

Surface Crosslinking of High-Density Polyethylene Beads in a Modified Plasma Reactor

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ABSTRACT: High-density polyethylene (HDPE) beads were successfully surface-crosslinked in a modified plasma reactor. The modified plasma reactor treats large amounts of beads, which are uniformly surface-crosslinked. In this study, effects of the gas pressure, radio-frequency (RF) power, and the treatment time on the degree of surface crosslinking were systematically investigated. Degree of surface crosslinking was measured by solvent extraction method (boiling xylene method, BXM). The gel content of plasma-treated HDPE increases from 0.0 to 1.05% within 10 min at 100 mTorr, 200 W. FTIR and DSC analyses show that the crosslinked layer after plasma treatment is limited only at HDPE surface without changing the bulk thermal property of HDPE. Through the analysis of FTIR, it was confirmed that main peaks corresponding to CH_2 bands were decreased and two peaks corresponding to CF_2 and CF_3 were observed after plasma surface modification. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2921–2929, 2002; DOI 10.1002/app.10295

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INTRODUCTION

Radio-frequency (RF) plasma treatment was mainly applied in the field of the surface modification of solid materials. A pure plasma is known to contain both positive and negative ions, atoms, and metastables of atoms, which were used to modify polymer surface properties such as crosslinking, wettability, and adhesion without changing bulk property.¹ Essentials of the technique are that electrons, atoms, and radicals in the plasma attack the surface of the polymeric materials and then remove hydrogen atoms from the polymeric surface to form radical sites at the surface, and finally, the radicals react with other

radicals to form crosslinked chains. The crosslinking mechanism in argon plasma is shown in Figure 1. Good contact of the polymer surface with plasma is an important factor for the efficient modification of polymer surface.² Beads are difficult to handle in the plasma treatment because of the large surface area per unit mass of beads. The untouched region of beads or powders are hardly modified. In a previous study, Anand et al. modified polyethylene particles in a fluorine plasma which was induced in a vibrating fluidized bed.³ Masuoka et al. used a rotary kiln as a plasma reactor to coat powders on polymer film.⁴ Kusakabe et al. observed that fine particles were smoothly fluidized at reduced pressures.⁵ Generally, the fluidized bed reactor is favorable to treat powders because of the uniformity in the bed and the ability of continuous powder handling.⁶ Therefore, all powders can be uniformly treated at the fluidized bed plasma reactor.

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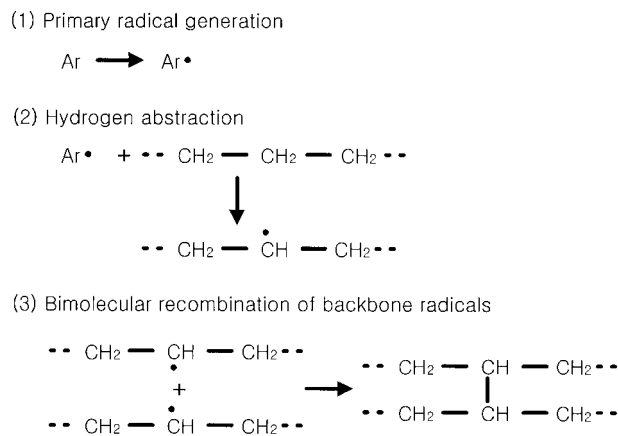


Figure 1 HDPE crosslinking mechanism in argon plasma condition.

Beads, however, can hardly be treated in the fluidized bed reactor because the fluidization of beads is very difficult because of their weight. The high-density polyethylene (HDPE) has good thermal properties such as a melting point of 120–135°C and latent heat of 180–210 J/g. Thus, it was reported that HDPE is suitable for use as a thermal energy storage material.⁷ Until now, three other methods of controlled chemical and physical crosslinking of HDPE were reported: (1) peroxide-initiated, free radical crosslinking; (2) vinyl triethoxy silane grafting and crosslinking;

and (3) electron beam crosslinking. However, the crosslinking using these methods penetrates into the inside of the HDPE bead and results in 20–30% losses of latent heat because of the decrease in linear HDPE's crystallinity, although it still shows high temperature from stability.⁸

Thus, the objective of this study was to crosslink only the surface of HDPE in a modified plasma reactor and to find optimum reaction conditions at various operations. The chemical and physical characterization of these crosslinked surfaces are performed by using boiling xylene method (BXM), Fourier transfer infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and image analysis.

EXPERIMENTAL

A schematic diagram of the apparatus used in this study is represented in Figure 2. A reactor for plasma modification consists of four main sections: reaction column, gas inlet part, vacuum system, and RF (radio-frequency) plasma-matching system. Gas flow rate is regulated and measured with a regulator and microneedle valve, respectively. The reduced pressure in the reactor is maintained by using both mechanical rotary vacuum pump (Woosung Vacuum Co., 200 L/min)

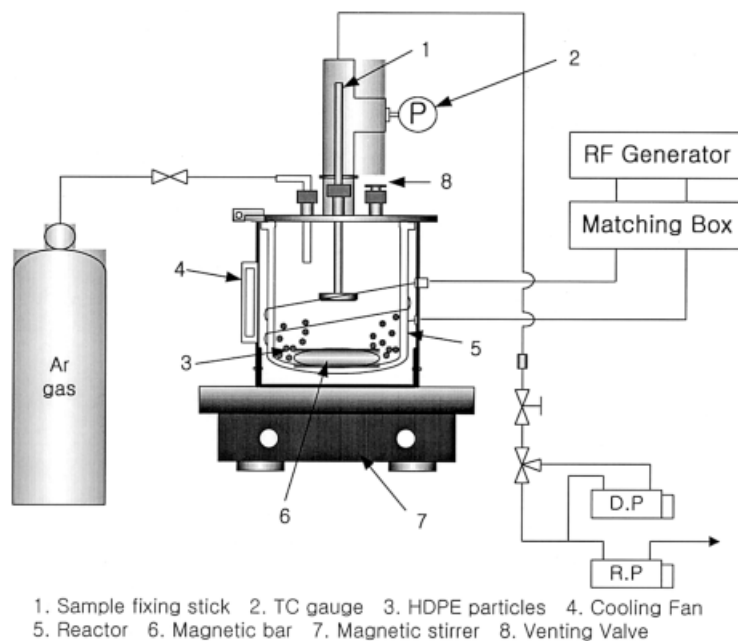


Figure 2 Reactor for plasma treatment of particles or film.

Table I Specifications and Properties of HDPE 8800

	Test Method	Values
Density (g/cm ³)	ASTM D1905	0.956
Melt index (dg/min)	ASTM D1238	0.04
Tensile yield strength (Kg/cm ²)	ASTM D638	230
Ultimate tensile strength (Kg/cm ²)	ASTM D638	300
Elongation at break (%)	ASTM D638	>500

and diffusion pump (Kodivac Co., 360 L/s). The TC gauge (Varian Co., 801, analog type) is used to measure pressure in the reactor. Entrained particles from the reactor are captured by a trap. An inductively coupled electrode (4-mm OD copper tube, two-turn) for glow discharge at 13.56 MHz frequency was coiled at a distance of 30 mm from gas inlet and was connected to an auto-matching network and an RF power generator (Youngsin Engineering Co., 0–300 W). To prevent overheating of the electrode and diffusion pump, a cooling system (mechanical fan) is installed at both electrode and diffusion pump. To mix HDPE beads, a magnetic stirrer (Tops Co., MS-300, rpm: max 1000) is used. The reactor (Plasmart Co., Taejon, Korea) is made of 90 mm ID and 110-mm high Pyrex glass column.

Resin specifications and physical properties of HDPE 8800 is shown in Table I. HDPE sample film is prepared from commercial grade HDPE pellets (density: 0.956 g/cm³, M.I.: 0.04 g/10 min, Yuzex Co., HDPE 8800) by hot press method. The HDPE beads of 20 g or film 2 × 3.5 cm (0.5 mm thickness) are loaded into the reactor and then gas in the reactor is evacuated to base pressure; argon gas (purity: 99.999%) is injected for approximately 10 min. The experimental pressures are 60, 100, 200, and 300 mTorr, respectively. The experimental variables and their ranges for plasma surface crosslinking of HDPE film or beads in the modified plasma reactor are summarized in Table II. HDPE particles are stirred in

the reactor at a rotation speed of 600 rpm with magnetic stirrer. Then, the power is adjusted to start glow discharge. After the desired treatment time, plasma is turned off, and samples are kept in the reactor for more than 20 min at the given gas flow rate. After plasma treatment, HDPE samples were characterized by following procedures.

Degree of Gel content

Gel content of the plasma treatment, which is regarded as the crosslinking degree, was measured by ASTM D2765-95 procedure.⁹ A known amount of a crosslinked HDPE film or beads was placed in a preweighed 150-mesh stainless steel basket. Crosslinked HDPE and stainless steel basket was weighed and then extracted in boiling xylene together with stabilizer (2,6-ditert-butyl-4-methylphenol) for 12 h. After extraction, the undissolved portion of HDPE film was dried under vacuum at 100°C for 10 h and then weighed and compared with the original weight. Finally, gel content was calculated as follows:

$$\text{Gel content (\%)} = \frac{M_b}{M_f} \times 100 \quad (1)$$

where M_b was the weight after extraction and M_f was the weight after plasma treatment.

To measure the plasma penetration depth into HDPE, we first prepared plasma-treated HDPE

Table II Experimental Conditions of Plasma Surface Crosslinking in a Modified Plasma Reactor

Gas	Argon (99.999% purity)
Size of HDPE film [mm]	20 (width) × 35 (length) × 0.5 (thickness)
Average diameter of particle [mm]	3
Pressure [mTorr]	60, 100, 200, 300
Treatment time [min]	1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 60
RF power [W]	50, 100, 150, 200
Magnetic stirrer speed [rpm]	600

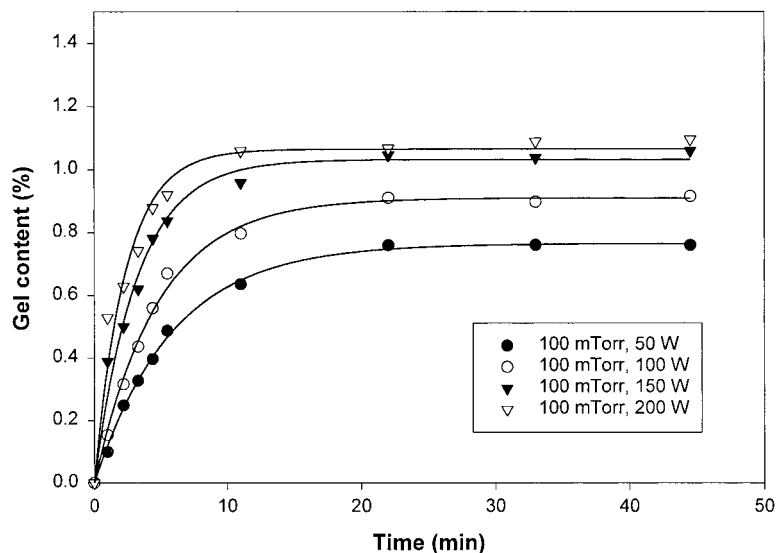


Figure 3 Effect of treatment time (min) on gel content (%) of argon plasma-treated HDPE beads.

films with constant size. Because we attached the film exposed to only one surface at the bottom of sample fixing stick, we were able to assume only the exposed surface to be crosslinked during the plasma treatment. After extracting the untreated portion of the film, we measured the weight of remaining crosslinked portion. Then, we indirectly estimated the plasma penetration depth into HDPE film from the following equation:

$$\text{Plasma penetration depth} = \frac{V_f}{A_a} \quad (2)$$

$$V_f = M_b/\rho, \quad A_a = M_a/\rho d$$

where V_f was the volume after plasma treatment, A_a was the area of HDPE film before plasma treatment, ρ was the density of HDPE, M_a was the weight of plasma-untreated HDPE film, and d was the thickness of plasma-untreated HDPE film.

FTIR

FTIR spectra of the argon plasma-treated HDPE were recorded on a Bomen FTIR spectrophotom-

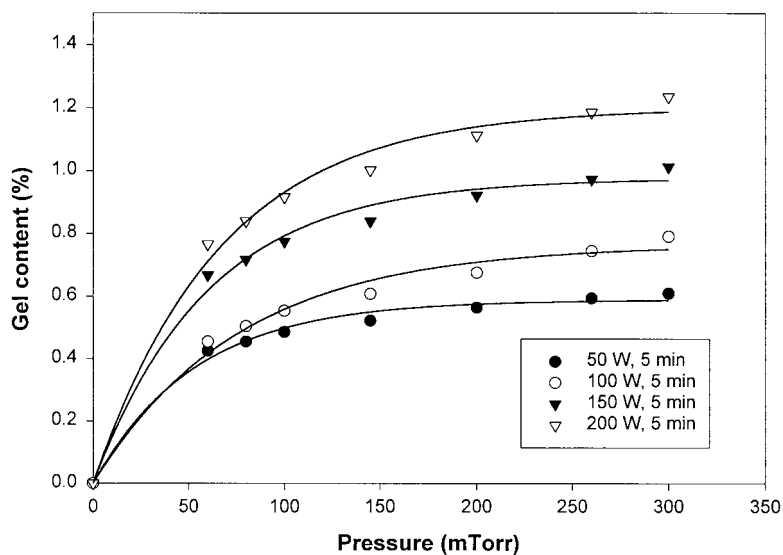


Figure 4 Effect of gas pressure on gel content (%) of argon plasma-treated HDPE beads.

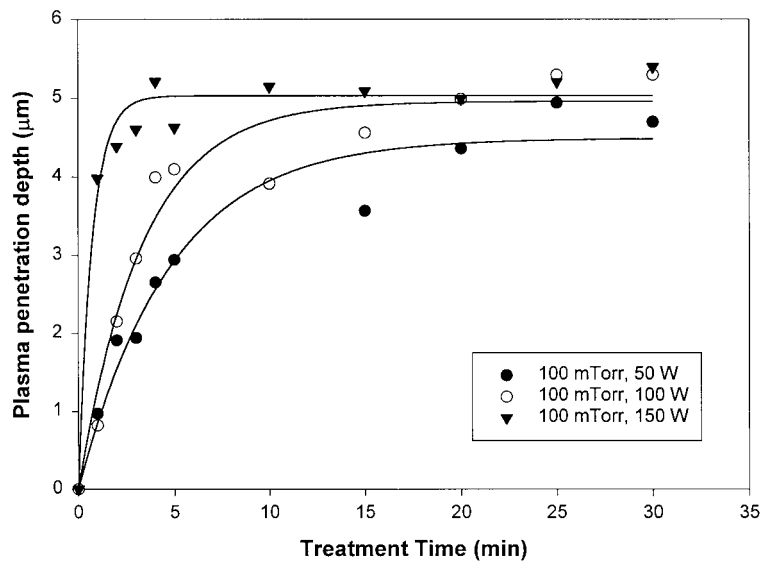


Figure 5 Effect of treatment time (min) on plasma penetration depth (μm) of argon plasma-treated HDPE film (at a constant pressure of 100 mTorr).

eter with a diffuse reflector (Applied System Inc., ReactirTM 1000). The FTIR technique is known as a simple and rapid method to confirm

the change in chemical and physical properties of polymers. In this article, we measured FTIR spectra of HDPE films prepared after hot-press-

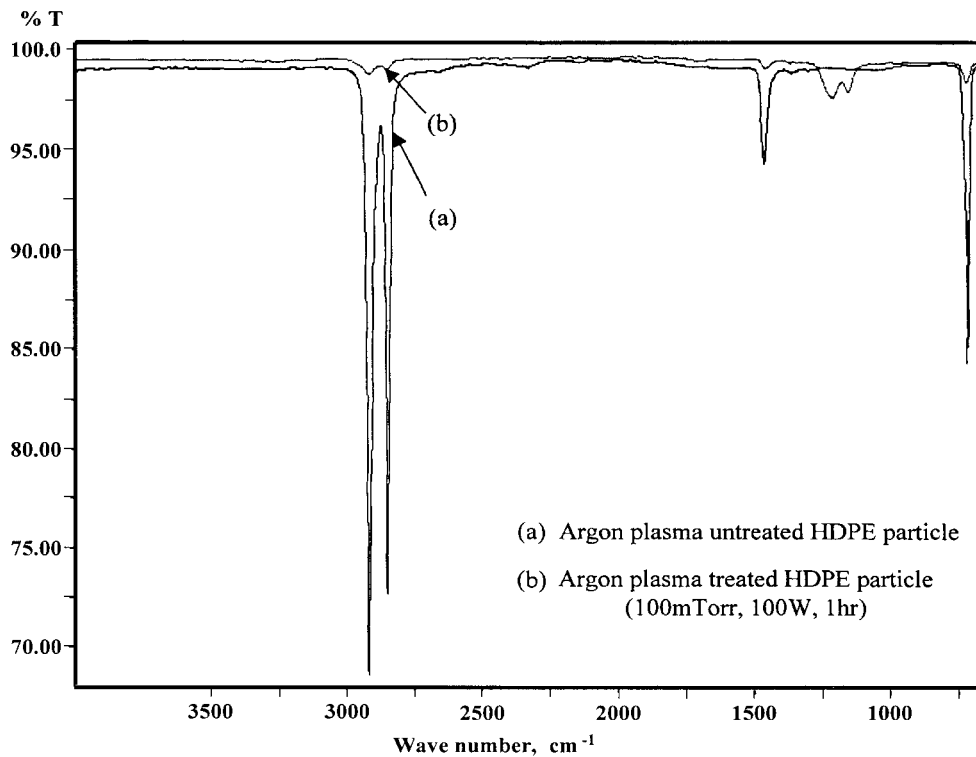


Figure 6 FTIR spectra of the argon plasma-treated HDPE beads in a plasma reactor with Teflon-coated magnetic bar: (a) plasma-untreated; (b) plasma-treated (100 mTorr, 100 W, 1 h).

Table III Summary of FTIR Absorbance Peak Position

Wave Number, [cm ⁻¹]	Functional Group
719.7	CH ₂ rocking (ρ CH ₂)
1000–1100	Monofluoroalkane
1162–1223	CF ₂ and CF ₃ groups
1470	CH ₂ bending (δ_s CH ₂)
2850	CH ₂ symmetry stretching (ν_s CH ₂)
2916	CH ₂ asymmetry stretching (ν_{as} CH ₂)

ing both plasma-treated and -untreated HDPE beads.

DSC

Melting point was determined by using a differential scanning calorimeter (V4.0B DuPont 2000). DSC equipped with an auto scanning zero was used for investigating the thermal changes of the crosslinked HDPE. Measurements were carried out under nitrogen purging at 10°C/min scan rate from 20 to 180°C. Both plasma-treated and -untreated beads were used in this measurement.

SEM

A SEM (Acc.V Spot Magn) was used for observing physical changes of the HDPE surfaces before and after argon plasma treatment.

Image Analysis

Surface change of HDPE film was observed by an optical microscope (Olympus BX60). The obtained images were stored in a computer through CCD camera and analyzed by an image analyzer system.

RESULTS AND DISCUSSION

The surface modification of polymer using a plasma reactor is influenced by pressure, RF power, treatment time, and type of gas parameters.¹⁰ The importance of these parameters are reconfirmed here for HDPE. In this study, surface modification properties of HDPE can be established by using argon plasma. Then, the physical properties of the modified HDPE surface are investigated.

The effect of treatment time on the gel content (%) of argon plasma-treated HDPE beads is shown in Figure 3. It is obvious that the gel content (%) of the plasma-treated HDPE increases with an increase in treatment time due to the formation of crosslinked structure at the surface layer, but levels off after further treatment. Under the RF power of 50 W, the gel content of plasma-treated HDPE increases from 0 to 0.75% during the time interval of 0 to 20 min. This figure also represents that in argon plasma (under 100 mTorr, 200 W) the gel content of plasma-treated HDPE rapidly increases from 0 to 1.05% as treatment time increases from 0 to 10 min and levels off after 15 min. The time required for the gel content until its becoming constant depends on the RF power: 25 min for the HDPE plasma-treated at 100 mTorr–50 W; 20 min for the HDPE plasma-treated at 100 mTorr–100 W; 10–12 min for the HDPE plasma-treated at 100 mTorr–150, 200 W. The total gel content is shown to be dependent on the plasma reactor parameters such as RF power and treatment time.

The effect of gas pressure (50–300 mTorr) in the reactor on gel content (%) is shown in Figure

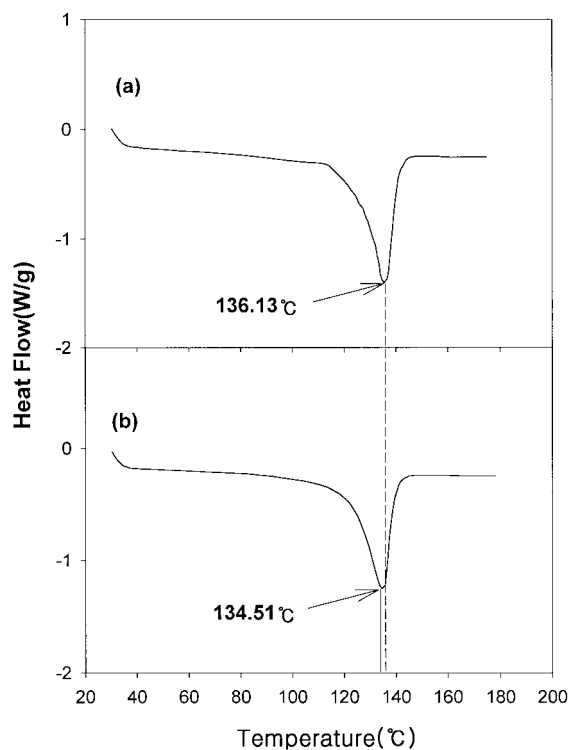


Figure 7 DSC diagrams of HDPE beads: (a) argon plasma-treated (100 mTorr, 100 W, 1 h); (b) argon plasma-untreated.

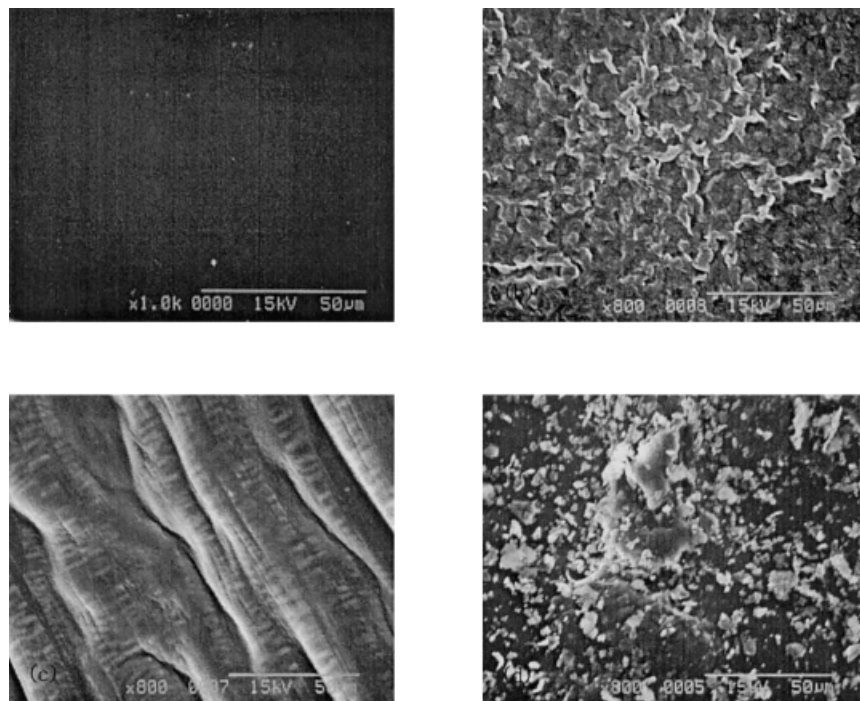


Figure 8 SEM photographs of (a) untreated HDPE film; (b) remainder after solvent extraction; (c) untreated HDPE bead; and (d) plasma-treated HDPE bead (100 mTorr, 100 W, 1 h).

4. This figure represents the degree of surface crosslinking of HDPE beads treated by argon plasma at given conditions. As can be seen in the figure, gel content of HDPE beads gradually increases with increasing RF power and pressure in the plasma reactor.

Figure 5 represents the change in the plasma penetration depth of plasma-treated HDPE film with increasing treatment time. Under the given RF power and pressure, the thickness of the crosslinked layer increases with increasing treatment time. At 50 W RF power, the plasma-treated HDPE thickness gradually increases from 0 to 4.5 μm , but levels off after 15 min. The results of 100 and 150 W RF power show rapid increase in the plasma penetration depth with increasing treatment time, but the penetration depths reach maximum values of 4.7 and 5 μm at 6 min (100 W) and 3 min (150 W) of treatment time, respectively. Treatment time taken for maximum plasma penetration is getting faster with increasing RF power.

The FTIR spectra of argon plasma-untreated HDPE beads and plasma-treated HDPE beads in a modified plasma reactor at different operating conditions are shown in Figure 6. On the IR spectrum for argon plasma-untreated HDPE beads,

strong absorption peaks appear at 2916, 2850, 1470, and 719.7 cm^{-1} , which correspond to CH_2 , CH_3 , and terminal vinyl groups, respectively.¹¹ The asymmetrical stretching ($\nu_{as} \text{CH}_2$) and symmetrical stretching ($\nu_s \text{CH}_2$) occur near 2916 and 2850 cm^{-1} , respectively.¹¹ The scissoring band ($\delta_s \text{CH}_2$) in the spectra of untreated HDPE appears near 1470 cm^{-1} , and CH_2 rocking is 719.7 cm^{-1} .¹¹ The plasma-treated HDPE shows less CH absorption peaks than that of the untreated one. This is because many C—H bonds on the surface were broken and removed by Ar plasma. We also observed new absorption peaks of fluorine functionalities in the range of 1162–1223 cm^{-1} . This is thought to be due to the transfer of fluorine-containing groups from a Teflon-coated magnetic bar. In general, the fluorine-containing compound shows various C—F bands between 730 and 1400 cm^{-1} . Monofluoroalkane has an IR band at 1000–1100 cm^{-1} . CF_2 and CF_3 show bands at 1120–1350 cm^{-1} . Thus, new absorption peaks observed in the range of 1162–1223 cm^{-1} result from the formation of CF_2 and CF_3 . It is possible that some of these groups are detected in-depth on the basis of a gradient in the polymer composition from a CH_2 — CH_2 state in the bulk to a CF_2 — CF_2 state

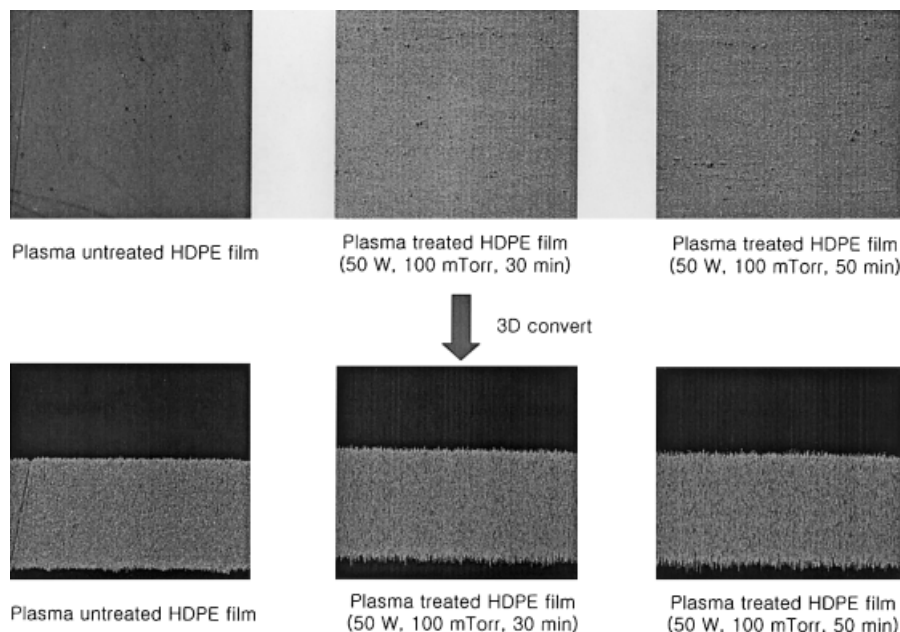


Figure 9 Optical observations of surface property on plasma-untreated HDPE film and plasma-treated HDPE film (50 W, 100 mTorr, 30 min, 50 min).

on the surface.^{12–14} The positions of FTIR absorption peaks are summarized in Table III.

Figure 7 shows the comparison of DSC diagram of the plasma-untreated HDPE particle with that of plasma-treated HDPE particle prepared under the condition of 100 W RF power for 1 h (at 100 mTorr). The melting points of plasma-treated and -untreated HDPE particles measured with DSC are 136.13 and 134.51°C, respectively. From this result, it is noted that the melting point of plasma surface-treated HDPE is about 1.62°C higher than that of plasma-untreated HDPE, but the profile of the plasma-treated diagram is almost the same for that of the plasma-untreated diagram. This means that the crystallinity of the HDPE is not changed after surface crosslinking of 100 W RF power, so endotherm peaks for phase change from crystalline to amorphous show almost the same change in both plasma-treated and -untreated HDPE. Because the crosslinking is bound only at a thin surface layer, the bulk thermal property does not change even after surface crosslinking.

Figure 8 represents SEM photographs of HDPE surface: Figure 8(a) for the untreated HDPE film, Figure 8(b) for the remainder after extraction, which is a 100% crosslinked HDPE. Figure 8(c,d) shows the morphological changes of HDPE beads before and after plasma treatment. Many small particles are adhered on the HDPE

surface after plasma treatment and this is thought to be due to the ablation of HDPE surface and the crosslinking between HDPE and debris during plasma reaction.

Figure 9 shows the surface of two plasma-treated HDPE films at 100 mTorr, 50 W for 30 and 50 min, respectively. From the three-dimensionally converted image, surface roughness increases with increasing plasma treatment time. Commonly, HDPE is known to have a lamella structure and the lamella structure usually has two phases, crystalline and amorphous. According to this result, plasma-treated HDPE surface layer may be converted from crystalline to amorphous after plasma treatment.

CONCLUSION

The crosslinking properties of argon plasma-treated HDPE are investigated by gel content measurements and FTIR analysis. The gel content (%) of plasma-treated HDPE increases (from 0.0 to 0.75 and 1.05%) with an increase in treatment time, but remains constant with further treatment. Penetration depth of plasma-treated HDPE is within the range of 4.5–5 μm. The plasma-treated thickness increases with increasing treatment time and RF power, but remains constant

after treatment. From the FTIR analysis, it is confirmed that the intensity of the main peaks corresponding to CH_2 bands becomes smaller after plasma surface modification. The functional groups observed at 1223 and 1162 cm^{-1} are found to be CF_2 . The crosslinked layer after plasma treatment is limited only at the HDPE surface and the influence of the surface crosslinking on the bulk thermal property is less observed. Thus, the HDPE beads surface-crosslinked by way of argon plasma treatment can be a promising material for thermal energy storage.

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