Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 6287–6295

polymer

www.elsevier.com/locate/polymer

Investigation of crystallinity effects on the surface of oxygen plasma treated low density polyethylene using X-ray photoelectron spectroscopy

Kwang Soo Kim[a], Chang Mo Ryu[b], Chan Sup Park[c], Gil Soo Sur[d], Chan Eon Park[a,*]

[a]Department of Chemical Engineering, School of Environmental Science and Engineering, Polymer Research Institute, Pohang University of Science and Technology, Hyojadong, Pohang 790784, South Korea
[b]Department of Physics, Pohang University of Science and Technology, Pohang, South Korea
[c]Steel Products and Process Research Group, Technical Research Laboratories, POSCO, Pohang, South Korea
[d]School of Chemical Engineering and Technology, Yeungnam University, Kyongsan, South Korea

Received 2 April 2003; received in revised form 8 July 2003; accepted 22 July 2003

Abstract

Plasma treated polymer surface shows rapid hydrophobic recovery after plasma treatment. Surface rearrangement and the hydrophilicity change of low density polyethylene (LDPE) films with different degrees of crystallinity after oxygen plasma treatment were investigated using X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. Since the mobility of polymer chain was restricted in the crystalline region, the chain movement of high crystalline polymer would be reduced. Water contact angles of quenched and annealed LDPE just after plasma treatment were almost same and oxygen contents of quenched LDPE was slightly higher than that of annealed LDPE. However, annealed LDPE showed slower contact angle raise and kept higher oxygen concentration than quenched LDPE with increasing aging time. By deconvolution of carbon XPS spectra, it was observed that major group contributed to decrease of oxygen contents was the hydroxyl groups and hydroxyl groups of quenched LDPE decayed faster than annealed LDPE while other oxygen species kept constant or decreased slightly. Increasing crystallinity reduce the surface rearrangement of polymer chain after plasma treatment.

Keywords: Plasma; Surface rearrangement; XPS

1. Introduction

Plasma treatment is very useful method to make hydrophobic polymer surface to hydrophilic surface for improving wettability and adhesion properties without changing bulk properties [1–3]. However, since the mobility of polymer chains enables polymer surface to respond to interfacial force and to adapt their surface chemical structure to their environment, polymer shows hydrophobic recovery after plasma treatment in air [4,5]. By rotational and translational motions of chains and chain segments, the surface composition can change in order to minimize the interfacial free energy between the polymer surface and environment [6]. If aged polymer in air was immersed in water, the polar groups would recover onto surface region. S. Kuroda showed the effect of aging media after plasma treatment [7]: When the plasma treated polymers were aged in nitrogen gas, the surface free energy value decreased with aging time, but when the polymers were aged in water, the surface free energy of polymers approached that of water.

This chain mobility mainly occurs in the amorphous region and the mobility in the crystalline region is fairly limited because of an orderly packed structure [7–10]. With high crystalline polymers, hydrophobic recovery would be reduced because highly restricted chain mobility in the crystalline region could limit the rotational and translational motions in surface region after plasma treatment. This restricted chain mobility decreased the aging rate of polar groups in the surface with crystalline polymer. Therefore, after aging there were more polar groups on the surface with crystalline polymer.

Crystallinity effects on surface arrangement would be important factors for preventing aging after plasma treatment in the view of surface dynamics. Surface chemistry

---

* Corresponding author. Tel.: +82-54-279-2269; fax: +82-54-279-8298.
E-mail addresses: cep@postech.ac.kr (C.E. Park).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00674-8

change during aging time was observed to study the effect of crystallinity of LDPE samples with different degree of crystallinity after oxygen plasma treatment.

Aging behavior of oxygen plasma treated LDPE with different crystallinity was examined using water contact angle meter and SEM was used to investigate the surface morphology change before and after plasma treatment. The diffusional movement of polymer chains incorporated with oxygen groups was observed using XPS. And deconvolution of XPS spectra revealed the detail change of oxygen groups during aging time.

2. Experimental

2.1. Materials

The polymer material used here was commercial low density polyethylene (LDPE, Hyundai Petrochem. Co.). LDPE pellets were pressed against chromium coated steel plates by a Carber Laboratory Press at 150 °C for 2 min, and then LDPE films were quenched into liquid nitrogen immediately after melting to prevent crystallization of the polymer. LDPE films were also annealed at 90 °C for 24 h to increase crystallinity. The film thickness was 0.5 mm. Melting point and the glass transition temperature measured by DSC (Perkin–Elmer DSC7) were 109 and −30 °C, respectively. Before plasma treatment LDPE films were washed with ethanol and water mixture using ultrasonicator to remove the dirt on the surface and to remove the LMWM (low molecular weight materials) after oxygen plasma treatment.

The crystallinity was obtained by the melting enthalpy from DSC and by wide angle X-ray scattering spectra from XRD. But the crystallinity from the calculation using DSC or XRD does not represent the surface crystallinity, so the surface crystallinity was checked using the grazing incident angle X-ray diffraction (GIXD) at 8C1 beam line of Pohang Acceleration Laboratory (PAL). For GIXD, 0.1 degree of incident angle was selected and the depth of penetration (τ) with 0.1 grazing angle was around 100 nm from calculating using the following equation [11].

$$\tau = \frac{\sin^2\theta - \sin^2\psi}{2\mu \sin\theta \cos\psi}(\alpha = \theta + \psi) \tag{1}$$

where α is the angle of incidence, θ is one-half the scattering angle, ψ is the tilt angle, and μ is the linear absorption coefficient. The crystallinities of quenched and annealed LDPE obtained from DSC, XRD, GIXD were shown in Table 1.

Table 1
Crystallinity of LDPE obtained using DSC and XRD

	DSC (%)[a]	XRD (%)[b]	GIXD (%)[b]
Quenched LDPE	31	35	28
Annealed LDPE	40	45	44

[a] The crystallinity was calculated by dividing the melting enthalpy with the fusion energy of 100% crystalline PE, 69 cal/g [12].

[b] The crystallinity was calculated from the areas under the amorphous peak and crystalline peaks of XRD spectra [13].

2.2. Plasma treatment

Plasma treatments were performed with the LDPE sample located on the grounded electrode using a parallel plate reactor. Scheme 1 shows a schematic diagram of plasma equipment. Prior to the plasma treatment, the chamber containing the samples was evacuated to about 1.0×10^{-5} Torr with mechanical and diffusion pumps. Pure oxygen (99.999%) gas was introduced into the chamber for 5 min before generation of plasma to assure uniform gas environment. The plasma parameters were as follows: excitation frequency 13.56 MHz, power 150 W, treatment time 1 min, pressure 20 mTorr, and gas flow rate 35–40 cm^3/min. After finishing the plasma treatment, oxygen gas was used to purge the reactor for the reaction of radicals with oxygen molecules. Aging experiment was done in a forced-air convection oven at room temperature.

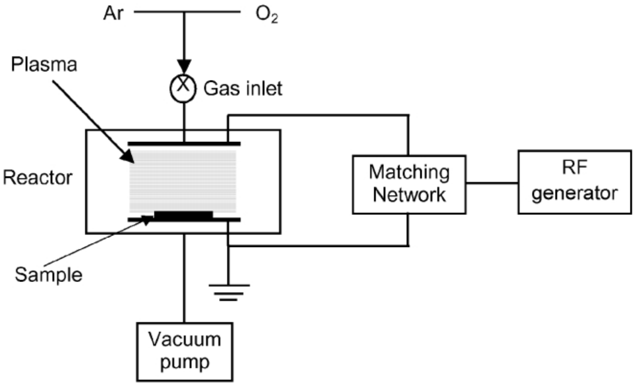
2.3. XPS

The oxygen atomic concentrations of the surface of oxygen plasma treated polyethylene were analyzed using X-ray photoemission spectroscopy at the 4B1 beam line of PAL with 650 eV X-ray source energy. Take-off angle of photoelectrons from the sample surface to photoelectron detector was varied from 20° to 50° and 90° for depth profiling, and sampling depth for each take-off angle can be calculated from Eq. (2) [14,15].

$$\zeta = 3\lambda \sin\theta \tag{2}$$

ζ : the sampling depth; λ : the inelastic mean free path; θ : take off angle.

First XPS analysis was carried out 2 h after plasma treatment because it took 2 h to make stable vacuum pressure (below 1×10^{-9} Torr) in the main chamber. And



Scheme 1. Schematic diagram of capacitor type plasma reactor.

C_{1s} and O_{1s} spectra were obtained after 1, 3, 7 days to observe the decay of oxygen species on the surface. From C_{1s} spectra shoulder peaks over 285 eV were observed and these sub peaks were discussed later. Oxygen atomic concentration of oxygen (C_{oxygen}) was calculated from respective peak area of assumed Gaussian–Lorentzian curves using following equation.

$$C_{\text{oxygen}} = \frac{A_{\text{oxygen}}/S_{\text{oxygen}}}{A_{\text{oxygen}}/S_{\text{oxygen}} + A_{\text{carbon}}/S_{\text{carbon}}} \qquad (3)$$

Area of carbon (A_{carbon}) and oxygen (A_{oxygen}) were calculated using PC software 'PeakFit' and the atomic sensitivity factors (S) based on peak area measurement were taken as 0.296 for C_{1s} and 0.711 for O_{1s} to normalize the intensities of the signals [16].

2.4. Contact angle measurement

Contact angle measurements were performed on the plasma treated LDPE at room temperature with distilled water. Water contact angles were obtained by the sessile drop technique using a contact angle measuring system (SEO Co., SEO 300A plus) with CCD camera image equipment after plasma treatment. The water contact angle of untreated LDPE was around 85°. Water contact angle of oxygen plasma treated LDPE which was aged in air were measured with increasing time.

Aged LDPE films were stored in water for 24 h and the water contact angle of these samples was checked again to observe hydrophilic recovery of oxygen plasma treated LDPE. Each contact angle reported was the average of 10 different measurements on a sample surface and at least five samples were used for every condition.

2.5. SEM

Before and after oxygen plasma treatment, LDPE surface morphology coated with platinum was investigated using field emission SEM (Hitachi, S-4200) with 8 kV. FESEM images have been recorded at a magnification of 30,000.

3. Results

3.1. Surface morphology

Surface lamellar structure was observed in the annealed LDPE, but the surface was smooth in the quenched LDPE as shown in Fig. 1. SEM surface morphology images showed that some crystalline region was generated in surface layer during annealing and the surface of quenched LDPE was covered with amorphous region. This fact was verified with surface crystallinity from GIXD. After oxygen plasma treatment, the lamellar structure was shown in the quenched LDPE and the lamellar structure was more embossed and thickened in the annealed LDPE. This rough surface was from the difference of plasma susceptibility because crystalline and amorphous polymer and crystalline region was etched more slowly than amorphous region [17,18]. According to Wenzel equation, the roughness of surfaces influences the contact angle [19,20].

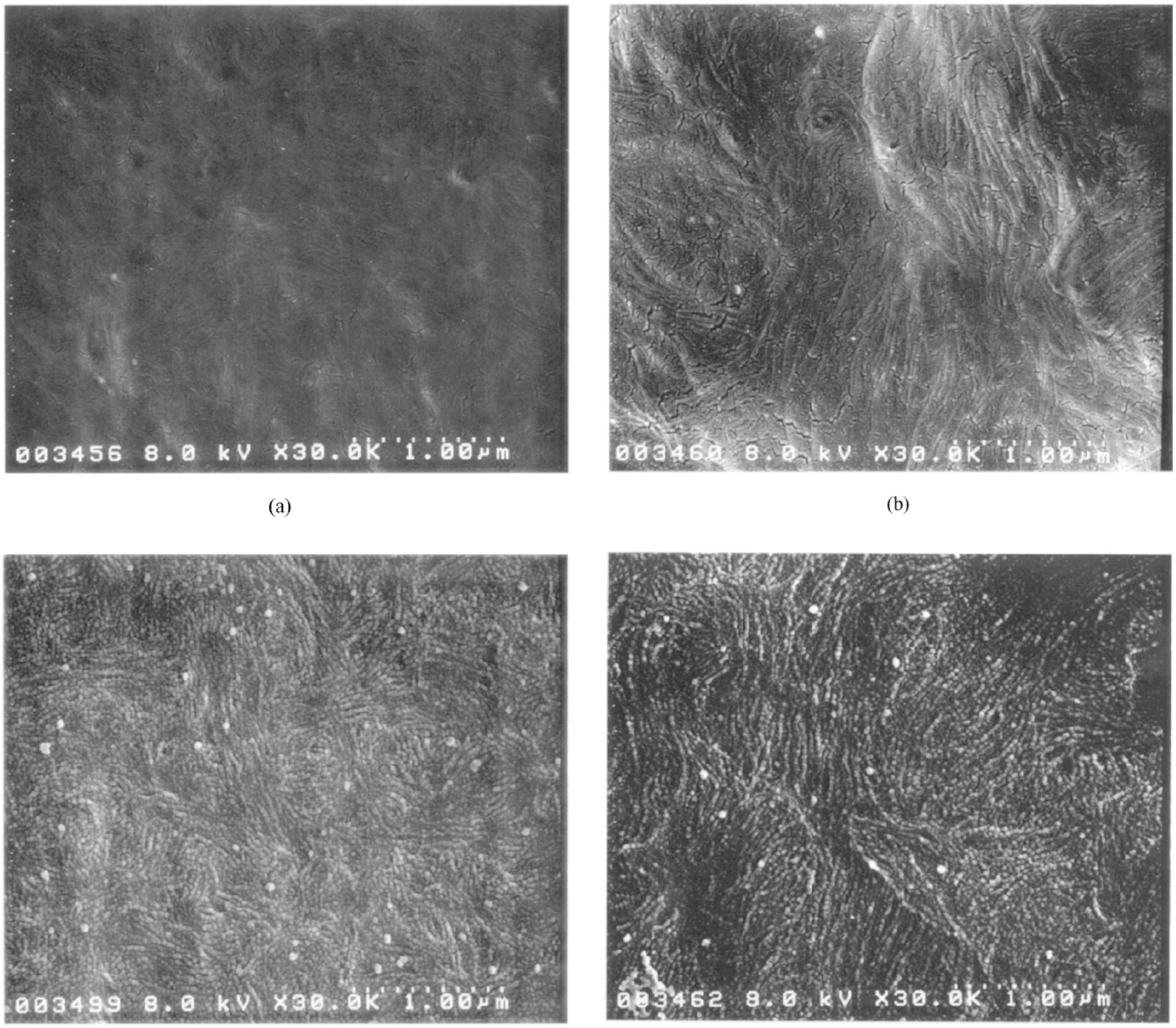
$$\cos \theta^{\text{rough}} = r \cos \theta_0 \qquad (4)$$

where θ^{rough} is the contact angle on a surface of sample, θ_0 is the thermodynamic contact angle on the smooth surface, and r is the roughness (ratio of the actual area of the interface to the geometric surface area). From this equation, for the surface having lower contact angle than 90°, increasing roughness decrease the contact angle. But Busscher et al. found that if the roughness is below 100 nm, there was no influence on the contact angle [21]. The roughness for oxygen plasma treated LDPE was around 100 nm (it was verified with AFM), so the contribution of roughness for the lowering the water contact angle was expected to be small and would not affect the aging phenomena.

3.2. XPS analysis

Atomic concentration of oxygen with increasing aging time is shown in Fig. 2. Before aging the oxygen concentration of the surface with 20° take off angle was 5% more than that of the surface with 90° take off angle. The linear decrease in oxygen concentration with the increasing depth from the surface reveals that reactions of polymer chains with oxygen plasma took place in the very shallow surface region. For the generation of the oxygen species, C-radicals have to be formed by accelerated oxygen ions in the plasma and have to meet the molecular oxygen. However, the oxygen ions cannot penetrate into the deep surface layer and the molecular oxygen cannot diffuse into the bulk easily, and the decreasing depth profile of oxygen concentration was obtained. Additionally, lower diffusion of molecular oxygen into the polymer matrix for low free volume of the high crystalline region was expected as the one of the reason for lower oxygen atomic concentration of annealed LDPE.

Oxygen concentration of quenched LDPE was a little higher than that of annealed LDPE through the surface region. The higher degree of oxygenation of quenched LDPE reflects a greater chemical reactivity of the quenched LDPE under the influence of plasma. Our previous report with HDPE having low or high crystallinity also showed similar results and this is due to the fact that the hydroperoxide as key intermediate from the reaction of the radicals and oxygen is relatively more mobile in the polymer matrix having lower crystallinity [22]. More oxygen corporate carbon can be generated in the low crystalline LDPE easily. Morra et al. has reported that the



(a) (b)

(c) (d)

Fig. 1. SEM images of untreated (a) quenched LDPE and (b) annealed LDPE, and oxygen plasma treated (c) quenched LDPE and (d) annealed LDPE.

higher reactivity of the polymer, having lower crystallinty fraction, is due to the greater freedom of motion granted by the higher percentage of the amorphous region of the polymer [23].

Oxygen concentrations decreased continuously just after oxygen plasma treatment for both LDPE samples. Although within the depth of 8 nm the decrease of oxygen concentration was not much, the atomic oxygen concentration of quenched LDPE had diminished more rapidly than that of annealed LDPE. With 20° take off angle for 2 nm penetration depth, quenched LDPE showed sharp decrease of oxygen concentration after oxygen plasma treatment. Within surface layer (≤ 1 nm) polar groups moved fast because of the difference of surface energy between the surface and air, but over the depth of 1 nm the driving force of migration of polar groups was not as strong as that of the surface layer.

After 7 days, there was 10% decrease in the oxygen concentration of quenched LDPE, but decrease of oxygen concentration of annealed LDPE was 4% only. There was a reduction of tendency towards surface migration because of higher structural regularity and lower free volume of the polymer matrix with the increase of crystallinity. And in the case of annealed LDPE, the movement of polymer chain participated in the rotational or diffusional movement for minimizing the interface energy was interrupted by the presence of crystalline region. The loss of polar functional groups from the surface would be discussed more in the contact angle measurement part with the view of immobile fraction of polymer surface.

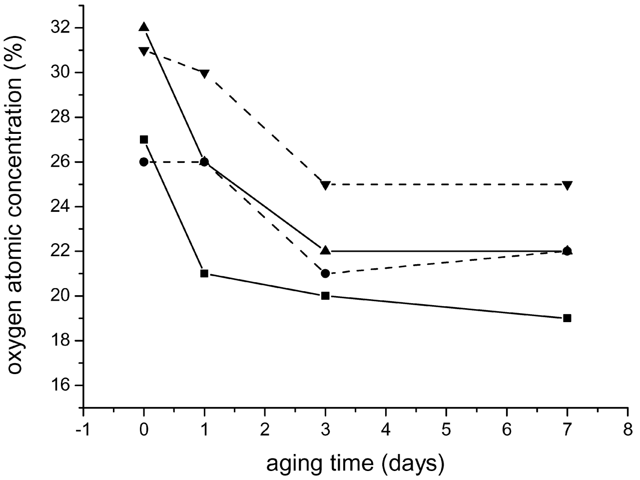


Fig. 2. Oxygen atomic oxygen concentration of quenched LDPE (solid line, ▲:20° take off angle ■:90°) and annealed LDPE (dashed line, ▼:20°, ●:90°) with increasing aging time for different take off angle.

3.3. Water contact angle

From water contact angle measurement it could be estimated that how much polar group in outer surface region (depth ≤ 1 nm) was formed after plasma treatment. The increase of water contact angles of quenched LDPE and annealed LDPE were shown with aging in Fig. 3. The increase of contact angles after aging was interpreted as a result of the migration of polar groups away from the surface to the bulk (depth ≥ 1 nm) [4]. The sharp increase of contact angle within 24 h was similar with the sharp decay of atomic oxygen concentration from XPS in the depth of 2 nm. Both quenched and annealed LDPE showed almost the same contact angle of 5° just after plasma treatment. However, as aging time increased, quenched LDPE showed more rapid hydrophobic recovery than annealed LDPE as like that oxygen atomic concentration from XPS decayed sharply. Contact angle of quenched LDPE increased up to 30° within 3 h and it was 10° higher than that of annealed LDPE after 7 days. Lower contact angle of annealed LDPE suggested that more portions of hydrophilic groups were still remained in annealed LDPE surface rather than quenched LDPE surface after aging, because crystalline region in the annealed LDPE restricted the diffusion of functional groups. Based on Hyun's model the fraction of immobile polar groups (f_{im}) was obtained [9]. Chatelier et al. have defined that 'immobile' polar groups are those that, for instance due to near by cross-linking, cannot participate in polymer chain motions that would transport them beyond the range of interfacial potentials [4]. Because, cross-linked structure was generated not by oxygen plasma, but the inert gas plasma like argon, limitation of polymer chain movement in well ordered crystalline region was the main reason for immobility of polar groups in this study. So, the polymer surface with higher f_{im} had persisted low contact angle after long period of aging.

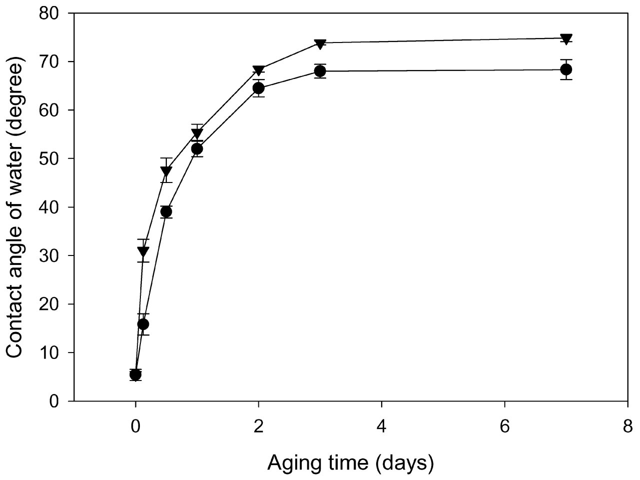


Fig. 3. Water contact angle with increasing aging time of annealed LDPE (●) and quenched LDPE (▼).

J. Hyun suggested the following equations for the calculation of the fraction of polar groups introduced in the crystalline region and that the fraction of immobile polar groups remaining after aging represented the crystallinity of a polymer. [9].

$$f_{\mathrm{m}} = (\cos\theta_{\mathrm{i}} - \cos\theta_{\mathrm{f}})/(\cos\theta_{\mathrm{p}} - \cos\theta_{\mathrm{np}}) \qquad (5)$$

$$f_{\mathrm{im}} = (\cos\theta_{\mathrm{f}} - \cos\theta_{\mathrm{np}})/(\cos\theta_{\mathrm{p}} - \cos\theta_{\mathrm{np}}) \qquad (6)$$

f_{m} : the fraction of mobile polar groups; θ_{i} : initial water contact angle after plasma treatment; θ_{f} : final water contact angle after aging; θ_{p} : water contact angle of completely polar surface (0°); θ_{np} : water contact angle of untreated polymer surface (85°).

The immobile polar groups (f_{im}) do not represent exact surface crystallinity, but it showed tendency of increase as increasing the crystallinity. Table 2 showed the fraction of immobile polar groups (f_{im}) of annealed LDPE were higher than those of quenched LDPE due to higher content of surface crystallinity. These immobile polar groups with limited movement caused the lower rate of chemical decay of oxygen species with high crystalline LDPE in the XPS experiment. Decreasing rate of oxygen concentration of annealed LDPE was lower than that of quenched LDPE, which was consistent with the results of contact angle measurement.

Table 2
The fraction of immobile polar groups of quenched and annealed LDPE after oxygen plasma treatment

	f_{m}	f_{im}	f_{np} [a]
Quenched LDPE	0.826	0.170	0.004
Annealed LDPE	0.699	0.297	0.004

[a] The fraction of non-polar groups, $f_{\mathrm{np}} = 1 - f_{\mathrm{p}}$, ($f_{\mathrm{p}} = f_{\mathrm{m}} + f_{\mathrm{im}}$).

4. Discussion

4.1. Surface chemical changes of LDPE during aging time

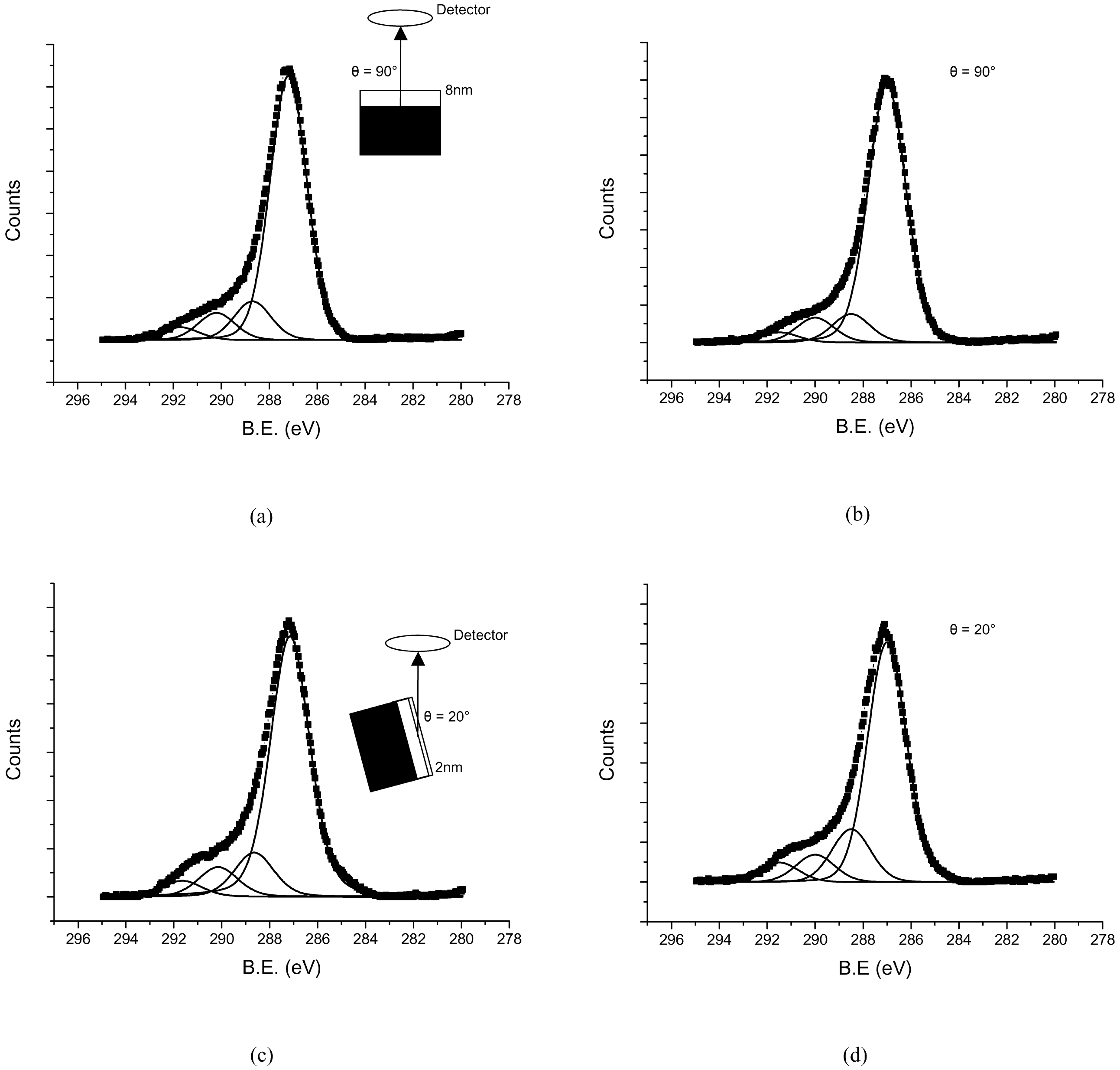
Fig. 4 displays the C_{1s} XPS spectra of oxygen plasma treated LDPE with different take-off angles after deconvolution for oxygen functional groups. Usually, the XPS spectrum of untreated polyethylene shows only the symmetric peak centered at 285.0 eV, but three new sub peaks resulting from the plasma-induced oxidation were revealed in Fig. 4 (solid line). These oxygen functional groups (alcohol, carbonyl, ester etc.) were the results of complex reactions of free radicals caused by oxygen plasma treatment. The scheme of these reactions leading to a variety of oxidation products was suggested by many literatures [20,24–26]. C-radical sites could react with oxygen when the LDPE was exposed to air, and peroxy radicals, and hydroperoxides were generated.

$$C^{\cdot} + {}^{\cdot}O{-}O^{\cdot} \rightarrow C{-}O{-}O\cdot$$

$$C{-}O{-}O^{\cdot} + RH \rightarrow C{-}O{-}OH + R\cdot$$

From this hydroperoxides, many kinds of oxygen functionalities like C–O (alcohol), C=O (carbonyl), COO (carboxylic acid, ester), etc. were formed.

After deconvolution of C_{1s} peak with fixing the BE of the



(a) (b) (c) (d)

Fig. 4. C_{1s} XPS spectra (solid line from sub peaks obtained by fitting) of oxygen plasma treated (a), (c) quenched, and (b), (d) annealed LDPE with 20° or 90° take off angle.

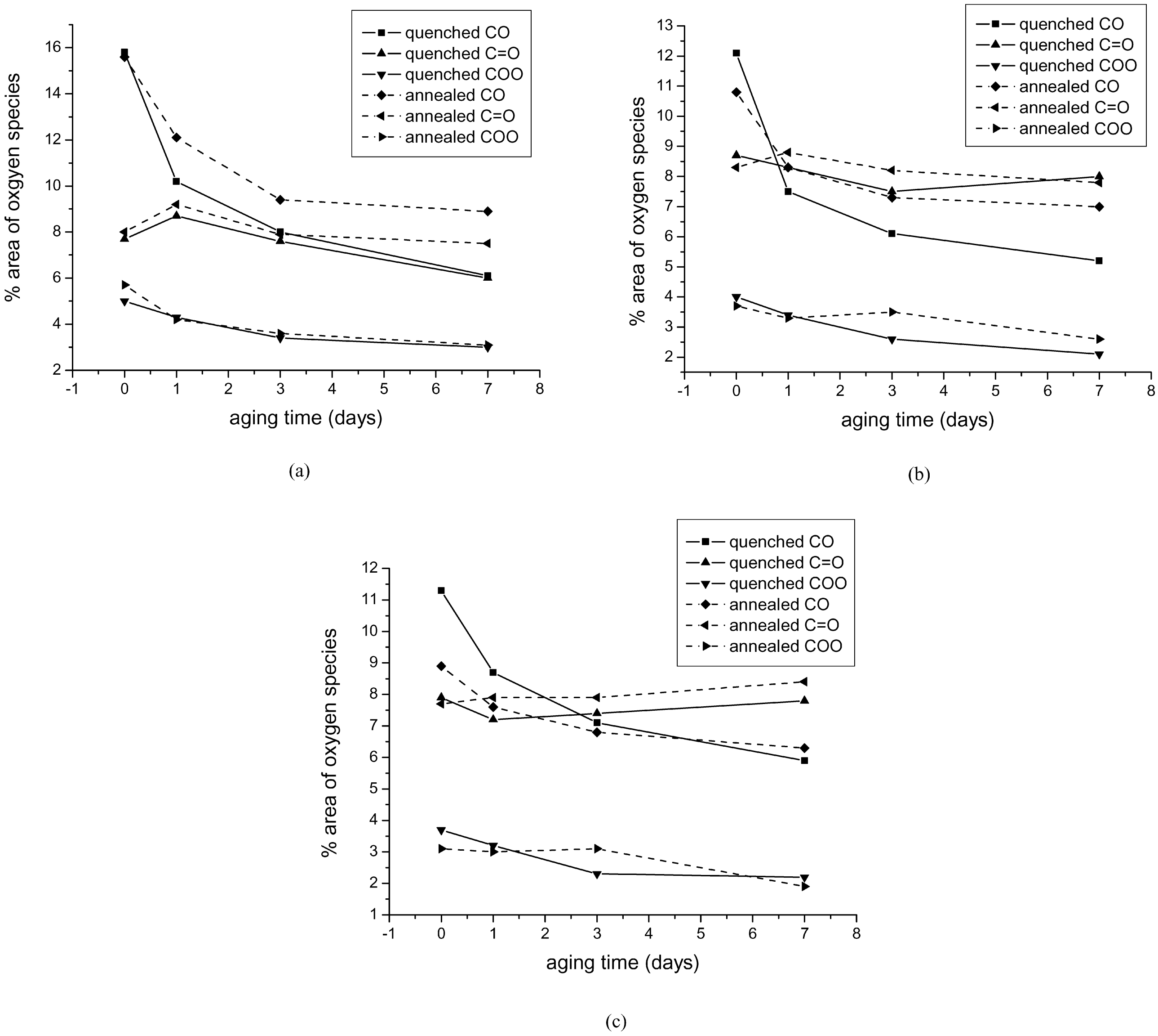
C–O (hydroxyl, ether) species to 286.5 eV, that of C=O (carbonyl or double ether) to 288 eV and that of COO (ester or carboxylic acid) to 289.5 eV and having same FWHM (full width at half maximum), we calculated the percentage area of these species on the surface of oxygen plasma treated LDPE. (Fig. 5) [25,26].

All over the surface region (~8 nm), there was no big variation of the percentage area of C=O and COO species. But C–O species concentrated on the outer surface region (~2 nm) rather than deep surface region (over 2 nm) and it decreased as depth increased. As mentioned on XPS analysis section it was not easy for oxygen molecules to diffuse into deep surface, the amount of the hydroperoxide in the deep surface was small. So the CO species of the inner surface was smaller than that of the outer surface.

During aging time the decrease of CO was very drastic while other oxygen species kept constant (C=O) or decreased slightly (COO). Rapid decrease of CO was mainly from the diffusion of polymer chains with CO groups into bulk side for its difference of interfacial energy with hydrophobic air environment. And at the same time conversion of CO into C=O or COO by further oxidation caused the fast decay of CO with keeping C=O or COO constant. The high diffusion rate of polymer chains of quenched LDPE from lower degree of crystallinity gave rise to a rapid drop of CO and especially drastic decrease of CO on the 2 nm surface (20° take off angle) could explained higher water contact angle of quenched LDPE after 7 day aging.

4.2. Hydrophilic recovery of plasma treated LDPE

In general, the decay of the hydrophilic character of the surface over time after plasma treatment is owing to rotation



(a)

(b)

(c)

Fig. 5. Percentage area of oxygen species of oxygen plasma treated LDPE surface with 20° (a), 50° (b), and 90° take-off angle (c).

or diffusional migration of hydrophilic moieties which are introduced only on the surface by plasma treatment, away from the surface. After aging in air, if the aged polymer was immersed in water, hydrophilicity of the polymer surface would be recovered by rotation or diffusion of hydrophilic moieties in order to minimize the free energy difference between polymer surface and water, and contact angle of water would decrease. Since the surface configurations were different between quenched and annealed LDPE, the hydrophobic recovery at surface would be also different. As shown in Fig. 6, annealed LDPE aged for 3 h in air recovered fully the initial contact angle of plasma treated LDPE after 24 h of water immersion. Whereas quenched LDPE aged for 3 h in air did not recover its initial contact angle. In the case of aged LDPE for 7 days in air, water contact angle of annealed LDPE was still 10° lower than that of quenched LDPE after 24 h of immersion in water. The decrease of contact angle originated from hydrophilic recovery could show how much polar group was remained in near surface region (≤ 1 nm) and how much polar group was diffused into deep bulk region, where polar groups were not affected by hydrophilic environment. Polymer chains in amorphous region can move freely, and much hydrophilic moiety can diffuse into bulk side within short time after plasma treatment. And due to continuous diffusion into bulk side during aging in amorphous region, the hydrophilic groups diffused into deep bulk region could not return to surface layer after 7 days of aging even in water environment. Quenched LDPE with more amorphous region had higher contact angle of water than annealed LDPE after 24 h of water immersion due to its unrecoverable diffusion of hydrophilic groups. For more crystalline polymer, more hydrophilic groups can remain in the surface layer because of restricted movement of polymer chains of crystalline region during aging.

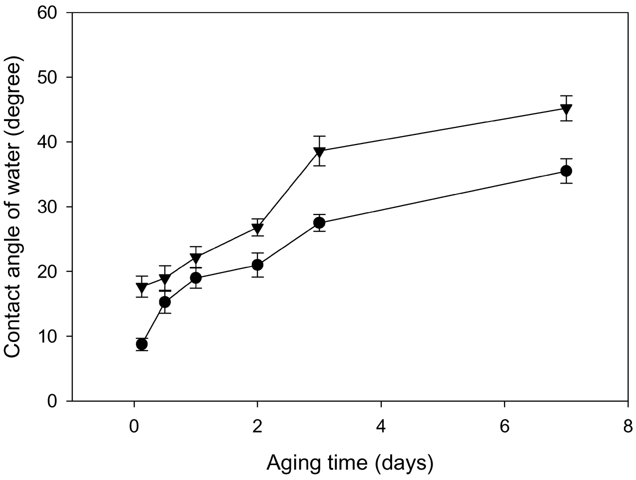


Fig. 6. Water contact angle of annealed LDPE (●) and quenched LDPE (▽) immersed in water for 24 h after aging in air.

5. Conclusions

The increase of crystallinity of LDPE was achieved by annealing and restricted the polymer chain motions. Limited chain motions reduced the diffusion rate of polar functional groups during aging and more hydrophilic moieties remained at the surface. Therefore, quenched LDPE with low crystallinity showed higher aging rate and lower hydrophilic recovery than annealed LDPE with high crystallinity. Since LDPE had low glass transition temperature (− 30 °C), the polymer chain motion would be very fast on room temperature. Therefore, the crystalliniy has critical effects on aging. Increasing crystallinity of LDPE could hinder the movement of the polymer chains and reduce the aging of plasma treated LDPE.

Acknowledgements

This work was supported by the grant from Ministry of Science and Technology (National Research Laboratories Program) and the Ministry of Education and Human Resources Development (BK21 Program), Korea.

References

[1] Chan CM, Ko TM, Hiraoka H. Surf Sci Rep 1996;24:1.
[2] Schamberger P, Abes J, Gardella J. Colloids Surf, B 1994;3:203.
[3] Liston EM, Martinu L, Wertheimer MR. J Adhesion Sci Technol 1993;71:1091.
[4] Chatelier RC, Xie X, Gengenbach TR, Griesser HJ. Langmuir 1995; 11:2576.
[5] Chatelier RC, Xie X, Gengenbach TR, Griesser HJ. Langmuir 1995; 11:2585.
[6] Andrade JD, editor. Polymer surface dynamics. New York: Plenum Press; 1988.
[7] Murakami T, Kuroda S, Osawa Z. J Colloid Interface Sci 1998;202: 37.
[8] Yasuda T, Okuno T, Yoshida K. J Polym Sci, Part B; Polym Phys 1988;26:1781.
[9] Hyun J. Polymer 2001;42:6473.
[10] Brennan WJ, Feast WJ, Munro HS, Walker SA. Polymer 1991;32: 1527.
[11] Murthy NS, Bednarczyk C, Minor H. Polymer 2000;41:277.
[12] Failla MD, Valles EM, Lyons BJ. J Appl Polym Sci 1999;71:1375.
[13] Rabek JF, Experimental methods in polymer chemistry: physical principles and applications, New York: Wiley; 1980.
[14] Chan CM. Polymer surface modification and characterization, New York: Hanser Publishers; 1993.
[15] Jama C, Quensierre JD, Gengembre L, Moineau V, Grimblot J, Dessaux O, Goudmand P. Surf Interface Anal 1999;27:653.
[16] Moulder JF, Stickle WF, Sobol DE, Bomber KD, Handbook of X-ray photoelectron spectroscopy, Minnesota: Physical Electronics; 1995.
[17] Choi DM, Park CK, Cho K, Park CE. Polymer 1997;38:6243.
[18] Olde Riekerink MB, Terlingen JGA, Engbers GHM, Feijen J. Langmuir 1999;15:4847.
[19] Youngblood JP, MacCarthy TJ. Macromolecules 1999;32:6080.
[20] Sprang N, Theirich D, Engermann J. Surf Coat Technol 1995;74:689.
[21] Busscher HJ, van Pelt AWJ, de Boer P, de Jang HP, Arends J. Colloids Surf 1984;9:319.

[22] Banik I, Kim KS, Yun YI, Kim DH, Ryu CM, Park CS, Sur GS, Park CE. Polymer 2003;44:1163.

[23] Morra M, Occhiello E, Garbassi F. In: Strobel M, Lyons CS, Mittal KL, editors. Plasma surface modification: relevance to adhesion. Utrecht: VSP; 1994.

[24] Kuzuya M, Niwa J, Ito H. Macromolecules 1993;26:1990.

[25] Retzko I, Friedrich JF, Lippitz A, Unger WES. J Electron Spectrosc Relat Phenom 2000;121:111.

[26] Briggs D, Seah MP. Practical surface analysis. Auger and X-ray photoelectron spectroscopy, vol. 1. Chichester: Wiley; 1990.