Macromolecular Research, Vol. 12, No. 1, pp 134-140 (2004)

AFM and Specular Reflectance IR Studies on the Surface Structure of Poly(ethylene terephthalate) Films upon Treatment with Argon and Oxygen Plasmas

Eun-Deock Seo

Division of Chemical Engineering, Kyungnam University, Masan 631-701, Korea

Received Dec. 4, 2003; Revised Jan. 5, 2004

Abstract: Semi-crystalline poly(ethylene terephthalate) (PET) film surfaces were modified with argon and oxygen plasmas by radio-frequency (RF) glow discharge at 240 mTorr/40 W; the changes in topography and surface structure were investigated by atomic force microscopy (AFM) in conjunction with specular reflectance of infrared microspectroscopy (IMS). Under our operating conditions, analysis of the AFM images revealed that longer plasma treatment results in significant ablation on the film surface with increasing roughness, regardless of the kind of plasma used. The basic topographies, however, were different depending upon the kind of gas used. The specular reflectance analysis showed that the ablative mechanisms of the argon and oxygen plasma treatments are entirely different with one another. For the Ar-plasma-treated PET surface, no observable difference in the chemical structure was observed before and after plasma treatment. On the other hand, the oxygen-plasma-treated PET surface displays a significant decrease in the number of aliphatic C-H groups. We conclude that a constant removal of material from the PET surface occurs when using the Ar-plasma, whereas preferential etching of aliphatic C-H groups, with respect to, e.g., carbonyl and ether groups, occurs upon oxygen plasma.

Keywords: plasma treatment, surface structure, preferential ablation, PET, AFM.

Introduction

Plasma-surface modification as an economical and effective materials processing technique has been of scientific and technological interest for over 30 years since it can improve wettability, adhesion, biocompatibility, etc. The applications for biocompatibility include cleaning, sterilization, deposition or coating, and implantation modification of a substrate.[1] Poly(ethylene terephthalate) (PET) is not only an important material for conventional uses such as fiber, food package, and information storage but also for specific biomedical uses with good stability against body fluid and high radiation resistance for sterilization.[2]

Plasma-surface modification of PET has been studied by some workers, and changes in the physical behavior and surface morphology has been reported.[2-5] For example, Piglowski *et al.*[5] have reported that PET can be modified into biomaterials by plasma treatment with argon or with perfluorohexane.

To be used as biomaterials, polymers are generally required to have biocompatibilities with blood and tissues and its compatibilities are closely related with the surface characteristics such as chemical composition, surface morphology, and wettability, and etc.[6-10] More importantly, it is believed that the surface morphology plays an important role in biocompatibility of biomaterials *in vivo*. Ohl *et al.*,[11] for example, have reported that the surface morphology of the cell scaffold materials affects the cell behavior and functions. Furthermore, the nature of the substrate material has been found to influence the "D-value" (where D-value is the time necessary to decrease the number of living microorganism by one order of magnitude) of a given microorganism.[12] At present, plasma techniques are used preferentially to produce different morphology on surfaces to investigate cell biological effects.[13,14] Thus, it has been of interest to get specific polymeric surfaces for applications in the field of biomaterials. The objective of this study is to investigate surface topographical changes in relation with the changes in fine chemical structure of PET surface due to Ar-plasma and oxygen plasma treatment by means of atomic force microscopy (AFM), contact angle measurement, and specular reflectance of infrared microspectroscopy (IMS). AFM and specular reflectance of IMS are a particularly powerful tool in the study of surface topography and fine chemical structure because AFM can provide high-resolution three-dimensional images of the film surface without any sample pretreatments and damages to the polymer surface, especially enough

*e-mail: seo2659@kyungnam.ac.kr

information on the film surface at the nano level in the height direction,[11] and specular reflectance of IMS also give detailed informations on outmost molecular layer of material without any sample pretreatments and damages to the polymer surface if the samples have a level and lustrous surface.

Experimental

Materials. Semi-crystalline PET without additives was supplied as a film (100 μm thickness) by Kolon Co., Korea. Argon and oxygen gas (purity 99.9%) were purchased from Union Gas. Acetone (spectral grade), which was used as solvent without further purification, was purchased from Sigma Chem. Co..

Surface Modification Procedures. A capacitatively coupled glow-discharge system[15] with a 13.56 MHz radio-frequency (RF) generator (Auto electronic, Korea, maximum power of 300 W), mass flow controller (MFC, MKS, USA), pressure transducer (MKS Baratron, USA), tubular reactor (76 cm long Pyrex glass tube with 5 cm diameter) and two-stage rotary pump (Welch, USA) were used for the modification of the PET surface.

The PET films were cleaned first with acetone in Soxhlet extractor. The films were then dried in the tubular reactor under vacuum at room temperature. The reactor chamber was pumped down to 5 mTorr to remove air, moisture and acetone that may have adsorbed on the PET surface and reactor wall. The ablation procedure was carried out by argon gas and oxygen plasma at 240 mTorr, 40 W of discharge power for 1, 3, and 5 minutes. After plasma treatment. the films were cleaned with acetone and then dried under vacuum again. The effects of surface modification by plasma treatments were analyzed by specular reflectance of IMS and AFM.

Instrumental Analysis. In order to obtain the images of Ar-, and oxygen-plasma modified surfaces, AFM measurement (Auto Probe CP Research System, USA, equipped with silicone tip) was carried out at room temperature, 40% RH, and at scanning rate of 0.5 Hz in noncontact mode. The mean spring constant of the tip was 17 N/m, the length was 85 μm. Ra (average roughness) was determined as the average deviation of Z values within given areas (1×1 μm). The PET samples of 1×1 cm size were attached to sample holder with double-sided carbon tape. For the evaluation of changes in chemical structure of the PET surface, Mid infrared (MIR) specular reflectance measurements on samples were carried out on Equinox 55 FT-IR (Bruker GmbH, Germany) equipped with IRscope II in the range of 600~4000 cm^{-1}. The reflectance spectrum obtained was then transformed into absorption spectrum by Kramers-Kronig Transformation (KKT). To ensure that no light is reflected from back surface of the PET film, the backside was roughened. Polarizing microscope (Olympus AX70, Japan) and contact angle meter (Erma G-1, Japan) were used as additional characterization tools for the surface.

Results and Discussion

Most polymers including PET simultaneously show the characteristics of both crystalline states and highly amorphous states. PET can crystallize, and with some fabrication methods, particularly those employed in the manufacture of film and fiber, molecular orientation may be introduced. Spherulites in Figure 1, observed from polarizing microscope, verify that the virgin PET film used in this study is a semi-crystalline polymer as manifested by Maltese cross.

The evolution of the topography observed by AFM for Ar-plasma-treated PET and oxygen-plasma-treated PET is illustrated in Figures 2 and 3, respectively. The virgin film ((a) in Figure 2) has a relatively smooth and uniform surface. In contrast, the surfaces which were treated by Ar-plasmas ((b), (c), and (d) in Figure 2), and by oxygen plasma ((a), (b), and (c) in Figure 3) become progressively rougher, and shows steep peaks and deep valleys with increasing treatment time. These observations strongly reveal that some moieties of the polymeric material are ablated regardless of the kind of gas used. But differences in the surface ablative ability by plasma between crystalline and amorphous region are considered to cause PET surface to change the topography of the outermost surface of PET film. This interpretation can be strengthened from the work of Ha *et al.*[16] and agrees well with the results of the literature.[3] However, the topographical results demonstrate a significant difference between plasmas employed. The surface by oxygen-plasma treatment is more severely damaged than that by Ar-plasma treatment. In addition, the sizes of peaks which are formed by the ablation become obtuse and thicker as the treatment time increases as shown in Figure 3. The extent of these changes can be measured quantitatively by instrumental analysis of related data such as Ra and SA (surface area) values.

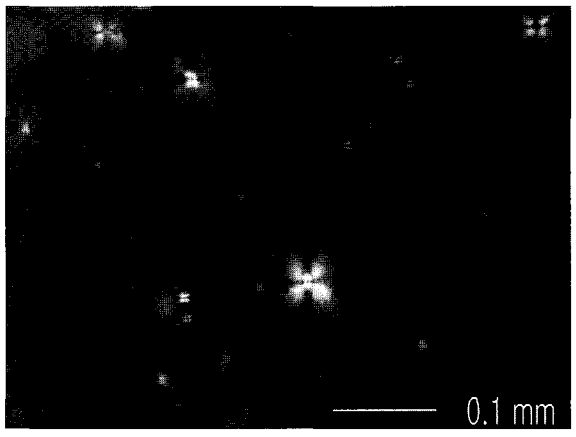

Figure 1. Photograph of spherulites by polarizing microscope for the virgin PET.

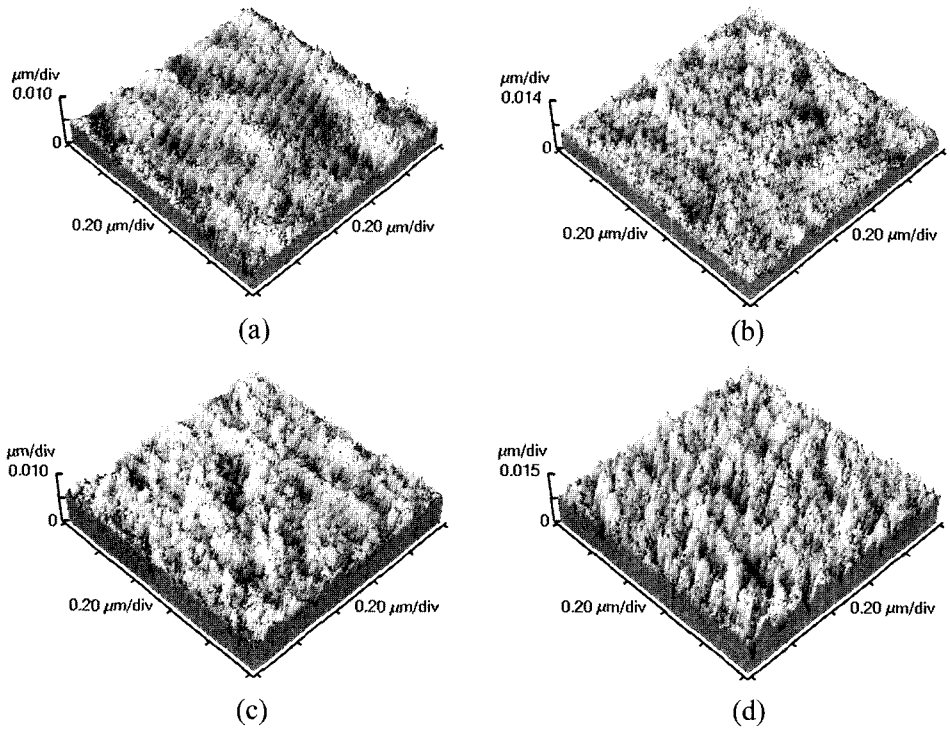

Figure 2. AFM images before and after Ar-plasma treatment. (a) virgin PET, (b), (c), and (d) Ar-plasma treated PET at 240 mTorr, 40 W for 1, 3 and 5 min, respectively.

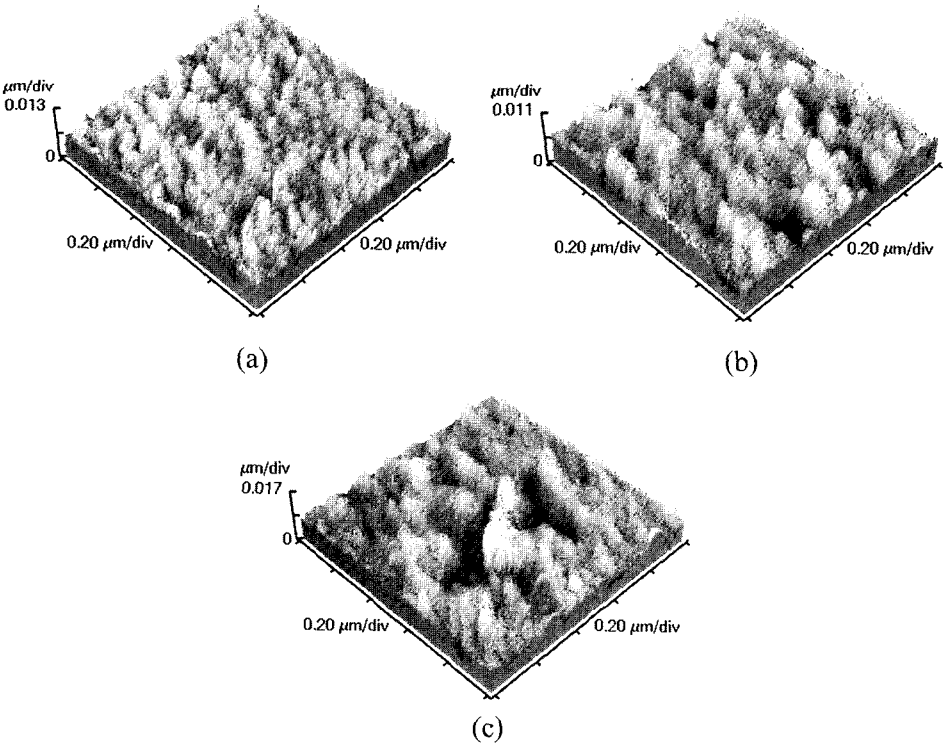

Figure 3. AFM images by oxygen-plasma treatment. (a), (b), and (c) oxygen-plasma treated PET at 240 mTorr, 40 W for 1, 3 and 5 min, respectively.

Ra and SA values plotted as a function of plasma treatment time are illustrated in Figure 4. Starting from a low Ra value of 1.145 nm for the virgin PET, the roughness increases by almost all the plasma ablation process. The Ra values increase with increasing the treatment time up to 2.6 and 2.0 times for Ar-plasma and oxygen-plasma treatment, respectively. The SA values also show similar results. However, the increasing pattern of the SA is entirely different depending upon the plasma source used. For the case of oxygen-plasma, for example, the SA value increases drastically during a short time exposure of 1 min and then decrease slightly but evidently. The reason for the decrease in the SA value by oxygen-plasma seems to be closely related with its topography. As mentioned above, the peaks are obtuse and somewhat agglomerated with some parts of neighbor peaks. From these changes in AFM images and parameters, it can be concluded that the mechanisms of ablation are significantly different with each other.

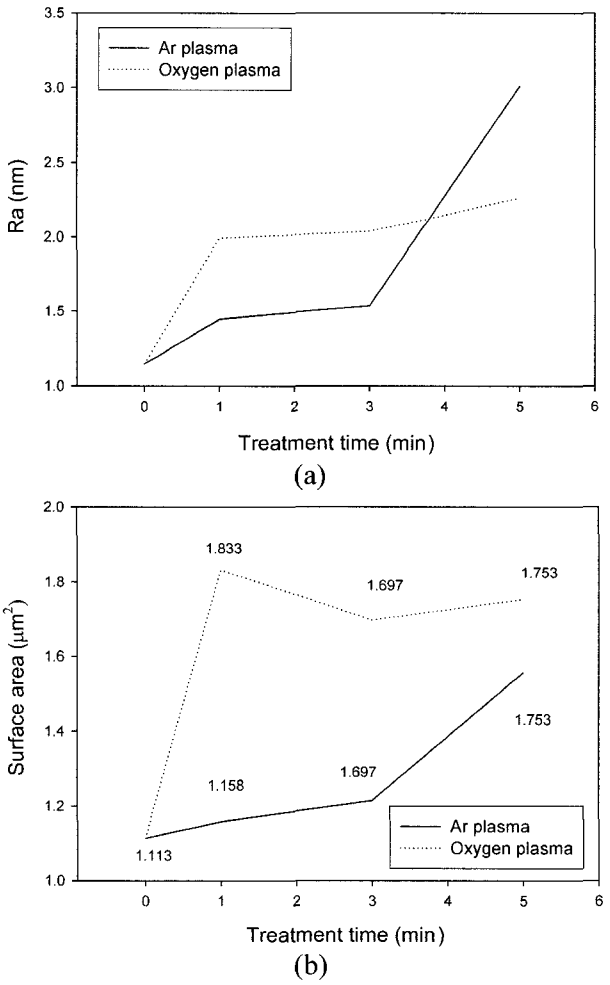

Figure 4. The changes in AFM parameters with increasing plasma treatment time. (a) Ra values versus treatment time and (b) SA versus treatment time.

It has been well-known by work of Yasuda[17] that ablation of materials by plasma can occur by two principle processes. One is physical sputtering and the other is chemical etching. The sputtering of materials by an inert gas such as argon is a typical example of physical sputtering by a momentum-exchange process, and oxygen is a typical example of chemical etching. After Clouet and Shi,[18] in Ar-plasma, the argon and excited species can not chemically react with the substrate and the formation of radical is attributed to the ion bombardment, whereas, in oxygen-plasma, atomic oxygen initiates the reaction, beside the ion bombardment, according to PH (polymer) + O $\rightarrow$ R$\cdot$ + $\cdot$OH.

Accordingly, AFM results obtained from Ar-plasma treatment in this work strongly suggest that the ablation through momentum-exchange process plays an important role to alter the topography of the PET surface in Ar-plasma. On the other hand, AFM results obtained from oxygen plasma treatment are due to oxidative ablation of oxygen.

In addition to the topography, it is of interest to investigate how the chemical fine structure of the surface may be changed by both treatments. For this purpose, specular reflectance spectra are analyzed, which are an appropriate tool for obtaining informations on chemical structure of outmost surface layer materials. Reflectance is given by Eq. (1) where n is reflective index. Using the Eq. (1) for the reflectance R along with the reflective index of 1.57 for PET, it is calculated that only 4.9% of the incident IR radiation is measurable. However, this principle drawback has been overcome by advanced instrumentation.

$$R = \frac{(n-1)^2}{(n+1)^2} \tag{1}$$

Figure 5 shows the specular reflectance spectra for the virgin PET (a), Ar-plasma-treated PET for 5 min (b), and their difference spectrum (c). Others with different treatment time are omitted because of no substantial differences with that of Figure 5(B). Characteristic absorption bands appearing at 1718 (C=O), 1253 (C-O), and 1127 cm^{-1}(C-O) confirm this material as an polyester. To our surprise, we can notice at a glance that spectrum (a) is nearly identical with that of (b). This observation can be verified by their difference spectrum (c) which shows negligible changes in the fine chemical structure between the virgin PET and argon plasma treated PET. As a result, this fact indicates that physical sputtering by argon plasma treatment leads to a constant removal of the material from the PET surface. Inagaki *et al.*[19] who carried out research on the surface modification of PET by Ar-plasma at RF powers of 75 W have also reported that changes in the chemical composition of PET film surface were small.

For comparison of the ablation by Ar-plasma with that by oxygen plasma, the specular spectra by oxygen-plasma treatment are shown in Figure 6. As expected, the spectrum

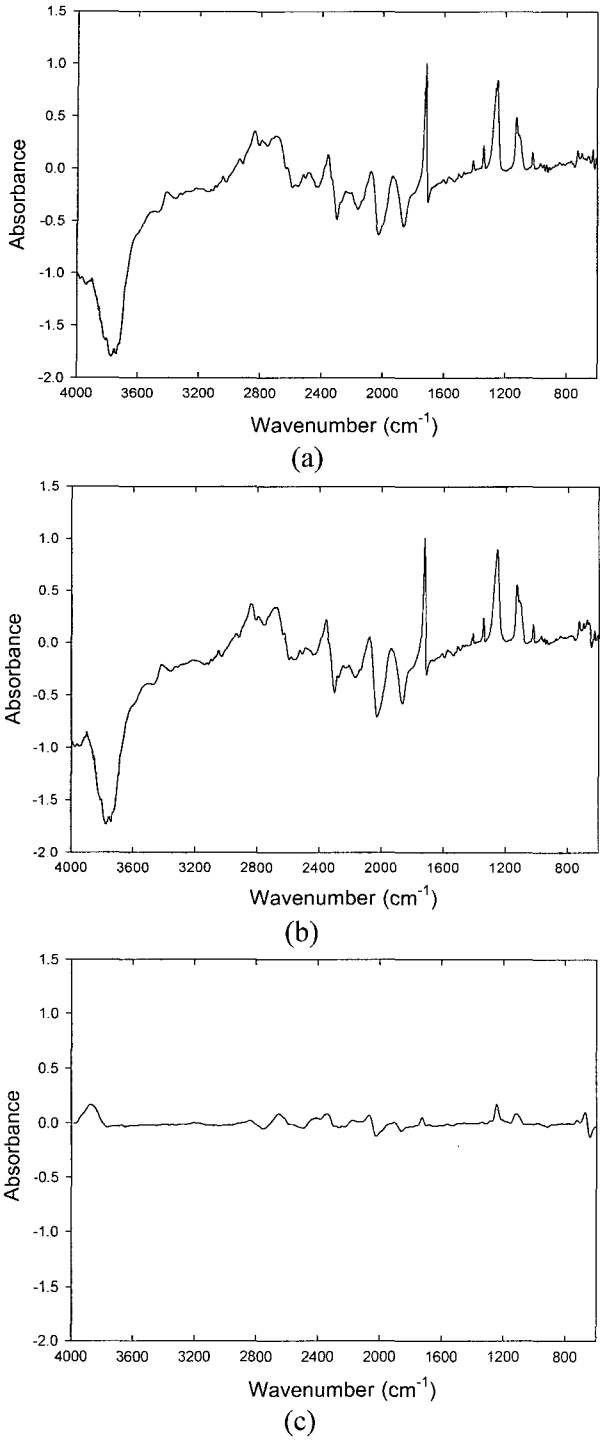

Figure 5. Specular reflectance spectra of Ar-plasma treated PET surface. (a) virgin PET (b) treated for 5 min at 240 mTorr, 40 W, and (c) difference spectrum between spectrum (b) and (c).

(a) in Figure 6 is almost entirely different with those of the spectrum (a) and (b) in Figure 5. A significant decrease in the intensity of aliphatic C-H stretching vibration band which has values of between 2800 and 3000 cm^{-1} is observed. The

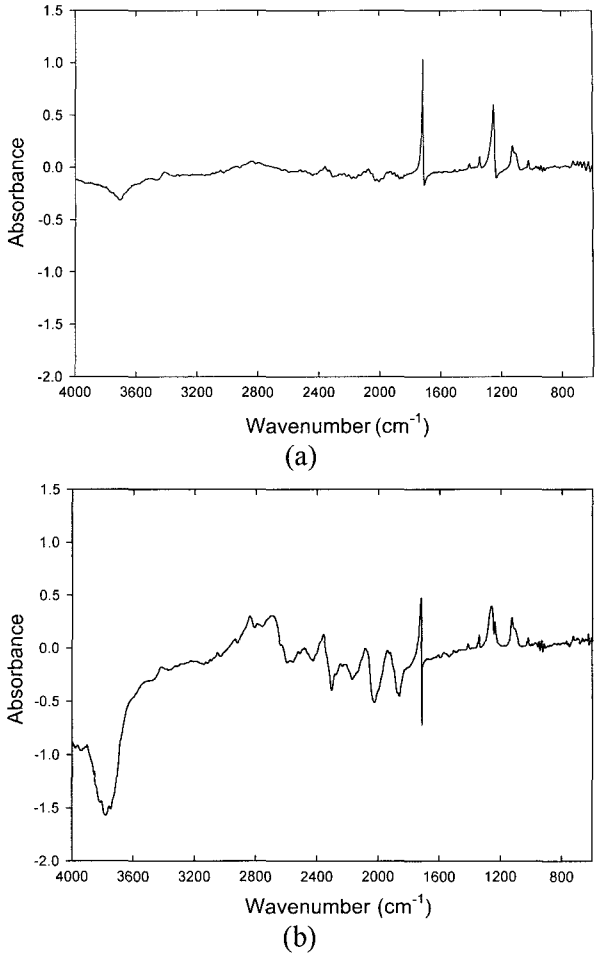

Figure 6. Specular reflectance spectra of oxygen-plasma treated PET. (a) treated for 5 min and (b) difference spectrum of oxygen-plasma treated PET surface with that of the virgin PET.

extent of the decrease can be monitored again from the difference spectrum in (b) of Figure 6 in which the extent of decrease in the C-H band is exhibited as high-rising absorbance bands between 2800 and 3000 cm^{-1}. These experimental facts, along with the result of topographical changes by oxygen plasma, lead us to conclusion that, during oxygen plasma treatment, the ablation proceeds mainly via preferential attack on C-H group rather than on carbonyl group and thereby some polymer chains of the outmost molecular layer of the PET film is considered to be in, at least, partially crosslinked state to maintain the bond valence of carbon-carbon between outmost layer component. On the other hand, the PET surfaces treated by Ar-plasma do not experience a serious surface chemical modification judging from its corresponding specular reflectance spectrum because no noticeable changes in surface chemical structures occur.

Another important aspect to discuss is the behavior of contact angle interacting with plasma-treated surfaces since surface characterization by contact angle measurement has

Table I. The Water Contact Angles for Plasma-Treated PET Films

Plasma	Treatment Time (min)			
	0	1	3	5
Ar	71	60	58	58
O_2	71	37	36	36

an advantage over other instruments such as electron spectroscopy for chemical analysis (ESCA) and attenuated total reflection infrared spectroscopy (ATR/IR) because it is of great value to get informations of outmost surface properties within the range of 5~10 Å depth.[20,21] In Table I, the data for the virgin, Ar-plasma-treated, and oxygen-plasma-treated PET surface are listed.

Water contact angle (WCA) value of untreated PET surface was determined to be 71°, whereas WCA values were lowered to around 58° and 36° for the Ar-plasma-treated surface and oxygen-plasma-treated surface, respectively. The WCA values reach saturation within 1 min of treatment time. It has been known that the main mechanism responsible for the behavior of WCA is actually the incorporation of polar groups and their mobility[20] as well as surface roughness.[22] For the case of nonuniform surface, the apparent contact angle, θ_r, is given by Eq. (2) where r is the ratio of actual to projected area.

$$\cos \theta_r = r \cos \theta_{true} \quad (2)$$

In this study, WCA value should be reduced to some extent since r values are larger than 1 as shown in Figure 4(b). The decreases by roughness, which can be calculated using Eq. (2) and the data presented in Figure 4(b), for Ar-plasma-treated and oxygen-plasma-treated surfaces, are within the range of 8° and 13°, respectively. As a consequence, it is considered that surface roughness is an important factor for the lowering of WCA for Ar-plasma-treated surface since the maximum contribution by roughness is 5/8. However, the lowering of WCA for oxygen-plasma-treated surface is at most 13/35. Accordingly, a primary reason for this fact seems to be due to remaining polar groups on the surface rather than roughness. An explanation for the discriminated behaviors between Ar-plasma and oxygen-plasma is also possible with the aid of specular reflectance spectra. The lowering of WCA for Ar-plasma treated surface seems to be not attributed to polar group but surface roughness effect since there are no distinctive variations in the corresponding spectrum, while that of oxygen-plasma-treated surface is mainly due to a significant decrease in hydrophobic -CH_2- group (or much more enhanced polar carbonyl group, compare to -CH_2- group) in PET surface as manifested by Figure 6(a).

It is worthwhile to examine the crosslinking by activated species in inert gas plasma (CASING)[23,24] phenomenon because it has been known to cause crosslinking of a polymer surface of a film by bombardment with energetic plasma species. However, in this study, CASING seems not to take place, although its possibility can not be excluded completely, during inert gas plasma treatment of argon but to occur during oxygen plasma treatment under our experimental conditions judging from the above mentioned viewpoints such as specular reflectance analysis and topography by AFM. For an elucidation on the exact mechanism, there are still many mysteries that await further studies. Unfortunately, there is little room for argument in this statement.

Conclusions

Semi-crystalline PET film was subjected to ablative plasma treatment under argon and oxygen gas. The changes in AFM topographies of the PET surfaces were investigated in conjunction with specular reflectance of IMS and contact angle measurement. The following results were obtained under our operating conditions.

The increase of plasma treatment time caused the PET surfaces to damage severely, regardless of the kind of plasma used. The surfaces became progressively rougher, and showed steep peaks and deep valleys with increasing treatment time, but their ablative behaviors are significantly different depending upon the plasma used. The specular reflectance spectrum analysis showed that a constant removal of surface material is an important ablative aspect for Ar-plasma, while a preferential ablation to -CH_2- group plays an important role for oxygen plasma. CASING seems not to take place during Ar-plasma treatment but to occur during oxygen-plasma treatment under our experimental conditions. For the surface modification of polymers as biomaterials, especially PET, these results have to be taken into account.

Acknowledgements. This work was supported through The 2002 Academic Research Project by Kyungnam University.

References

(1) P. K. Chu, J. Y. Chen, L. P. Wang, and N. Huang, *Mater. Sci. Eng. R*, **36**, 143 (2002).
(2) B. Gupta, J. Hilborn, C. H. Hollenstein, C. J. G. Plummer, R. Houriet, and N. Xanthopoulos, *J. Appl. Polym. Sci.*, **78**, 1083 (2000).
(3) Y. L. Hsieh and M. Wu, *J. Appl. Polym. Sci.*, **38**, 1719 (1989).
(4) A. M. Wrobel, M. Kryszewski, W. Rakowski, M. Owkoniewski, and Z. Kubacki, *Polymer*, **19**, 908 (1978).
(5) Piglowski, I. Gancarz, J. Staniszewska-Kus, D. Paluch, M. Szimonowicz, and A. Konieczny, *Biomaterials*, **15**, 909 (1994).
(6) R. Singhvi, A. Stephanopoulos, and D. J. C. Wang, *Biotechnol. Bioeng*, **43**, 764 (1994).

(7) A. F. van Rectum and T. G. van Kooten, *J. Biomater. Sci., Polym. Ed.*, **7**, 181 (1995).
(8) S. J. Lee, Y. M. Lee, G. Khang, I. Y. Kim, B. Lee, and H. B. Lee, *Macromol. Res.*, **10**, 150 (2002).
(9) G. Khang, J. M. Lee, P. Shin, I. Y. Kim, B. Lee, Y. M. Lee, H. B. Lee, and I. Lee, *Macromol. Res.*, **10**, 158 (2002).
(10) G. Khang, J. H. Jeon, J. M. Rhee, and H. B. Lee, *Polymer(Korea)*, **23**, 861 (1999).
(11) A. Ohl and K. Schroder, *Surf. Coat. Tech.*, **116**, 820 (1999).
(12) S. Lerouge, M. R. Wertheimer, and L'H. Yahia, *Plasmas Polym.*, **6**, 175 (2001).
(13) H. B. Lee and J. H. Lee, *Biocompatibility of Solid Substrates Based on Surface Wettability*, in *Encyclopedic Handbook of Biomaterials and Bioengineering: Part A. Materials*, D. L. Wise, D. J. Trantolo, D. E. Altobelli, M. J. Yaszemski, J. D. Gresser, and E. R. Schwarz, Eds., Maecel Dekker, New York, 1995. Vol. 1, pp 371-398.
(14) G. Khang, M. K. Choi, J. M. Lee, S. J. Lee, H. B. Lee, Y. Iwasaki, N. Nakabayashi, and K. Ishihara, *Korea Polym. J.*, **9**, 107 (2001).
(15) Y. R. Kang, H. S. Lym, and E. D. Seo, *Polymer(Korea)*, **15**, 570 (1991).
(16) S. W. Ha, R. Hauert, K. H. Ernst, and E. Wintermantel, *Surf. Coat. Tech.*, **96,** 293 (1997).
(17) H. Yasuda, *Plasma Polymerization*, Academic Press, New York, 1985.
(18) F. Clouet and M. K. Shi, *J. Appl. Polym. Sci.*, **46**, 1955 (1992).
(19) N. Inagaki, S. Tasaka, and S. Shimada, *J. Appl. Polym. Sci.*, **79**, 808 (2001).
(20) D. M. Cho, C. K. Park, K. Cho, and C. E. Park, *Polymer*, **38**, 6243 (1997).
(21) M. E. Schrader and G. I. Loeb, *Modern Approaches to Wettability*, Plenum, New York, 1992.
(22) A. W. Adamson, *The Physical Chemistry of Surfaces*, 5th Ed., John Wiley & Sons, Inc., New York 1990.
(23) H. Schonhorn and H. Hansen, *J. Appl. Polym. Sci.*, **11**, 1461 (1967).
(24) A. Grill, *Cold Plasma in Materials Fabrication-from Fundamentals to Applications*, IEEE Press, New York, 1994.