



Plasma induced graft polymerization of hydrophilic monomers on polysulfone gas separation membrane surfaces



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ABSTRACT

Active groups were induced on the surface of polysulfone (PSF) membranes by DC Ar/O₂-plasma and hydrophilic monomers, acrylic acid (AA) and polyethylene glycol (PEG), were post-grafted. Membrane samples were characterized by several techniques to confirm the tailoring of membrane surfaces. Hydrophilic properties were evaluated in terms of water contact angle in sessile drop mode measurement. Morphological structures were analyzed through SEM and AFM images. Creation of functional groups was determined by ATR-FTIR while grafting yield was estimated by weighing of membrane both before and after grafting. Permeation of CO₂ and CH₄ gases through membrane was also measured. Results showed that the hydrophilic property of PSF membrane surface grafted by PEG was permanently improved over 120 days. The CO₂/CH₄ separation performance was slightly enhanced from 54.06 to 60.05.

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1. Introduction

Polysulfone is used for gas separation membrane preparation because it has many excellent properties such as a high mechanical, chemical, and thermal resistance and film-forming is easy. Moreover, the separation and plasticization properties are in an acceptable range [1, 2]. However, applications of PSF membrane are limited because of its hydrophobic property nature. Various research groups endeavored to improve this limitation by using several physicochemical techniques, like UV radiations, electron beams, gamma rays and plasmas. Plasma is one of the mostly high potential techniques for modification of material surfaces, because it has many advantages, including several conditions that can be adjusted, like plasma gas pressure, plasma gas type, treatment time, discharge power and power supply source; and further it is simple, fast and friendly to the environment. Importantly, cold plasma takes effect only on the skin surface of membrane materials without the effect to the desired bulk structures and properties [3–5]. Glow discharge plasma is an ionized gas comprising of equal concentrations of positive and negative charge particles and a large number of neutral species as well as a broad spectrum of electromagnetic radiation. The different particles and radiations present in plasma induce the formation of free radicals in the polymeric chain and in this way it

is possible to insert or interact with certain functional groups on the polymer surface which will enhance the surface properties of the polymeric membranes [6–8]. Various types of power sources can be used to generate plasma, such as radiofrequency (RF), microwave (MW), photons, and DC high voltage [9]. However, low pressure DC glow discharge plasma has advantage that it is more convenient and efficient for processing of polymeric materials [6]. Besides, DC plasma is technically simple and no electromagnetic wave matching unit is required and it is also quite low cost compared to the other sources. It was well known that the hydrophilicity of polymeric membrane surface can be improved by plasma treatment [10–14]. In the field of polymeric gas separation membranes, it was confirmed that the hydrophilic property has an important role on the gas separation performance [15]. Although the hydrophilic property of polymeric membranes can be improved by the plasma treatment, however, this improvement is not permanently sustain [13,16,17]. In order to improve this drawback, plasma induced graft polymerization (PIGP) is used by applying hydrophilic monomers, like *N*-vinyl-2-pyrrolidone (NVP) [18], polyacrylic acid (PAA), acrylic acid (AA), 2-hydrox-ethylmethacrylate (HEMA), methacrylic acid (MEA), polyethylene glycol (PEG), and polyvinylpyrrolidone (PVP), both in liquid and vapor forms [15,16,19].

Chen and Belfort [18] grafted the NVP on the He-plasma treated polyethersulfone (PES) membranes. They found that the filtration performance of the plasma treated and plasma-grafted PES membranes is higher than of virgin membranes. They also found that the hydrophilic property was stabilized by plasma induced graft polymerization of NVP on the PES membrane surfaces. Song et al. [20] grafted the PEG

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onto the plasma treated PSF membrane surfaces. After the PSF membranes were immersed in 0.5% PEG-4000 in the solution composed of 25 wt% isopropanol (IPA) and 75 wt% water for 24–36 h, PSF membranes were air dried and treated with plasma using N_2 as working gas. They confirmed that PEG was grafted on the surface of PSF membranes. They also found that the hydrophilicity and performance of membranes can be improved by plasma induced graft polymerization. However, they have not studied the permanence of hydrophilic property of PEG-grafted PSF membranes. Acrylamide (AAM) in vapor phase was plasma grafted on the surface of porous polyethersulfone (PES) to improve the hydrophilic property and reduce the protein fouling. It was found that the permanency of hydrophilic property depended on the grafting yield and the graft reaction was confirmed by Fourier transform infrared (FTIR) spectroscopy [13]. Generally, the plasma induced graft polymerization for hydrophilic modification of polymeric membranes has two main steps. In the first step, the membrane is treated adequately by plasma; and in the second step, the plasma treated membrane is put in contact with the vapor of hydrophilic monomer or immersed in the aqueous solution of monomer at normal or elevated temperature [21]. Ulbricht and Belfort [22] grafted hydrophilic monomers onto the polyacrylonitrile (PAN) and PSF membrane surfaces. They summarized that plasma induced graft polymerization of hydrophilic monomer on ultrafiltration membranes can be used to improve both of surface hydrophilicity and permeability. The one important advantage of the plasma initiated graft polymerization is that it offers the possibility of modifying surfaces locally [23].

This research attempted to improve the permanence of hydrophilicity and gas separation property of PSF membranes using the post Ar/O₂-PIGP. The acrylic acid (AA) and polyethylene glycol (PEG) were grafted on plasma treated PSF membrane surfaces. Characteristics of resulted membranes were investigated in details through several analytical techniques. Gas permeation through un-grafted and plasma grafted PSF membranes was also studied in detail.

2. Experiments

2.1. Materials

Pellets of PSF (Udel P-1700 NT II) were supplied from Solvay, China. Solvents including 1-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF; 95%, $M_w = 72.11$ g/mol), were purchased from Sigma-Aldrich Co. Ltd. (Singapore) and Ajax Finechem Pty Ltd., (Australia), respectively. The reagent grade ethanol (EtOH; C₂H₅OH, $M_w = 46.07$ g/mol, purity of 99.5%) and methanol (MeOH; CH₃OH, $M_w = 32.04$ g/mol, purity of 99.5%) were supplied by Merck Co. Ltd. (Thailand). AA and PEG with molecular weight of 200, 1000 and 10,000 Da were supplied from Sigma-Aldrich Co. Ltd., (Singapore). Ar and O₂ gas mixtures with a ratio of 20:80 (w/w) were purchased from Linde Co. Ltd. (Thailand). All of these chemical substances were used as received.

2.2. Preparation of asymmetric PSF membranes

The casting solutions consisted of 22.5 wt% PSF, 30.5 wt% NMP, 30.5 wt% THF and 16.5 wt% EtOH were prepared for this study. Pellets of PSF materials were dried in vacuum electric oven (BINDER, VD53) at the temperature of 85 °C for 24 h before usage. The dried PSF was weighed (SARTORIUS, BS 4202 S; $d = 0.01$ g) and gradually dissolved in the mixtures of low and high volatile solvents (NMP and THF, respectively) and non-solvent (EtOH). For this study, the dissolving temperature was controlled in the range of 55–60 °C. After the polymer material was completely dissolved, the polymer solution was subjected to the ultrasonic cleaner (GT SONIC, VGT-1620T) for 30 min and free placed in the room temperature for 1–2 h to remove any air bubbles. Afterwards, the casting solution was carefully poured and casted on the clear and smooth glass plate. The casting temperature and relative humidity were in the range of 25–27 °C and 58–60% (Traceable Digital

Thermohygrometer, Cole-Palmer (Thailand)), respectively. The wet thickness of nascent membrane was controlled at about 150 μ m. To control the shear effect, the casting rate was carefully controlled at the similarly rate. To generate the dense skin selective layer, the nascent membrane was placed in the normal air for 90 and 120 s before immersed in the first coagulation bath. The immersion times in first and second coagulation baths were about 15 min and 2 h, respectively. Reverse osmosis (RO) water and methanol (MeOH) were respectively used as the first and second coagulation medium, in this study. The process of PSF membrane preparation is shown in Fig. 1.

2.3. Plasma treatment and plasma induced graft polymerization

In order to study the effect of plasma treatment time (PTT) and discharge power (DP) on the grafting yield (GY), samples of PSF membranes were treated by the low temperature and pressure DC glow discharge plasma using Ar and O₂ gas mixtures as working gas. The DC plasma system used in this study is shown in Fig. 2. Further details of this plasma system were described in our previous work [24]. In brief, the plasma system consisted of three main parts; vacuum chamber, DC high voltage power supply and electrodes, and vacuum pump set. In this study, PTT was varied for 30–600 s while DP was varied from 10 to 50 W. The process of plasma treatment started from placing of PSF membrane sample on the anode electrode, pumping of gas pressure in the chamber down to about 5.0×10^{-2} mbar, feeding of Ar/O₂ gas mixtures into the chamber till the gas pressure reach about 2.0×10^{-1} mbar and applying of electric high voltage to generate the glow discharge plasma. The inter-electrode gap was fixed at about 3.5 cm. After the sample of PSF membrane was plasma treated, it was free placed in the normal air for 5 min before immersed in the monomer. From literature [25], when a small amount of Ar was added to a pure O₂ discharge, the overall positive-ion density increases, whereas the ratio of negative ion to electron density decreases. It may lead to the increase of the plasma surface modification efficiency. Furthermore, it was found that the decrease of water contact angle (WCA) increases with increase in the percentage of O₂ in Ar-O₂ plasma [26]. Therefore, the O₂ and Ar gas mixtures with the percentage of O₂ about 80 wt% was used in this present work.

Two types of hydrophilic monomer, acrylic acid (AA) and polyethylene glycol (PEG) with a molecular weight of 10,000 Da, solution with a concentration of 10 wt% in RO-water, were used for post grafting. Grafting (immersing) time (GT) was varied for 15–180 min, in this study. To remove the un-grafted monomer, the grafted membranes were washed with the running RO-water before drying. In this research, PEG with a molecular weight of 200 and 1000 Da was also used. However, the results were not presented in this report, because the preliminary experimental results showed that the GY of these two types of PEG was very low.

2.4. Characterizations

To confirm the permanence of hydrophilicity, water contact angle (WCA) in sessile drop mode using a video based optical contact angle measuring instrument (Model OCA 15EC, Data Physics Instruments GmbH, Germany) was measured at different storage times. The reported value was averaged from 5 to 7 points. Chemical and morphological structure changes were analyzed through the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum (400–4000 cm^{-1} and 4 cm^{-1} resolution), scanning electron microscope (SEM, JEOL JSM-5800 LV) and atomic force microscopy (AFM, Nanosurf-easyscan 2 from Nanoscience (instruments) Co. Ltd.), respectively. For surface roughness determination by AFM, the PSF membrane surface was scanned over an area of $20 \times 20 \mu m^2$.

To determine the grafting quantity of AA and PEG monomers on the surface of PSF membrane, the mass of membrane sample was weighed using the 0.0001 g weighing scale (METTLER, AE200) both before and

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