ELSEVIER

Polymer 44 (2003) 1163–1170

polymer

www.elsevier.com/locate/polymer

A closer look into the behavior of oxygen plasma-treated high-density polyethylene

Indranil Banik[a,1], Kwang Soo Kim[a], Yo Il Yun[a], Dae Ho Kim[b], Chang Mo Ryu[b],
Chan Sup Park[c], Gil Soo Sur[d], Chan Eon Park[a,*]

[a]*Department of Chemical Engineering, Polymer Research Institute, Pohang University of Science & Technology (POSTECH), Hyoja Dong, Pohang, Kyungbuk 790784, South Korea*
[b]*Department of Physics, Pohang University of Science & Technology (POSTECH), Hyoja Dong, Pohang, Kyungbuk 790784, South Korea*
[c]*Technical Research Laboratories, POSCO, Pohang, South Korea*
[d]*School of Chemical and Technology, Yeungnam University, Kyongsan 712037, South Korea*

Received 26 April 2002; received in revised form 7 October 2002; accepted 12 November 2002

Abstract

X-ray photoelectron spectroscopy and near edge X-ray absorption fine structure investigation have been used to characterize the surfaces of two oxygen plasma-treated high-density polyethylene (HDPE) samples having different crystalline fractions. Both the observations indicate that a higher degree of crystallinity restricts the mobility of the polar functional groups on the HDPE surface. An increased crystalline order lowers the amount of oxidation and the aging of polar functional groups on the substrate surface. The results are supported by contact angle measurements and field emission scanning electron microscopic observations.

Keywords: High-density polyethylene; Oxygen-plasma; Crystallinity

1. Introduction

The plasma modification of chemically inert polyethylene is used to increase its hydrophilicity and is an important research area in the plastics industry [1,2]. Owing to its low cost and good surface properties [2,3], there has been a number of important applications of this plasma treated polymer in the area of composites [4], packaging for microelectronic components [5], printing and coating [2,6], biomaterials [7,8] and so on.

Although the use of plasma for the modification of polymer has become a mature technology, research is still continuing into the behavior of treated surfaces with time of storage. One commonly observed and troublesome phenomenon is the deterioration of the beneficial surface properties (hydrophilicity) through aging. Commonly these effects are manifested in contact angle measurements, where one observes an increase in contact angle on long-term storage. It has been suggested that this hydrophobic recovery is mainly due to a combination of two processes [2,9–11]. One involves the reorientation of polar chemical groups into the bulk of the material to reduce the surface energy. The other is due to the diffusion of polar chemical groups into the polymer matrix. These chain relaxation processes [2,11] at the surface can be reduced by increasing the crystallinity of the polymer. Although this degree of reduction can be estimated, there has so far been a lack of proper report highlighting this reduced reorientation and diffusion of polar groups in a plasma-modified HDPE subjected to aging. This can be detected by carrying out X-ray photoelectron spectroscopy (XPS) measurements parallel to those by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. These may reveal more insight into the situation at the polymer surfaces. Meanwhile literature continues to update the research on the plasma-modification of polyethylene [1,4–9,12–15].

NEXAFS spectroscopy [16–20] is an analytical method providing molecular-specific information (the excitation of electrons into unoccupied molecular orbitals from core

---

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

[1] Present address: CRASP, Department of Chemical Engineering; Ecole Polytechnique, C.P. 6079, Succ. Centre-Ville; Montreal, Que. H3C 3A7, Canada.

0032-3861/03/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00847-9

levels are probed). Here incident photon energy is scanned through an X-ray absorption edge such as that of C 1s or O 1s electron shell. Peaks appear in the core-level photon absorption spectrum when the photon energy corresponds to the energy difference between the occupied core level and an unoccupied state [21]. Furthermore, the molecular orientation of the samples can be determined by monitoring changes in the NEXAFS spectrum as function of the angle of incidence between the X-ray photon beam and the sample surface [16–21].

In this report, the plasma treatment of high-density polyethylene (HDPE) has been performed and the changes in molecular mobility investigated by the NEXAFS spectra as the samples are subjected to aging. The results have been clarified using XPS and contact angle measurements. To examine the influence of crystallinity on aging and to judge the nature of mobility (reorientation and diffusion), observations have been made on HDPE samples of different crystallinities. In addition, surface morphologies have been investigated by field emission scanning electron microscopy (FESEM).

2. Experiments

2.1. Material

HDPE has been supplied in the form of pellets by Daehan Yuwha Co. (Ulsan, Korea). For contact angle measurements distilled water have been used. The weight average molecular weight of HDPE has been reported to be around 78,000 and the polydispersity index 3.25.

2.2. Fabrication of HDPE sheets

HDPE pellets have been pressed and formed into thin sheets at 180 °C for 3 min with a mould pressure of 12 lbf. The molded sheets have then been cleaned thoroughly in an ultrasonicator using 1:1 ethanol/water solvent mixture.

2.3. Crystallization experiments

The crystallization studies have been conducted by molding the HDPE samples as mentioned in Section 2.2 and then annealing in vacuum oven at various temperatures and for different periods of time. However, thermal treatment for a long time (24 h) at high temperature (126 °C) has been found to increase the degree of crystallinity from 56 to 66%. The crystallinity of the various HDPE samples has been determined by differential scanning calorimetry (DSC) according to the standard procedure mentioned in the literature [22]. The empirical heat of fusion for 100% crystalline PE has been set at 293 J/g. The HDPE samples, having crystallinities of 56 and 66% have been designated as S-1 and S-2, respectively. Earlier crystallinity changes of polymer samples have been measured by DSC and the effect of these changes on plasma surface functionalization reported [22–24].

2.4. Plasma treatment of HDPE samples

Cleaned HDPE samples have been treated with oxygen plasma using a home made parallel plate plasma generator operating at 13.56 MHz. The effective pressure during the treatment has been maintained at around 2×10^{-2} Torr. Optimum conditions have been observed when the plasma treatment has been carried out at a plasma power of 100 W for 60 s. At still higher power (150 W), the concentration of oxygen atoms has been found to increase [25]. An optimized gas flow rate 30 sccm (standard cubic centimeter per minute) has been used in all the cases. Following the plasma treatment, the samples have been washed ultrasonically in a 1:1 ethanol/water mixture to remove the chain scissored low molecular weight materials [24] and then dried. For the aging studies, the samples have been stored in a vacuum desiccator for extended periods of time.

2.5. Contact angle studies

The contact angle measurements of the plasma treated samples have been performed at ambient temperature by a sessile drop method with a contact angle goniometer (CA-A, Kyowa Surface Science, Japan). The equilibrium contact angle of untreated HDPE has been found out to be 96°. An average of at least six readings has been reported in each case. The error limit in the measurement of contact angle was around ±2%. Brennan et al. [10] has reported the aging behavior of plasma treated poly(ether ether ketone) samples, having different crystallinities, by contact angle measurements.

2.6. XPS analysis

The chemical surface atomic composition of the plasma treated polymer samples have been investigated by XPS. The measurements have been performed with a Perkin–Elmer Phi-5400 photoelectron spectrometer using Mg K_α X-ray source (1253.6 eV, 350 W). The high-resolution spectra of the samples were recorded and a Gaussian line shape was used to obtain the experimental spectra as it provided the best fit for the HDPE surface. A similar approach has been used earlier [26]. The area under O 1s peaks has been taken as a measure of the concentration of oxygen atoms incorporated on the polymer surface by plasma. The area of a peak has been calculated after a background correction and the concentration calculated following the method as mentioned in the literature [2].

The operating pressure during analysis has been in the range of 10^{-9} Torr. Angle resolved XPS measurements [2, 11] have been used at take-off angles of 15, 45 and 85° for depth profiling the treated surfaces both before and after aging. The depth of penetration (D in nm) has been calculated using the relation as reported in the literature [26]. As prominent changes have been observed within first few hours of the treatment, the XPS data have been reported just after the plasma treatment and within first 24 h of aging.

2.7. SEM analysis

The surface morphology of the polymer samples has been studied by FESEM. The samples have been analyzed with a Hitachi S-4200 cold field emission SEM (5 kV) instrument. FESEM photographs have been recorded at a magnification of 30,000 × .

2.8. NEXAFS studies

Thin HDPE samples have been spin-coated on silicon-wafers employing 0.5 wt% solution of the polymer in *p*-xylene at 2000 rpm. The resulting film thickness has been around 100 nm. Before taking the NEXAFS spectra, all the samples have been cleaned thoroughly in an ultrasonicator using 1:1 ethanol/solvent mixture and then dried.

Total electron yield (TEY) [16] X-ray absorption experiments have been carried out at Pohang light source with a resolution better than 0.2 eV at the O 1s electron shell. All the spectra have been normalized by dividing the TEY signal from the sample with the signal simultaneously obtained from a reference gold coated grid monitor [16]. Reproducibility of the spectra has been checked by multiple scanning. The information depth of the NEXAFS method in TEY mode can be estimated to be ≤5 nm for the O 1s signal [16,18,19] assuming that Auger electrons predominantly contribute to the signal.

To look for the crystallinity effects, the angle of incidence of the linearly polarized synchrotron light has been varied between 90° (electric field vector *E* lies in the surface plane) and 20° (*E* nearly parallel to the surface normal). Since distinct changes have been observed within first few hours of plasma treatment, the data are reported for the features evolving within 24 h after the plasma treatment. An almost similar variation in the intensity of the O 1s signals have been observed when the data have been compared at different polar angles of incidence. However almost no change in the NEXAFS O 1s intensities, measured at 20°, have been observed especially after first 10 h of plasma treatment. Hence to maintain the clarity of the spectra these have not been shown here.

3. Results and discussion

3.1. XPS observations

Fig. 1 shows the relative concentration of oxygen atoms (O%) on the surface of oxygen plasma treated HDPE films having the crystallinities of 56% (a) and 66% (b), respectively. The oxygen% evaluated by XPS has been plotted as a function of penetration depth of the incident X-rays from the film surface (*D*). The results indicate a higher concentration of atomic oxygen for the sample having lower crystallinity (56%). Fig. 2 displays the difference in the oxygen concentration of the above two samples before and after plasma treatment. It is observed that the extent of decrease in the amount of oxygen, on aging, is also reduced as the crystallinity (%) is increased, especially within a penetration depth of about 2 nm. Both the samples, however, show a sharp decrease in the topmost layer (2 nm), but then it becomes gradual and levels-off in the surface layers beyond 5.7 nm. The results are in line with the literature [2] and also one of the recent observations [15] which say that the amount of oxygen in the first few layers decreases much faster.

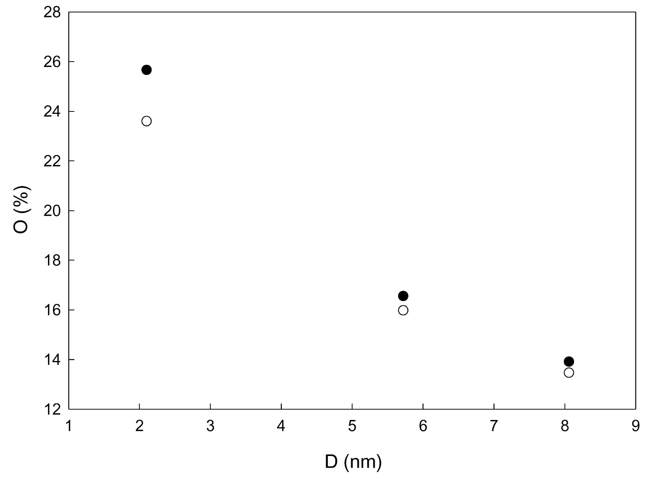

Fig. 1. XPS of the two plasma treated HDPE samples: (a) (●) S-1 (56% crystallinity) and (b) (○) S-2 (66% crystallinity).

The higher degree of oxygenation of the low crystallinity sample indicates a greater chemical reactivity of the sample under the influence of plasma. The reason is probably due to the fact that the reaction intermediates (mainly the radicals) are relatively more mobile in the polymer matrix having lower crystallinity [27] and hence expected to react more easily with the oxygenated species in the plasma. Morra et al. [7] has reported on the influence of crystallinity on the plasma modification of the polymer surface. They have concluded that the higher reactivity of the polymer, having lower crystalline fraction, is due to the greater freedom of motion granted by the higher percentage of the amorphous domains of the polymer. The effect is also prominent in aging.

When the comparative aging behavior is considered, it is observed that there is a lowering of oxygen concentration for the sample having higher crystallinity, especially in surface layers within a depth of 5 nm. Although the decrease is not large at depths higher than 5 nm, the migration of polar functional groups is much reduced as compared to the sample having lower crystallinity. With the increase of crystallinity, there is a reduction in tendency towards surface migration because of higher structural regularity and

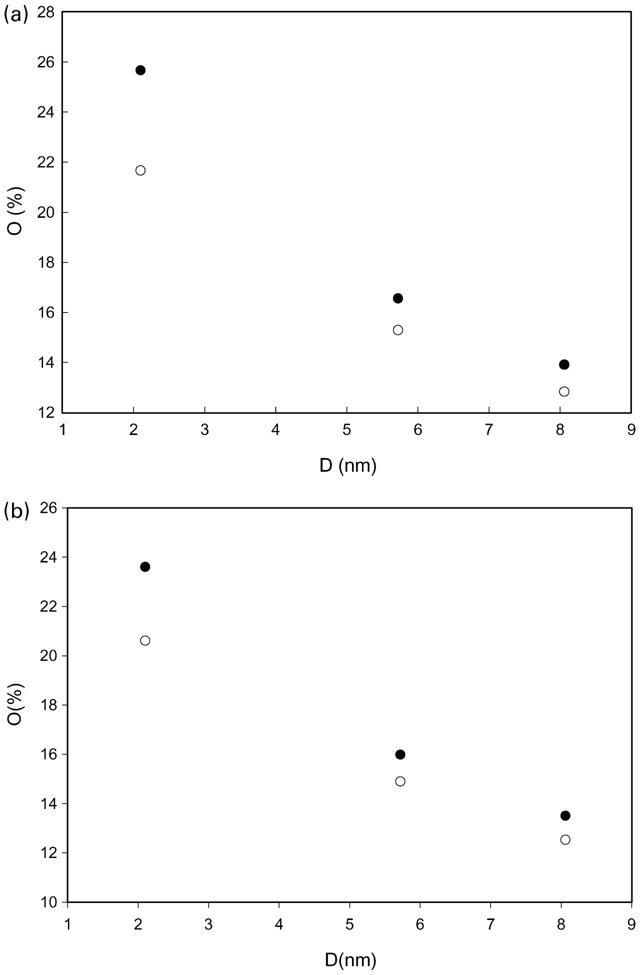

Fig. 2. XPS of the HDPE samples modified by oxygen-plasma at 100 W for 60 s: (a) (●) S-1 (after plasma treatment) and (○) S-1 (aged for 24 h), (b) (●) S-2 (after plasma treatment) and (○) S-2 (aged for 24 h).

lower free volume of the polymer matrix [10]. Increase in crystallinity hinders the movement of the polymer chains and therefore slows the aging process of orientation and diffusion. Although the diffusion appears to be responsible for the loss of polar functional groups from the surface, reorientation effects are not reported. This has been explained by NEXAFS in Section 3.4.

3.2. Contact angle measurements

Table 1 presents the data related to the aging studies of the plasma treated samples investigated by contact angle measurements. It is observed that though the contact angle of both the samples is almost the same after plasma treatment, there is a significant increase on prolonged storage. The increase is less marked for the material having higher crystallinity and the retention of hydrophilicity is also relatively high. The decrease in contact angle after plasma treatment is due to surface oxygenation, which leads to an increase of surface energy. However, surface roughness [2,4] caused by plasma treatment can also be responsible for lowering of the contact angle. And the decrease of hydrophobic recovery with increase of crystallinity is due to the restriction imposed on the loss of polar surface groups by the ordered crystalline environment. This has also been justified by XPS in Section 3.1. Hyun [23] has also reported a decrease of the mobility of the plasma-incorporated polar surface groups owing to an increase in crystallinity.

Table 1
Contact angle of oxygen plasma treated HDPE samples at various times of storage

Aging condition	Contact angle (°)	
	S-1 (56% crystallinity)	S-2 (66% crystallinity)
Just after plasma treatment	5	5
Sample aged for 1 day	59	50
Sample aged for 2 days	71	59

3.3. SEM investigations

The chemical changes at the surface of a polymer are often related to the morphological changes caused by plasma [2,14]. Hence to find a correlation between the surface morphology and level of plasma modification, SEM observations have been made on the oxygen plasma treated HDPE samples.

Fig. 3 shows the SEM micrographs of the two untreated materials having different crystallinities of 56% (a) and 66% (b). Both the samples show the presence of lamellar structure characteristic of polyethylene [28] and the density and thickness of lamellae are increased after annealing. Presence of lamellar structures on HDPE surface has also been reported [22] earlier: the amount of crystallite thickening is governed by the crystallization time and temperature [28]. An increase of crystallinity, hence the macromolecular chain-alignment, occurs through enhanced molecular mobility at higher temperatures and longer annealing times. The details of the mechanism can be found in the literature.

However the change in morphology of the HDPE surface after plasma treatment is of more concern in the present report. Fig. 4 shows the morphology of the two oxygen plasma treated HDPE samples having crystallinities of 56% (a) and 66% (b), respectively. It is observed that the surface of the sample having lower crystallinity (56%) is more granulated after the treatment. This indicates the greater etching (chemical oxidation leading to the formation of volatiles) and hence more damage of the polymer surface owing to the higher amorphous fraction. Such observations have also been reported [22].

Due to the greater degree of surface oxidation, the surface of the oxygen plasma treated lower crystalline

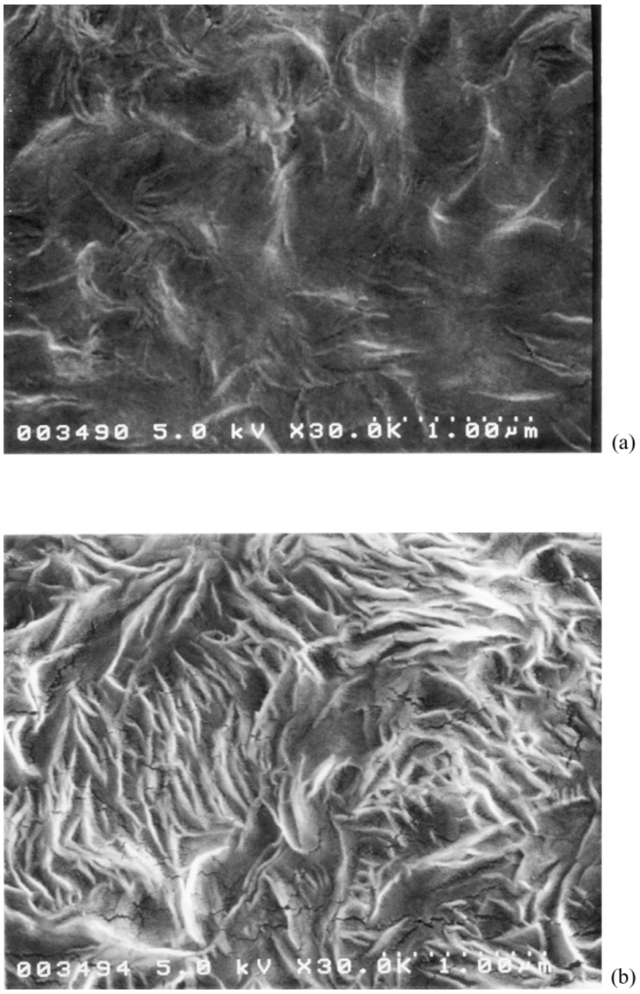

Fig. 3. SEM micrograph of the untreated HDPE samples: (a) S-1 (56% crystallinity) and (b) S-2 (66% crystallinity).

sample shows the presence of granular particles distributed uniformly across the surface. Such observations have already been cited in the literature [29]. This is justified by the fact that when argon–oxygen (in the presence of argon and absence of oxygen, crosslinking [2,29–30] predominates because of less favorable energetic intermediates for chemical reaction) mixture in a ratio of 9:1 is used [25], instead of only oxygen, the granular features have been found to disappear although the surface of the sample is roughened. On the other hand less surface damage has been observed for the HDPE sample having higher crystallinity (66%) because of some resistance provided (against the chemical attack) by its ordered structure. This has been already verified by XPS in Section 3.1.

3.4. NEXAFS investigations

The orientation aspects [16,31] of the macromolecular chains of the plasma treated HDPE samples have been studied by NEXAFS. Since the main target of the study has been to focus and investigate the mobility of the polar oxygenated groups (CO, C=O) generated by plasma, O 1s electron shell signals have been reported. As indicated by DSC measurements on the molded samples, the annealed spin-coated HDPE would also have a higher degree of crystallinity than the unannealed material although the relative values of the degree of crystallinity and the lamellar aggregation in the molded and spin-coated samples may be different.

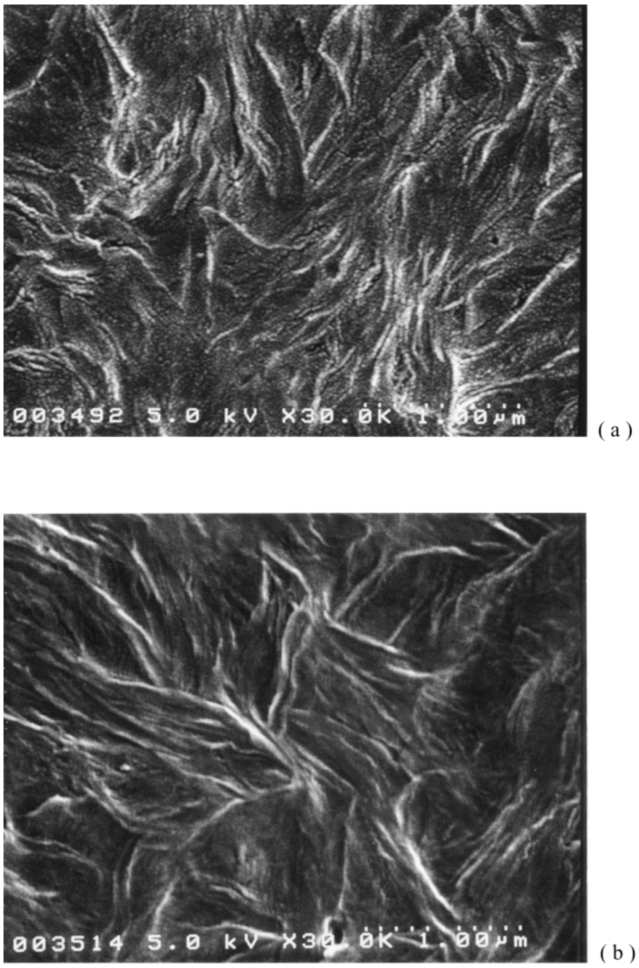

Fig. 4. SEM micrograph of the HDPE samples oxidized by plasma at 100 W for 60 s: (a) S-1 (56% crystallinity) and (b) S-2 (66% crystallinity).

Fig. 5 shows the O 1s spectra of unannealed (a) and annealed (b) HDPE samples recorded, at various angles, immediately after treatment by oxygen-plasma at a power of 150 W for 60 s. Transitions are observed at around 534 and 542.5 eV and these, according to the literature [16–20], correspond to the signals arising out of O 1s → $\pi^*_{C=O}$ and O 1s → σ^*_{C-O} valence excitations, respectively. As it can be seen that the orientation of oxygenated carbon moieties is different in two HDPE samples. This can arise from the differences in molecular environment on the surface of the two polymers having different crystalline fractions. A comparison of the spectra reveals that for the annealed material having high crystallinity, the intensity of O 1s signal is lowered and there is a shift in its position to lower excitation energy.

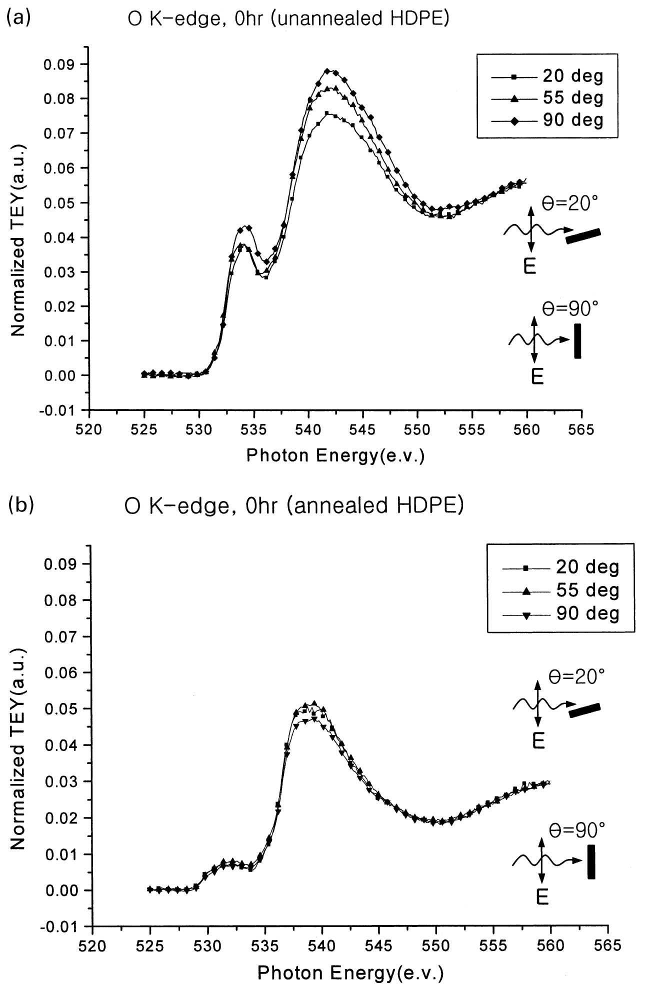

Fig. 5. NEXAFS spectra of the HDPE samples treated by oxygen-plasma at 150 W for 60 s and at various angles of incidence: (a) unannealed HDPE (▼: 90°, ▲: 55°, ■: 20°) and (b) annealed HDPE (◆: 90°, ▲: 55°, ■: 20°).

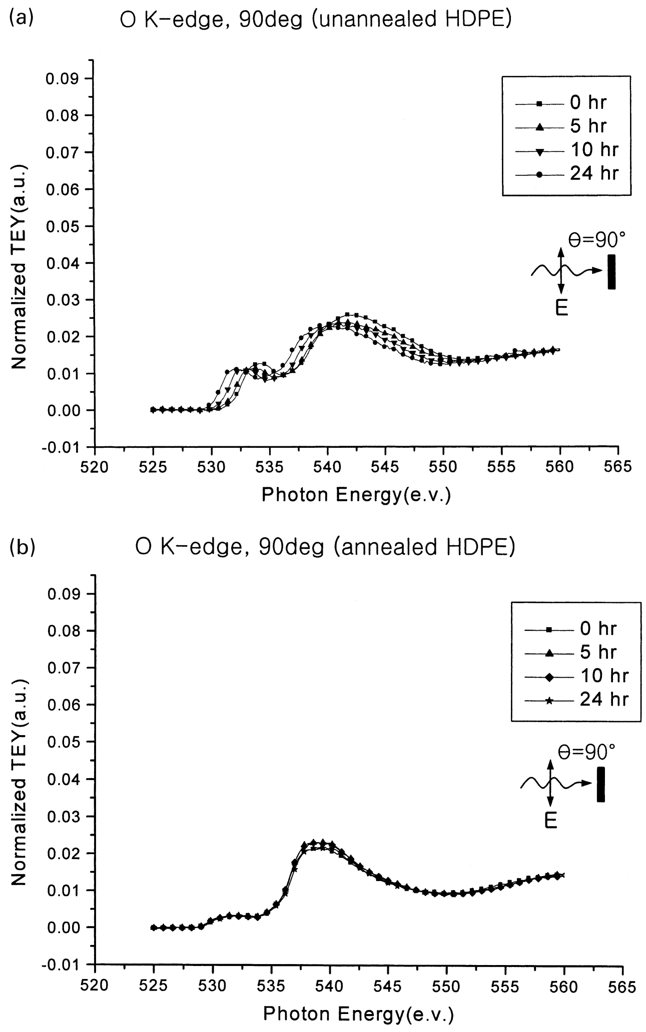

Fig. 6. O–K edge spectra of the HDPE surfaces modified by oxygen plasma at 100 W for 60 s and aged for various times: (a) unannealed HDPE (■: 0 h, ▲: 5 h, ▼: 10 h, ●: 24 h all measured at 90°) and (b) annealed HDPE (■: 0 h, ▲: 5 h, ◆: 10 h, ∗ : 24 h all measured at 90°).

The decrease of O 1s intensity of the HDPE sample having higher crystallinity indicates the restricted orientation of its plasma treated polymer chains. Because of the higher crystalline order, the free volume in the polymer matrix is reduced [10] and the chances that the polar chemical bonds can orient with X-ray field are lowered. The reason is also in line with the XPS observation, which has also indicated that the concentration of atomic oxygen, incorporated by plasma treatment, is decreased on increasing the crystallinity of HDPE. Due to the reduction of this atomic concentration, the number of oxygenated groups orienting with the electric vector of the X-ray field is reduced and this accounts for the lowering of the intensity in O 1s signal. However the reason for the shift in the position of the O 1s peaks is not clearly understood.

To compare the aging behavior, the spectra have been collected for the two HDPE samples at the same angles of incidence with different aging times. Figs. 6 and 7 show the variation of O 1s signals of the unannealed (a) annealed (b) HDPE surfaces having different crystallinities. The NEXAFS spectra presented in Fig. 6 has been recorded at 90°, whereas those in Fig. 7 at 20° polar angle of incidence. It is observed that, with the increase in aging time, for the low crystallinity sample there is a reduction in the intensity of the signal with a concomitant shift in its position to lower energy. However the corresponding changes for the annealed material are small. These indicate that the molecules of the low crystallinity (unannealed HDPE) sample have lost their tendency to orient with the applied X-ray field on storage (aging). This reflects a more mobile nature of the polar functional groups on the surface of HDPE having lower crystallinity. Earlier, XPS observations have shown that there is a sharp drop in concentration of oxygen, especially from 2 to 5.7 nm of the surface layers; the decrease is higher for the sample having lower crystallinity i.e. the unannealed material. Contact angle measurements have also indicated a higher hydrophobic recovery for the low crystallinity material. Hence from the studies of XPS and contact angle, it can be said that both the reorientation and diffusion processes are higher for the

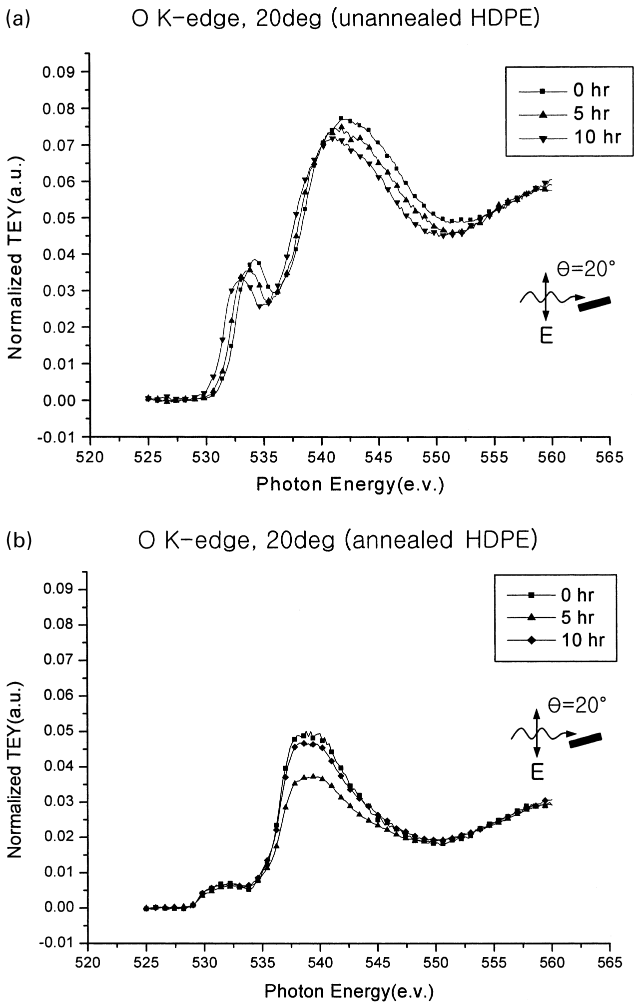

Fig. 7. NEXAFS data of the HDPE samples oxidized by plasma at 100 W for 60 s and aged for various times: (a) unannealed HDPE (■: 0 h, ▲: 5 h, ▼: 10 h all measured at 20°) and (b) annealed HDPE (■: 0 h, ▲: 5 h, ◆: 10 h all measured at 20°).

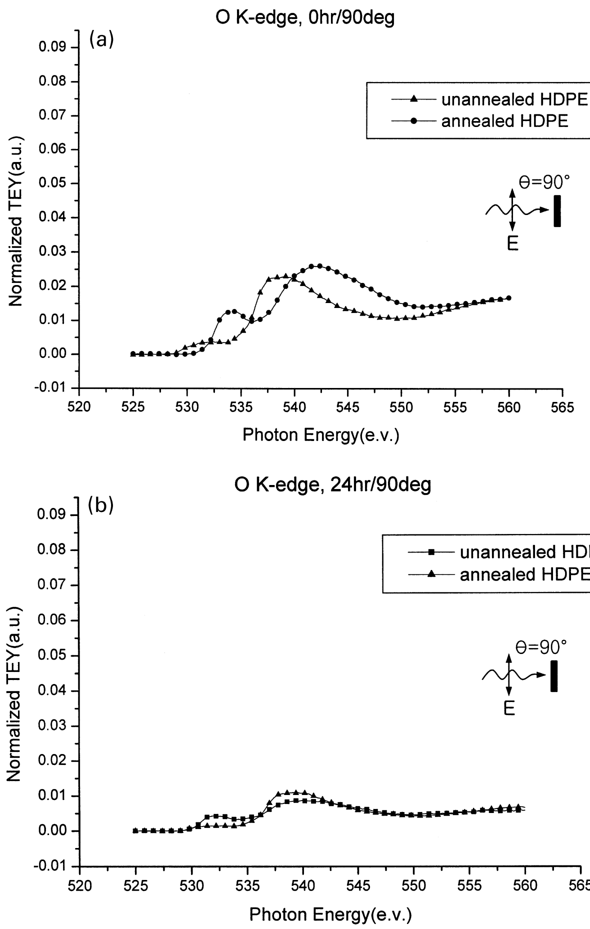

Fig. 8. O–K edge spectra of the HDPE materials of different crystallinities surface functionalized by oxygen plasma and aged for different times: (a) 0 h at 90° polar angle of incidence (▲: unannealed HDPE, ●: annealed HDPE) and (b) 20 h at 90° polar angle of incidence (■: unannealed HDPE, ▲: annealed HDPE).

plasma treated sample having lower degree of crystallinity. An increased diffusion pulls the polymer chain molecules inward and as a result, they loose their tendency to align with the X-ray photon beam of the linearly polarized synchrotron light. However the behavior of the HDPE sample having higher crystallinity looks to be different. Because of the higher crystalline order, the diffusion is restricted and the chain molecules are somewhat locked-up in their disposition. As a result, both the orientation and diffusion effects are reduced to some extent.

To verify the crystallinity effects on the orientation (of the polar oxygenated groups, C–O, C=O), NEXAFS results have been collected at 90° angle of incidence. Fig. 8 shows the relative effects of the two different HDPE samples immediately after plasma treatment and on storage. It is observed that in either of the two cases, the O 1s peak intensity is reduced for the unannealed sample having lower crystallinity. There is a shift in its position to lower value as compared to the annealed sample having higher crystallinity. The observed features for the HDPE sample having lower crystallinity, as explained earlier, arise from the higher mobility of its plasma treated polymer chains [2], which register more reorientation and diffusion into the bulk on aging. Owing to the preferential etching of the amorphous region, the molecules at the surface of the polymer are more disintegrated and this enhances the freedom of motion of polar oxygenated groups into the bulk. Once again, the reason for the shift in the peak position of the O 1s signal is not clearly understood. This may arise either from an enhanced tendency towards diffusion which can affect the interaction between various bonds owing to a change in molecular environments or the increased degree of modification/damage on the HDPE surface due to its higher amorphous fraction. An increased surface damage and level of modification have already been identified using FESEM and XPS investigations, respectively. Similar trends have been noted when the results have been compared and analyzed by varying the angles of incidence.

Finally it needs to be mentioned that, the O 1s intensity (at 0 h and 90° angle of incidence), as shown in Fig. 5, is observed to be higher than those reported either in Figs. 6 or

8. This reflects a greater concentration of atomic oxygen on the HDPE surface treated at higher plasma powers [25]. As the build of polar oxygenated groups is enhanced with a rise in plasma power, the number O 1s transitions are also increased. This then accounts for the observations as reported here.

4. Conclusion

The behavior of the HDPE surfaces, of varying degrees of crystallinity towards oxygen plasma has been studied with XPS and NEXAFS. XPS, NEXAFS and the FESEM observations indicate a higher degree of plasma modification on the surface of a polymer having lower crystalline fraction. The mobility of the polar groups is reduced with increase in degree of crystallinity. The aging effect has been observed to be lower in the sample of higher degree of crystallinity and this is explained due to lower reorientation and diffusion in the surface. Contact angle measurements also point to more hydrophilic nature of the plasma treated surface having a higher crystalline fraction.

Acknowledgements

This work was supported by the grant from National Research Laboratories Program (Development of nanopolymer binder for microelectronics and information technology using molecular design and interfacial engineering), Ministry of Science and Technology, Korea.

References

[1] Wheale SH, Barker CP, Badyal JPS. Langmuir 1998;14:6699.
[2] Chan CM. Polymer surface modification and characterization. Munich: Hanser; 1994.
[3] Brydson JA. Plastic materials. Oxford: Butterworth; 1989.
[4] Choi DM, Park CK, Cho K, Park CE. Polymer 1997;38:6243.
[5] Simon D, Liesegang J, Pigram PJ, Brack N, Pura JL. Surf Interf Anal 2001;32:148.
[6] Liston M, Martinu L, Wertheimer MR. J Adhes Sci Technol 1993;7: 1091.
[7] Morra M, Occhiello E, Garbassi F. In: Strobel M, Lyons CS, Mittal KL, editors. Plasma surface modification: relevance to adhesion. Utrecht: VSP; 1994.
[8] Lin JC, Ko TM, Cooper SL. J Colloid Interf Sci 1996;164:99.
[9] Paynter R. Surf Interf Anal 2000;29:56.
[10] Brennan WJ, Feast WJ, Munro HS, Walker SA. Polymer 1991;32: 1527.
[11] Chan CM, Ko TM, Hiraoka H. Surf Sci Rep 1996;24:1.
[12] Sprang N, Theirich D, Engemann J. Surf Coat Technol 1995;74/75: 689.
[13] Hollander A, Wilken R, Behnisch J. Surf Coat Technol 1999;116/119: 788.
[14] Jama C, Quensierre JD, Gengembre L, Moineau V, Grimblot J, Dessaux O, Goudmand P. Surf Interf Anal 1999;27:653.
[15] Maas AJH, Vitranen MM. Brongersma Surf Interf Anal 2000;30:3.
[16] Stohr J. NEXAFS spectroscopy. Berlin: Springer; 1992.
[17] Ade H, Urquhart SG. In: Sham TK, editor. NEXAFS spectroscopy and microscopy of natural and synthetic polymers. Singapore: World Scientific; 2000.
[18] Lippitz A, Freidrich JF, Unger WES, Schertel A, Woll Ch. Polymer 1996;37:3151.
[19] Lippitz A, Koprinarov I, Freidrich JF, Unger WES, Weiss K, Woll Ch. Polymer 1996;37:3157.
[20] Koprinarov I, Lippitz A, Friedrich JF, Unger WES, Woll Ch. Polymer 1998;14:3001.
[21] Sutherland DGJ, Carlisle JA, Elliker P, Fox G, Hagler TW, Jimenez I, Himpsel FJ, Shuh DK, Tong WM, Jia JJ, Callcott TA, Ederer DL. Appl Phys Lett 1996;68:2046.
[22] Riekerink MBO, Terlingen JGA, Engbers GHM, Feijen J. Langmuir 1999;15:4847.
[23] Hyun J. Polymer 2001;36:6473.
[24] Poncin-Epaillard F, Brosse JC, Falher T. Macromolecules 1997;30: 4415.
[25] Banik I, Kim KS, Yun YI, Kim DH, Ryu CM, Park CE. J Adhes Sci Technol 2002;16:1155.
[26] Le QT, Pireaux JJ, Caudano R. J Adhes Sci Technol 1997;11:735.
[27] Clough RL. In: Kroschwitz JI, editor. Encyclopedia of polymer science and engineering, vol. 6. New York: Wiley; 1988.
[28] Dosiere M. Crystallization of polymers. Boston: Kluwer; 1993.
[29] Greenwood OD, Hopkins J, Badyal JPS. Macromolecules 1997;30: 1091.
[30] Vallon S, Drevillion B, Poncin-Epaillard F. Appl Surf Sci 1997;108: 177.
[31] Gross Th, Lippitz A, Unger WES, Friedrich JF, Woll Ch. Polymer 1994;35:5590.