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Hydrophilic surface-grafted poly(tetrafluoroethylene) membranes using in pervaporation dehydration processes

Chen-Yuan Tu [a,b], Ying-Ling Liu [a,b,*], Kueir-Rarn Lee [b,c], Juin-Yih Lai [a,b]

[a] Department of Chemical Engineering, Chung Yuan University, Chungli, Taoyuan 32023, Taiwan
[b] R&D Center for Membrane Technology, Chung Yuan University, Chungli, Taoyuan 32023, Taiwan
[c] Department of Chemical Engineering, Nanya Institute of Technology, Chungli, Taoyuan 32034, Taiwan

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Abstract

Preparation of hydrophilic poly(tetrafluoroethylene) (PTFE) membranes was performed by means of combined hydrogen plasma and ozone treatment and surface-initiating grafting polymerization. Acrylamide (AAm) and sodium 4-styrenesulfonate (NaSS) were used as monomers in grafting polymerization. Grafted PTFE membrane exhibited high hydrophilicity with a water contact angle of 38° and showed superior performance of pervaporation dehydration for various aqueous solutions of organic compounds. A high permeation flux of 422 g/m^2 h and a high separation factor of 4491 were observed with PTFE-g-PSSA membrane in pervaporation dehydration of a 90 wt.% aqueous solution of isopropanol (IPA) at 65 °C. The PTFE-g-PSSA membrane also exhibits advantages of wide application scopes, low temperature-sensitivity, good membrane stability, and operation durability in pervaporation dehydration processes.

Keywords: Poly(tetrafluoroethylene); Surface modification; Pervaporation; Dehydration

1. Introduction

Pervaporation receives a lot of studies as it has shown great achievements on separation of azeotropic mixtures or liquid mixtures containing substances of close boiling points, which are hard to be separated by conventional distillation processes. Aqueous solutions of alcohols and other organic compounds are major targets for pervaporation separation. Hydrophilic membranes, such as poly(vinylalcohol) and chitosan-based membranes, are good candidates for using in pervaporation dehydration owing to their water-permselectivity and high permeation fluxes [1–10]. However, hydrophilic membranes are highly swollen in aqueous solutions, and the swollen membranes usually lose their permselectivity and suffer with poor stability. Great efforts, therefore, attempt to improve the stability and mechanical properties of hydrophilic membranes. Some approaches are bringing cross-linked structures to membranes [11–18], blending chitosan with other polymers [19–21], and adding inorganic reinforcements into membranes [22,23]. Reduction of permeation flux is accompanied with these modifications. On the other hand, composite membranes prepared from casting hydrophilic polymers on another porous substrate exhibit some effectiveness on maintaining high permeation fluxes [11,24–26]. However, the stability of composite membranes was still not good enough for most of aqueous solutions of various organic compounds. In addition, preparation of such composite membranes involved complicated processes. Seeking for stable alternatives for pervaporation dehydration processes is attractive.

Poly(tetrafluoroethylene) (PTFE) membranes are attractive for using in pervaporation process owing to their superior chemical resistance, good thermal stability, and high mechanical strength. However, PTFE is highly hydrophobic, so as to be suitable for organic compound-selective pervaporation

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* Corresponding author. Tel.: +886 3 2654130; fax: +886 3 2654199.
E-mail address: ylliu@cycu.edu.tw (Y.-L. Liu).

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processes. For example, PTFE membranes were applied in removal of volatile organic compounds from water and gases [27–31]. On the other hand, Huang et al. [32,33] used resintered PTFE membranes for dehydration of ethanol aqueous solutions by means of vapor permeation process. Unfortunately poor performance was observed. One major problem of using PTFE membranes for pervaporation dehydration is their poor surface hydrophilicity to result in low water permeation flux and selectivity. In 1972, Aptel et al. [34] grafted *N*-vinylpyrrolidon and 4-vinylpyridine onto PTFE membranes through ^{60}Co irradiation-initiated polymerization. However, the permselectivity of the surface-grafted PTFE membrane was very low. Later, Tealdo et al. [35] prepared sulfonated-polystyrene grafted PTFE membranes for pervaporation dehydration. With increasing the surface hydrophilicity of PTFE membranes, a significant increase of permeation flux was achieved but the water permselectivity was still not high enough.

Continuing our studies on pervaporation dehydration, this work attempts to develop high performance PTFE membranes for pervaporation dehydration processes. Surface modification on PTFE membrane was performed with hydrogen plasma/ozone treatment and followed surface-initiating grafting polymerization. PTFE membranes possessing highly hydrophilic surfaces were obtained to show high performance in pervaporation dehydrations for various aqueous solutions of organic compounds, including hydrocarbon alcohols, tetrafluoropropanol (TFP), and dimethylformamide.

2. Experimental

2.1. Materials

Porous and crystalline poly(tetrafluoroethylene) membranes with a thickness of 80 μm were received from Nitto Denko Co., Ltd. Japan. Acrylamide (AAm) and sodium 4-styrenesulfonate (NaSS) were purchased from Merck Chemical Company and Fluka Chemie, respectively.

2.2. Surface activation on PTFE membranes

Hydrogen plasma treatment was performed with a capacity coupling electrodes (Dressler HF-Technik GmbH, Germany; model CESAR-1310) under the conditions of a hydrogen flow rate of 10 sccm (standard cm^3/min), a radio frequency of 13.56 MHz, a power of 50 W, a pressure of 13.3 Pa (0.1 Torr), and a reaction time of 180 s. After plasma treatment, PTFE membranes were immersed in 80 ml isopropanol (IPA). A continuous O_3–O_2 mixture stream (flow rate: 6 L/min.; O_3 concentration: 28 g/m^3) generated from an ozone generator (Ozone Group, Taiwan) was bubbled through the liquid at room temperature for about 15 min. The liquid was icy cooled. PTFE membranes were drawn out and then dried at room temperature under vacuum.

2.3. Surface-initiating polymerization of PTFE membranes [36]

Two monomers of AAm and NaSS were utilized in the polymerization. First, the selected monomer was dissolved in water to form a 15 wt.% aqueous solution (50 mL). The activated PTFE membranes were immersed in the monomer solution. The reaction solutions were then degassed by argon purge and frozen degas process for three times. Under stirring the reaction system was heated to 80 °C with a silicon oil bath. After reaction at 80 °C for 24 h, the reaction system was cooled with an ice bath. The PTFE membranes were then drawn out from the solutions, washed with water and acetone under ultrasonic, and dried at room temperature under vacuum. The obtained PTFE membranes were coded as PTFE-g-PAAm and PTFE-g-PNaSS, respectively. PTFE-g-NaSS membrane was further treated with 1 M $HCl_{(aq)}$ solution at room temperature for 5 h to convert the sodium sulfonate groups to sulfonic acid groups (PTFE-g-PSSA). The degree of grafting polymerization (DG) was determined from

$$\mathrm{DG} = \frac{W_b - W_a}{A} \tag{1}$$

where W_a and W_b are the weights of PTFE membranes before and after grafting polymerization, respectively; and A is the area of PTFE membrane.

2.4. Instrumental analysis

Water contact angles were measured with an angle meter (Automatic Contact Angle Meter, Model CA-VP, Kyowa Interface Science Co., Ltd. Japan) at room temperature. Distilled water (5 μL) was dropped on the sample surface at 10 different sites. The average of 10 measured values for a sample was taken as its water contact angle. Scanning electron micrographs (SEM) were recorded with a Hitachi S-3000N SEM. PTFE membrane fixed at the sample holder was coated with Au by sputtering and was then applied to observation. FTIR-ATR spectra were obtained with a Perkin Elmer Spectrum One FTIR equipped with a multiple internal reflectance apparatus and a ZnSe prism as an internal reflection element. The angle of incidence of IR beam is 45°. X-ray photo spectroscopy (XPS) analysis was conducted with using a Thermo VG-Scientific Sigma Probe ESCA (British) using an Al Kα line as a radiation source. The background pressure of the analytical chamber was 267×10^{-8} Pa (2.0×10^{-8} Torr) and the take-off angle of photoelectrons was 90° with respect to sample surface. The sensitivity factor for C, F, O, N, S, and Na is 1.00, 4.43, 2.93, 1.80, 1.67, and 8.52, respectively. Software of XPSPEAK was applied for curve fitting with using the Gaussian–Lorentzian mixture function (mixture ratio: 80/20).

2.5. Measurement of degree of swelling

PTFE membrane was completely dried under reduced pressure at room temperature and then weighed. The dried