Influence of argon plasma treatment on polyethersulphone surface

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Abstract. Polyethersulphone (PES) was modified to improve the hydrophilicity of its surface, which in turn helps in improving its adhesive property. The modified PES surface was characterized by contact angle measurement, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and Vicker's microhardness measurement. The contact angles of the modified PES reduces from 49° to 10° for water. The surface free energy (SFE) calculated from measured contact angles increases from 66.3 to 79.5 mJ/m^2 with the increase in plasma treatment time. The increase in SFE after plasma treatment is attributed to the functionalization of the polymer surface with hydrophilic groups. The XPS analysis shows that the ratio of O/C increases from 0.177 to 0.277 for modified PES polymer. AFM shows that the average surface roughness increases from 6.9 nm to 23.7 nm due to the increase in plasma treatment time. The microhardness of the film also increases with plasma treatment.

1. Introduction

Polyethersulphone (PES) is a high-temperature and high-performance engineering thermoplastic [1]. This polymer has good oxidative, thermal, mechanical and film-forming properties. PES is used in a wide range of areas such as electrical, automotive, aerospace, medical, consumer products and separation processes. Hydrophilic, hydrophobic and ionic species are always used as modifiers depending on specific application. The reconstructable surfaces change their wettability and permeability, as well as their adhesive, adsorptive, mechanical and optical properties [2]. Graft polymerization can be initiated

without a photoinitiator. Thus, UV light is particularly useful for chemically attaching hydrophilic monomers to PES membranes for antifouling. Malaisamy *et al* [3] used a hydrophilic, positively charged, quaternary ammonium derivative of a vinyl monomer, [2-(acryloyloxy)ethyl] trimethyl ammonium chloride (AETMA) to modify a commercially available PES microfiltration membrane.

Lee *et al* [4] reported a novel method for producing a selective protein adhesion pattern on a PES film surface using atmospheric pressure plasma with reactive gases. Zhu *et al* [5] modified the surface of PES membrane by graft polymerization of acrylic acid using corona discharge treatment, which helps to improve hydrophilicity and antifouling properties at the surface. Vatuňa *et al* [6] found that PES fabric RF plasma modification seems to be more effective than that of MW plasma. Bruggen [7] found that the plasma treatment introduces functional groups on the membrane surface; by varying plasma treatment parameters, surfaces with different properties can be obtained. Possible gases include CH_4, Ar, O_2, H_2, He, Ne, N_2 and CO_2 in addition to H_2O. He *et al* [8] introduced the concept of composite membrane with a coating layer of sulphonated polyethersulphone (SPES) onto a polysulphone (PS) support. The sulphonated polymer itself will be investigated in terms of mechanical properties as well as adhesion onto the PSf support. Steen *et al* [9] studied H_2O plasma treatment of PES membrane to investigate the role of membrane material (chemical composition) and structure (i.e. degree of asymmetry) in hydrophilic modification. Wavhal and Fisher [10] studied the surface and permeation properties of membranes before and after plasma treatment and subsequent grafting with acrylic acid (AA). Kull *et al* [11] examined the influence of nitrogen-containing plasmas, especially N_2, NH_3, Ar/NH_3 and O_2/NH_3 on PES membranes. Kroll *et al* [12] developed a strategy for modifying hollow fibre surface with a wide variety of different reactive ligands. Such membranes find application in high speed separations of amino acid and protein mixtures. Vesel and Mozetic [13] studied the surface modification of various polymers by oxygen plasma. Increased concentration of oxygen was detected on all polymer surfaces, by observing groups such as $C-O$, $C=O$ and $O=C-O$ on the surface. The concentration of these groups depends on the type of polymer. Hegazy *et al* [14] studied the membrane obtained by radiation grafting for separation process and waste water treatment from heavy and toxic metals, low-level nuclear waste management and separation of Zr from uranium in their wastes and enzyme immobilization.

The aim of this work is to improve superficial hydrophilic properties of PES films by measuring contact angle (surface free energy, SFE), chemical composition using X-ray photoelectron spectroscopy (XPS) analysis, microhardness by indentation technique and surface roughness by atomic force microscopy (AFM) at different argon (Ar) plasma treatment times.

2. Experimental method

PES samples (size: 15 mm × 15 mm) were cleaned in isopropyl alcohol and dried before inserting into the plasma chamber. The schematic of the experimental set-up is shown in figure 1. It consists of 60 cm long cylindrical chamber having 30 cm diameter. It has two rectangular parallel stainless steel plates of 16 cm × 7.5 cm dimension, which work as electrodes as shown in figure 1. The interelectrode gap was maintained at 2 cm in all the
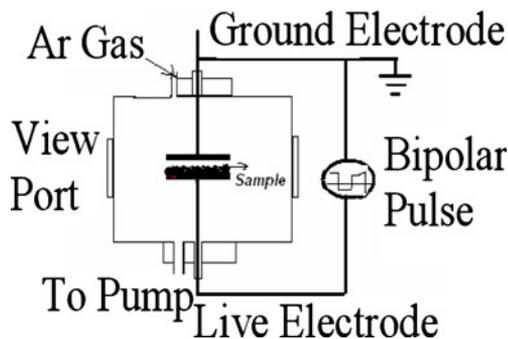
Figure 1. Schematic of the experimental set-up.

experiments. Bipolar pulsed power source was used to generate the desired Ar plasma [15]. The applied voltage and current were measured with the help of high voltage probe (Tektronix P6015A, 1000X) and current transformer, respectively. Tektronix (TDS 2024, 200 MHz) digital oscilloscope was used to record the voltage and current waveforms (figure 2). The initial base pressure was of the order of 5×10^{-5} mbar. Chamber pressure of 0.1 mbar was maintained during the Ar plasma treatment. The samples were treated in Ar plasma for 5, 10 and 50 minutes, respectively.

Contact angle goniometer (NRL C.A. Goniometer, Model 100-00-230) was used to analyse surface wettability by sessile drop method. Two different measuring modules (water and glycerine) were employed to calculate SFE as a sum of polar and dispersion components. About 3 to 5 drops of 5 μl water drops were injected onto a dried surface for calculating the average contact angle at ambient temperature. From the measured contact angles, the polar and dispersion components were calculated using Owen method [16,17].

XPS measurements of the above samples were carried out using VSW ESCA machine with AlK$_\alpha$ radiation (1486.6 eV) [18]. During the experiment, chamber vacuum was
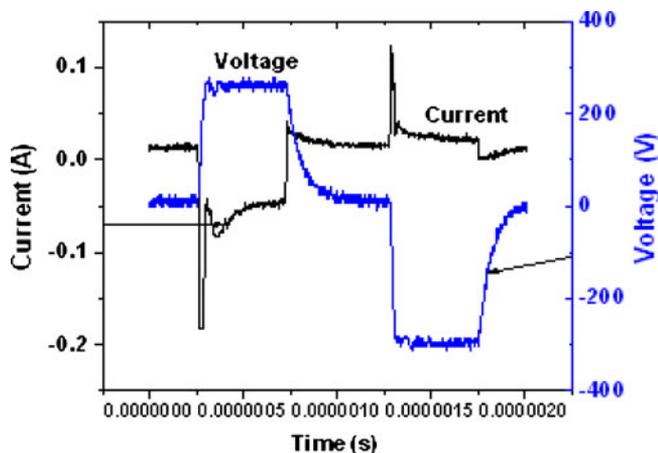

Figure 2. Voltage and current waveforms.

maintained at 10^{-9} torr. The electron take-off angle was 40° and the X-rays were operated at 10 kV and 10 mA emission current. The pass energy of the hemispherical energy analyser was set at 48 eV. To compensate for the charging effects, the carbon peak was assumed to be lying at 284.8 eV. Curve fitting has been done using the Gaussian/Lorentzian curve fitting programme.

The surface topography and cross-sectional roughness of modified PES films were characterized in contact mode AFM (Digital Nanoscope IIIa Instrument Inc.).

Digital Microhardness Tester (FM 700–Future-Tech Corporation, Kawasaki-Japan) was used to determine Vicker's hardness number (Hv) by indentation technique. Microhardness measurements on pristine and treated films were carried out using Vicker's microhardness tester. Indentation was made with a Vicker's diamond pyramidal indenter housing a square base and pyramidal angle of 136° between the opposite faces attached to an optical microscope using a pilar micrometer/image analyser. The samples were fixed with non-reactive adhesive on an optical glass plate in such a way that the surface to be indented was perfectly horizontal. The plate along with the sample was then mounted on the stage of the microscope so as to avoid only displacement of samples during indentation. The load ranging from 10 to 500 gf was applied for a constant loading time of 20 s.

3. Results and discussion

3.1 *Contact angle measurements*

The contact angle measurement was used to study the SFE, wettability and adhesion of low surface energy materials. The knowledge of this parameter is useful in studies on adsorption and wettability processes, which play an important role in many industrial applications of the material. Measurement of contact angle of a liquid with the solid surface permits a rapid and qualitative evaluation of the SFE of the polymer. The water contact angle of the untreated sample was about 49°. With an increasing treatment time, it was decreased to about 10°. This shows the improvement in wettability of PES surfaces. Similarly, the contact angle for glycerine on PES surface changes from 61° to 20° with increasing treatment time. Five measurements were made for each sample to determine the average (shown in figure 3). Lower contact angles confirm that the plasma-modified surfaces were changed to more hydrophilic surfaces.

Analysis of the SFE of PES has been made on the basis of dispersive and non-dispersive components. SFE (γ_s) and its polar (γ_s^p) and dispersion (γ_s^d) components of the sample were determined from two sets of contact angles (water and glycerine) according to Owens–Wendt–Kaelble equation [16].

$$\gamma_l \left(1 + \cos\theta\right) = 2\left[\gamma_l^d \gamma_s^d\right]^{1/2} + 2\left[\gamma_l^p \gamma_s^p\right]^{1/2},$$

where γ_l, γ_l^p and γ_l^d are the total SFE, the polar component and the dispersion component of the SFE of the liquid, respectively.

The values of the SFEs of the test liquids obtained from the literature are given in table 1. The values of SFE and its components before and after the treatment in Ar plasma are compared in figure 4. The increase in SFE is attributed to the functionalization of the polymer surface with hydrophilic groups on the surface.
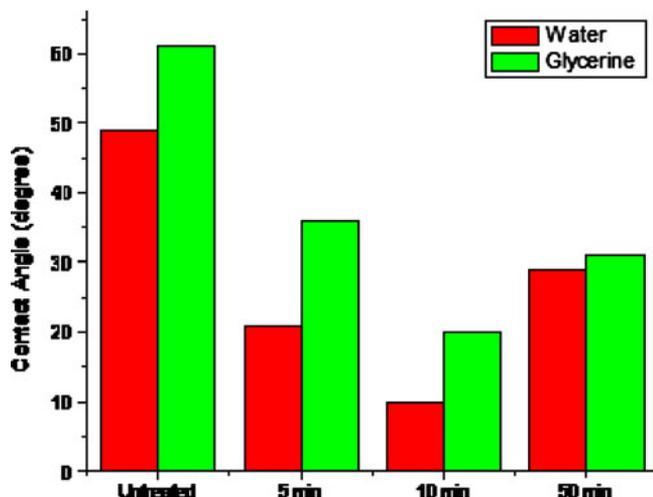
Figure 3. Contact angles for untreated and Ar plasma-treated PES samples.

Initially for untreated PES, the values of polar and dispersion components of SFEs are lower and comparable, but there is a small increase in the polar component after all subsequent treatments, whereas remarkable change in the dispersion component was observed. An important information obtained from the surface energy measurement is that the increase in polar component indicates the formation of covalent bonds on the surface.

3.2 *XPS analysis*

XPS is the most suitable method for determining functional groups on a polymer surface. For detailed analysis of chemical changes induced by plasma treatment on PES surfaces, high resolution XPS spectra were recorded as shown in figures 5a–d. It is observed that there is an overlap of the peaks due to C–C bond at 284.8 eV and C–S bond at 285.3 eV [13]. A basic problem in polymer analysis is the surface charging due to the loss of surface electrons by X-ray irradiation. In common practice, manual shifting of unfunctionalized C 1s peak (C–C) to 284.8 eV is performed. Carbon peak of the untreated PES consists

Table 1. Surface free energy (SFE) and its polar and dispersion components of water and glycerine used to determine the SFE of PES [19].

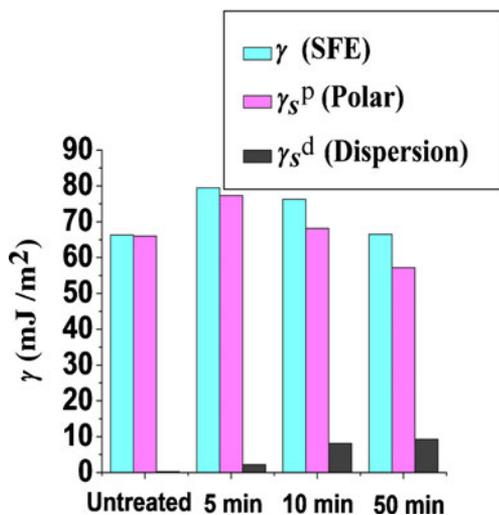| Liquid	Total surface energy γ_1 (mJ/m^2)	Polar component γ_1^p (mJ/m^2)	Dispersion component γ_1^d (mJ/m^2)
Water	72.8	51	21.8
Glycerine	63.4	29.7	33.6

Figure 4. Comparison of SFE and its components before and after the treatment in Ar discharge.
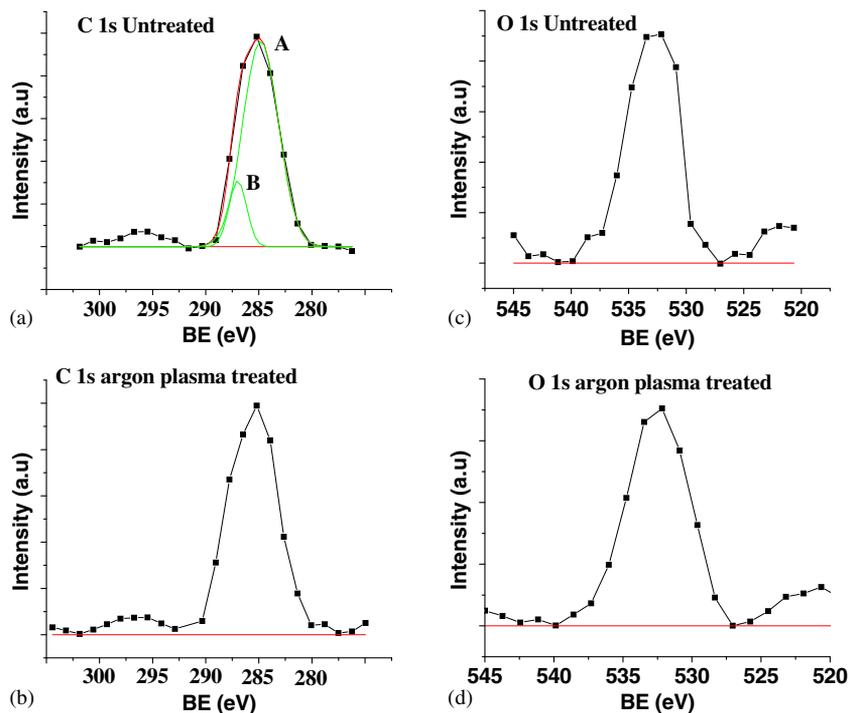

Figure 5. C 1s peak of the XPS spectra of **(a)** untreated and **(b)** Ar plasma-treated samples; O 1s peak of the XPS spectra of **(c)** untreated and **(d)** Ar plasma-treated samples.

Table 2. Surface composition of PES before and after plasma treatment.

Sample	C	O	O/C
Untreated	84.9	15.09	0.177
Treated in Ar (10 min)	78.26	21.74	0.277

of two peaks; one A at 284.8 eV corresponds to C–C bonds and the other B at 286.5 eV corresponds to C–O bonds. The surface composition of PES before and after the plasma treatment is tabulated in table 2.

Carbon atoms in PES are oxidized during plasma activation. O/C ratio increases due to the oxidation on its surface. This indicates the formation hydrophilic group such as C–O, etc. on the surface.

3.3 *Microhardness*

Vicker's hardness number (Hv) was determined by indentation technique performed with a microhardness tester in the load range from 10 to 500 gf for a constant loading time of 20 s. Indentation was made with a Vicker's diamond pyramidal indenter housing a square base and a pyramidal angle of 136° between the opposite faces attached to an optical microscope using a pilar micrometer/image analyser. An average value of the diagonal of indentation was used for the calculation of hardness value. Hv was calculated using the relation:

$$Hv = (1854.4 \times P)/d^2 Kgf/mm^2,$$

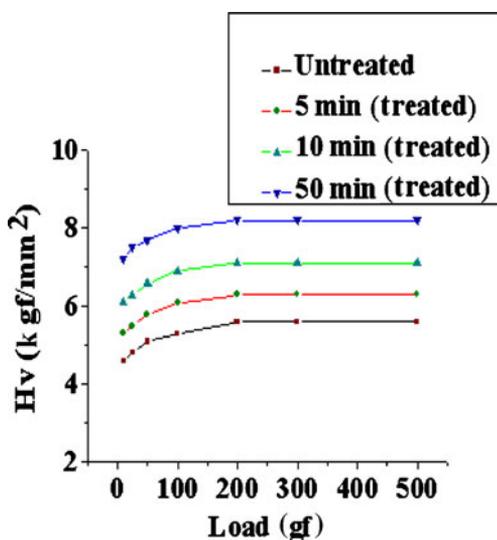**Figure 6.** Plot of hardness vs. applied loads.

where P is the indenter load in gf, d is the average of the two diagonal lengths in micrometres. Several indentations were obtained at each load and the average hardness number was calculated. The variation of Hv with load ranging from 10 to 500 gf for both untreated and Ar plasma-treated PES is illustrated in figure 6.

Vicker's hardness increases as load increases. However, on reaching a certain load value, the rate of increase of hardness slows down and then becomes constant. At higher loads, above 200 gf, the interior of the bulk specimen is devoid of surface effects. Hence, hardness value at higher loads represents the true value of the bulk and is consequently independent of the load. Hardness is found to increase as treatment time increases. This may be attributed to the cross-linking phenomenon at the polymer surface [20,21]. It is also corroborated with XPS analysis.

3.4 *Atomic force microscopy*

The surface morphology of Ar plasma-treated PES samples was measured by AFM in contact mode on a 5×5 μm^2 area and are shown in figures 7a,b. Each AFM image was analysed in terms of surface average roughness (R_a). The data show that the average surface roughness (rms) increases with treatment time. The rms for untreated film and Ar plasma-treated film for 10 min are 6.9 nm and 23.7 nm, respectively. The roughness of the PES surfaces increases with treatment time, hence it can support the adhesion improvement. This result is corroborated with SFE results.

4. Conclusion

Ar plasma was found to be an effective method for the surface modification of the PES polymer. The SFE of PES film increases with Ar plasma treatment. This will increase the hydrophilic groups on the surface. The XPS analysis reveals an increase in O/C ratio due to plasma treatment, i.e. the surface contains hydrophilic functional groups. The hardness
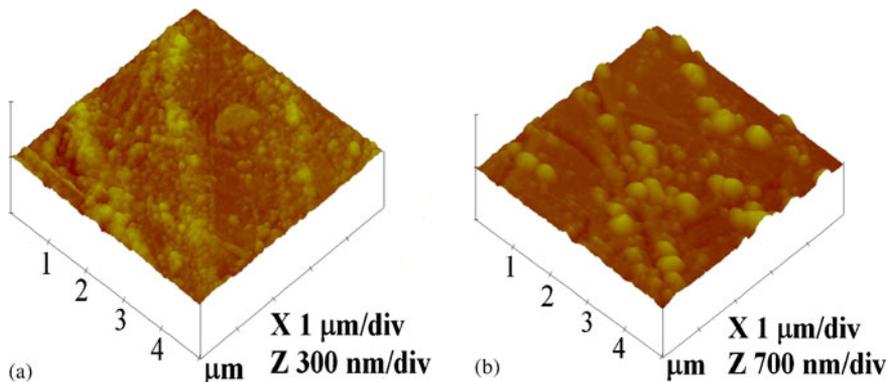

Figure 7. AFM photomicrographs of **(a)** untreated PES film; **(b)** Ar plasma-treated PES for 10 min.

increases with increase in treatment time. Increase in hardness is observed due to the cross-linking at the surface. The surface of the untreated PES film is rough. However, the surfaces of the PES films modified by Ar plasma are even rougher than that of the untreated PES film. The AFM images clearly show variations in the morphology of the PES film before and after the plasma treatment.

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