Surface Properties and Characterization of PSII-modified Polymers

Yeonhee Lee[1*], Seunghee Han[1], Moonhee Kwon[1], Youngsoo Kim[2], Hyejin Chun[2]
[1]*Advanced Analysis Center, Korea Institute of Science & Technology, Seoul 136-791, Korea*
[2]*Department of Chemistry, Korea University, Seoul 136-701, Korea*
yhlee@kist.re.kr

(Received: Nov. 17, 2002; Accepted: Jan. 30, 2003)

The Plasma Source Ion Implantation (PSII) technique was utilized to improve the surface electrical properties of various synthetic polymers such as poly(ethylene terephthalate), modified poly(phenylene oxide), and poly(styrene-butadiene copolymer). They were implanted with inert ion species such as Ar and Xe, and with reactive ion species such as N_2 and O_2 to render the surface more electrically conductive. The effect of ion energy and treatment time on the surface resistivity of polymer was investigated. Depending on ion energy, dose, and ion species, the surface resistivity of the film was reduced by several orders of magnitude. In this study we also provide a method for surface modification of 3-dimensional bulk polymers, which is capable of implanting plasma ions into surface of 3-dimensional bulk polymer sample by mounting a metallic grid over a sample stage. Electrical property improvement was measured by high resistance electrometer. Polymer surfaces were characterized by using TOF-SIMS and XPS before and after PSII treatment. From these measurement it was found that the reduction in surface resistivity after PSII treatment was related to graphitic carbon or cross-linked carbon double bond species formed on the surface.

1. Introduction

Many research groups have been concentrated on the possibility of obtaining electrically conducting structures in polymeric materials ever since conducting polymers were discovered [1]. Electrical conductivity of polymers can be achieved by incorporating dispersible conducting fillers, the deposition of conducting materials, and use of conducting polymers [2]. To enhance the surface electrical properties of the polymers a variety of modification techniques have been evaluated [3-6].

Although ion implantation has long been proven to modify the surface properties of metals, semiconductors, and ceramics, only in recent years has great effort been devoted to the surface modification of polymers by ion implantation. Recent studies have shown that ion implantation very effectively improves polymer surface properties such as wettability, surface hardness, wear resistance, and electrical properties [7-9]. Ion-beam surface modification involves use of conventional ion implantation and recently developed hybrid plasma-enhanced ion implantation techniques. Whereas conventional ion implantation has attracted much attention and achieved great success in the surface modification of materials, plasma enhanced ion implantation such as plasma source ion implantation (PSII) is an emerging technology in the field of surface modification for a variety of materials [10-12]. Our group has investigated the use of PSII for modification of polymeric materials [13,14]. It was found that the PSII process very effectively makes the surface hydrophilic and produces a stable surface layer of modified polymer.

Polymer surfaces can also be modified by use of a high-energy ion-beam. High-energy ions are introduced into the polymer structure at high velocity and initiate a large amount of chemical bonding between molecular chains. After treatment by high energy ion beam processes the modified polymers have a highly cross-linked three dimensionally connected rigid network structure and significantly improved electrical properties, hardness, and resistance to wear and chemicals [15,16].

In this study we have explored improvement of the surface resistivity of polymer surface. We focused on the effect of PSII treatment on the polymer surface, using a high energy of more than 20 keV to reduce the surface resistivity. Surface analysis of the modified polymers was performed by X-ray photoelectron spectroscopy (XPS) and Time-of-flight secondary ion mass spectrometry (TOF-SIMS).

This paper was presented at the 4th KVS-SASJ Int'l Symposium in Hiroshima, Japan, November 18-19, 2002.

2. Experimental

2.1 Materials

The sample materials studied were commercial poly(ethylene terephthalate) (PET), poly(styrene-butadiene copolymer) (PS-BD), and modified poly(phenylene oxide) (MPPO) manufactured by Yulchon Chemical (Seoul, Korea). The films and plates were used after cleaning with methanol.

2.2 PSII apparatus

The experiments were performed with a plasma source ion implanter built in-house. A detailed description of this apparatus and the PSII modulator characteristics have been presented elsewhere [17]. Polymer specimens were placed on the oil-cooled stage immersed in the plasma. A metallic grid was mounted over the sample stages so that ions from plasma surrounding the sample were accelerated into a three-dimensional shaped polymer sample when the pulse was on (Fig. 1). The grid having a diameter of 21 cm was electrically connected to the sample stage with the post. Samples were pulse-biased to a high negative potential up to –30 kV.

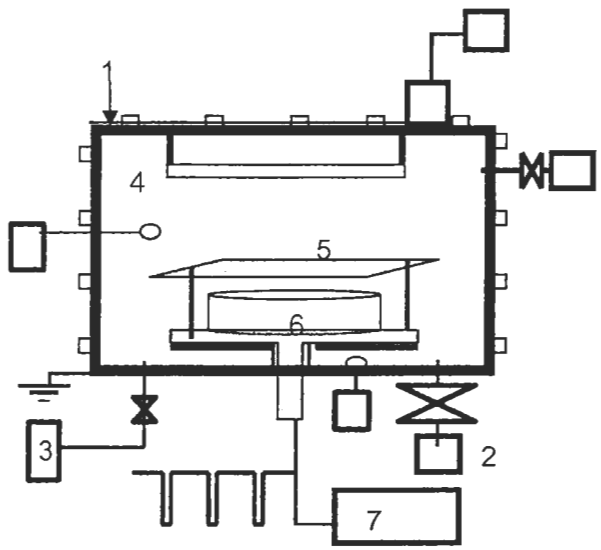

Fig.1 Schematic diagram of PSII system used in the experiment: (1) vacuum chamber (2) turbo molecular pump (3) gas inlet system (4) antenna (5) metal grid (6) sample (7) high voltage pulse generator

2.3 Instrumental evaluation

A Physical Electronics model PHI 7200 TOF-SIMS/SALI instrument, with the Cs^+ ion gun operated at 8 keV, at an ion current of 1 nA, was used for the TOF-SIMS study; the analysis spot size was approximately 50 μm in diameter. Charge neutralization was used when modified polymer plates were analyzed. XPS spectra were obtained by use of a Physical Electronics model PHI 5800 spectrometer with monochromatic AlK_α radiation of the power of 350 W at focused mode. Charging of the polymer samples, as a result of photoemission, was corrected by setting the energy of the main hydrocarbon component of the C1s spectrum at 284.6 eV for MPPO. A pass energy of 23.5 eV was employed for all spectra.

3. Results and Discussion

PSII was used to evaluate the possibility of reducing the surface resistivity of polymer films. Fig. 2 shows the dependence of the surface resistivity for poly(ethylene terephthalate) (PET) and modified poly(phenylene oxide) (MPPO) on ion species at an ion energy of 30 keV for 5 min. treatment time. For poly(styrene-butadiene copolymer) (PS-BD) an ion energy of 20 keV was used to reduce the surface resistivity without severe heat deformation of the surface. Several different ion species, including N_2, O_2, Ar, and Xe were implanted in a variety of polymers, resulting in a significant reduction in surface resistivity.

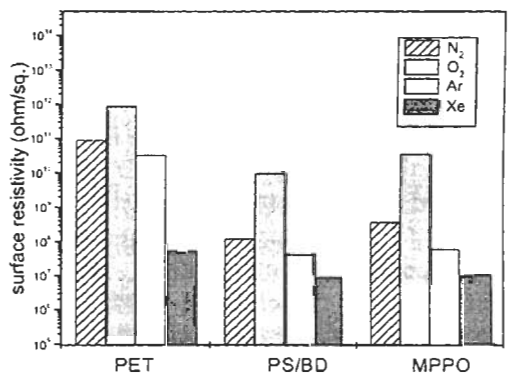

Fig. 2 Surface resistivity of PET, PS-BD, and MPPO after 20 or 30 keV PSII with different ion species

It was observed that, in general, PSII reduced the surface resistivity of the polymers and that the extent of the decrease varied with the nature of the ion species. The surface resistivity of the untreated polymers was approximately $3x10^{15}$ Ω/sq. Overall, Xe gas had the most significant effect on the polymer studied. The surface resistivity of PS-BD was reduced by more than eight orders of magnitude when the polymer was treated with Xe gas. Inert gases such as Ar and Xe had better effect than reactive gases such as N_2 and O_2. The electrical properties were apparently related to the degree of cross-linking double bond

formation, and ion species with a large electronic collision cross-section, e.g. Ar and Xe, are expected to induce more cross-linking and unsaturation, which increases conductive paths.

Fig. 3 represents the surface resistivity of a treated PS/BD film as a function of the grid height above the polymer surface. At 20 keV ion energy, the surface resistivity of PS-BD decreased to about 6×10^6 Ω/sq. with a color change to dark brown. A considerable difference in the surface resistivity was observed by employing a grid regardless of ion dose. The surface resistivities of the treated samples in the presence of the grid decreased by 3-6 orders of magnitude uniformly independent of the post height.

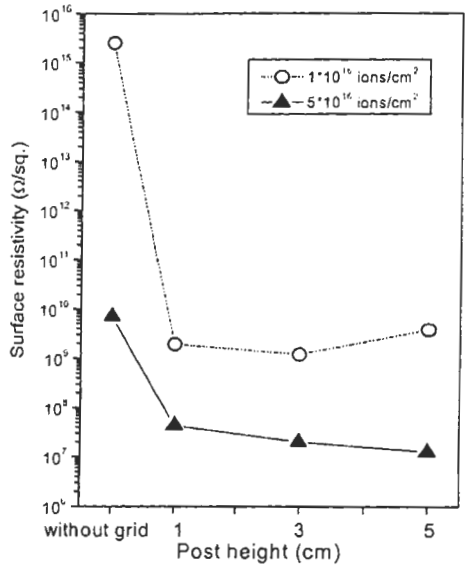

Fig. 3 Surface resistivities of Ar implanted PS/BD at a center area as a function of the post height

For the sample treated without the grid, the surface resistivity of the PS-BD sample did not decrease after treatment at a dose of 1×10^{16} ions/cm^2, but decreased by 5 orders of magnitude at a dose of 5×10^{16} ions/cm^2. The use of the grid enabled to prevent the ineffective potential drop and charging on the polymer surface. Because a conductive grid makes ions accelerate perpendicularly to the sample, the polymer sample yields more uniform and lower resistivity than that treated without the grid. The lower resistivity of the sample treated with the grid is possibly related to the larger sheath size and the implantation with fully applied potential.

Ar and Xe plasma ion treatments of MPPO sample resulted in a drastic reduction in the surface resistivity. As expected, on the basis of MPPO polymer composition, the XPS survey spectrum revealed the presence of carbon and oxygen. In Fig. 4 we illustrate, by means of curve-fitted C1s core level spectra, the carbon functionality of MPPO surfaces undergoing Ar- or Xe-PSII treatment. The fits are based on reference measurement of poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) by Beamson and Briggs [18].

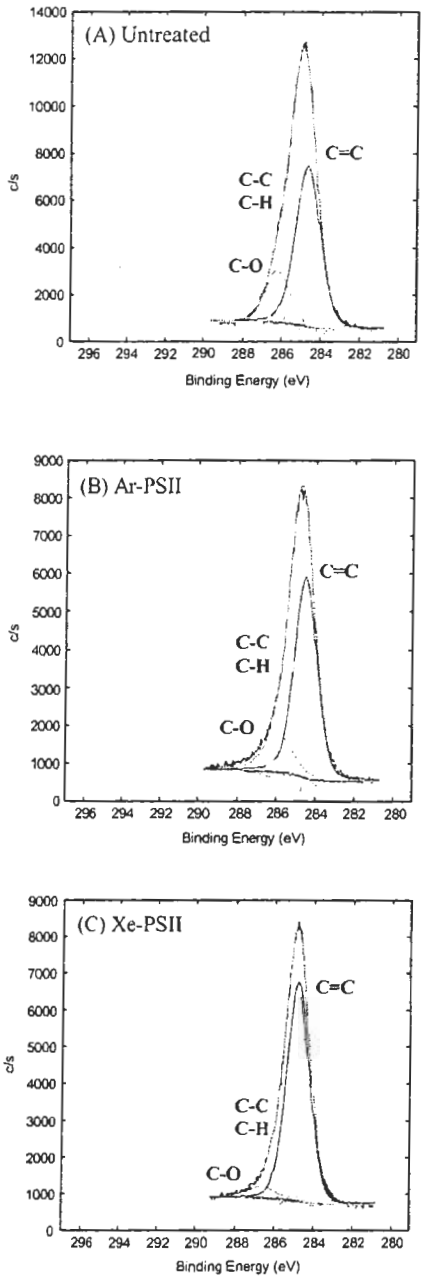

Fig. 4 Deconvoluted C1s XPS spectra of MPPO obtained (A) as received;(B) after Ar PSII treatment; (C) after Xe PSII treatment

The spectra reveal that Ar- and Xe-PSII increase the number of double bonds or the

amount of graphite carbon on the polymer surfaces, as indicated by the higher intensity of the corresponding peaks, labeled C=C for MPPO, compared with the peaks obtained from the untreated polymers. The increase of the C=C peak is much larger for Xe-treated MPPO than for the Ar-treated sample. The spectra also show that the peaks assigned to the C-C (or C-H) bond and the C-O bond for the treated surfaces decrease much more than for the untreated surfaces. This result means that C=C double bonds or graphite carbon are closely related to surface resistivity. Contributions from the aromatic π-π^* satellites disappear from the C1s peaks after treatment (not shown in the figure).

The negative ion TOF-SIMS peak intensity ratios, and the surface resistivities of the modified MPPO are given in Table 1. The positive ion TOF-SIMS spectrum of the untreated MPPO is dominated by the intense characteristic peaks at m/z 77, 91, and 103 ($C_6H_5^+$, $C_7H_7^+$, and $C_8H_7^+$, respectively) whereas intensities of those peaks are much lower in the spectrum of the treated surface. For Ar- and Xe-treated samples the peak ratios C_2^-/OH^-, C_2H^-/OH^-, C_3^-/OH^-, and C_4^-/OH^-, are larger in the negative ion TOF-SIMS spectrum. As the peak ratios C_2^-/OH^-, C_2H^-/OH^-, C_3^-/OH^-, and C_4^-/OH^- increase the surface resistivity decreases. The C_2^-, C_2H^-, C_3^-, and C_4^- peaks might be associated with graphite carbon or double bonds formed on the surface after surface modification. Peak intensity ratios were obtained by integrating the peak areas of the two fragment ions. From the tabulated data it is obvious that the amount of graphite carbon or double bond carbon species on the treated surface increased and that the original MPPO structure was substantially modified by the treatment.

Table 1. TOF-SIMS peak intensity ratios, and surface resistivities for MPPO as a function of the working gas

	TOF-SIMS				Surface Resistivity
	C_2^-/OH^-	C_2H^-/OH^-	C_3^-/OH^-	C_4^-/OH^-	(Ω /sq.)
Untreated	1.02	1.33	0.06	0.04	2.7×10^{15}
Ar PSII	1.17	1.38	0.11	0.15	6.0×10^{7}
Xe PSII	1.67	1.59	0.14	0.17	4.0×10^{6}

4. Conclusions

The electrical properties of PET, PS-BD, and MPPO treated by PSII with a mesh-type conducting grid were investigated by measurement of surface resistivity. The effect of low-pressure plasmas of oxygen, nitrogen, argon, or xenon on the surface resistivities of the polymers was studied. Depending on ion energy and treatment time, surface resistivities of MPPO were reduced by several orders of magnitude. Intense inert gas ion bombardment led to more conductive and stable surfaces as a function of aging time. The Ar- and Xe-PSII treated MPPO were characterized by XPS and TOF-SIMS. TOF-SIMS and XPS data indicated the formation of double bonds or graphite carbon on the MPPO surface after treatment and were correlated with the decrease in the surface resistivity of the treated surface.

5. Acknowledgements

This work was supported by National Research Lab. Program from MOST.

6. References

[1] J. Mort, Science. 208, 819 (1980).
[2] M. Narkis, A. Ram, Z. Stein, J. Appl. Poly. Sci. 25, 1515 (1980).
[3] KL. Mittal and KW. Lee, Polymer surfaces and interfaces, characterization, modification, and application. VSP, Utrecht, The Netherlands (1997).
[4] F. Garbassi, M. Morra and E. Occhiello, Polymer surfaces. Wiley, New York (1994).
[5] YQ. Wang, SS. Mohite and LB. Bridwell, Mater. J. Res. 8, 388 (1993).
[6] EH. Lee, GR. Rao, MB. Lewis and LK. Mansur, Nucl. Instrum. Methods B. 74, 326 (1993).
[7] KL. Mittal, Polymer surface modification, relevance to adhesion. VSP, Utrecht, The Netherlands (1996).
[8] H. Tsuji, H. Satoh, S. Ikeda, N. Ikemoto, Y. Gotoh and J. Ishikawa, Surf. Coat. Technol. 103/104, 124 (1998).
[9] CM. Lopatin, TL. Alford, VB. Pizziconi, M. Kuan and T. Laursen, Nucl. Instrum. Methods B. 145, 522 (1998).
[10] JR. Conrad, JL. Radtke, RA. Dodd, FJ. Worzala and NC. Tran, J. Appl. Phys. 62, 4591 (1987).
[11] J. Shao, EC. Jones and NW. Cheung, Surf. Coat. Technol. 93, 254 (1990).
[12] JR. Conrad, RA. Dodd and S. Han, J. Vac. Sci. Technol A. 8,3146 (1990).
[13] S. Han, Y. Lee, H. Kim, J. Lee, J. Yoon and G. Kim, Surf. Coat. Technol. 93, 261 (1997).
[14] Y. Lee, S. Han, J. Lee, J. Yoon, H. Lim and K. Kim, J. Vac. Sci. Technol A. 16, 1710 (1998).
[15] MK. Ghosh and KL. Mittal, Polyimides,

fundamentals and applications. Marcel Dekker, New York (1996).
[16] K-H. Bather and U. Hermann, Surf. Coat. Technol. 74/75, 670 (1995).
[17] S. Han, H. Kim, Y. Lee, J. Lee and S. Kim, Surf. Coat. Technol. 93, 254 (1996).
[18] G. Beamson and D. Briggs, High resolution XPS of organic polymers. Wiley, New York (1992).