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CHARACTERIZATION OF PLASMA ION IMPLANTED SURFACES USING TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMATRY

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ABSTRACT

Plasma Source Ion Implantation (PSII) technique was used for the hydrophilization or hydrophobization of polymer surfaces. Polymers were modified with different plasma gases such as oxygen, nitrogen, argon, and tetrafluoromethane, and for varying lengths of treatment time. Plasma ion treatment of oxygen, nitrogen, argon and their mixtures increased significantly the hydrophilic properties of polymer surfaces. More hydrophobic surfaces of polymers were formed after the treatment with tetrafluoromethane. A study of plasma source ion implanted polymers was performed using contact angle measurements and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The TOF-SIMS spectra and depth profile were used to obtain the information about the treated surfaces of polymers. The permanence of this technique could be evaluated with respect to ageing time. The surfaces treated with PSII gave better stability than other surface modification methods.

INTRODUCTION

When polymeric materials are used in industrial applications, a variety of interactions can occur between the polymer surface and the industrial environment. The hydrophilicity of the polymer surface can play an important role in determining how these interactions proceed. Thus, in order to gain more hydrophilic surface, various modification methods have been developed¹⁻⁴⁾. This study used new technique, namely Plasma Source Ion Implantation (PSII) to modify the polymer surfaces. PSII technique has been studied to apply it in a variety of materials' surface modification^{5,6)}. PSII has several advantages in the modification of solid surfaces.

In this work different kinds of plasma source ion implantation treatment conditions were chosen, focusing on the behavior with time of the treated surface in contact with air. The treated surfaces and the behavior of treated surfaces with time were studied by a combination of surface-sensitive techniques. Water contact angle measurements and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)⁷⁾ were used to characterize the modified surfaces.

EXPERIMENTAL PROCEDURE

PSII treatments were performed in an "in-house" built PSII chamber at Korea Institute of Science and Technology (KIST). A deta-

iled description of this instrument has been presented⁸. Modifications of polymer samples were performed using different kinds of gases such as O₂, N₂, Ar, CF₄, and their mixtures. Commercial polymer samples were located on the oil-cooled high voltage pulse stage. The PSII parameters adopted were as follows: pressure 1 mTorr, RF power 200W, high voltage pulse -5kV, pulse width 10 μ s, pulse frequency 500 Hz, treatment time 1min. to 15min.

Water contact angle measurements were taken using a Rame-Hart model 100 contact angle goniometer.

Static secondary ion mass spectrometry studies were performed using a PHI Φ -7200, TOF-SIMS/SALI. Spectrometer with a Cs⁺ ion gun operated at an ion energy of 8keV at an ion current of 15nA.

RESULTS AND DISCUSSION

Table 1 gives a list of contact angles for untreated and plasma ion-implanted polystyrene measured as a function of the gas type and the length of treatment time. The plasma ion implanted samples were prepared at 1 mTorr using pulses of -5kV, 10 μ s, 500Hz and 200W RF power. Oxygen, nitrogen, and argon plasma ion treatment caused a drastic reduction of water contact angles. Contact angles for untreated polystyrene were 79° and after PSII treatment they were reduced to below 10°. Oxygen treated surfaces showed more hydrophilic properties than other gas treated samples.

Another advantage of this technique is that the surface of polymer can be altered to be hydrophobic. Contact angles for CF₄ plasma

Table 1. Contact angles for untreated and plasma ion implanted polystyrene as a function of treatment time

Treatment Time	Contact Angle		
	Oxygen	Nitrogen	Argon
Untreated	79°	79°	79°
1 min.	7°	35°	40°
5 min.	4°	18°	14°
30 min.	2°	5°	5°

Table 2. Contact angles for CF₄ plasma ion implanted polystyrene as a function of treatment time

Treatment Time	Contact Angle
Untreated	79°
1 min.	101°
5 min.	103°
10 min.	106°

ion implanted polystyrene as a function of treatment time are shown in Table 2. With 1 min. of CF₄ treatment, an increase is observed reaching contact angles of about 101° for polystyrene.

TOF-SIMS has the potential to provide molecular structure and composition information from the uppermost layers of polymer surfaces. The Cs⁺ source provides the high mass spectral resolution for chemical identification. Figure 1 shows positive ion TOF-SIMS spectra for the untreated, Ar treated and O₂ treated polystyrene. Positive ion TOF-SIMS spectra for the modified polystyrene show an enhancement of the low mass fragments and introduction of oxygen containing functional groups. TOF-SIMS instrument has the high mass resolution for separating inorganic or organic species occurring at the same nominal mass. Peaks at m/z 43 can be

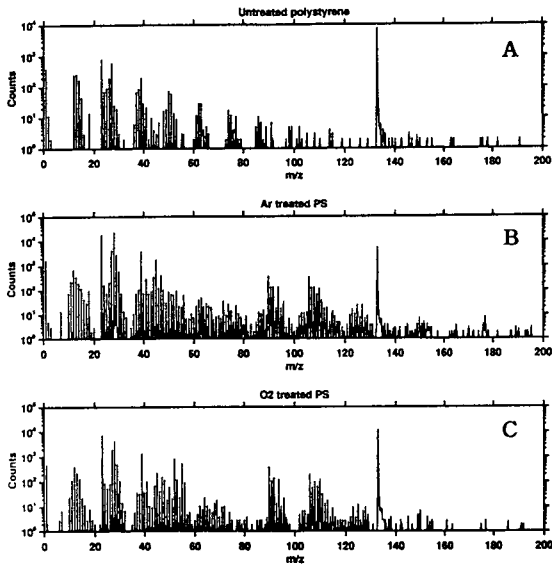


Fig. 1. Positive ion TOF-SIMS spectra of (A) untreated (B) Ar treated (C) O₂ treated polystyrene in mass range $m/z=0-200$.

attributed to C₂H₃O⁺ (exact mass m/z 43.0183) and C₃H₇⁺ (exact mass m/z 43.0546), respectively (Fig. 2). The negative ion TOF-SIMS spectrum of the untreated plate is dominated by the very intense characteristic peaks at m/z 13 and 25 (CH⁻ and C₂H⁻, respectively); whereas the spectrum of the treated surface shows an abundance of oxygen containing. After treatment with Ar and O₂ plasma ion, oxygen containing peaks increase and the intensities of hydrocarbon peaks decrease in the spectra.

As shown in Figure 3, SIMS depth profile also indicates that plasma ion-implanted polystyrene surfaces involved more abundant CO containing species and less hydrocarbon fragments than the unmodified polystyrene.

The rate and extent of hydrophobic recovery was studied as a function of aging time using water contact angle measurement. In Figure 4 the behavior of water contact angles is plotted according to the aging time. It

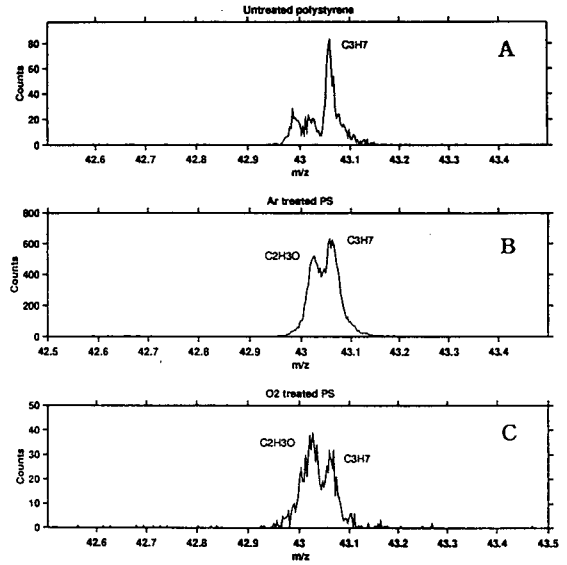


Fig. 2. Positive ion TOF-SIMS spectra of (A) untreated (B) Ar treated (C) O₂ treated polystyrene in mass range $m/z=42.5-43.5$

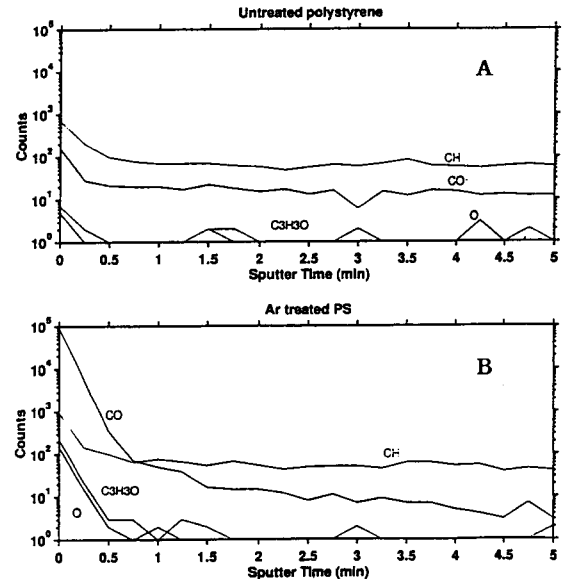


Fig. 3. Positive ion TOF-SIMS depth profile of (A) untreated (B) Ar treated polystyrene

is evident that the rate of recovery is much lower for the O₂ treated sample surface than for the N₂ and Ar treated. The contact angle of O₃ treated surface showed a rapid increase

for about 24h, then stabilized at a value. The initial very rapid change in contact angle observed after PSII modification is probably due to the reorientation of highly mobile fragments created by the treatment.

PSII method was also applied to modify the surfaces of other polymers, such as poly(ethylene terephthalate), polyethylene, poly(vinyl chloride), poly(ethylene naphthalene), polycarbonate, and silicone rubber. The untreated polymer surface was hydrophobic, with contact angles in agreement with literature values. With treatment, a sharp decrease of the contact angle was observed for the polymers studied in this work.

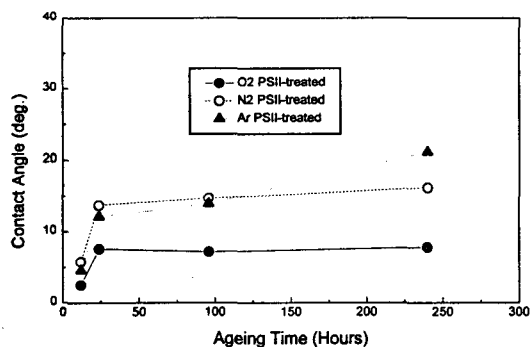


Fig. 4. Water contact angles for O₂ treated, N₂ treated, and Ar treated polystyrene as a function of ageing time

CONCLUSIONS

PSII was performed to modify the polymer surfaces, and water contact angle measurements and TOF-SIMS were used to charac-

terize the treated surfaces. This study shows that PSII is a potentially powerful technique for the modification of polymer surfaces to improve the hydrophilicity or hydrophobicity and to stabilize the treated surfaces.

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REFERENCES

1. F. Garbassi, M. Morra, and E. Occhiello, *Polymer Surfaces*, John Wiley & Sons, New York (1994)
2. J. Pochan, L. Gerenser, and J. Elman, *Polymer*, 27, 1058 (1986)
3. M. Morra, E. Occhiello, and F. Garbassi, *J. Colloid Interface Sci.*, 132, 504 (1989)
4. Y. Iriyama, T. Yasuda, D. L. Cho, and H. Yasuda, *J. Applied Polymer Sci.*, 39, 249 (1990)
5. J.R. Conrad, J. L. Radke, R. A. Dodd and F.J. Worzala, *J. Appl. Phys.*, 62, 4591 (1987)
6. M. Tuszewski, J. T. Scheuer, L.H. Campbell, and B. K. Laurich, *J. Vac. Sci. Technol. B*, 12, 973 (1994)
7. A. Benninghoven, *Secondary Ion Mass Spectrometry*, John Wiley & Sons, 1987
8. S. Han, H. Kim, Y. Lee, J. Lee and S. G. Kim, *Surf. Coat. Technol.*, 82, 270 (1996)