Surface Characterization of Polystyrene Treated with Plasma Source Ion Implantation

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Polystyrene plate was modified with different kinds of gases to improve the surface wettability by Plasma Source Ion Implantation (PSII) technique. Hydrophobic recovery of treated polystyrene has been studied with regard to its dependence on ageing time and treatment parameters. PSII-treated surfaces were characterized and compared with surfaces which were treated by plasma. The permanence of these two treatment methods was evaluated with respect to ageing time and ageing temperature. A study on the PSII-treated and plasma-treated polystyrene surfaces and their hydrophobic recovery was performed using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), and water contact angle measurements. Oxygen PSII-treated polystyrene combined with various inert gas treatments showed very stable surfaces as a function of ageing time. Oxygen isotope gas, $^{18}O_2$, and CF_4 gas were used to identify the effect and mechanism of PSII treatment on the polystyrene surfaces. TOF-SIMS spectra of $^{18}O_2$ PSII-treated samples provided the information about the presence of ^{18}O-containing peaks in clusters from the modified surfaces.

1. Introduction

The chemical and physical properties at the surface of every material are essentially different from those of the bulk. Many people had a great deal of interest in the surface properties of polymer materials[1]. The most interesting field is the interactions between the polymer surface and other materials, such as adhesion, wettability, biocompatibility, dyeability, printing, antielectrostaticity, water repellance, etc. Those important interactions are closely related to the surface properties of polymer materials. The surface modification of polymer materials is a useful way to obtain functional polymers by controlling their surface properties. Surface modification techniques of polymers generally include plasma treatment, corona treatment, radiation treatment, and ion beam treatment[2-5].

Oxygen plasma treatments have long been known to increase wettability and adhesion of polystyrene. Occhiello and coworkers have studied plasma treatment on the polystyrene as a function of molecular weights and radio frequency power[6]. For polystyrene both argon and oxygen plasma increased the amount of the oxygen content on its surface. It has been reported that different kinds of plasma added oxygen in the form of aldehyde, ester, carboxylic acid and ketonic species to polystyrene surface[7].

This paper is concerned with the nature of plasma source ion implantation (PSII) modified surface of polystyrene for hydrophilicity. The advantages of PSII process for polymer treatment involves (1) uniform treatment, (2) stable surface layer of modified polymer, (3) effects of both plasma and ion implantation, and (4) intrinsic charge compensation on the surface. PSII was utilized to modify polystyrene using various treatment parameters such as kinds of gases, pressure, plasma power, pulse frequency, pulse voltage, etc in the previous study[8]. In this study we focused on the effect of PSII treatment on the polymer surface and comparison with plasma treatment. Surface analysis for modified polystyrene was performed using time-of-flight secondary ion mass spectrometry (TOF-SIMS), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and water contact angle measurements.

2. Experimental

The experiment was conducted using an in-house built plasma source ion implanter. Fig. 1 shows schematically the most important components of an apparatus for PSII. A detailed description of this apparatus and PSII modulator characteristics have been presented elsewhere[9]. The stainless-steel vacuum chamber is cylindrical and measures 50 cm in diameter and 60 cm in height. An antenna for 13.56 MHz, 600 W RF plasma source is positioned inside top of the chamber to produce RF plasma of high density. The radio frequency (RF) instrumental conditions were:gas pressure $1.0x10^{-3}$Torr, RF input power 200W. The PSII facility consists of a tube-based high voltage pulse generator up to 100 kV with pulse lengths between 1 and 100 μs

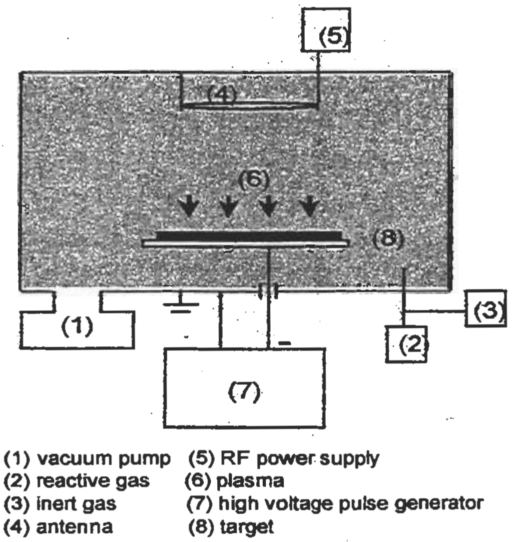

Fig. 1 Schematic diagram of Plasma Source Ion Implanter

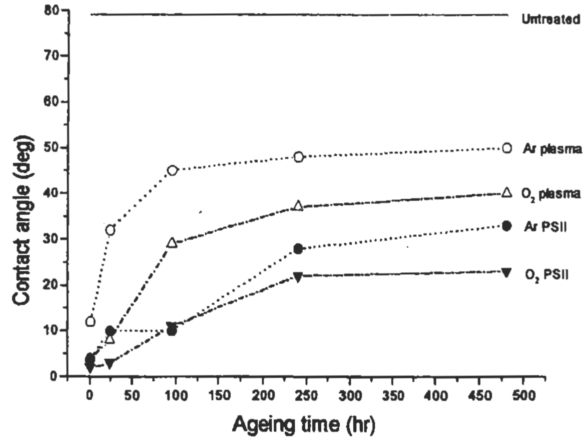

Fig. 2 Water contact angles for plasma- and PSII treatments with O_2 and Ar as a function of ageing time

and frequencies up to 2 kHz. For the experiments mainly 10 μs pulses with 1 kHz frequency were used with a fast rise time. 100% of the indicated voltage was reached within 1 μs. Polystyrene specimens, 3.5 mm in diameter and 1 mm in thickness, were placed on the oil-cooled stage surrounded by the plasma source. Its density is varied from $1x10^9$ to $1x10^{10}$ /cm^3. Samples were pulse-biased to a high negative potential, mainly -5kV. For this experimental condition the ion dose is varied from $1x10^{16}$ to $5x10^{17}$ /cm^2.
For the TOF-SIMS study, a Physical Electronics model PHI 7200 TOF-SIMS/SALI instrument was used with Cs^+ ion gun operated at 8 keV and at an ion current of 10 nA. XPS spectra were obtained using Physical Electronics model PHI 5700 spectrometer with monochromatic AlKα radiation at a power of 350 W. Spectra were obtained at the following take-off angles from the surface: 45 deg. for survey spectra, and 15, 45, 80 deg. for elemental high-resolution spectra. Water contact angle was measured by the static sessile drop method, on a Rame-Hart model 100 contact angle goniometer. SEM micrographs were collected using a Hitachi model S-4100 microscope.

3. Results and Discussion

Polystyrene plates were treated with two different methods: plasma and plasma source ion implantation (PSII). The plasma treatment and PSII treatment were carried out with oxygen and argon plasma. The behavior of contact angles of water as a function of ageing time is a very good indication of hydrophobic recovery. The surface wettability before and after treatment with aging time is given in Fig.2. The water contact angles for plasma-treated and PSII-treated samples changed to very low values from 79 deg. of untreated samples. To assess the effect of ageing in air on plasma- and PSII- treated polystyrene, their contact angles were measured as a function of ageing time. The contact angles of plasma treated polystyrene with oxygen and argon gas increase more rapidly than the PSII-treated one within 4 days at the room temperature. The PSII-treated polystyrene still keep a very low contact angle after 20 days, especially O_2 PSII treated polystyrene stabilized at 20 deg. The effect of ageing temperature has been reported elsewhere [8] and results essentially in faster recovery rates at higher ageing temperature. Contact angles of oxygen plasma- and PSII-treated polystyrene were 65 deg. and 45 deg., respectively after they stored for 24 hrs at 80℃. PSII-treated polystyrene aged at high temperature showed the slower hydrophobic recovery and better hydrophilic surface than plasma-treated.
In systems where the surface is morphologically smooth as checked by SEM, the contact angle can be considered as representative of the wettability of the surface. In order to show the surface features plasma exposed and PSII treated polystyrene were studied by SEM. SEM images for plasma and PSII treated polystyrene as a function of duration time of treatment are shown in Fig. 3. The polystyrene as received showed relatively flat surface structures. With increasing oxygen plasma treatment times for samples the surface is structured by a fibrous pattern. The sample treated by PSII looks like the untreated material with small size granules

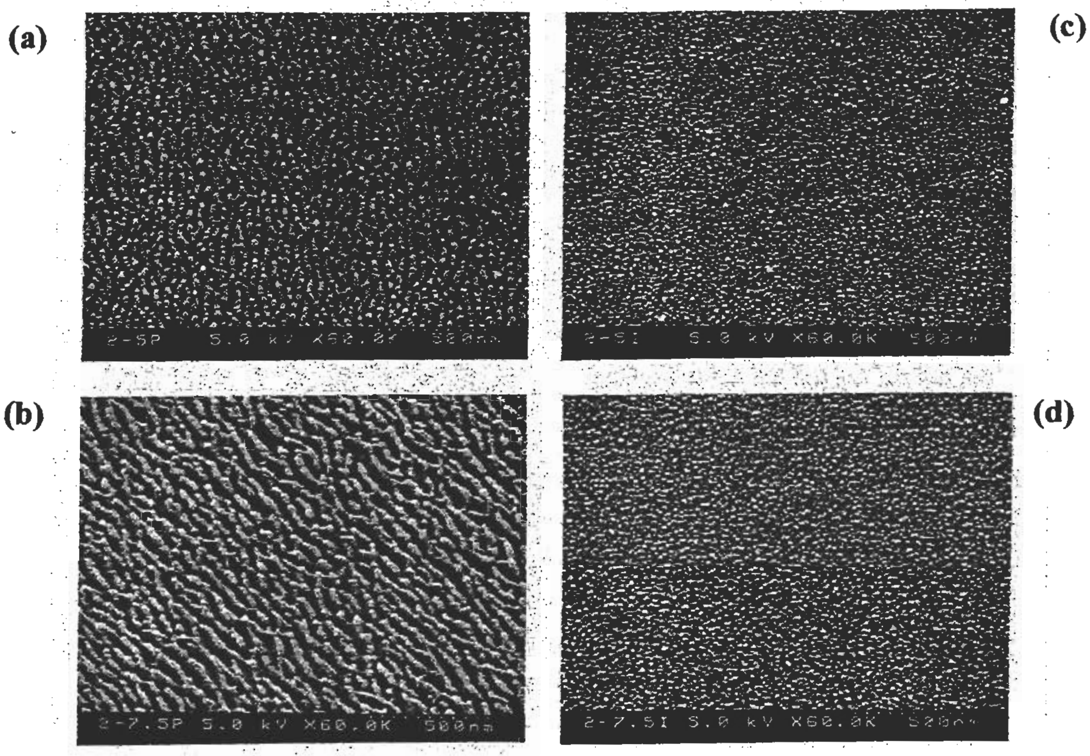

Fig. 3 SEM images of treated polystyrene surfaces: (a) 5 min O_2 plasma, (b) 7.5 min O_2 plasma, (c) 5 min O_2 PSII, and (d) 7.5 min O_2 PSII treatment.

and only weakly enhanced surface roughness. The oxygen plasma exposed sample showed more and larger cones than oxygen PSII treated surface. A long duration plasma treatment generally leads to surface degradation combined with an increased roughness, which can be explained by high energy particle bombardment and contact with activated species from plasma. The contact angles provided by plasma treated surfaces include the effect of the surface roughness as generally the measured angle decreases with increasing roughness for the contact angle, $\theta < 90$ deg. [10]. Plasma-treated polystyrene showed a larger roughness development for shorter treatment times than in PSII-treated samples.
Further comparison of two methods and evidence on hydrophilic composition is provided in Table 1. TOF-SIMS CH^-/O^- and CH^-/OH^- ratios and XPS O/C ratios at different take-off angles are compared for plasma and PSII treated samples aged for 24 hrs. Contact angle and angle resolved XPS evidence are parallel in showing more hydrophilic properties for PSII-treated surfaces than for plasma treated surfaces. Angle resolved XPS results indicated that the treatment with oxygen PSII provided more oxygen-containing functional groups at each sampling depth than with oxygen plasma. To make sure that the derease of contact angles is accompanied by a change in chemisty, we used TOF-SIMS, a uppermost layer chemical probe. CH^-/O^- and CH^-/OH^- ratios in TOF-SIMS data also showed the dependence on the treatment method paralleling that of contact angles and XPS results. This indicates that ion implanted samples from plasma source provides a more oxygen-containing modified surfaces than the plasma does.

Table 1. Water contact angles, TOF-SIMS peak ratios and XPS peak ratios of O_2 plasma treated and O_2 PSII treated polystyrene.

	Sample / Treatment		
	Untreated	**O_2-Plasma**	**O_2-PSII**
Contact Angle (deg.)	79	8	3
TOF-SIMS			
(CH^-/O^-)	4.4	0.3	0.2
(CH^-/OH^-)	12.0	1.1	0.7
Angle-resolved XPS (C/O)			
10 °	110	2.62	2.14
45 °	115	3.85	2.84
80 °	158	4.64	3.48

Although the stability of a treated polymer surface is an important issue, a modified surface by the treatment goes back to a less hydrophilic surface with time. The ageing

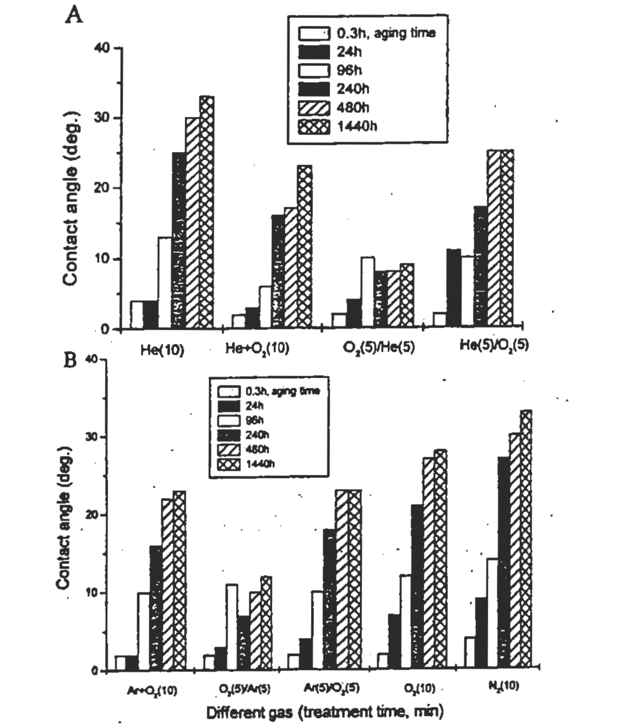

Fig. 4. Water contact angles for O_2 PSII treated polystyrene in combination with (A)He and (B)Ar.

phenomenon could be slowed down by stabilizing the surface layer using a inert gas plasma. As shown in Fig. 4, polystyrene treated using helium or argon and oxygen plasma source ions alternately or their mixtures shows still very wettable surface after 2 months. Inert gas plasmas induce scissions of the polymer chains and favor the formation of carbon-carbon bonds. So PSII treatment using inert gas generates crosslinking and new bonds such as C=C to improve the bond strength of the surface. Combination of inert gas and reactive gas plasma provided the stabilized surface layer to minimize the surface reorganization of polystyrene upon contact with air.

The effect and mechanism of PSII treatment on the polystyrene surface was investigated using oxygen isotope gas, $^{18}O_2$, and CF_4 gas. Negative ion TOF-SIMS spectra of differently prepared samples with $^{18}O_2$ and CF_4 were obtained in Fig. 5. The $^{18}O_2$ treated sample shows ^{18}O containing peaks at m/z 18 and 19 for $^{18}O^-$ and $^{18}OH^-$, respectively. Some ^{16}O is observed, which may come from the contaminants and chamber wall. The samples treated reactive gas, O_2 , did not provide the significant evidence for reaction with storage gas. The spectrum of a sample treated with Ar and stored in CF_4 shows the abundant fluorine peak and indicates the introduction of fluorine on the sample sürface. After inert gas treatment, it can be called another surface-modification step for the sample to expose to air and to involve the oxygen containing functional groups.

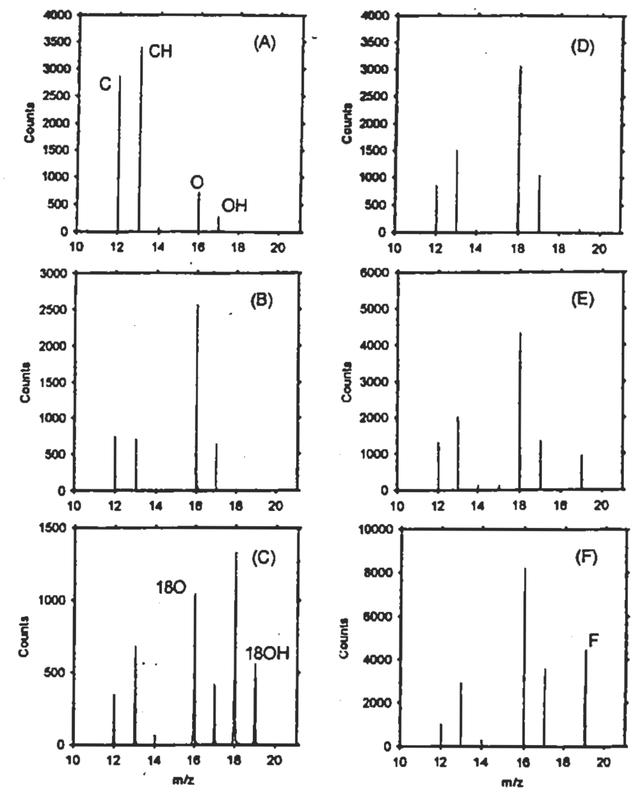

Fig. 5. Negative ion TOF-SIMS spectra (a) untreated, (b) O_2 PSII, stored in $^{18}O_2$, (c) $^{18}O_2$ PSII, stored in O_2, (d) O_2 PSII, stored in CF_4, (e) N_2 PSII, stored in CF_4, and (f) Ar PSII, stored in CF_4.

4. Conclusions

The PSII treated polystyrene surfaces were characterized and compared to the typical plasma treated samples using surface sensitive methods such as contact angle measurement, TOF-SIMS, XPS and SEM. The combined treatment of oxygen and inert gas provided very stabilized surface layer via crosslinking. TOF-SIMS results showed that specific peaks can be used to monitor the effect and mechanism of reactive gas and inert gas PSII treatment.

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