Thermal Characteristics of Surface-Crosslinked High Density Polyethylene Beads as a Thermal Energy Storage Material

Jae-Woo Kim, Young-Sun Kim and Ho-Suk Choi[†]

Department of Chemical Engineering, Chungnam National University, 220 Gung-dong, Yusong-gu, Daejeon 305-764, Korea

Abstract–High density polyethylene (HDPE) beads were surface-crosslinked in a modified plasma reactor by using argon plasma. The modified plasma reactor can treat a large amount of beads to be uniformly surface-crosslinked. The objectives of this study were to develop a shape-stabilized functional thermal energy storage material and to find an optimum plasma reaction condition out of various operations. To achieve these objectives, we systematically studied the effects of the gas pressure, the radio frequency (RF) power and the treatment time on the degree of crosslinking. The degree of crosslinking was measured by solvent extraction method (BXM: boiling xylene method). The chemical and physical characterization of the material was performed by using fourier transform infra-red (FT-IR) spectroscopy, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). Finally, we confirmed the thermal stability of surface-crosslinked HDPE through about 50 thermal cycling tests.

Key word: Plasma, Crosslinking, HDPE, Thermal Energy Storage Materials

INTRODUCTION

Radio frequency plasma treatment has been mainly applied in the field of the surface modification of solid materials [Kim et al., 2000]. A pure plasma is known to contain both positive and negative ions, atoms and metastables of atoms, which have been used to modify polymer surface properties such as crosslinking, wettability and adhesion without changing bulk property [Clark and Dilk, 1997]. Essential to the technique is that electrons, atoms and radicals in the plasma attack the surface of the polymeric materials, 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 a crosslinked chain. Crosslinking mechanism in argon plasma is shown in Fig. 1. By the way, good contact of the polymer surface with plasma is an important factor for the efficient modification of polymer surface. Thus, in this study, we focus on the homo-

geneous surface crosslinking of high density polyethylene (HDPE) beads [Hudis, 1972]. Beads are difficult to handle in plasma treatment because of the large surface area per unit mass of beads. The unexposed region of beads or powders is hardly modified. In the previous studies, Anand et al. [1981] modified polyethylene particles in the fluorine plasma which was induced in a vibrating fluidized bed. Masuoka et al. [1984] used a rotary kiln as a plasma reactor to coat powders with polymer film. Kusakabe et al. [1989] observed that fine particles were smoothly fluidized at reduced pressures. Generally, the fluidized bed reactor is favorable to treat powders because of the uniformity in the bed and the ability of continuous powder handling [Inagaki et al., 1992; Park and Kim, 1999]. Therefore, all powders can be uniformly treated in the fluidized bed plasma reactor. Beads, however, can hardly be treated in the fluidized bed reactor because the fluidization of beads is very difficult due to their weight.

By the way, HDPE has good thermal properties such as melting point of 120-135 °C and latent heat of 180-210 J/g. Thus, it has been reported that HDPE is suitable for its use as a thermal energy storage material [Salyer and Davision, 1983]. Until now, three other methods of controlled chemical and physical crosslinking of HDPE have been reported: (1) peroxide-initiated, free radical crosslinking, (2) vinyl triethoxy silane grafting and crosslinking, and (3) electron beam crosslinking. When we apply the above three methods for the crosslinking of HDPE, however, the crosslinking reaction can occur in the inside of HDPE beads which results in 20-30% losses of latent heat due to the decrement of linear HDPE's crystallinity, although it still shows high temperature form stability.

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 was performed by using boiling xylene method (BXM), fourier transfer infra-red (FT-IR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA)
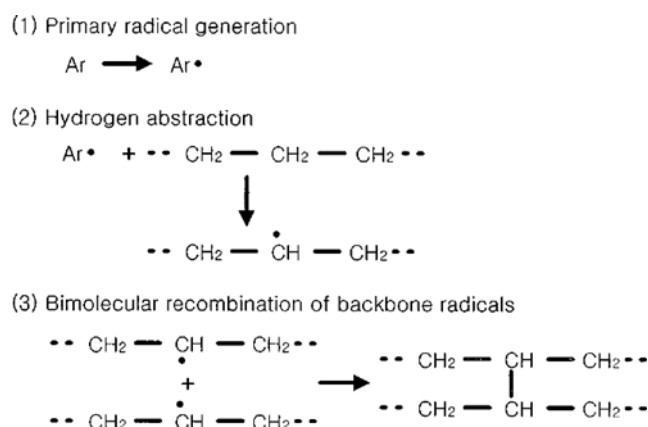
(1) Primary radical generation

$$Ar \longrightarrow Ar\bullet$$

(2) Hydrogen abstraction

$$Ar\bullet \; + \; {}^{\bullet\bullet}CH_2 \longrightarrow CH_2 \longrightarrow CH_2{}^{\bullet\bullet}$$

$$\downarrow$$

$${}^{\bullet\bullet}CH_2 \longrightarrow \overset{\bullet}{C}H \longrightarrow CH_2{}^{\bullet\bullet}$$

(3) Bimolecular recombination of backbone radicals

$${}^{\bullet\bullet}CH_2 \longrightarrow \overset{\bullet}{C}H \longrightarrow CH_2{}^{\bullet\bullet} \quad + \quad {}^{\bullet\bullet}CH_2 \longrightarrow \overset{\bullet}{C}H \longrightarrow CH_2{}^{\bullet\bullet} \longrightarrow {}^{\bullet\bullet}CH_2 \longrightarrow CH \longrightarrow CH_2{}^{\bullet\bullet}$$

$${}^{\bullet\bullet}CH_2 \longrightarrow \overset{\bullet}{C}H \longrightarrow CH_2{}^{\bullet\bullet} \qquad {}^{\bullet\bullet}CH_2 \longrightarrow CH \longrightarrow CH_2{}^{\bullet\bullet}$$

Fig. 1. Crosslinking mechanism in argon plasma.

[†]To whom correspondence should be addressed.
E-mail: hchoi@cnu.ac.kr

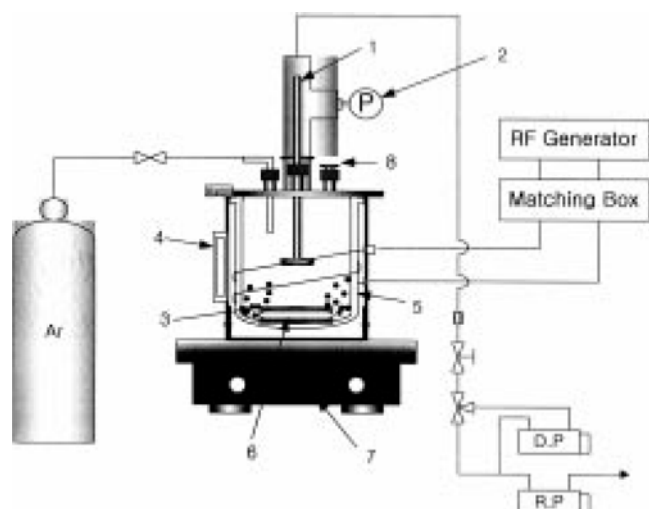**Fig. 2. Reactor for plasma treatment of particles or film.**

1. Sample fixing stick	5. Reactor
2. TC gauge	6. Magnetic bar
3. HDPE particles	7. Magnetic stirrer
4. Cooling fan	8. Venting valve

and image analyzer.

EXPERIMENTAL

A schematic diagram of the apparatus used in this study is represented in Fig. 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 micro needle valve, respectively. The reduced pressure in the rector is maintained by using both a mechanical rotary vacuum pump (Woosung vacuum Co., 200 l/min) and diffusion pump (KODIVAC Co., 360 l/sec). TC gauge (Varian Co., 801, analog type) is used to measure pressure in the reactor. An inductively coupled electrode (4 mm-OD copper tube, 2turn) 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 a RF power generator (YOUNG-SIN Engineering Co., 0-300 W). To prevent overheating of the electrode and diffusion pump, a cooling system (mechanical fan) is installed at both the electrode and diffusion pump. To mix particles, a magnetic stirrer (TOPS Co., MS-300, rpm: max 1000) is used. The reactor is made of 90 mm ID and 110 mm-high Pyrex glass column.

Resin specifications and physical properties of HDPE 8800 are shown in Table 1. HDPE sample film was prepared from commercial grade HDPE pellets (density: $0.956 \, g/cm^3$, M.I.: 0.04 g/10 min,

Table 1. Specifications and properties of HDPE 8800

	Test method	Values
Density (g/cc)	ASTM D1905	0.956
Melt index (dg/min)	ASTM D1238	0.04
Tensile yield strength (kg/cm²)	ASTM D638	230
Ultimate tensile strength (kg/cm²)	ASTM D638	300
Elongation at break (%)	ASTM D638	>500

Table 2. Experimental conditions and ranges

Gas	Argon (99.999% purity)
HDPE film [mm]	20×35×0.5
Particle [mm]	3
Pressure [mTorr]	60, 100, 200
Treatment time [min]	1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 60
RF power [Watt]	50, 100, 150, 200, 250
Magnetic stirrer speed [rpm]	600

YUZEX Co., HDPE 8800) by hot press method. After the HDPE particles of 20 g were loaded into the reactor and then gas in the reactor was evacuated to base pressure, argon gas (purity: 99.999%) was injected for approximately 10 min. The experimental pressures were 60, 100, 200 mTorr, respectively. The experimental variables and their ranges for plasma surface crosslinking and thermal cycling of HDPE beads are summarized in Table 2. HDPE particles were stirred in the reactor at a rotation speed of 600 rpm with a magnetic stirrer. Then, power was adjusted to start glow discharge. After the desired treatment time, plasma was turned off, and samples were kept in the reactor for more than 20 min at the given gas flow rate. After plasma treatment, HDPE samples were characterized by the following procedures.

1. Degree of Gel Content

Gel content of the treated HDPE particles, which is regarded as the crosslinking degree, was measured by ASTM D2765-95 procedure. A known amount of a crosslinked HDPE sample was placed in a pre-weighed 150 mesh stainless steel basket. Crosslinked HDPE and stainless steel basket were weighed and then extracted in boiling xylene (p-xylene, Oriental Chemical Co.) together with stabilizer (2,6-Di-tert-butyl-4-methylphenol) for 12 hours. After extraction, the undissolved portion of HDPE was dried under vacuum at 100 °C for 10 hr, then weighed and compared with the original weight. Finally, gel content was calculated as follows:

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

Where, M_b is a weight after extraction and M_f is a weight after plasma treatment.

2. Fourier Transform Infra-Red Spectroscopy

FT-IR spectra of the argon plasma-treated HDPE were recorded on a Bomen FT-IR spectrophotometer with a diffuse reflector (APPLIED SYSTEM INC., REACTIR™ 1000). The FT-IR technique is known as a simple and rapid method to confirm the chemical bond of polymer surface.

3. Differential Scanning Calorimetry (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. The measurement was carried out under nitrogen purging at 10 °C/min scan rate from 20 to 180 °C.

4. Scanning Electron Microscope (SEM)

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

5. Thermogravimetric Analyzer (TGA)

A TGA (951 Thermogravimetric Analyzer, TA instrument) was used for investigating the thermal stability change of surface-cross-

linked HDPE after 50 thermal cycling tests.

6. Image Analysis

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

7. Thermal Cycling Test

We repeatedly performed melting and solidification of surface crosslinked HDPE beads. For melting and solidification, we repeatedly heated and cooled the HDPE beads submerged in liquid ethylene glycol (Oriental Chemical Co.) between 50 and 150 °C. After 50 thermal cycles, we compared the thermal characteristics of plasma-treated beads with those of plasma-untreated beads through the analysis of DSC and TGA results. During this thermal test, we also used an antioxidant (butylated hydroxy toluene: BHT) to investigate the effect of the oxidation on the thermal stability of crosslinked HDPE.

RESULTS AND DISCUSSION

Pressure, RF power, treatment time and type of gas are main parameters which control the plasma surface modification of polymeric materials [Park and Kim, 1994]. The importance of these parameters was reconfirmed here for HDPE. In this study, surface properties of argon plasma-treated HDPE were compared with those of plasma-untreated HDPE. Then, the morphological features of HDPE surface layer were investigated.

The effect of treatment time on the gel content (%) of argon plasma-treated HDPE is shown in Fig. 3. It is obvious that the gel content (%) of the plasma-treated HDPE increases with increasing treatment time because of the formation of crosslinked structure at the surface layer, but levels off after further treatment. Under the RF power of 50 Watt, the gel content of plasma-treated HDPE increases from 0 to 0.75% during the time interval of 0 to 10 min. This figure also represents that, in case of argon plasma operation under 100 mTorr and 150 Watt, the gel content of plasma-treated HDPE rapidly increases from 0 to 0.92% as reaction proceeds for 5 min, and levels off after 5 min. The time required for a constant gel content depends on the RF power: 15 min for the HDPE plasma-treated at
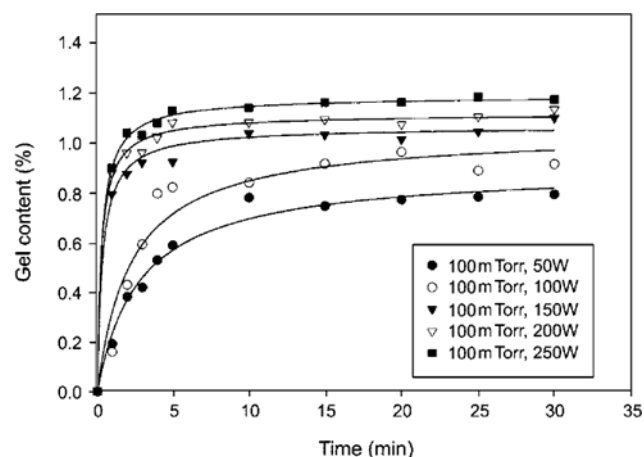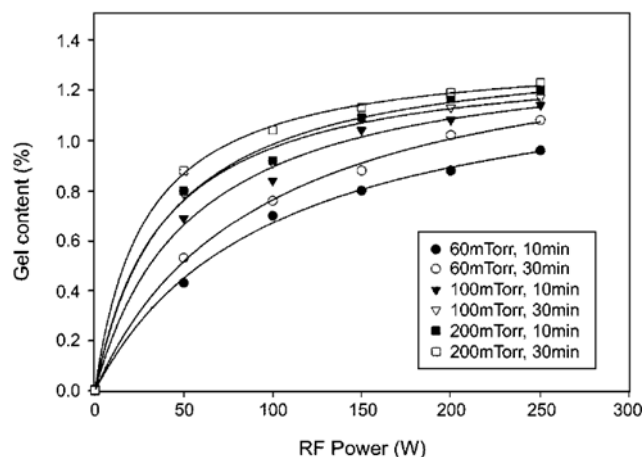

Fig. 4. Effect of rf power on gel content (%) of argon plasma HDPE film.

100 mTorr-50 Watt, 5 min for the HDPE plasma-treated at 100 mTorr-100 Watt, 3-4 min for the HDPE plasma-treated at 100 mTorr-150, 200, 250 Watt. The total gel content is also affected by the plasma power, as shown in the Fig. 3. It increases with increasing the plasma power. This is because Ar gases can have more kinetic energies as the plasma power increases and then can penetrate more deeply from surface to bulk.

The effect of the RF power supplied (50-250 W) by plasma on gel content (%) is shown in Fig. 4. This figure represents the degree of surface crosslinking of HDPE film treated by argon plasma at given conditions. As can be seen in the figure, gel content of HDPE film gradually increases with increasing RF power. At low pressure, gel content is still increasing with increasing RF power while it levels off with increasing RF power at high pressure. As the pressure increases, the mean free path of gas reduces due to the collision with nearby gas molecules but the collision frequency of plasma gas to polymer surface increases.

The FT-IR spectra of argon plasma-untreated HDPE particle and plasma-treated HDPE particle in a modified plasma reactor are shown

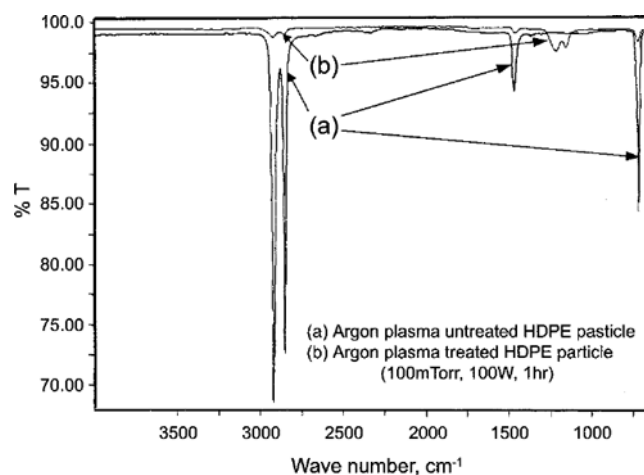Fig. 3. Effect of treatment time on gel content (%) of argon plasma treated HDPE film.

Fig. 5. FT-IR spectra of the argon plasma-treated HDPE particles in a plasma reactor with teflon coated magnetic bar: (a) plasma-untreated, (b) plasma-treated (100 mTorr, 100 W, 1 hr).

Table 3. Summary of FT-IR absorbance peak position

Wave number [cm^{-1}]	Functional group
719.7	CH$_2$ rocking (CH$_2$)
1162	CF$_2$ symmetry stretching
1223	CF$_2$ asymmetry stretching
1470	CH$_2$ bending (δ_s CH$_2$)
2850	CH$_2$ symmetry stretching (v_s CH$_2$)
2916	CH$_2$ asymmetry stretching (v_{as} CH$_2$)

in Fig. 5. The positions of FT-IR absorption peaks are summarized in Table 3. Fig. 5(a) represents the IR spectrum for argon plasma untreated HDPE particles. It shows strong absorption peaks at 2,916, 2,850, 1,470 and 719.7 cm^{-1} which are due to CH$_2$, CH$_3$ and terminal vinyl groups. The asymmetrical stretching (v_{as}CH$_2$) and symmetrical stretching (v_sCH$_2$) occur near 2,916 and 2,850 cm^{-1}, respectively [Silverstein et al., 1991]. The frequency of methylene stretching is increased when the methylene group, which has four bending vibrations, is scissoring, rocking, wagging and twisting. Here, the scissoring band (δ_sCH$_2$) in the spectra of untreated HDPE appears near 1,470 cm^{-1}, and CH$_2$ rocking is 719.7 cm^{-1}. As shown in Fig. 5(b), the plasma-treated HDPE shows fewer CH absorption peaks than the untreated one, but new absorption peaks of fluorine functionalities appear in the range of 1,162-1,223 cm^{-1} due to the transfer of
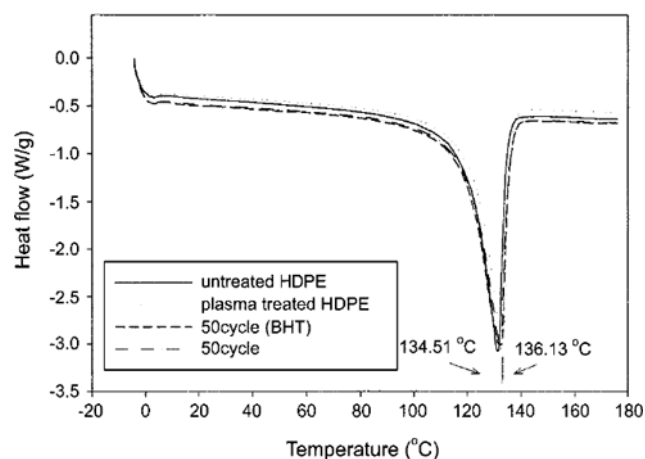
Fig. 6. DSC diagrams of HDPE beads.

fluorine from Teflon-coated magnetic bar. In general, the region of IR bands from about 1,000 cm^{-1} to 1,350 cm^{-1} is assigned to various fluorine-carbon bands. Polytetrafluoroethylene shows two strong bands at 1,223 cm^{-1} and 1,162 cm^{-1} which corresponds to CF$_2$ asymmetrical and symmetrical stretching, respectively. The fluorine compound usually lowers the surface energy of material so that it prevents the coagulation between particles [Das et al., 1994]. Due to this additional advantage from the fluorine compound, the surface-
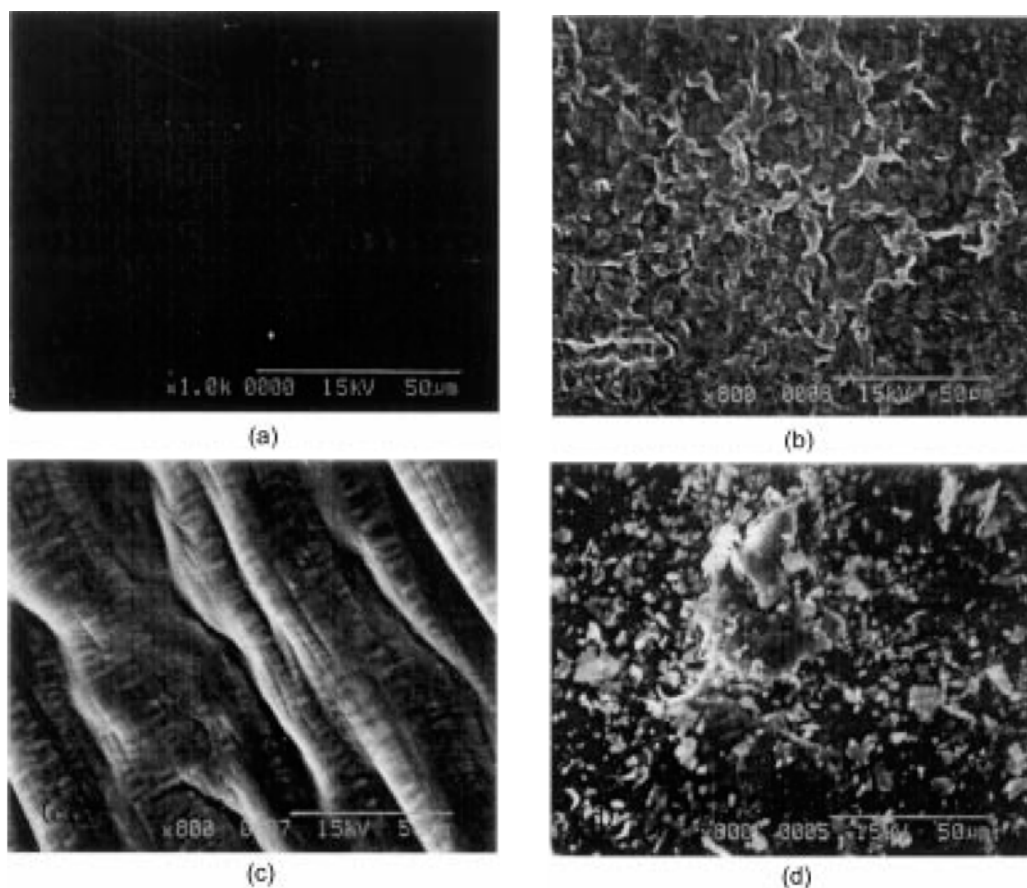
Fig. 7. SEM photographs of (a) untreated HDPE film, (b) remainder after the solvent extraction of the treated HDPE film, (c) untreated HDPE particles and (d) plasma treated HDPE particle (100 mTorr, 100 W, 1 hr).
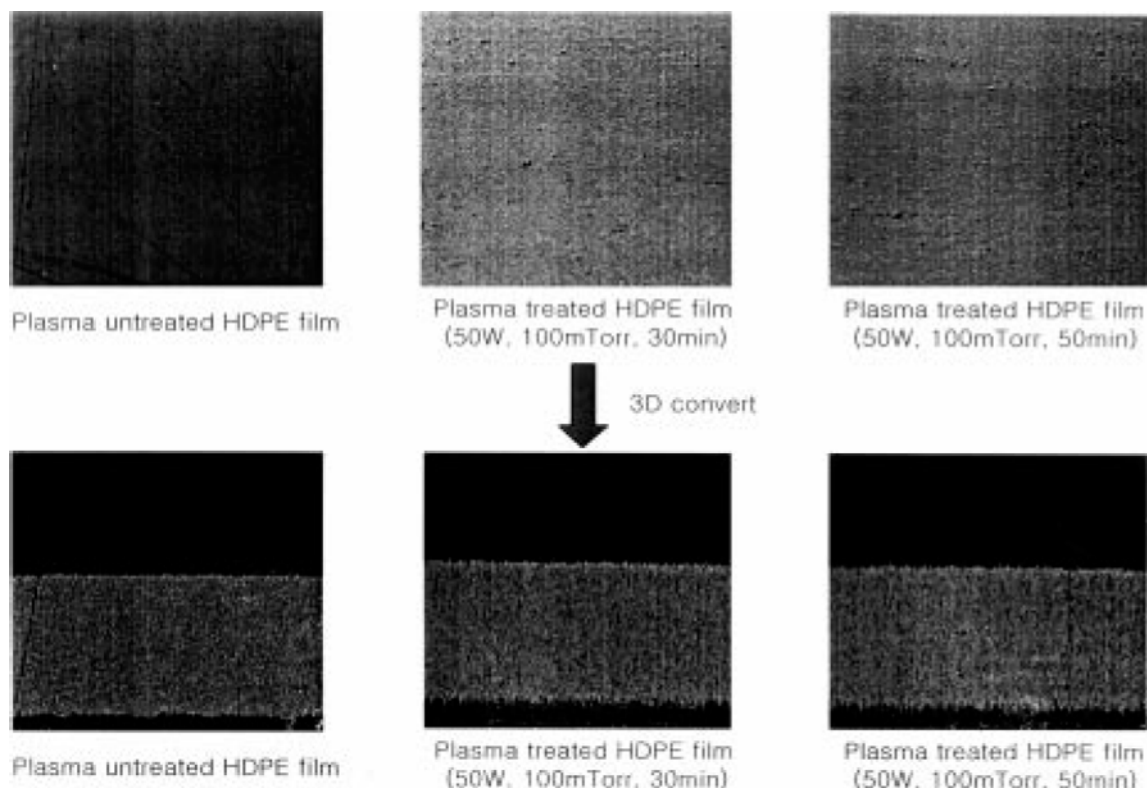
Fig. 8. Optical observations of surface property on plasma untreated HDPE film and plasma treated HDPE film (50 W, 100 mTorr, 30 min).

crosslinked HDPE can be more effective thermal energy storage material for both the storage and the transportation of thermal energy.

Fig. 6 shows the comparison of DSC diagrams of the plasma-untreated HDPE particle with that of plasma-treated HDPE particle prepared under the condition of 100 Watt RF power for 1 hr at 100 mTorr. The melting points of plasma-treated and -untreated HDPE particles measured with DSC are 136.13 °C and 134.51 °C, respectively. From this result, 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 diagram in case of plasma-treated HDPE is almost the same as the profile in case of plasma-untreated HDPE. It means that the crystallinity of the HDPE does not change after crosslinking of 100 W RF power, so endothermic peak for phase change from crystalline to amorphous shows almost the same change both in plasma-treated HDPE and untreated HDPE. Since the cross-linked layer is bounded only at thin surface layer, the bulk thermal property does not change even after crosslinking. After 50 melting and solidification cycles, the thermogram does not show any significant difference from the untreated HDPE. The peak area calculation showed that the plasma-treated sample had 92% latent heat of original untreated sample and the sample tested with adding anti-oxidant had 5% more latent heat than the sample tested without adding antioxidant after 50 thermal cycling tests. We were also able to observe that the addition of antioxidant prevented the coagulation of crosslinked HDPE beads after 50 thermal cycling tests.

Fig. 7 represents SEM photographs of HDPE surface. Fig. 7(a) shows the untreated HDPE film. Fig. 7(b) is the remainder after the extraction of the treated HDPE film. It is a 100% crosslinked HDPE. Figs. 7(c) and (d) represent the untreated and the treated

HDPE particles, respectively. From Figs. 7(c) and (d), the effect of argon plasma treatment on morphological features of HDPE can be observed. Many small particles and debris are adhered on the HDPE surface. This result may result in the ablation and crosslinking during argon plasma treatment.

Fig. 8 shows the surface of plasma-treated HDPE at 100 mTorr, 50 Watt and 1 hr. From 3 dimensionally converted images, 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. Due to the crosslinking of HDPE surface layer, we can guess that plasma-treated HDPE surface layer becomes crosslinked amorphous struc-
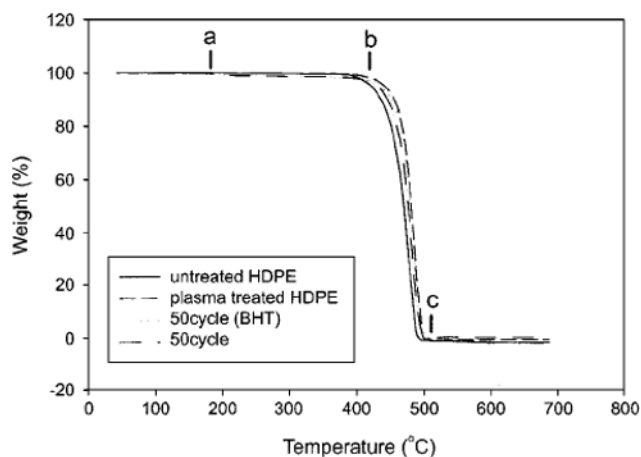

Fig. 9. TGA diagram of HDPE.

ture after plasma treatment while the bulk still has both crystalline and amorphous structures.

Fig. 9 represents the behavior of thermal decomposition of four different samples. As shown in the figure, each sample shows three step decompositions (a-b-c). At around 200 °C (first step), some components that are weakly bonded or connected with branches are evaporating and decomposing from the main chain of polymeric material. At a temperature of 400 to 500 °C (second step), the main chains are explosively decomposed and thermally stable graphite chars are formed. After 500 °C (third step), the graphite chars are slowly decomposed. The surface crosslinked HDPE shows the second step decomposition at higher temperature than the untreated HDPE. This is because the former is more thermally stable than the latter due to the crosslinking of backbone chain. After 50 cycling tests, more decompositions occurred from 200 °C to 400 °C and also the second step decomposition occurred a little faster than that of the original crosslinked HDPE. This means that oxidization during thermal cycling deteriorates the thermal stability of crosslinked HDPE. However, we were able to observe that the addition of antioxidants slowed down the deterioration of the thermal stability.

CONCLUSIONS

The crosslinking properties of argon plasma-treated HDPE were investigated by gel content measurements and FT-IR analysis. The HDPE crosslinked by argon plasma has 0.75-1.04% gel content. The gel content (%) of plasma-treated HDPE increases with increasing treatment time, but it remains constant with further treatment. From the analysis of FT-IR, it is confirmed that CH_2 bands become smaller after plasma surface modification. The functional groups observed at 1,223 cm^{-1} and 1,162 cm^{-1} are proved to be CF_2 bands due to the transfer of fluorine from a Teflon-coated magnetic bar. Based upon the analysis of DSC and TGA, the crosslinked layer after plasma treatment is limited only at HDPE surface and the influence of the surface crosslinking on the bulk thermal property is less observed. Thus, the HDPE beads surface-crosslinked in the modified argon plasma reactor can be a promising material for thermal energy storage and transfer, since they show good shape-stability and thermal storage characteristics above their melting point without any significant drop of latent heat even after 50 thermal cycling tests.

ACKNOWLEDGEMENT

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