

# Surface modification with nitrogen-containing plasmas to produce hydrophilic, low-fouling membranes

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## Abstract

Nitrogen-based plasma systems such as  $N_2$ ,  $NH_3$ ,  $Ar/NH_3$ , and  $O_2/NH_3$  were used to modify microporous polyethersulfone membranes. Treatments were designed to alter the surface chemistry of the membranes to create permanently hydrophilic surfaces. Contact angle measurements taken initially, as well as 1 year post-treatment confirmed that treatments using  $O_2/NH_3$  plasmas (with a 5:3 gas flow ratio) were successful in achieving our designed goals. Analyses by FT-IR and XPS established the incorporation of  $NH_x$  and OH species in the PES membranes. Moreover, the plasma penetrates the thickness of the membrane, thereby modifying the entire membrane cross-section. Optical emission spectroscopy studies of excited state species present in the modifying gases revealed the presence of  $OH^*$ , which was not present in a 100% ammonia plasma, suggesting  $OH^*$  must play a critical role in the membrane modification process. Investigations using bubble point analysis, differential scanning calorimetry, and scanning electron microscopy demonstrate there is no damage occurring under these specific treatment conditions. The usefulness of this treatment is revealed by increased water flux, reduced protein fouling, and greater flux recovery after gentle cleaning when compared to an untreated membrane.

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## 1. Introduction

Polyethersulfone (PES) is a commercially available, thermally stable polymer used in high-performance applications because of its toughness, high thermal resistance and chemical inertness [1,2]. As a result, PES has been adopted as the membrane material for important separation processes including biological, pharmaceutical, and sterilization filtration [1,3]. One issue with PES is its high hydrophobicity, which severely limits its long-term applicability and in many cases requires the use of a wetting agent prior to filtration. Thus, achieving the desired surface properties without modification of the advantageous properties of PES membranes is an important goal for the membrane industry.

Plasma treatments can alter the surface energy of most polymers, changing their surface polarity, wettability, and

adhesive characteristics [4]. Surface activation takes place during the plasma processing mainly by hydrogen abstraction and radical formation, which results in modification of only the top-most nanometers of the polymer structure being altered [5]. This means that the surface can be selectively modified for a specific application while the bulk properties of the polymer are unaffected. Moreover, plasma processes can also induce changes that cannot be produced by conventional methods [6]. Plasma modification of porous polymers can significantly improve the wetting properties of PES and polysulfone (PSf) membranes [7–9].

Nitrogen-containing plasma systems have been used extensively for treatment of metals, polymers, and polymeric membranes [10–14]. These systems are often used for their ability to introduce amine, imine, amide, nitrile, and other functionalities to the polymer surface [15–17]. Implanted amine groups, with their associated polarity and reactivity, can be useful in the preparation of blood compatible materials or in promotion of adhesion for directed, controlled

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covalent attachment of antibodies in a solid support [18]. In some systems, control of plasma parameters and plasma density can result in selective grafting of  $-\text{NH}_2$  to the polymer surface [17]. Implanted nitrogen functional groups, as well as post-treatment atmospheric oxidation produces highly hydrophilic surfaces, significantly reducing the contact angle of treated surfaces [10]. One distinct advantage of membranes with hydrophilic surfaces is the increase in water flux through the membrane and the concomitant reduction of protein fouling [19–22]. Although the mechanisms for protein fouling are not well understood, significant reductions in fouling behavior have been reported for membranes with modified hydrophilic surfaces.

One drawback to plasma treatment is that the changes in hydrophilicity induced by implantation of polar functional groups can be time-dependent. Chain migration in the surface region can result in gradual deterioration of the surface properties [11,15,23–25]. This process, called aging or hydrophobic recovery, restores the original hydrophobic surface to the extent that it adapts composition to interfacial forces [11,16,26]. Aging of surface modified polymers is attributed to migration of polar surface groups into the polymer along with movement of untreated polymer chains to the surface; to structural rearrangement that buries chemical groups introduced at the surface; and/or to chemical reactions occurring upon exposure to atmospheric oxygen and moisture. These changes in the surface properties can limit the usefulness of modified membrane materials [26]. For example, use of well-characterized surfaces is critical for the study of interactions with proteins and cells. Reorientation of surfaces on unknown time scales prevents careful control experiments from being performed. In addition, materials with mobile surface compositions cannot be reliably used in biomedical devices because of possible uncontrolled interfacial interactions. Thus, hydrophobic recovery should be reduced or eliminated to extend the shelf life for practical applications of modified membranes.

The goal of this work was to examine the influence of nitrogen-containing plasmas, specifically  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{Ar}/\text{NH}_3$ , and  $\text{O}_2/\text{NH}_3$ , on PES membranes. Treated membranes were characterized with surface analytical techniques such as contact angle measurements, FT-IR, and XPS. The changes in structural, mechanical, and thermal properties were also studied using scanning electron microscopy (SEM), bubble point, and differential scanning calorimetry (DSC). The amount of protein absorbed and the reversibility of fouling were measured and compared to control membranes using bovine serum albumin (BSA) as a model protein.

## 2. Experimental details

### 2.1. General

Asymmetric micro-porous polyethersulfone (PES) membranes (Millipore Inc.) were soaked in methanol for 15 min to

remove extractables and air dried thoroughly before plasma treatment. All membrane treatments were performed in a tubular, glass inductively coupled, rf (13.56 MHz) reactor described previously [27,28]. A cylindrical substrate holder orients the membrane (3.8 cm diameter) perpendicular to the flow, allowing maximum penetration of the plasma species [7,8]. Downstream placement of the membranes ( $\sim 9$  cm from the coil) minimizes damage to the membrane and facilitates modification of the entire cross-section. The orientation of the membrane in the holder (i.e. whether the large pore side or the small pore side of the asymmetric membranes faced the plasma) was found to be critical for complete modification. This is in contrast to previous work in our laboratory in which orientation did not affect the outcome of the treatments [7]. Thus, in this work, all treatments were performed with the open side of the membrane facing the plasma, designated as the upstream side.

Reactant gases (95–99.995%, General Air ( $\text{N}_2$ ,  $\text{Ar}$ ,  $\text{O}_2$ ), Matheson ( $\text{NH}_3$ )) were introduced into the reactor through MKS flow controllers, keeping the amount of gas admitted to the reactor constant ( $\pm 2\%$ ). The chamber pressure was monitored with an MKS Baratron capacitance manometer, which is insensitive to differing gas compositions. The parameters investigated included treatments using applied rf powers of 15–120 W, reactor pressures of 50–400 mTorr (2–15 standard cubic centimeters per minute (sccm) flow rates), and treatment times from 2 to 25 min. Unless otherwise noted, all treatments shown used 25 W applied rf power and treatment time of 5 min for the  $\text{Ar}/\text{NH}_3$  (5:10 sccm ratio) and  $\text{O}_2/\text{NH}_3$  plasmas (with a range of gas flow ratios), and 60 W with a 3 min treatment time for the  $\text{N}_2$  plasmas.

### 2.2. Methods of analysis

Changes in membrane hydrophilicity induced by plasma treatment were assessed using static contact angles (CAs) measured by the sessile drop method with a contact angle goniometer (Krüss DSA10) equipped with video capture by applying 1–1.3  $\mu\text{L}$  drops of room temperature deionized (DI) water to the surface. CAs were measured on each side of the membrane (open and tight) for both treated and untreated membranes. For each sample, three drops were placed at different locations and the average of these measurements is reported. Except in the aging studies, CAs were measured immediately after plasma treatment.

Optimization of treatment variables was realized when the membranes were completely wettable and static CAs could no longer be measured by the goniometer. Thus, for most of our modified membranes, it was impossible to perform static contact angle measurements as the water drop quickly ( $< 2$  s) disappeared into the membrane (i.e. CA of  $0^\circ$ ). In comparison, water drops on untreated PES remained for  $> 25$  min without obvious change due to evaporation. 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. In a typical acquisition, an image was recorded ev-

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