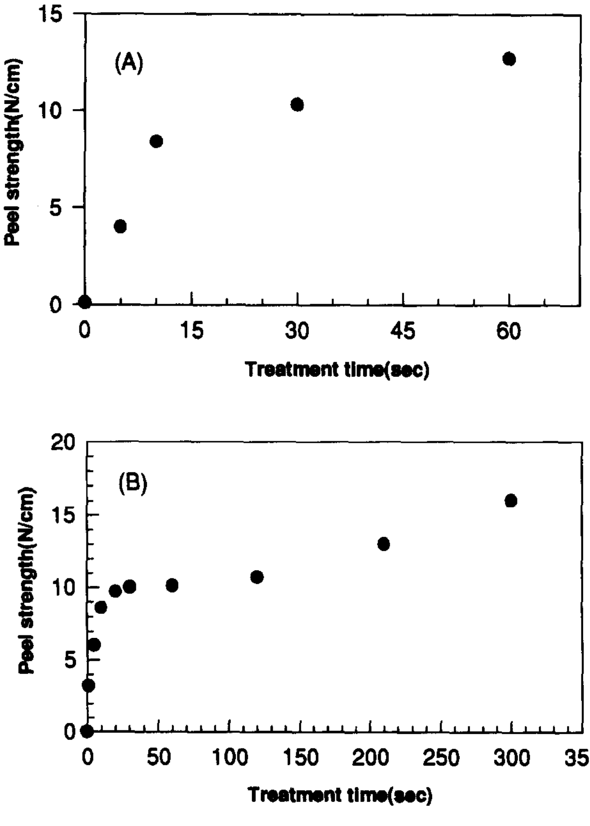

Figure 4 Peel strengths of epoxy resin/plasma-treated LDPE joints with increasing the plasma treating time: (A) O_2 plasma and (B) N_2 plasma

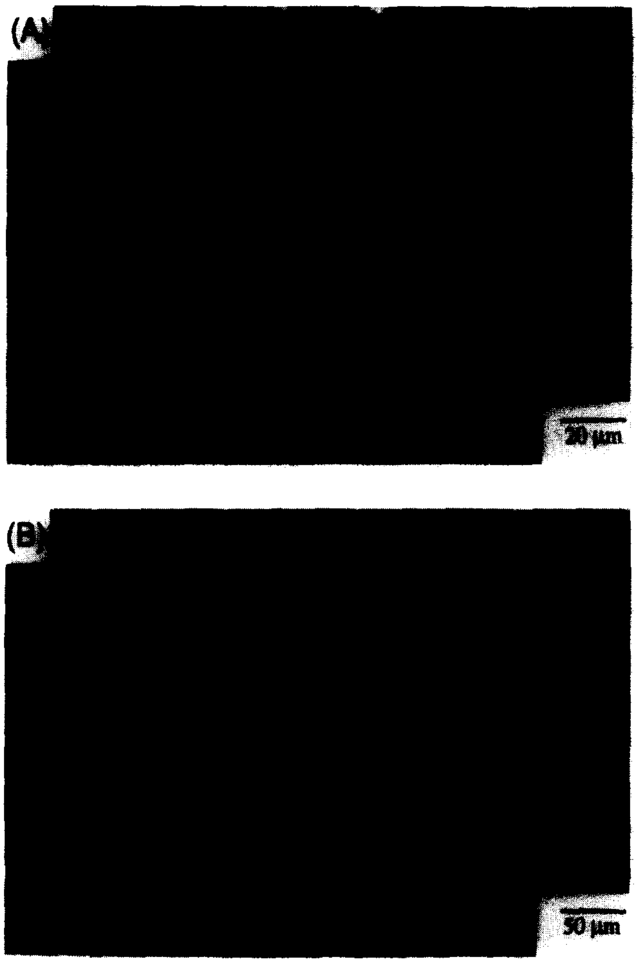

Figure 5 Optical reflection micrographs of peeled surfaces of epoxy resin/plasma-treated LDPE joints: (A) peeled LDPE side and (B) peeled epoxy side

Preparation of the epoxy resin/polyethylene joints

One hundred parts of epoxy resin and 20 parts of TETA were mixed at room temperature. The mixture was poured onto the polyethylene sheet in a silicone rubber mould and then cured at 40°C for 2 h and 70°C for 2 h.

Peel tests

The adhesion strength of epoxy resin/polyethylene joints was measured by a 90° peel test at a peel rate of 5 mm min^{-1} using an Instron Model 4206. Polyethylene strips 5 mm wide with a thickness of 3 mm were cut with a razor blade and peeled from the epoxy resin at room temperature.

Scanning electron microscopy (SEM)

The morphologies of plasma-treated polyethylene were observed by SEM with two different plasma gases (O_2 and N_2) depending on plasma treating time. After peel tests, fracture surfaces of both polyethylene side and epoxy resin side were examined by SEM.

RESULTS AND DISCUSSION

Low density polyethylene (LDPE)

Figure 1 shows the SEMs of the LDPE surface treated by O_2 and N_2 plasmas. O_2 plasma was more reactive than N_2 plasma and became more etched and rough surfaced with the increase of plasma treating time. The roughness of the LDPE surface appears to increase since the noncrystalline part can be easily etched. In the peel tests, the maximum plasma treatment time was 1 min for O_2 plasma and 5 min for N_2 plasma, respectively, to avoid mechanical interlocking through the etched surface.

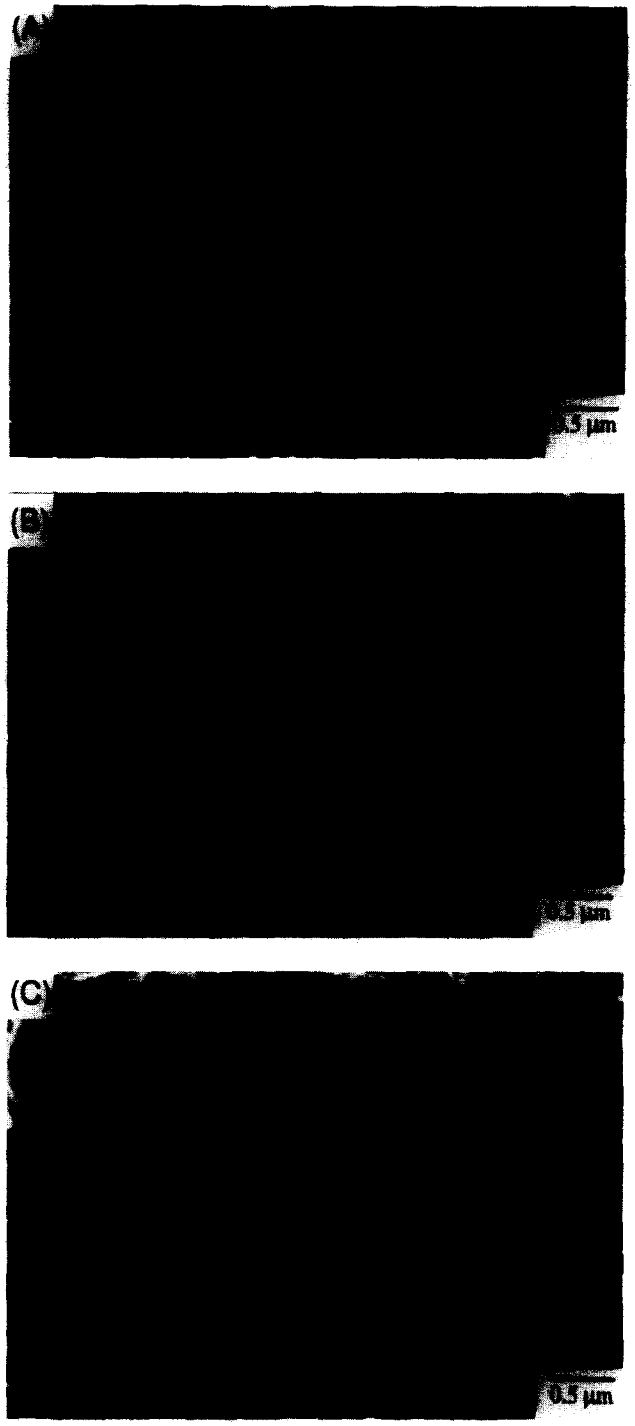

Figure 6 SEMs of O_2 plasma-treated HDPE: (A) untreated, (B) treated for 1 min and (C) treated for 5 min

Figure 2 shows the surface free energies of plasma treated LDPE with the increase of plasma treating time. The polar component of surface free energy of LDPE increased rapidly to around 20 mJ m^{-2} with 5 s and 10 s of plasma treating time for O_2 plasma and N_2 plasma, respectively, and then saturated. This indicates that the concentration of polar group within the depth of contact angle measurement (about 5–10 Å)[28] reached the

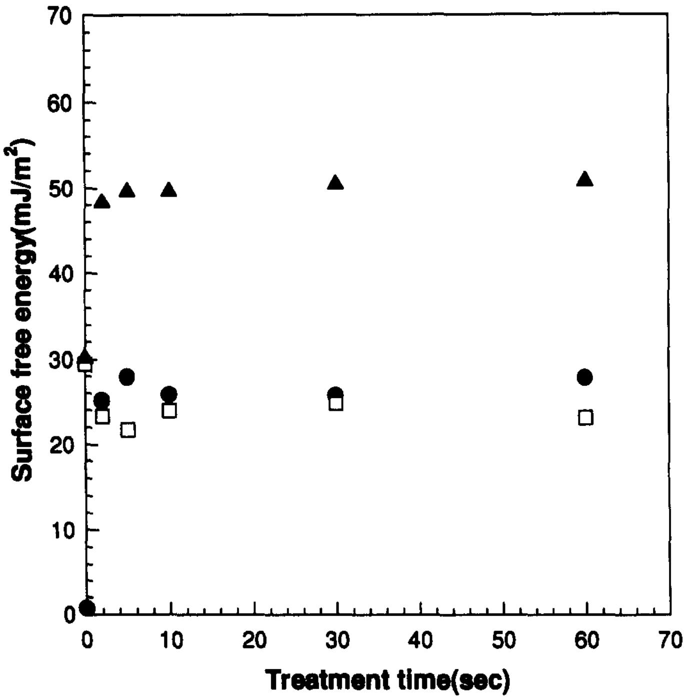

Figure 7 Surface free energies of O_2 plasma-treated HDPE: ▲ surface free energy (γ), □ dispersive component (γ^d) and ● polar component (γ^p)

Table 3 X.p.s. analysis of O_2 plasma-treated HDPE

Functional group (%)		Binding energy (eV)	Treatment time (s)		
			3	30	60
C_{1s}	$-CH_2-$	284.6	83.5	82.5	82.9
	$-C-OH$	286.2	9.2	9.8	9.6
	$-C=O$	287.5	4.4	4.8	4.6
	$-\overset{\overset{O}{\|}}{C}-O-$	288.6	2.9	3.0	2.9
O/C (%)		533.6(O_{1s})	17.6	19.2	18.6

saturation point within 5–10 s of plasma treating time. *Tables 1* and *2* show the atomic concentration of O_2 and N_2 plasma-treated LDPE surfaces, respectively, measured by X.p.s. depending on the plasma treating time. O/C ratio increased up to 9–10% with 5–10 s of plasma treating time and then saturated, which is consistent with the results of surface free energy. Oxygen concentration was also observed in N_2 plasma treatment. It appears that radicals formed by N_2 plasma treatment react with oxygen in the air to form hydroxyl, carbonyl and carboxyl groups. Ueda observed the formation of radicals in

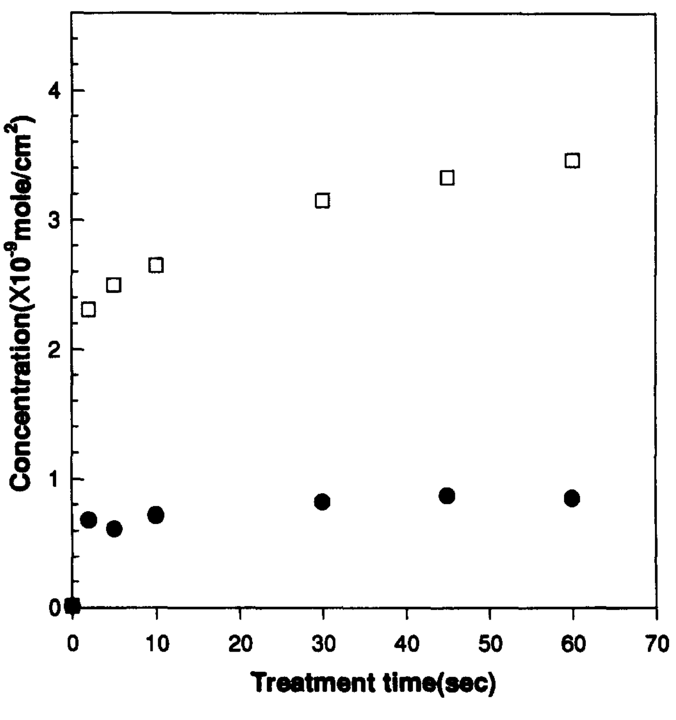

Figure 8 Concentration of functional group with increasing the plasma treating time: □ hydroxyl group and ● carbonyl group

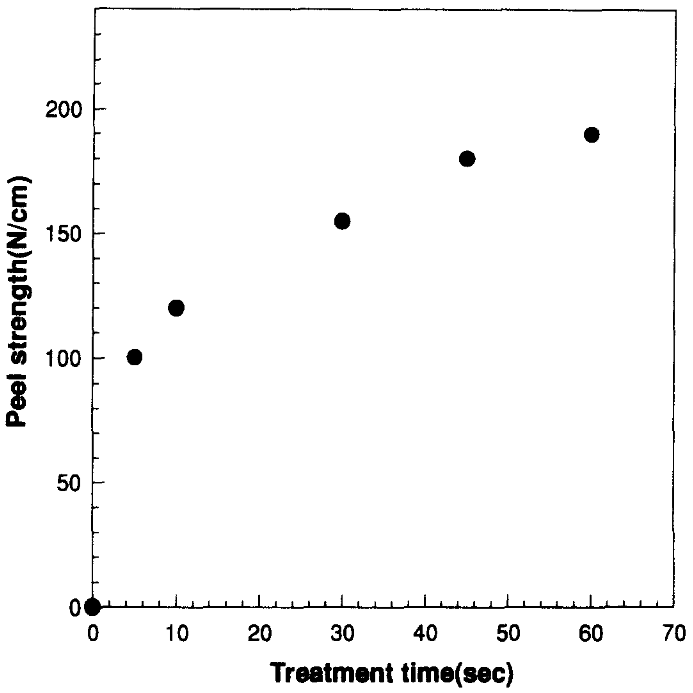

Figure 9 Peel strength of epoxy resin/plasma-treated HDPE joints with increasing the plasma treating time

plasma-treated polyethylene surface by O_2 and N_2 plasmas using e.s.r. spectroscopy and reported that the half-life of the radical was about 4 days[17]. The concentration of hydroxyl, carbonyl and carboxyl groups measured by the deconvolution of the C_{1s} peak was approximately 12–13%, 3–4% and 2%, respectively. N/C ratio also increased up to about 3% with N_2 plasma treatment. The decrease of N/C ratio with 300 s of treatment cannot be explained currently.

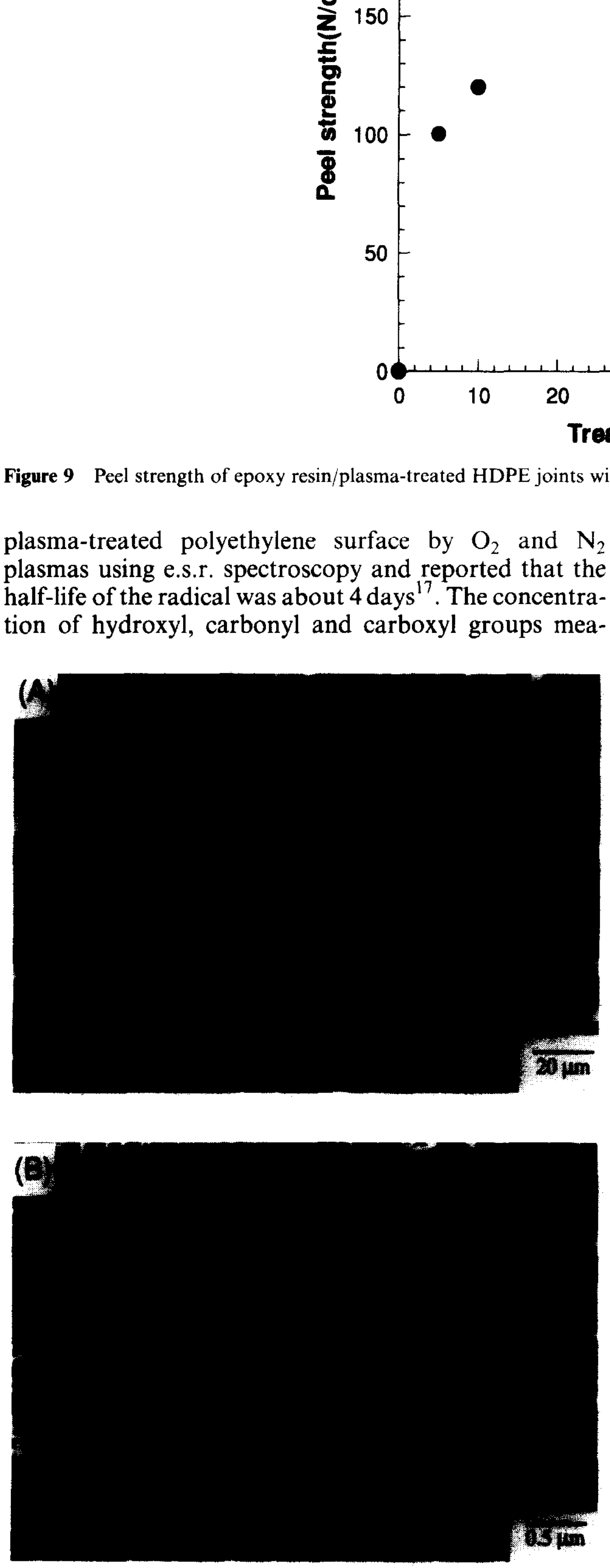

Figure 10 Optical reflection micrographs of peeled surfaces of epoxy resin/O_2 plasma-treated HDPE joint: (A) peeled HDPE side and (B) peeled epoxy side

From both the ATR *FT*i.r. spectra of O_2 and N_2 plasma-treated polyethylene subtracting the spectrum of untreated polyethylene, a hydroxyl group at 3225 cm^{-1}, a carbonyl group at 1720 cm^{-1} and a double bond at 1630 cm^{-1} and 966 cm^{-1} were observed. The concentration of functional groups was calculated from the absorbance of each peak in the difference spectrum. The concentration of hydroxyl and carbonyl groups increased rapidly within 5–10 s and then slowly with the increase of plasma treating time (*Figure 3*). In X.p.s. analysis, the concentration of functional groups did not increase after saturation since the penetration depth is about 50–60 Å. But in ATR *FT*i.r. analysis, the concentration of the functional group increases gradually with plasma treating time since the penetration depth is about 1 μm. The nitrogen containing functional group was not observed from ATR *FT*i.r. spectrum due to a small amount.

Although the peel strength of epoxy resin/plasma-treated LDPE joints was almost zero without plasma treatment, the peel strength increased rapidly at the beginning of plasma treatment and then gradually up to 1200 N m^{-1} with O_2 plasma in 60 s of plasma treating time and 1600 N m^{-1} with N_2 plasma in 300 s of plasma treating time (*Figure 4*). The increasing trend of adhesion strength was the same as that of concentration of functional groups. This indicates that all the functional groups formed by plasma treatment, not only on LDPE surface detected by contact angle measurement but also near LDPE surface detected by ATR *FT*i.r., participated in chemical and physical bondings with epoxy resin. The functional groups near the LDPE surface detected only by ATR *FT*i.r. appear to participate in bondings through the diffusion of epoxy resin.

Figure 5 shows the optical reflection micrographs of peeled surfaces of epoxy resin/plasma-treated LDPE joints. In the peeled epoxy resin side, fibrous polyethylene texture was observed. It appears that the locus failure was mainly the cohesive failure in polyethylene. In the peeled polyethylene side, a lot of plastic deformation of polyethylene was observed.

High density polyethylene (HDPE)

Figure 6 shows the SEMs of O_2 plasma-treated HDPE surface. Fibrous texture was seen in untreated HDPE surface owing to high crystallinity. Since the amorphous region was selectively etched by O_2 plasma, the fibrous texture was more pronounced and thickened with the increase of plasma treating time. Therefore, O_2 plasma treating time was limited to 1 min to avoid mechanical interlocking through etched surface. *Figure 7* shows the surface free energies of O_2 plasma-treated HDPE with the increase of plasma treating time. The increasing trend of polar component of surface free energy of HDPE was very similar to that of LDPE except for a $10\,\mathrm{mJ\,m^{-2}}$ higher polar component of surface free energy at the saturation point. *Table 3* shows the atomic concentrations of O_2 plasma treated HDPE surface depending on the plasma treating time. O/C ratio increased up to about 18% with 3 s of plasma treating time and then saturated, which is about twice that of O_2 plasma-treated LDPE and consistent with the results of surface free energy. The concentration of hydroxyl, carbonyl and carboxyl groups measured by the deconvolution of C_{1s} peak was approximately 9.5%, 4.5% and 3%, respectively.

In ATR *FT*i.r. analysis of O_2 plasma-treated HDPE, the same difference spectrum as that of plasma-treated LDPE showing hydroxyl, carbonyl and double bond peaks at the same position was obtained. The increase of hydroxyl and carbonyl groups in O_2 plasma-treated HDPE surface with the increase of plasma treating time (*Figure 8*) was similar to that in O_2 plasma-treated LDPE surface (*Figure 3*). The increase of the peel strength of epoxy resin/O_2 plasma-treated HDPE joints was proportional to the increase of polar functional groups as shown in *Figure 9*, which was consistent with that of epoxy resin/O_2 plasma-treated LDPE joints. However, the peel strength of epoxy resin/O_2 plasma-treated HDPE joints was about 10 times that of epoxy resin/O_2 plasma-treated joints since the deformation energy of HDPE was about 10 times that of LDPE confirmed by tensile tests, and the polar functional group of O_2 plasma-treated HDPE interacting with epoxy resin was about twice that of O_2 plasma-treated LDPE.

Figure 10 shows the SEMs of peeled surfaces of epoxy resin/O_2 plasma-treated HDPE joints. Fibrous texture of HDPE in the peeled epoxy resin side and severe ductile deformation in the peeled HDPE side were clearly seen.

CONCLUSIONS

The wettability and polar component of surface free energy of LDPE and HDPE increased rapidly within 5–10 s and then saturated by N_2 and O_2 plasma treatment of LDPE and HDPE. O_2 plasma was more reactive in etching the polyethylene surface. The formation of hydroxyl, carbonyl and carboxyl groups was confirmed by X.p.s and ATR *FT*i.r. The quantitative amount of hydroxyl and carbonyl groups measured by ATR *FT*i.r. increased rapidly at the beginning of plasma treatment and then very slowly. Since the penetration depth of ATR *FT*i.r. is about 1 μm and that of contact angle measurement is approximately 5–10 Å, the concentration of polar functional groups measured by ATR *FT*i.r. increased further beyond the limit measured by contact angle measurement with the increase of plasma treating time. The adhesion strength of epoxy resin/plasma-treated polyethylene joints increased with the same pattern as the increase of polar functional groups. This indicates that the functional groups near the polyethylene surface also participate in forming chemical and physical bonding with the epoxy resin diffused into the polyethylene layer. The higher adhesion strength of epoxy resin/plasma-treated HDPE joints than that of epoxy resin/plasma-treated LDPE joints originated from higher deformation energy of HDPE during the peel tests and more polar functional groups formed on HDPE surface.

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