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Polymer evolution of a sulfonated polysulfone membrane as a function of ion beam irradiation fluence

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Abstract

Ion beam irradiation was used to modify the surface of a sulfonated polysulfone water treatment membrane. A beam of 25 keV H^+ ions with three irradiation fluences (1×10^{13} ions/cm^2, 5×10^{13} ions/cm^2, and 1×10^{14} ions/cm^2) was used for membrane irradiation. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) analyses were performed on the virgin and irradiated membranes in order to determine the changes to chemical structure incurred by ion beam irradiation. The results show that some of the sulphonic and C–H bonds were broken and new C–S bonds were formed after irradiation. Atomic force microscope (AFM) analyses show that membrane roughness decreased after irradiation. A significant increase in flux after ion beam irradiation was also observed, while the amount of cake accumulation on the membrane was decreased after ion beam irradiation. Hydrophobicity, pore size distribution and selectivity of the membrane were not affected by ion beam irradiation.

Keywords: Ion beam radiation; Surface modifications; Membrane; Ion fluence

1. Introduction

Membranes are becoming a common means of separation in the water treatment field because they can be designed to meet stringent standards while requiring significantly less space and time than other separation techniques. Ideal membranes would be able to maintain high throughput of a desired permeate with a high degree of selectivity. Unfortunately, these two parameters are mutually counteractive. The reason is that a high degree of selectivity is normally only achievable using a membrane having small pores and inherently high hydraulic resistance (or low permeability). Fouling is another severe problem associated with water treatment membranes, which is the deposition of solute constituents onto the surface of the membrane. Fouling of membrane elements often causes a significant increase in hydraulic resistance and applied pressure drop, which increases operating cost and decreases the life of the membrane [1].

For membranes to be competitive with conventional technologies, a membrane process needs to operate with a high rate of flux, have a high degree of selectivity and have a high resistance to fouling. There are three main areas of interest when it comes to improving membrane performance: the synthesis process, the application process, and post-synthesis modification. Synthesis process improvement involves the techniques, methods, and materials of the manufacturing processes to produce a high performance membrane. The application process involves the specific operating parameters for a membrane system. These include selecting the raw water characteristics, operating pressure, and cleaning intervals to allow the system to operate at maximum efficiency. Post-synthesis modification involves modifying the membrane after the initial manufacturing process is complete, which was the focus of the study discussed here.

1.1. Ion beam irradiation

One such post-synthesis modification is achieved through ion beam irradiation. Ion beam irradiation has long been recognized as an effective method for the synthesis and modification of

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diverse materials, including polymers [2–4]. Ion beam irradiation is the bombardment of a substance with energetic ions. When the ions penetrate through the surface of a membrane, they may eliminate the tall peaks and deep valleys, resulting in an overall reduction in surface roughness [5]. As the ions penetrate the membrane, they lose energy to their surroundings (membrane structure) by two main processes: interacting with target nuclei (nuclear stopping) and interacting with target electrons (electronic stopping [6]). Nuclear stopping energy losses arise from collisions between energetic particles and target nuclei. Atomic displacement occurs when the colliding ion imparts energy greater than certain displacement threshold energy. If the energy is not great enough for displacement, the energy dissipates as atomic vibrations known as phonons. Electronic stopping energy losses arise from electromagnetic interaction between the positively charged ions and the target electrons. Excitation and ionization are two common forms of electronic energy loss. Excitation is the process in which an electron jumps to a higher energy level, while in ionization an orbital electron is ejected from the atom.

There have been a number of studies examining the effects of ion beam irradiation on gas separation membranes [5,7–9]. These studies exposed polyimide gas separation membranes to different ion irradiation fluences and energies. Ion irradiation fluences refer to the number of ions implanted into a unit of area of the membrane. Ion energy is directly related to the depth the ions will penetrate into the membrane. As discussed earlier, ion beam irradiation provides energy to the electrons and nuclei of the membrane. The intensive energy deposition in polymers can lead to the following: (1) formation of volatile molecules and free radicals which leave defects in the polymer matrix, (2) creation of additional crosslinking between polymer chains, (3) formation of new chemical bonds, and (4) chemical reactions with chemical atmosphere such as oxidation [8]. These four events can, in turn, lead to membrane microstructure alterations. Previous studies [7–9] found ion beam irradiation resulted in gas separation membranes with both increased permeability and selectivity; two characteristics which have a trade-off relationship toward each other. The improvements in membrane performance were believed to be results of microstructure modification, which was proven by a narrow but intensive free volume distribution. Studies of atomic force microscopy (AFM) of ion beam irradiated polyimide films showed that ion beam irradiation eliminates deep valleys and tall peaks on the surface of the polyimide films even at very low doses of irradiation and that a very smooth surface can be observed after ion beam irradiation [5].

1.2. Objectives

The goal of the study described here was to determine the effects of ion beam irradiation on surface morphology, microstructure, and chemical structure and on the performance of a modified commercial sulfonated polysulfone water treatment membrane.

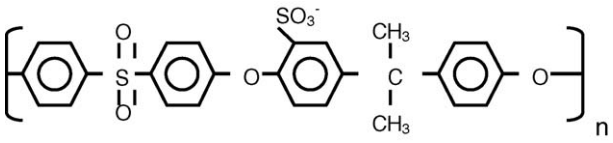

Fig. 1. Structure of sulfonated polysulfone.

2. Experimental

2.1. Membrane properties

A commercially available nanofiltration composite membrane with a selective layer of sulfonated polysulfone was used for testing. The structure of the sulfonated polysulfone is shown in Fig. 1. The membrane is negatively charged (at pH 7.0, the charge is −6.26 mV), hydrophobic (contact angle of 58° [10]) and has a molecular weight cutoff (MWCO) of 500 Da. The operating temperature range is 0–45 °C and pH range is 2–11, and the membrane is able to withstand chlorine concentrations of several hundred ppm.

2.2. Ion beam irradiation

Each membrane was irradiated with H^+ ions at an energy level of 25 keV. The incident energy of 25 keV was determined using a well-known program titled "The Stopping and Range of Ions in Matter" (SRIM [11]) to ensure that the entire upper semipermeable sulfonated polysulfone layer was modified. The thickness of the upper layer was obtained from the SEM images shown in Fig. 2, which show the cross-section of the membrane. Membrane top layer thickness usually ranges from 1000 to 2000 Å. SEM images were obtained using a JSM 6100 SEM (JEOL Inc., Peabody, MA). The SEM images show that the composite membrane was characterized by a thin semipermeable sulfonated polysulfone membrane layer (0.2 μm thick, which agrees with literature values [12]), supported on a porous polysulfone substrate (about 50 μm thick) that, in turn, is bonded to a fibrous layer, which provides mechanical strength to the top layers without adding significant hydrodynamic resistance. The incident energy of 25 keV is chosen to ensure that the entire upper layer of approximately 0.2 μm thick is modified by the ion beam irradiation. Three irradiation fluences (1×10^{13} ions/cm^2, 5×10^{13} ions/cm^2, and 1×10^{14} ions/cm^2) were used for ion beam irradiation of the membranes. The beam current density was maintained at low levels (<1 μA/cm^2) to avoid heating of the samples. All samples were irradiated at room temperature and in a vacuum chamber at a pressure less then 2.5331×10^{-5} Pa (1.9×10^{-7} Torr). The incident beam was perpendicular to the samples. The irradiation was performed using a 1.7 MV high current Tandetron Accelerator at the University of Michigan (Ann Arbor, MI, USA). To provide support to the membrane through the irradiation process, a foil tape masking was utilized. Only the active area of the membrane, which was about a circular area of 95 cm^2, was irradiated.