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Polyarylethersulfone with cardo/poly (vinyl pyrrolidone) blend membrane for pervaporation of methanol/methyl *tert*-butyl ether mixtures

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ABSTRACT

Polyarylethersulfone with cardo (PES-C) and poly (vinyl pyrrolidone) (PVP) blend membranes with various PVP contents were prepared for pervaporation separation of methanol (MeOH)/methyl *tert*-butyl ether (MTBE) mixtures. The membranes were characterized using Fourier transform infrared (FTIR), wide angle X-ray diffraction (WAXRD), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), contact angle metering and positron annihilation lifetime spectroscopy (PALS). The influence of PVP content on the swelling behavior and mechanical properties was studied. The effect of PVP content on the pervaporation performance was investigated and discussed in terms of the solution-diffusion mechanism. With incorporation of PVP, the permeation flux increased and the separation factor increased as well in the PVP content range of 0–16 wt%. Of all the as-fabricated blend membranes, the one containing 84 wt% PES-C and 16 wt% PVP showed the highest separation factor of 889 and a permeation flux of $3.44 \text{ kg } \mu\text{m}^{-2} \text{ h}^{-1}$ for a 15 wt% MeOH feed mixture at 40°C .

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1. Introduction

The industrial production of methyl *tert*-butyl ether (MTBE) is via reaction of methanol (MeOH) with isobutylene. Up to 20% excess MeOH is normally used to improve the reaction conversion rate. This encounters a difficulty in purification because MeOH and MTBE form an azeotrope consisting of 14.3 wt% MeOH at atmospheric pressure [1]. In the chemical industry, MeOH/MTBE mixture is first prefractionated by water washing, and then further separated via distillation to recycle the MeOH to the reactor [2]. However, this conventional process has two main drawbacks of high capital investment and energy consumption. Pervaporation (PV) has recently gained much attention as an alternative or supplement for the separation process mentioned above. The main advantages of PV over the conventional processes include energy-saving, modularity and easy scale-up, the ability to separate heat-sensitive components and the lack of theoretical limitation in the final product purity [3]. Extensive efforts have been devoted to designing the optimal membrane for PV separation of MeOH/MTBE mixture. The most studied polymers include cellulose acetate (CA) [4–12], poly (vinyl alcohol) (PVA) [13–17] and

chitosan (CS) [18,19]. Nevertheless, most of the membranes in the literature show an obvious trade-off behavior in pervaporation.

Polyarylethersulfone with cardo (PES-C) is a new kind of thermoplastics engineering material [20]. It is a thermally stable polymer with high mechanical properties and chemical resistance. With regard to its chemical structure, PES-C can be taken as poly (ether sulfone) modified by the introduction of the rather bulky and polarizable phenolphthalein group in place of oxygen atom. The presence of the cardo group on the PES-C backbone reduces its crystallinity. As confirmed in our previous work, the intermolecular distance (0.51 nm) between the PES-C polymer chains lies between the kinetic diameter of MeOH (0.40 nm) and MTBE (0.62 nm). The separation factors for MeOH/MTBE mixtures are at a reasonable industrial level; however, the comparatively low permeation fluxes need to be enhanced.

In the present work, poly (vinyl pyrrolidone) (PVP) was chosen as an additive to blend with PES-C in order to increase the permeation flux without appreciably reducing the separation factor. PVP is soluble in water rather than MTBE. The much stronger interaction between PVP and MeOH than that between PVP and MTBE makes it reasonable to believe that the separation performance of pristine PES-C may be enhanced by incorporating PVP into the PES-C matrix. In addition, the low crystallinity of PVP may induce a suppression of total crystallinity of the blend membranes. This is favorable to the transport of penetrant molecules. In the literature, PVP has already been used to blend

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with other polymers to prepare PV membranes applied to separate tetrahydrofuran (THF)/water [21–23], THF/MeOH [23], ethanol (EtOH)/ETBE [24], EtOH/cyclohexane (CHx) [25,26] and MeOH/MTBE [5,27] mixtures. The separation performance is enhanced as a result of the high affinity of pyrrolidinone sites towards water, MeOH and EtOH. Additionally, PVP can influence the membrane structure and further improve the separation performance.

Herein, PES-C/PVP blend membranes with various PVP contents were prepared for pervaporation separation of MeOH/MTBE mixtures. Scanning electron microscopy, water contact angle metering, wide angle X-ray diffraction, Fourier transform infrared, thermo gravimetric analysis and positron annihilation lifetime spectroscopy were used to characterize the as-prepared blend membranes. Swelling and mechanical property were studied. The effect of PVP content on the microstructure and separation performance of the membranes was also investigated.

2. Experimental

2.1. Materials

PES-C ($M_w=117000\text{ g mol}^{-1}$) was purchased from Xuzhou Engineering Plastic Factory (Jiangsu, China). PVP ($K30$, $M_w=40000\text{--}60000\text{ g mol}^{-1}$) was supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). *N*-methyl pyrrolidone (NMP), methanol (MeOH) and methyl *tert*-butyl ether (MTBE), of analytical grade, were obtained from Shanghai Chemical Reagent Store (Shanghai, China) and used without further purification.

2.2. Membrane preparation

Seven membrane casting solutions were prepared with different PVP concentrations. The polymer concentration was 6 wt% in all the solutions, while weight percentage of PVP in the final membranes was varied from 0 to 24 wt% with an interval of 4 wt%. Desired amount of PES-C and PVP for each blend was dissolved in NMP under vigorous stirring at room temperature for 24 h to get a homogeneous mixture. The solution was placed statically overnight to get rid of bubbles. Then the bubble-free solution was cast onto a clean glass plate followed by drying at 80 °C for 8 h. The obtained membranes were rapidly peeled off, dried and stored for further use. The as-prepared blend membranes were designated as M0, M1, M2, M3, M4, M5 and M6 with respect to the weight percentage of PVP (Table 1). The thickness at random 5 points of the transparent membranes was measured with a digital micrometer (DP-25, Beijing Yaou Depeng Co. Ltd., China). The average thickness was around $21 \pm 1\ \mu\text{m}$, as confirmed by SEM.

The membranes were dried in a vacuum oven at 100 °C, weighted and then immersed in a MeOH (15 wt%)/MTBE mixture at 40 °C to investigate the extraction of the PVP from the membranes. After tens of hours, they were dried again in the vacuum oven at 100 °C and weighed to get the dried weight. The same procedure was repeated 4 times to study the leaching of PVP.

Table 1

Membrane thickness, glass transition temperature (T_g), crystallinity and degree of swelling in 15 wt% MeOH feed at 40 °C.

Membrane	M0	M1	M2	M3	M4	M5	M6
PVP content (wt%)	0	4	8	12	16	20	24
Actual PVP content (wt%)	0	2.9	6.3	9.8	13.6	17.2	21.4
Thickness (μm)	20	21	22	20	21	22	21
T_g (°C)	260.2	257.8	256.5	254.8	252.4	250.6	–
Degree of swelling (%)	6.2	7.1	8.4	9.6	11.2	13.8	15.3
Crystallinity (%)	53.2	49.2	47.1	42.7	37.2	35.1	31.6

The results show that PVP fraction suffers extraction in the MeOH (15 wt%)/MTBE mixture. However, the weight of the membrane begins to level off after 24 h. This suggests that the membrane is stable and the PVP does not extract after being immersed into the feed for 24 h. In this work, the membrane samples were immersed in the liquid mixture for 48 h. After that, they were assembled to perform pervaporation. Therefore, separation performance of the as-prepared membranes is stable and reliable. Moreover, the actual PVP content can also be calculated from the difference in the mass of the membranes before and after leaching, as listed in Table 1.

2.3. Membrane characterizations

The morphology of cross-section of the membranes was measured using a scanning electron microscope (SEM, LEO 1530, Oxford instruments) operating at EHT=20 kV. Fourier transform infrared (FTIR) spectra of the as-prepared blend membranes were recorded in the range 600–2000 cm^{-1} with an accumulation of 16 scans on a Nicolet Avatar 300. The thermal stability of the membranes was analyzed using differential thermal analysis and thermo gravimetric analysis (TGA) (Netzsch DSC 204 Phoenix). Accurately weighted (5 mg) samples were placed into aluminum cups and heated from room temperature to 900 °C at a constant heating rate of 10 °C min^{-1} under constant nitrogen purging at 10 ml min^{-1} . The structure of the membranes was characterized by wide angle X-ray diffraction (WAXRD) (XRD Panalytical X'pert Philip, Holland) using Cu $K\alpha$ radiation. The diffraction was operated at 40 kV and 30 mA in the 2θ range of 5–27° using a step size of 0.0167° and a counting time of 10 s per step to identify the change in the crystal structure of the membranes. From WAXRD pattern of the blend membranes, the crystallinity can be obtained after smooth treatment and peak separation with the help of MDI Jade6.0 software. The mechanical properties of the membranes were studied using a testing machine (WDS-5, Tianshui Hongshan Testing Machine Co. Ltd., China). Static contact angle of the membranes was measured by pendant drop method using a contact angle meter (SL200B, SOLON TECH, Shanghai, China) at room temperature. The value is the average over 10 measurements taken at different locations on the same membrane and the errors are less than 4%. Positron annihilation lifetime spectroscopy (PALS) experiments were performed using an ORTEC fast–fast coincident positron lifetime spectrometer with a time resolution of about 250 ps. The positron source ^{22}Na sealed in 7 μm thick Kapton foil (grade HN from Goodfellow) was sandwiched between two pieces of identical blend membranes (sample–source–sample). All spectra were collected with total counts of about 1.5×10^6 . The PATFIT program was used to analyze the spectra into three mean lifetime components, in which neither constraint nor source correlation was applied.

2.4. Swelling behavior and sorption experiments

Pre-dried membranes were weighed and immersed in a MeOH (15 wt%)/MTBE mixture at 40 °C for 48 h to reach equilibrium swelling. The sample was taken out at regular intervals, wiped with tissue paper rapidly to remove the surface solvent, and weighed as quickly as possible, then dipped into the solution again. The same procedure was continued until the weight of the swollen sample constant. All the experiments were repeated at least for three times to get the average results with the errors less than 3%. Based on the weight of the adsorbate, the degree of swelling (DS) is calculated as follows:

$$DS(\%) = \frac{m_w - m_d}{m_d} \times 100 \quad (1)$$

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