

Journal of Korean Institute of surface Engineering
Vol. 29, No. 5, Oct., 1996

POLYMER SURFACE MODIFICATION WITH PLASMA SOURCE ION IMPLANTATION TECHNIQUE

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ABSTRACT

The wetting property of polymer surfaces is very important for practical applications. Plasma source ion implantation technique was used to improve the wetting properties of polymer surfaces. Poly(ethylene terephthalate) and other polymer sheets were mounted on the target stage and an RF plasma was generated by means of an antenna located inside the vacuum chamber. High voltage pulses of up to -10kV, 10 μ sec, and up to 1 kHz were applied to the stage. The samples were implanted for 5 minutes with using Ar, N₂, O₂, CH₄, CF₄ and their mixture as source gases. A contact angle meter was used to measure the water contact angles of the implanted samples and of the samples stored in ambient conditions after implantation. The modified surfaces were analysed with Time-Of-Flight Mass Spectrometer (TOF-SIMS) and Auger Electron Spectroscopy (AES). The oxygen-implanted samples showed extremely low water contact angles of 3° compared to 79° of unimplanted ones. Furthermore, the modified surfaces were relatively stable with respect to aging in ambient conditions, which is one of the major concerns of the other surface treatment techniques. From TOF-SIMS analysis it was found that oxygen-containing functional groups had been formed on the implanted surfaces. On the other hand, the CF₄-implanted samples turned out to be more hydro-phobic than unimplanted ones, giving water contact angles exceeding 100°. The experiment showed that plasma source ion implantation is a very promising technique for polymer surface modification especially for large area treatment.

INTRODUCTION

Polymeric materials have a wide range of usage and the wetting property of polymer surface, which is hydrophobic(non-wetting) in nature, is especially important in practical

applications because it affects the wettability, paintability, colorability, bio-compatibility, anti-electrostaticity, anti-fogging, adhesion, etc. A lot of methods have been devised and commercially used to hydrophilize the polymer surfaces^[1, 2]. Among them, oxygen plas-

ma treatment is rather extensively studied for it is a very effective way to give the hydrophilicity to polymer surface especially of large area.

In this study, the plasma source ion implantation technique^[3] was used to improve the wetting property of polymer surfaces, and the results will be discussed.

EXPERIMENTAL

The implantation device used in the experiment is shown schematically in Fig. 1 and is described in detail elsewhere^[4]. Commercial poly(ethylene terephthalate) and other polymer sheets of various thickness from 0.1mm to 2mm were mounted on the flat target stage and the vacuum chamber was evacuated to

the base pressure of 10^{-5} Torr. After filling the chamber with 1m Torr of working gas (Ar, N₂, O₂, CH₄, CO, He, CF₄, and their mixtures), a 200 W RF plasma was generated by means of an antenna located inside the vacuum chamber. High voltage pulses of up to -10kV, 10 μ sec, and up to 1 kHz were applied to the target stage for varying lengths of time. A contact angle meter (Rame-Hart Model 100-10) was used to measure the water contact angles of the implanted samples and of the samples stored in ambient conditions after implantation. The modified surfaces were analyzed with PHI-7200 TOF-SIMS and PHI-670 Scanning Auger Electron Microscopy.

RESULTS AND DISCUSSION

In Table 1, the water contact angles of various polymers after oxygen ion implantation are summarized. The samples were implanted for 5 minutes using pulses of -5kV, 10 μ sec, and 500Hz. It can be seen that by oxygen ion implantation the surfaces of most polymers became completely wetting.

With the Auger depth-profiling analysis of oxygen-implanted poly(ethylene terephthalate), the implanted sample was found to be richer in oxygen compared to the unimplanted sample, as shown in Fig. 2. The Auger experiment was performed with an 1keV electron beam to prevent sample charging. Furthermore, the implanted oxygen was incorporated into the polymer forming oxygen-containing hydrophilic functional groups such as CO, COOH, OH, etc., which were responsible for the drastic change of water contact angles. Such functional groups were easily

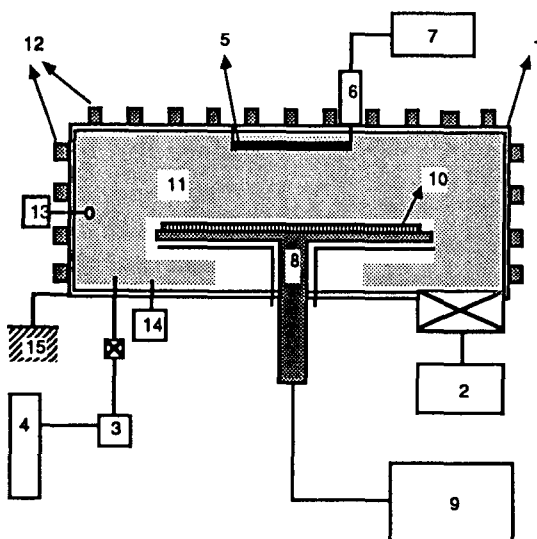


Fig. 1. Schematic diagram of PSII system used in the implantation experiment; 1. vacuum chamber; 2. vacuum pump; 3. gas inlet system; 4. gas; 5. antenna; 6. matching network; 7. RF power supply; 8. sample holder; 9. high voltage pulse generator; 10. sample; 11. plasma; 12. permanent magnet; 13. Langmuir probe; 14. ion gauge; 15. vacuum chamber ground

Table 1. Water contact angles of various polymers after oxygen ion implantation compared to unimplanted ones.

Polymer	Water contact angles	
	Untreated	O ₂ PSII-treated
polystyrene(A)	79°	2°
polystyrene(B)	88°	2°
poly(ethylene terephthalate)(A)	74°	2°
poly(ethylene terephthalate)(B)	75°	3°
poly(ethylene terephthalate)(C)	71°	3°
poly(ethylene terephthalate)(D)	73°	3°
polyethylene(A)	92°	2°
polyethylene(B)	88°	2°
poly(vinylchloride)	78°	7°
poly(ethylene naphthalene)	69°	3°
polycarbonate	90°	3°
silicone rubber	105°	8°

recognized with TOF-SIMS analysis. In Fig. 3, the TOF-SIMS spectrum of oxygen-implanted polystyrene is compared with that of the unimplanted sample. It can be seen that functional groups such as C₃H₃O or C₃H₄O, which were not found in the unimplanted sample, were formed after oxygen ion implantation.

The conventional plasma-treated polymers are known to undergo hydrophobic recovery (or aging), in which the hydrophilic surfaces achieved via plasma treatment get changed to be hydrophobic again with time^[5]. In conventional plasma treatment, the samples are just immersed in the plasma and there is no active control of the energies of the bombarding ions. The modified layer is very thin and is vulnerable to recovery by means of reorientation and diffusion of functional groups in order to lower the increased surface energy. In Fig. 4 and Fig. 5, the effects of process gases and target bias voltage on the hydrophobic recovery of PSII-treated poly(ethylene

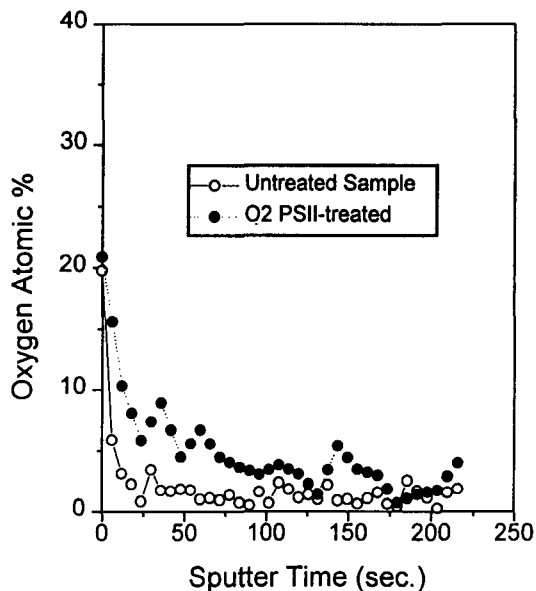


Fig. 2. Oxygen depth distributions of untreated and oxygen-implanted poly(ethylene terephthalate).

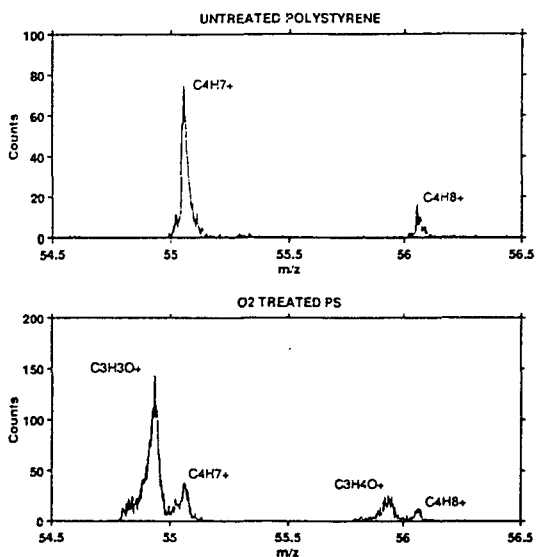


Fig. 3. TOF-SIMS spectra of untreated and oxygen-implanted polystyrene.

terephthalate) are shown. The samples in Fig. 4 were implanted at 1m Torr and 200 W RF power using pulses of -5kV, 10 μ sec, 1kHz for 5minutes. It can be seen that after rapid

recovery within 24 hours the water contact angles approached some limiting values, which are dependent on the process gas. It was also found that the mixture of CH_4 and O_2 gave the lowest contact angle after recovery.

In Fig. 5 we can see that by increasing the pulse voltage the water contact angle settled down to a lower value, which is very promising for practical applications. The samples were implanted at 1 mTorr and 200 W RF power except for the sample marked as HP (high pressure). The HP sample was implanted at high pressure of 30m Torr without using the RF power. In this operation mode, the plasma was generated by the high voltage pulses when the pulse was on and the implantation of ions was followed until the pulse got off. Hence, in most of the implantation time the sample was in neutral gas environment, not in a plasma. In the figure, the sample marked as No Bias was just immersed in

the RF plasma without pulse biasing, which was quite similar to the conventional plasma treatment. The unique feature of plasma source ion implantation applied to polymer surface modification lies in that when the pulse is on the ions are implanted at high energies enough to break the polymer chains and while the pulse is off the polymer surface with an abundance of active sites gets immersed in the plasma, which is rich in reactive species.

In Fig. 6, the uniformity of oxygen treated poly(ethylene terephthalate) of A4 size is shown. It was found that plasma source ion implantation is very suitable for uniform treatment of large areas.

On the other hand, by using CF_4 plasma the polymer surfaces became more hydro-phobic resulting in water contact angles larger than 100° which would be very beneficial for water-proof of polymeric fabric.

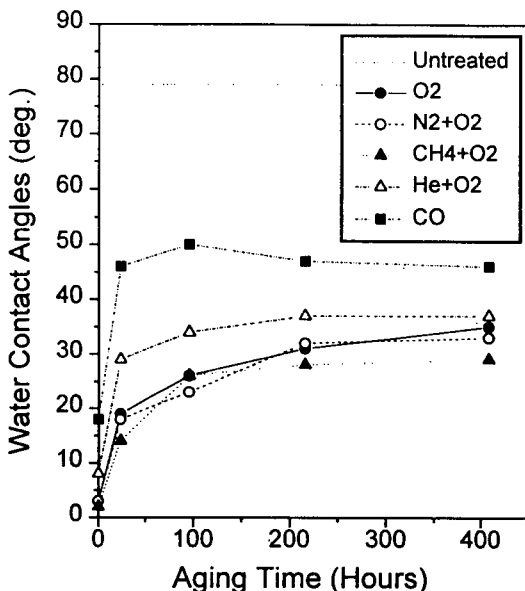


Fig. 4. Gas dependence of poly(ethylene terephthalate)'s hydrophobic recovery.

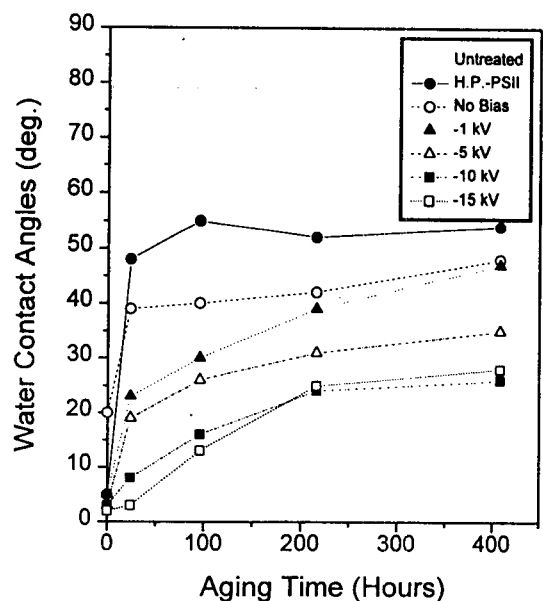


Fig. 5. Pulse voltage dependence of poly(ethylene terephthalate)'s hydrophobic recovery.

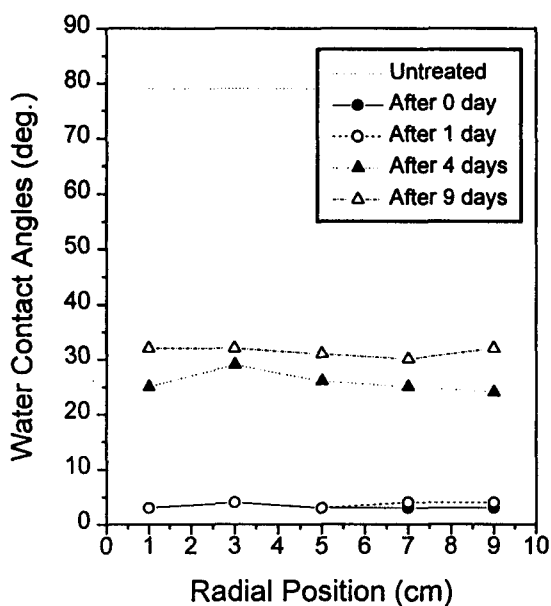


Fig. 6. Positional dependence of poly(ethylene terephthalate)'s hydrophobic recovery.

CONCLUSION

Plasma source ion implantation is a very promising technique for polymer surface mod-

ification due to its capability of active species control for treatment, active energy control of implanted species, intrinsic charge neutralization by using plasma and pulsing technique, and uniform treatment of large areas. Furthermore, it is simple in principle and also in machine, which allows the easiness of scale-up for production.

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