Hydrophilic modification of polyethersulfone membranes by low temperature plasma-induced graft polymerization

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Abstract
A complete and permanent hydrophilic modification of polyethersulfone (PES) membranes is achieved by argon plasma treatment followed by polyacrylic acid (PAA) grafting in vapor phase. Both Ar plasma treatment alone and post-PAA grafting rendered a complete hydrophilicity to the PES membranes. The hydrophilicity of the membranes treated with only the Ar plasmas is not, however, permanent. In contrast, the PES membranes treated with Ar plasma and subsequent acrylic acid (AA) grafting are permanently hydrophilic. High energy resolution X-ray photoelectron spectroscopy (XPS) confirmed the grafting of PAA to all surfaces of the membrane. Furthermore, water bubble point measurements remain unaffected. The pore sizes of the grafted membranes at higher grafting yield are slightly decreased. The modified membranes are less susceptible to protein fouling than the unmodified membranes and the pure water flux for the modified membranes was tremendously increased by plasma treatment. Furthermore, the modified membranes are easier to clean and required little caustic to recover permeation flux.

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1. Introduction
High temperature resistant polymers like polyether-sulfone (PES) are becoming increasingly important for many applications, especially for biological, pharmaceutical, and sterilizing filtration [1–3]. The performance of these membranes decreases because of membrane fouling, which is likely related to the hydrophobic character of PES. In general, fouling occurs on hydrophobic surfaces as a result of protein adsorption, denaturation, and aggregation at the membrane–solution interface [4]. Thus, hydrophilic surface modification of the membrane is an attractive approach to solving this problem [5]. Indeed, various investigations [6–8] have shown that an adsorbed hydrophilic polymer on the membrane surface alleviates protein fouling during ultrafiltration and microfiltration. There are several methods for the hydrophilic modification of membrane surfaces, including photolytic [9,10], wet chemistry for modification prior to casting [11], and low temperature plasma treatment [12–15].

Low temperature plasma techniques, which are very surface selective, have been used to modify various types of membranes. With plasma treatment, specific surface chemistries can be created for reducing protein–surface attractive interactions, thereby minimizing protein adsorption and hence membrane
fouling. For example, simple treatment with inert gas, nitrogen, or oxygen plasmas have been used to increase the surface hydrophilicity of asymmetric membranes [16], and ammonia plasmas have successfully functionalized polysulfone (PSf) membranes [17]. A water plasma treatment that renders asymmetric PSf membranes permanently hydrophilic was recently reported from our laboratory [18]. This treatment was also successfully applied to PES membranes and, to a lesser extent polyethylene (PE) membranes [19]. It is well known, however, that plasma treatment of materials with non-polymerizing gases has one serious drawback. On most polymer surfaces, the gained hydrophilicity is usually not permanent, and disappears or diminishes significantly after treatment. Often these changes occur within hours or days of treatment [20–24]. Conventional polymers usually possess significant segmental mobility and can rearrange their surface composition in response to interfacial forces. This may lead to time dependency in the surface properties of plasma treated polymers. Any such alteration of surface properties with time may cause a change in membrane performance. One method to reduce this loss of surface properties is to graft and polymerize monomers onto a plasma treated material to “lock-in” a desired surface chemistry [25–27]. The grafted polymer layers that are chemically bound to the surface are expected to provide a much more stable and long-lasting surface. Thus, an important reason for extending plasma treatment with post-grafting of monomers and subsequent polymerization is the possible reduction of surface restructuring.

The goal of this work was to use Ar plasma treatment followed by in situ exposure to acrylic acid (AA) vapor to render PES membranes completely hydrophilic. This sequential treatment avoids the restructuring of the surface and potentially reduces membrane fouling through formation of a hydrophilic polyacrylic acid (PAA) layer. The exposure of the Ar plasma treated membrane to atmosphere causes the attachment of oxygen and nitrogen moieties on and into the polymer matrix making the membrane completely hydrophilic. This hydrophilicity decreases with time, however, because restructuring occurs. The addition of post-plasma grafting of AA prevents possible surface restructuring and the resulting hydrophilicity is long-lasting. Our plasma treated and grafted membranes have been characterized with various analytical techniques such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), electron microscopy, and bubble point measurements. The effect of the modification on hydraulic permeability was also measured. The permeation and fouling properties of treated and grafted PES membranes were characterized by protein ultrafiltration experiments. The surface and permeation properties of membranes were compared before and after plasma treatment and subsequent grafting with AA.

2. Materials and methods

2.1. Materials

PES membranes used in this study were obtained from Millipore Corporation and were cleaned in methanol prior to use. The inhibitor with the AA monomer (99%, Sigma) was removed by degassing using freeze-pump-thaw cycles immediately prior to use. The sodium hydroxide (Fisher Chemical) was of analytical grade purity and the hydrion buffer was purchased from Micro Essential Laboratory Inc. Argon and nitrogen gases (General Air) were of ultrahigh purity and used as is. Bovine serum albumin (BSA, initial fractionation by heat shock, >98%, A9430) was obtained from Sigma. All protein solutions were prepared in hydrion buffer solution and filtered with a 0.22 μm Nylon filter.

2.2. Plasma

The plasma reactor used in this study has been described in detail elsewhere [18,28]. An additional cylindrical glass membrane holder (30 mm diameter) was used to orient the membrane perpendicular to the gas flow, ∼18 cm downstream from the most intense region of the plasma glow to reduce plasma-induced damage to the membrane. The orientation of the membrane allows penetration of the plasma through the porous membrane thickness and facilitates modification of the entire membrane cross-section.

The entire system was first evacuated to a pressure of ∼8 mTorr and Ar gas was purged into it a minimum of three times. By adjusting the gas flow rate, the pressure in the reactor was set to 0.3 Torr and a plasma was created (rf power, 13.56 MHz). An extensive para-
A meter study was performed including 25, 40, and 50 W applied rf powers, and treatment times from 5 to 360 s. When the plasma treatment was complete, Ar flow was stopped and the chamber was again evacuated. The AA vapor was introduced into the reactor and the flow was adjusted using a Nupro bellows-sealed metering valve until a pressure of 0.1 Torr was obtained. After the desired grafting reaction time, ranging from 5 to 45 min, the chamber was evacuated and inert gas was reintroduced to the chamber.

2.3. Grafting yield

The amount of polyacrylic acid grafted onto the membrane surface can be calculated as a grafting yield (GY) in μg/cm² using Eq. (1):

\[ GY = \frac{W_a - W_b}{A} \]  

where \( W_a \) and \( W_b \) represent the weight of the membrane before and after grafting, respectively, and \( A \) is the area of the membrane. For the current experiments, the grafting yields obtained correspond to ∼1.6–4.0% actual weight uptake. For example, a 100 μg/cm² GY corresponds to ∼2% weight uptake.

2.4. Surface characterization

All IR spectra were obtained using a Nicolet Magna 760 FTIR spectrometer in transmission mode (resolution of 4 cm⁻¹ and averaging over 2000 scans). XPS analysis was performed using a Physical Electronics PH5800 spectrometer. This system has a monochromatic Al Kα X-ray source (1486.6 eV photons), a hemispherical analyzer and resistive multichannel detector. A low energy (∼5 eV) electron gun was used for charge neutralization on the non-conducting samples. For all samples, multiple spots were analyzed. The composition was determined from 0 to 1000 eV survey scans acquired at an analyzer pass energy of 93.9 eV. The high resolution C1s, O1s, and S2p spectra were collected at a 45° take-off angle, which is the angle between the surface normal and the axis of the analyzer lens.

Static water contact angles were measured by the sessile drop method with a contact angle goniometer (Krüss DSA10) equipped with video capture. For the plasma treated membranes, static contact angle measurements were impossible to perform as the water drop disappeared into the membrane immediately. To quantify the time it takes for the water drop to completely disappear, a series of images were acquired in the movie mode of the DSA10. Contact angle as a function of the age of the water drop was plotted to determine the time it takes for the membrane to absorb the drop. This method allows comparison between different treatments and provides a semi-quantitative measure of the effects of aging on the hydrophilicity of the treated membranes.

Scanning electron microscopy (SEM) images were obtained using a Philips 505 microscope with an accelerating voltage of 15 kV and spot size of 50 nm. Cross-sectional SEM images were obtained by freeze-fracture of the membrane in liquid nitrogen. A thin gold film of ∼20 nm thickness was sputtered onto the surface prior to SEM analysis. Multiple spots on each membrane were analyzed. Images shown are representative of the entire membrane surface (or cross-section) for each of the membrane treatments.

2.5. Bubble point measurements

The most widely used non-destructive integrity test for membranes is bubble point analysis, which is based on the retention of liquids in pores by surface tension and capillary forces. The minimum pressure required to force liquid out of the pore space is the bubble point. Here, bubble point measurements were obtained using a home built apparatus consisting of a sample holder (4.9 cm²), a pressure gauge, and a compressed air cylinder (4.8 grade). Because of the hydrophobicity of the unmodified PES membranes, they were initially immersed in 50:50 mixtures of isopropyl alcohol (IPA) and water. All modified membranes, which were highly hydrophilic, wetted by deionized water prior to bubble point measurement. The wet membrane was placed in the sample holder between two protective metal screens with the tight side of the membrane upstream of the airflow. The delivery pressure was then slowly increased until rapid, continuous bubbling was observed at the outlet. This pressure is the bubble point.
2.6. Protein ultrafiltration

In this work, we employed the filtration parameters detailed by Chen and Belfort [29]. The hydrion buffer solution was prepared by dissolving known quantities of the salts in the desired volume of deionized water. Protein solution was prepared by dissolving BSA powder in a hydrion buffer solution (pH 7 ± 2) at room temperature, which was filtered with a 0.22 μm Nylon filter, stored at 4 °C, and used within 48 h of preparation. The concentration of the BSA was measured with an UV-Vis spectrometer (Varian, Cary 500 Scan) at 280 nm. The ultrafiltration experiment was performed in a dead ended stirred cell (Model 8050, Amicon Div., Millipore Corp.) with an active membrane area of 12.57 cm². The filtration apparatus used in this study included a membrane test cell, nitrogen pressure to the feed reservoir; permeate collection reservoir and pressure gauges.

Filtration performance of treated membranes was performed within 24 h of plasma treatment using a filtration protocol similar to that used by Chen and Belfort [29]. The stirred cell and reservoir were initially filled with deionized water and the membrane was precompacted for 15 min at a pressure of 15 psi. The pressure was then reduced to 5 psi and water flux, $J_0$, was measured after reaching a stable value. Modified membranes, which were highly hydrophilic were used without such preconditioning. Without removing the membrane from the test cell, it was then exposed to 10 g/l BSA in a hydrion buffer solution for 1 h without permeation. A pressure of 5 psi was then applied to the cell, and the permeate flux, $J_p$, was collected. The protein solution was then removed and the membrane surface quickly rinsed twice with deionized water. The water flux, $J_1$, was then measured at a pressure of 5 psi after reaching a stable value.

Cleaning of the membranes was also performed to determine if the original water flux could be recovered. Immediately following the BSA fouling experiment, the cell was then filled with a 0.25N NaOH solution and stirred for 30 min. After rinsing with ionized water, the membrane was reversed in the cell and the same procedure was followed to clean the other side of the membrane. Subsequent to these cleaning steps, the flux $J_2$ was measured. Then the membrane was reversed to its original orientation and water flux $J_3$ was measured.

Three ratios were calculated to evaluate the antifouling properties of the modified membranes and for comparison to the unmodified membranes. (1) $J_p/J_0$: This ratio measures the tendency of the membrane to foul with BSA solution. (2) $J_1/J_0$: This measures the ability to clean the membrane by water. (3) $J_3/J_0$: This ratio measures the extent of flux recovery by cleaning both sides of the membrane. Generally, ratio (3) was less than unity, with the higher ratios indicating more effective caustic cleaning. If this ratio is greater than unity, however, the caustic could be damaging the pore structure of the membranes.

3. Results and discussion

3.1. Grafting degree

Many researchers [30–34] have studied the grafting of AA on plasma treated polymer surfaces in the vapor phase. The extent of grafting, as measured by GY, depends on the chemical structure of the polymer to be grafted, on the radicals formed on the surface during the plasma process, and on the grafting method (i.e. vapor or solution phase). Hence, it varies significantly from polymer to polymer. Moreover, all plasma processes are strongly dependent on reactor geometry and other plasma processing parameters.

In this study, we treated PES membranes with Ar plasmas and then, without removal from the reactor, exposed the activated membranes to AA vapor in the same chamber. Plasma powers of 25, 40, and 50 W; activation times of 5–410 s; and grafting times of 2–45 min were selected. The plasma parameters, grafting time and grafting yield of AA on PES are listed in Table 1 for a variety of treatment conditions. Note that the “GA V” designation in Table 1 allows us to distinguish between different treatment conditions and originates from “grafting of acrylic acid in the vapor phase”. A similar designation system was used by Garcanz et al. [34]. It is clear that the GY increases with plasma treatment time and decreases with plasma power (membranes GA V4, GA V8, and GA V14). Furthermore, GY increases almost linearly with grafting time of the AA up to 30 min, and then the rate of grafting decreases. Depending on experimental conditions, we can achieve GY = 80–210 μg/cm². These values are roughly comparable to those found...
Table 1
Grafting yields as a function of reaction parameters

<table>
<thead>
<tr>
<th>Membrane label</th>
<th>Plasma treatment parameters</th>
<th>Grafting time (min)</th>
<th>GY (µg/cm²)</th>
<th>Bubble point (psi)</th>
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<tr>
<td></td>
<td>Power (W)</td>
<td>Time (s)</td>
<td></td>
<td></td>
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<tr>
<td>GA V1</td>
<td>25</td>
<td>300</td>
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<td>–</td>
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<tr>
<td>GA V2</td>
<td>25</td>
<td>5</td>
<td>5</td>
<td>130 ± 6</td>
</tr>
<tr>
<td>GA V3</td>
<td>25</td>
<td>30</td>
<td>5</td>
<td>130 ± 2</td>
</tr>
<tr>
<td>GA V4</td>
<td>25</td>
<td>120</td>
<td>5</td>
<td>130 ± 5</td>
</tr>
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<td>GA V5</td>
<td>25</td>
<td>300</td>
<td>5</td>
<td>158 ± 3</td>
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<td>GA V6</td>
<td>40</td>
<td>300</td>
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<td>–</td>
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<td>85 ± 6</td>
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<td>30</td>
<td>15</td>
<td>132 ± 4</td>
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<td>GA V9</td>
<td>40</td>
<td>300</td>
<td>2</td>
<td>115 ± 4</td>
</tr>
<tr>
<td>GA V10</td>
<td>40</td>
<td>300</td>
<td>5</td>
<td>155 ± 5</td>
</tr>
<tr>
<td>GA V11</td>
<td>40</td>
<td>300</td>
<td>15</td>
<td>168 ± 4</td>
</tr>
<tr>
<td>GA V12</td>
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<td>300</td>
<td>30</td>
<td>176 ± 4</td>
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<td>GA V13</td>
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<td>203 ± 3</td>
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<td>GA V14</td>
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<td>360</td>
<td>30</td>
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<td>GA V15</td>
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<td>159 ± 4</td>
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<td>GA V19</td>
<td>50</td>
<td>300</td>
<td>30</td>
<td>162 ± 3</td>
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<td>GA V20</td>
<td>50</td>
<td>300</td>
<td>45</td>
<td>203 ± 3</td>
</tr>
</tbody>
</table>

a Labels indicate grafting of acrylic acid was performed in vapor phase and are used primarily to distinguish samples obtained under different experimental conditions.

b Grafting yields (GY) are calculated using Eq. (1). Membranes GA V1, GA V6, and GA V15 were only treated with Ar plasma, so there are no grafting yields for these samples. Errors are one standard deviation of the mean from several samples.

c Bubble point for untreated PES is 75 ± 2 psi.

by Garcanz et al. [34] for similar grafting treatments.

3.2. FTIR spectroscopy

The plasma penetrates the entire thickness of the membrane, thereby modifying the entire cross-section. Hence, we recorded FTIR spectra in transmission mode. Fig. 1 shows FTIR spectra of unmodified PES membranes along with Ar plasma treated membranes exposed to AA vapor for various times. A new absorption band at ~1725.5 cm⁻¹ appears in the spectrum, indicating the presence of PAA. With increasing GY, the intensity of this band increases and is resolved into two peaks, one at 1727.5 cm⁻¹ and the other at 1701 cm⁻¹. This suggests that as the amount of PAA increases on the surface of the membrane, both intra- and interchain interactions occur between carboxylic groups [34].

3.3. XPS

Table 2 shows binding energies and relative peak areas of the C 1s and O 1s spectra for unmodified PES membranes. The fits are based on reference measurements of Beamson and Briggs [35]. The binding energies and relative peak areas are in good agreement with the theoretically predicted values. We shall first consider the effect of Ar plasma on the elementary decomposition processes on the PES surface. Fig. 2 shows XPS spectra for C 1s, O 1s, and S 2p core levels of the unmodified PES surface and an Ar plasma treated PES membrane. In the C 1s spectra (Fig. 2a) of the unmodified membrane, the π-π* shake-up satellite peak is at 291.64 eV. After Ar plasma treatment (Fig. 2b), this peak has decreased considerably (% area reduced from 7.8 to 3.9), possibly as a result of graphitization
Fig. 1. Transmission FTIR spectra of: (a) unmodified PES membrane; treated membranes: (b) GA V7, (c) GA V10, (d) GA V19, and (e) GA V14. See Table 1 for details of plasma and grafting parameters used for each treated membrane.

of the polymer surface due to dehydrogenation of the phenyl ring and disruption in the aromaticity [36]. In addition, there are other structural changes in the C 1s spectrum after Ar treatment, including a significant decrease in carbon content (Table 3). Analysis of the C 1s peak reveals the presence of two additional components: (1) a peak at 287.6 ± 0.2 eV, corresponding to carbonyl functionality; (2) a second peak at 289.0 ± 0.2 eV, attributed to carboxylic acid groups, –COOH. This indicates that oxygen containing groups are incorporated into the membrane matrix when it is exposed to atmospheric oxygen after plasma treatment [37–39].

The O 1s spectra (Fig. 2c and d) show that the Ar plasma treatment primarily attacks the oxygen in the sulfonic group, which is indicated by a stronger decrease of the corresponding peak at 531.7 ± 0.15 eV (% area decreased from 65.1 to 49.6). In addition, there is a significant increase in the intensity and area of the spectral feature at 532.8 eV (from 34.9 to 50.5%), corresponding to oxygen in the ether group. This may be the result of a decrease in oxygen from sulfonic groups or it may also be attributed to formation of new carbon–oxygen functionalities after post-plasma reaction of the activated surface with atmospheric

<table>
<thead>
<tr>
<th>Sample</th>
<th>284.7</th>
<th>65.9 ± 2.0</th>
<th>-C–C–</th>
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<tbody>
<tr>
<td>PES</td>
<td>285.32</td>
<td>17.2 ± 1.0</td>
<td>-C–S–</td>
</tr>
<tr>
<td></td>
<td>286.36</td>
<td>16.9 ± 1.0</td>
<td>-C–O–</td>
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<tr>
<td></td>
<td>291.6</td>
<td></td>
<td>µ–µ*</td>
</tr>
<tr>
<td>O₆₄</td>
<td>531.71</td>
<td>65 ± 2</td>
<td>O=S=O</td>
</tr>
<tr>
<td></td>
<td>532.90</td>
<td>35 ± 2</td>
<td>-C=O–C-</td>
</tr>
<tr>
<td>AA grafted</td>
<td>284.7</td>
<td>61.0 ± 2.0</td>
<td>C–C</td>
</tr>
<tr>
<td>PES</td>
<td>285.32</td>
<td>15.9 ± 1.0</td>
<td>-C–S–</td>
</tr>
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<td></td>
<td>286.36</td>
<td>15.2 ± 0.5</td>
<td>-C–O–</td>
</tr>
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<td></td>
<td>287.3</td>
<td>3.6 ± 0.5</td>
<td>-C=O</td>
</tr>
<tr>
<td></td>
<td>289.9</td>
<td>4.3 ± 0.5</td>
<td>COOH</td>
</tr>
<tr>
<td></td>
<td>291.6</td>
<td></td>
<td>µ–µ*</td>
</tr>
<tr>
<td>O₆₄</td>
<td>531.71</td>
<td>40 ± 1</td>
<td>O=S=O+O</td>
</tr>
<tr>
<td></td>
<td>533.12</td>
<td>60 ± 2</td>
<td>-C=O</td>
</tr>
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</table>

Data were taken with a take-off angle 55°. Fitted peak areas were taken from high resolution spectra. Results for the AA grafted PES are for GA V6.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak binding energy (eV)</th>
<th>Fitted peak area (%)</th>
<th>Assignment</th>
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<td>Unmodified PES</td>
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<td>65.9 ± 2.0</td>
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<tr>
<td>PES</td>
<td>285.32</td>
<td>17.2 ± 1.0</td>
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<td></td>
<td>286.36</td>
<td>16.9 ± 1.0</td>
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<td></td>
<td>291.6</td>
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<td>µ–µ*</td>
</tr>
<tr>
<td>O₆₄</td>
<td>531.71</td>
<td>65 ± 2</td>
<td>O=S=O</td>
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<tr>
<td></td>
<td>532.90</td>
<td>35 ± 2</td>
<td>-C=O–C–</td>
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<tr>
<td>AA grafted</td>
<td>284.7</td>
<td>61.0 ± 2.0</td>
<td>C–C</td>
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<tr>
<td>PES</td>
<td>285.32</td>
<td>15.9 ± 1.0</td>
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<td>3.6 ± 0.5</td>
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<td></td>
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<td>60 ± 2</td>
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Table 3

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<th>Material</th>
<th>XPS atomic percent</th>
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<tr>
<td>Unmodified PES</td>
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<tr>
<td>Ar plasma treated PES</td>
<td>70.1 ± 0.4</td>
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<tr>
<td>AA grafted PES</td>
<td>69.5 ± 0.7</td>
</tr>
</tbody>
</table>

* Results shown are for GA V6.

Table 1

<table>
<thead>
<tr>
<th>XPS atomic percent</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Sulfur</th>
<th>Nitrogen</th>
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<td>Unmodified PES</td>
<td>75.8 ± 0.7</td>
<td>19.2 ± 0.2</td>
<td>5.0 ± 0.1</td>
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</tr>
<tr>
<td>Ar plasma treated PES</td>
<td>70.1 ± 0.4</td>
<td>24.2 ± 0.1</td>
<td>3.9 ± 0.1</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>AA grafted PES</td>
<td>69.5 ± 0.7</td>
<td>26.9 ± 0.1</td>
<td>3.5 ± 0.1</td>
<td>–</td>
</tr>
</tbody>
</table>

* Results shown are for GA V13.
Fig. 2. XPS core level spectra for untreated and Ar plasma treated PES membranes (40 W, 5 min, GA V6). C 1s spectra are shown for: (a) untreated and (b) treated membranes. Similarly, O 1s spectra are shown for: (c) untreated and (d) treated membranes. S 2p spectra are shown for: (e) treated and (f) untreated membranes.

Oxygen (oxygen content increased from 19.2 to 24.2%). A small amount of nitrogen (1.7%) is observed on the treated PES surface, clearly indicating the activated surface reacts with both atmospheric oxygen and nitrogen.

The most prominent change in the membrane structure after Ar plasma treatment is observed in the S 2p spectrum (Fig. 2e and f). In the untreated sample, there is a single peak at 167.6 eV, whereas there are two peaks in the spectrum for the treated sample, the...
second peak occurring at a binding energy of 163.5 ± 0.2 eV, typical for sulfur located in a sulfide (–S–) group, and suggests the sulfone group (SO₂) in the PES is reduced during plasma treatment. From the XPS spectra, it is clear that Ar plasma attacks the polymer primarily at the oxygen in the sulfone group and the carbon in the phenyl ring.

Activation of the surface and graft polymerization of AA takes place in the same chamber, with no exposure to atmosphere. Hence, there is no opportunity for incorporation of atmospheric oxygen or nitrogen and polymerization is induced directly by radicals created in the polymer by the Ar plasma. Fig. 3 shows core level C 1s, O 1s, and S 2p spectra for plasma-induced AA grafted PES membranes. Binding energies, relative peak areas of the C 1s and O 1s spectra and their respective assignments are listed in Table 2 for the AA grafted membranes. There are several significant changes that have occurred in the surface composition of the membranes. First, the amount of sulfur incorporation is much reduced (3.64%) after AA grafting. Second, the oxygen content is increased from 19.2% in the unmodified PES to 26.9% after AA grafting. As there is no exposure of the membrane to atmosphere, this increase must be the result of grafting of AA moieties onto the surface. Third, the satellite peak located at 291.6 ± 0.2 eV in the C 1s spectrum and the sulfide peak at 163.5 ± 0.2 eV are significantly reduced in intensity relative to the spectra for the Ar plasma treated membranes (Fig. 2). This strongly indicates we are covering the surface with the AA polymer. Finally, the relative intensities of the two peaks in the C 1s spectrum attributable to carbonyl (287.3 ± 0.2 eV) and carboxylic acid groups (288.9 ± 0.2 eV) have changed. In comparison to the Ar plasma treated membrane, the contribution to the C 1s spectrum from the carboxylic acid is higher in the AA grafted membrane. All of these data confirm that AA polymer grafting is indeed occurring at the membrane surface.

3.4. Contact angle

Contact angle measurements are one of the simplest available methods for determining the hydrophobic or hydrophilic nature of chemical groups attached to the outer layer of a surface. Liquids similar in character to the chemical composition of the film wet the surface well and result in smaller contact angles. The average water contact angles of the open and tight sides of the unmodified membrane were ∼90 and ∼66°, respectively. Water contact angles were measured for samples both after Ar plasma treatment and after AA grafting. The contact angle measurements were performed on both sides of the membrane within 1 h of
removing the membrane from the reactor. As noted above, contact angle measurements on both sides of Ar plasma treated and AA grafted membranes were impossible to perform as the drop immediately disappeared into the membrane, with the exception of membranes GA V2, GA V3, GA V7, and GA V8. For these membranes, the open side is completely hydrophilic, but the drop never completely disappears from the tight side of the membrane. The contact angle on the tight side has, however, decreased substantially to $\sim 40^\circ$. This suggests that when plasma treatment time is less than $\sim 90$ s, only the upstream side (open side) is modified. To render complete hydrophilicity throughout the membrane, the Ar plasma exposure time must be $\geq 120$ s.

To study the effects of aging, modified membranes were stored in ambient conditions and the contact angle was measured after various periods of time. Fig. 4 shows the effect of aging on the Ar plasma treated membrane GA V6. The most significant result is that the hydrophilic modification of this membrane is not permanent, with a change in contact angle observed within 2 days of plasma treatment. After 1 week, the time for complete wetting had increased to 12 s for the upstream side of the membrane and 20 s for the downstream side. Further loss of hydrophilicity was observed after aging for 2 months, with wetting times increasing to 65 and 95 s for the upstream and downstream sides, respectively. Similar losses in hydrophilicity upon storage are typical, and have been observed for many plasma treated polymers [20–24].

Grafting and polymerization of AA onto the surface allows us to “lock-in” a desired surface chemistry, eliminating the deleterious effects of aging. Fig. 5 shows the effect of aging on AA grafted PES membranes (GA V10–GA V14, $G_H = 155–210 \mu g/cm^2$). Immediately after grafting, we measured the contact angle and found completely hydrophilic surfaces for both sides of the membrane. After a week of aging, the drop took 3–4 s to completely disappear. After this initial rearrangement on the surface, no further change in hydrophilicity was observed over a 2-month

![Fig. 4. Contact angle as a function of water drop age for unmodified and Ar plasma treated (GA V6) PES membranes. Open and closed circles are for the open and tight sides of an untreated PES membrane, respectively. Open and closed triangles are for upstream (open) and downstream (tight) sides, respectively, of an Ar treated PES membrane aged 1 week after treatment. Open and closed squares are for the upstream (open) and downstream (tight) sides, respectively, of an Ar treated PES membrane aged 2 months after treatment.](image-url)
time period. This demonstrates that after 1 week, the surface is stabilized and hydrophilicity is permanent. When \( \text{GY} \leq 115 \mu g/cm^2 \) (e.g. GAV9), however, some change in hydrophilicity is observed upon aging (Fig. 6). After 2 months, the time for the drop to disappear was 19 and 24 s for the downstream and upstream sides, respectively. Although there is a very small difference in wetting time for the two sides, it appears the downstream side is slightly more hydrophilic than the upstream side. This may simply be the result of the higher hydrophilicity of the tight side of the unmodified membrane. From these data, it is clear that Ar plasma treated membranes are regaining their original hydrophobicity, whereas AA polymer grafted membranes are permanently hydrophilic when \( \text{GY} > 115 \mu g/cm^2 \).

3.5. Morphology

The effect of Ar plasma treatment and plasma-induced AA polymer grafting on the morphology of PES membranes was investigated with SEM. The open sides of the membranes were imaged as these sides were oriented closest to the plasma glow during treatment and were, therefore, more likely to be physically damaged by the plasma than the downstream side. SEM images of the untreated, Ar plasma treated, and AA polymer grafted PES membranes are shown in Fig. 7. After Ar plasma treatment, Fig. 7b, the PES appears undamaged and is quite uniform. Although it appears there is a white layer on the surface of the polymer, which could correspond to degradation of the polymer, there is no apparent change in the pore size. Note that the downstream placement of the membrane (\( \sim 18 \) cm from the glow) significantly minimizes exposure of the membranes to ionizing radiation [40]. When grafted with AA for a relatively long time (GAV14), the membrane surface is covered with a small amount of polymer (Fig. 7c), somewhat reducing the surface porosity. Comparison of Fig. 7a and c reveals that smaller pores in the membrane surface are clearly coated following grafting. In addition, globular
structures originally present in the membranes have increased slightly in size as well as number. The cross-sectional morphology (Fig. 8), however, showed no visible change in the pore size for Ar plasma treated PES membranes. From the image in Fig. 8c, there is a clear change in the small pore size region (tight side) of the membrane (bottom of image). In this image, these pores are not as clearly visible as in the untreated membrane and it appears they may have begun to fill. Thus, the grafting time must be long enough to get a sufficient grafting yield, yet short enough to ensure pore structure is not significantly altered.

3.6. Bubble point measurements

Bubble point measurements for selected membranes are listed in Table 1. None showed any change from unmodified PES (75 ± 2 psi), with the exception of GAV14. The constant bubble point for these modified membranes may be the result of a decrease in contact angle and concomitant increase in the pore size. An overt change in pore size would, however, be observable in by SEM. As the SEM images in Figs. 7 and 8 demonstrate, there is no adverse physical alternation in membrane structure as a result of plasma modification. For the membrane GAV14, the bubble point increased by 5 psi, which is likely the result of a slight decrease in pore size as this treatment has the highest GY (Table 1).

3.7. Protein filtration

With plasma treatment, specific surface chemistries can be created for reducing protein–surface attractive interactions, thereby minimizing protein adsorption and ultimately membrane fouling. Similar to PSf, it is likely that the hydrophobic character of PES leads to an increase in protein fouling. Filtration results for the unmodified membrane, membranes modified by Ar treatment alone, and membranes grafted with AA polymer after Ar plasma exposure are shown in Table 4. The pure water flux values are tremendously
Fig. 7. SEM micrographs of the open sides of PES membranes. The images are for: (a) an untreated membrane; (b) Ar plasma treated membrane (GA/V6); (c) AA grafted membrane (GA/V14). See Table 1 for details of plasma and grafting parameters for the treated membranes.

Fig. 8. Cross-sectional SEM micrographs of PES membranes. The images are for: (a) an untreated membrane; (b) Ar plasma treated membrane (GA/V6); (c) AA grafted membrane (GA/V14). See Table 1 for details of plasma and grafting parameters for the treated membranes.
increased for modified membranes. The flux ratios after protein fouling \( \frac{J_p}{J_0} \) were 38–48% higher for Ar plasma treated membranes and 54–60% higher for AA grafted membranes. Also, cleaning of the membrane was more effective for plasma modified membranes \( \frac{J_1}{J_0} \). The flux recovery after water cleaning was 20–24% higher for Ar plasma treated membranes and 74–87% higher for AA grafted membranes. Likewise, flux recovery after caustic cleaning was 20–24% higher for Ar treated membranes and 47–49% higher for AA grafted membranes. The retention factor for all modified membranes was slightly higher. The higher filtration performance results for the AA modified membranes support the assertion that plasma grafting increases the hydrophilicity of the membranes, leading to an overall decrease in protein fouling.

### Table 4
Filtration performance for treated and untreated PES membranes

<table>
<thead>
<tr>
<th>Material</th>
<th>( J_0 ) (L/(m² h psi))</th>
<th>( J_p/J_0 )</th>
<th>( J_1/J_0 )</th>
<th>( J_3/J_0 )</th>
<th>Membrane treatment*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>58.5</td>
<td>0.24</td>
<td>0.46</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>Ar plasma</td>
<td>216.6</td>
<td>0.35</td>
<td>0.54</td>
<td>0.77</td>
<td>5 min, 25 W (GAV1)</td>
</tr>
<tr>
<td>Ar plasma</td>
<td>244.5</td>
<td>0.33</td>
<td>0.57</td>
<td>0.81</td>
<td>5 min, 40 W (GAV6)</td>
</tr>
<tr>
<td>AA grafted</td>
<td>195.8</td>
<td>0.36</td>
<td>0.80</td>
<td>0.94</td>
<td>5 min, 40 W, ( G = 30 \text{ min} ) (GAV12)</td>
</tr>
<tr>
<td>AA grafted</td>
<td>175.0</td>
<td>0.38</td>
<td>0.86</td>
<td>0.95</td>
<td>5 min, 40 W, ( G = 45 \text{ min} ) (GAV13)</td>
</tr>
</tbody>
</table>

*Error limits are \( \sim \pm 10\% \).

Increased for modified membranes. The flux ratios after protein fouling \( \frac{J_p}{J_0} \) were 38–48% higher for Ar plasma treated membranes and 54–60% higher for AA grafted membranes. Also, cleaning of the membrane was more effective for plasma modified membranes \( \frac{J_1}{J_0} \). The flux recovery after water cleaning was 20–24% higher for Ar plasma treated membranes and 74–87% higher for AA grafted membranes. Likewise, flux recovery after caustic cleaning was 20–24% higher for Ar treated membranes and 47–49% higher for AA grafted membranes. The retention factor for all modified membranes was slightly higher. The higher filtration performance results for the AA modified membranes support the assertion that plasma grafting increases the hydrophilicity of the membranes, leading to an overall decrease in protein fouling.

### 3.8. Comparison to previous grafting studies

As noted above, a number of studies have been published on the grafting of hydrophilic moieties to PES and PSf membranes using either UV or plasma activation. For example, acrylic acid has been used to modify poly(vinylidene fluoride) (PVDF) [41] and silicone rubber [14,42] membranes. We will limit this discussion, however, to those materials most relevant to the present work. Belfort and coworkers have used both UV excitation and plasma activation to graft a variety of hydrophilic monomers including 2-hydroxy-ethyl-methacrylate (HEMA), acrylic or methacrylic acid, and N-vinyl-2-pyrrolidinon (NVP), onto PSf, PES, and polyacrylonitrile (PAN) membranes [12,13,29,43]. In nearly all of these studies, solution phase grafting was employed following plasma treatment and subsequent atmospheric exposure. The grafting yields on PES or PSf membranes were considerably lower (i.e. \( \sim 12 \mu g/cm² \)) for methacrylic acid on PSf than those found here for vapor phase grafting with no exposure to atmosphere prior to the grafting step. Likewise, a study by Garcanz et al. [34] also found solution phase grafting yields to be fairly low (i.e. \( \sim 3–12 \mu g/cm² \)) for AA grafting onto PSf membranes following plasma activation. This study also examined vapor phase grafting, however, and found similar GY values (\( \sim 3–260 \mu g/cm² \)) compared to those reported here (Table 1), which were dependent on plasma treatment and grafting times. The somewhat lower vapor phase GY values reported by Garcanz et al. under all but the most aggressive conditions could be related to the orientation of the membrane, relative to the plasma. Specifically, their membranes were attached to a table, whereas our membranes are oriented perpendicular to gas flow, thus allowing for maximum exposure of the entire membrane cross-section to plasma treatment. With respect to transport properties, in general Belfort and coworkers report an increase in filtration performance and a decrease in fouling with grafted materials as compared to the unmodified materials. This is true for all hydrophilic monomers used for grafting, despite the relatively low GYs obtained with the solution phase dip method. Interestingly, Garcanz et al. report a dependence on pH for their vapor phase AA grafted PSf membranes, with a decrease in performance under acidic conditions, but better performance under basic conditions. The latter is similar to what we observe under neutral conditions (pH = 7) [34]. Thus, the results presented here are comparable to those reported for similar systems, although we do find slightly increased GYs under our treatment conditions. Additional ongoing studies in our laboratory on grafting of acrylamide onto PES membranes.
membranes have shown extremely low fouling behavior, with higher performance characteristics than the AA grafted materials discussed here [44].

4. Summary

Depending on plasma and grafting parameters, grafting yields of 80–210 μg/cm² were achieved with Ar plasma exposure followed by AA monomer vapor exposure. XPS analysis demonstrates that Ar plasma alone attacks the carbon in the phenyl group and to some extent, graphitization of the surface occurs. Furthermore, XPS, FTIR, and electron microscopy results confirm the grafting of AA. Bubble point measurements and SEM studies revealed no physical damage to the polymer surface after treatment. Contact angle measurements showed that for plasma treatment times >120 s, both sides of the membrane become highly hydrophilic, with the water drop immediately disappearing. For the Ar plasma treated membranes without grafting, hydrophilicity is not permanent. These changes can be attributed to structural rearrangement of polymer chains to decrease surface energy. A hydrophilic surface modification for the entire membrane cross-section can be “locked-in”, however, by post-plasma grafting of AA. The hydrophilicity of grafted membranes remained essentially unchanged for a minimum of 2 months. The pure water flux for modified membranes increased largely because of its high hydrophilicity. The protein fouling is considerably reduced for modified membranes. Furthermore, the modified membranes are easier to clean and required less caustic to recover permeation flux.

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References


