



Induced super hydrophilicity due to surface modification of polypropylene membrane treated by O₂ plasma

B. Jaleh^{a,*}, P. Parvin^b, P. Wanichapichart^{c,f}, A. Pourakbar Saffar^d, A. Reyhani^e

^a Physics Department, Bu-Ali Sina University, Mahdeyh Street, 65174 Hamedan, Iran

^b Physics Department, Amirkabir University of Technology, Hafez Ave, P.O. Box 15875-4413, Tehran, Iran

^c Membrane Science and Technology Research Center, Department of Physics, Prince of Songkla University, Thailand

^d Physics Department, Islamic Azad University Central Tehran Branch, Young Researchers Club, Tehran, Iran

^e Material Research School, P.O. Box 14395-836, Tehran, Iran

^f Thailand center of excellent in physics, commission on higher education, 328 SI Agutthaya road, Bangkok 10400, Thailand

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ABSTRACT

Radio frequency (RF) plasma offers a unique route for the surface modification of polymer. The influence of the plasma treatment on the basic properties of the porous membranes such as effective void volume and the flow rate were investigated. It was shown that the polymer ablation significantly alters the hydrophilicity leading to the enhancement of the water flux. Here, the polypropylene membrane was tested by O₂ plasma to emphasize that the contact angle nonlinearly decreases with the treatment time. The XPS surface sensitive technique was applied to confirm the drastic skin change of the oxygen content showing that membrane becomes super hydrophilic due to the significant O₂ implant.

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1. Introduction

Plasma technology is widely used to treat polymers in order to alter the surface properties. The method was found many attractive applications in automobile manufacturing, microelectronics, chemical, biomedical and pharmaceutical industries. The capability of RF plasma to modify polymer surface without affecting major bulk properties is advantageous for the design, development and manufacturing of biocompatible polymers. After the treatment, the surface properties such as hydrophobicity, chemical structures, roughness and conductivity are modified to meet the specific requirements. Major effects observed in the treatment include micro-etching, cross-linking and surface chemistry modification as well as cleaning of the organic contamination. For instance, low-pressure plasma is used to decontaminate polymer surface from air pollutants, oxide layers, weakly bonded surface layers and the other surface additives. Different inert and reactive gases can incorporate large varieties of chemical groups such as hydroxyl, carbonyl, carboxylic, amino or peroxy groups leading to the further enhancement of the electrochemical properties. In bio-

compatible materials, physico-chemical properties such as surface free energy and morphology influence on the cell–polymer interaction, protein–surface interaction, antimicrobial property, and cell adhesion which in turn can be altered significantly using various surface treatments. Surface modification of materials by plasma treatment is mainly achieved by using different gases including oxygen, nitrogen, argon, helium and air. The application of oxidizing gases such as O₂, air, H₂O and N₂O resulted in the removal of organic matters on the surface and introduction of oxygen containing species on the polymeric skin layer [1–9].

The modification of polymer materials is done through radiation cross-linking, degradation and grafting. Radiation processing, using plasma, electron-beams, UV and X-rays as well as laser beams has been demonstrated on a large commercial scale to be very effective means of improving end-use properties of various polymers [10–15].

Plasma treatment also leaves active sites on the surfaces, which are subject to the post-reactions. Polar functional groups can be introduced on the polypropylene (PP) membrane surface after breaking C–C and C–H bonds. Its content and effect on the material surface depend on the gaseous species of the discharge, the composition of treated sample and the process parameters [16].

Among the various surface modification techniques, plasma treatment is regarded as the most advantageous ones. The upper

* Corresponding author. Tel.: +98 9122114707; fax: +98 8118280440.

E-mail addresses: jaleh@basu.ac.ir, bjaleh@yahoo.com (B. Jaleh).

molecular layer of the surface is activated to improve wettability, adhesion and biocompatibility without affecting the bulk of the polymer. The PP microporous membranes obviously exhibit high potentials for comprehensive applications due to their high void volume, well-controlled porosity, high thermal and chemical stability, and low cost. An attempt to improve the antifouling characteristics of PP microporous membranes was previously reported based on the air plasma treatment [17]. In addition, the formation of strong covalent carbon–oxygen bonds with a great number of polar and reactive agents was evidenced. The surface modification of polypropylene microporous membrane (PP hollow fiber microporous membrane (PPHFMM) and PP flat microporous membrane (PPFMM) with a porosity of 45–50% and an average pore diameter of 0.10 μm) was done in order to improve the antifouling characteristics in a submerged membrane bioreactor (SMBR) for wastewater refinement, using O_2 plasma treatment such that the water contact angle decreases from 130° to 70° in terms of plasma treatment time. On the basis of systematic experiments considering surface etching and modification induced by plasma, 30 W was chosen as the applied rf power. The O_2 atmosphere in the chamber was kept at 10 Pa, while the plasma was generated for given times (0–10 min). It was shown that the relative pure water flux for the modified membranes increases with plasma treatment time up to 1 min, then it decreases with further increase of plasma treatment time. However, with the further increase of plasma treatment time, the relative pure water flux decreases continuously. It is commonly known that pore size, porosity and surface hydrophilicity are the dominant parameters affecting water flux. Results of XPS clearly indicate that the plasma treatment introduces oxygen containing polar groups on the membrane surface. The increase of permeability could be explained by enlargement of membrane skin pore size and/or the increase of porosity after plasma treatment. Apart from that, the increase of membrane surface hydrophilicity plays an important role in the enhancement of membrane permeability [18]. Similarly, this work deals with O_2 plasma treatment of membrane such that the contact angle is reduced drastically. It was shown that super hydrophilicity takes place due to strong O_2 implant in the skin layers. The water flux increases over a wide range of plasma treatment time up to 5 min employing 25 W plasma generator and there is no reduction with further increase of plasma treatment time. Moreover, it explains how oxygen plasma could alter the morphology and the permeability of PP membranes during the treatments. In the mean time, the corresponding physico-chemical properties of skin layer are also changed. Particularly, it was shown that the growth of hydraulic conduction corresponds the dielectric constant reduction.

2. Experimental

2.1. Materials and methods

PP membranes of 47 mm diameter, 190 μm thick and 0.22 μm mean pore size manufactured by Osmonics Germany, were used for subsequent plasma treatment. Radio frequency glow discharge plasma (EMITECH KX1050) was employed to produce the oxygen plasma. The samples were first cleaned by organic solvents, such as acetone and dried using hot air blower, the treatment was done using 25 W O_2 plasma from 1 to 5 min at 0.1 mbar pressure.

2.2. Membrane characterization

Surface hydrophobicity of plasma treated membranes was evaluated using contact angle measurements with (Kruss G10) goniometer equipped with an image analysis software. Static contact angles of 5 μl water were measured on the PP samples by means of a goniometer. The CCD camera has captured the droplet

images. The membrane morphology has been studied using a scanning electron microscopy (Philips SEM model XL30) accompanied with a sputter coater (BAL-TEC model SCD005). SEM with secondary electron detector (SE) was employed to observe the surface. The polymeric surface usually has no electrical conductance; hence a 10–15 nm gold layer must be provided by sputter coating, to remove electrostatic charge from the surface due to electron beam radiation. Analysis of polymer surface functional groups after plasma treatments was performed by FTIR/ATR (Bruker-Equinox 55) instrument.

Precision LRC meter Agilent 4258A with 16451b dielectric test fixture at various frequencies 75 kHz to 30 MHz with 1 MHz steps was exploited to determine dielectric constants for the reference and plasma treated membranes.

Resistivity of the material was calculated using equation $\rho = A/(2\pi f C_p D t)$ (Ωm) and dielectric permittivity, $\epsilon = C_p/C_0$, where C_p is the capacitance measured using an LCR meter, f the frequency, D dielectric loss and the C_0 the vacuum capacitance = $\epsilon_0 A/t$, A and t are the cross-sectional area of the electrode and thickness of the sample, respectively. ϵ_0 is the permittivity of vacuum to be equivalent to 8.85×10^{-12} F/m.

Experiments were carried out using distilled water as a feed and permeate volume was collected under various applied pressures. The reference and treated membranes were placed on a support using a dead end filtering set-up. In a preliminary study, water absorption of the membrane was measured. It was found to last ~ 20 min before water content in the membrane reaches to maximal level. Each one was therefore immersed in distilled water for at least 1 h to assure that any change in flux measurement was quite independent of this water swelling property. According to the Hagen–poissuille equation, hydraulic permeability coefficient (L_p) can be obtained from the slope of graph between the flux (J) and the applied pressure (ΔP) according to $J = L_p \Delta P$ [19].

Moreover, X-ray photoelectron spectroscopy (XPS) as a sensitive technique was carried out with an Al K_{α} X-ray source at 1486.6 eV. The samples were irradiated with monoenergetic soft X-rays and the subsequent emitted electrons have been energy analysed. The base pressure of analyzer chamber was usually set $\sim 5 \times 10^{-8}$ mbar. Subtle variations in binding energies can be used to identify the chemical state of materials being analysed. Binding energies were calibrated using characteristic carbon (C1s = 284.7 eV).

3. Results and discussion

Several sets of PP membranes were treated with O_2 plasma at various treatment durations, ranging from 1 to 5 min at 25 W. Fig. 1 illustrates SEM micrographs of the membranes for the reference and the plasma treated ones with various treatment times of 1, 3 and 5 min. Those exhibit that the pore size is apparently enlarged at higher treatment times due to plasma ablation. The corresponding contact angle was measured as a function of treatment time and plotted as shown in Fig. 2. The smaller contact angle is corresponding to the longer plasma treatment showing a significant drop from 135° of untreated sample to $\sim 20^\circ$ after 5 min treatment. The treated membranes with O_2 plasma exposure longer than 5 min have shown a completely wetting property, supporting the fact that membrane surface becomes highly hydrophilic. Here, the effect exhibits to be stronger than previously reported using the same O_2 plasma treatment [18]. Even though different treatment conditions on various PP samples may lead to different results, O_2 plasma treatments for similar instrument were compared numerically while air plasma treatment is shown at the same time for comparison.

In addition, the alteration of the corresponding chemical structures were investigated using, FTIR/ATR and XPS spectroscopy. Fig. 3 displays FTIR/ATR spectra of the untreated and treated PP

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