



Effect of TiO₂ nanoparticles on the surface morphology and performance of microporous PES membrane

Jing-Feng Li^{a,b}, Zhen-Liang Xu^{a,*}, Hu Yang^a, Li-Yun Yu^a, Min Liu^a

^a State Key Laboratory of Chemical Engineering, Chemical Engineering Research Center, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

^b SINOPEC Beijing Research Institute of Chemical Industry, Beijing 100013, China

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ABSTRACT

PES–TiO₂ composite membranes were prepared via phase inversion by dispersing TiO₂ nanoparticles in PES casting solutions. The crystal structure, thermal stability, morphology, hydrophilicity, permeation performance, and mechanical properties of the composite membranes were characterized in detail. XRD, DSC and TGA results showed that the interaction existed between TiO₂ nanoparticles and PES and the thermal stability of the composite membrane had been improved by the addition of TiO₂ nanoparticles. As shown in the SEM images, the composite membrane had a top surface with high porosity at low loading amount of TiO₂, which was caused by the mass transfer acceleration in exposure time due to the addition of TiO₂ nanoparticles. At high loading amount of TiO₂, the skinlayer became much looser for a significant aggregation of TiO₂ nanoparticles, which could be observed in the composite membranes. EDX analysis also revealed that the nanoparticles distributed in membrane more uniformly at low loading amount. Dynamic contact angles indicated that the hydrophilicity of the composite membranes was enhanced by the addition of TiO₂ nanoparticles. The permeation properties of the composite membranes were significantly superior to the pure PES membrane and the mean pore size also increased with the addition amount of TiO₂ nanoparticles increased. When the TiO₂ content was 4%, the flux reached the maximum at 3711 L m^{−2} h^{−1}, about 29.3% higher than that of the pure PES membrane. Mechanical test also revealed that the mechanical strength of composite membranes enhanced as the addition of TiO₂ nanoparticles.

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1. Introduction

Polyethersulfone (PES) is a kind of polymer with good performance and now has been widely used for microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and gas separation application [1–5]. It has lots of merits like high temperature and good chemical resistance, wide pH tolerances, easy to be fabricated into membrane or modules of variable configurations, broader range of pore sizes. Phase inversion process is the most common used method for the preparation of PES membranes. In this process a homogeneous solution was formed at first and then immersed in a non-solvent bath to form the membrane [6–8].

To improve the properties of polymeric membranes including antifouling, permeation, thermal stabilities, and mechanical properties, inorganic nanoparticles have been introduced as filler to prepare composite membrane in recently years, and their application fields have covered microfiltration [9,10], ultrafiltra-

tion [11–17], gas separation [18,19], as well as pervaporation [20]. Among the mostly used inorganic nanoparticles, nano-sized titanium dioxide (TiO₂) is special interested for its good performance like high hydrophilicity, good chemical stability, antibacterial property, avirulent et al. [21], and anatase TiO₂ could also be used as a photocatalyst in waste water treatment [22]. Three methods have been reported to prepare polymer–inorganic composite membranes: (1) Disperse the nanoparticles in the casting solution directly and prepare the composite membranes via phase inversion [11–16]; (2) Add the prepared sol containing nanoparticles in the casting solution and prepare the composite membranes via phase inversion [17,23,24]; (3) Dip the prepared membrane in the aqueous suspension containing nanoparticles and prepare the composite membranes via self-assembling [25,26].

Some authors have reported that the membrane morphology could be modified by the addition of nanoparticles. Yang's [11,17] work showed that as the addition amount of TiO₂ nanoparticles increased, cross section changed from macrovoid to sponge-like for the increasing viscosity of casting solution. In additional, Cao et al. [14] investigated the surface roughness of the membrane with and

* Corresponding author. Tel.: +86 21 64252989; fax: +86 21 64252989.

E-mail address: chemxuzl@ecust.edu.cn (Z.-L. Xu).

without nanoparticles by SEM or AFM and found that the surface became smoother as the addition of nanoparticles. But there is no report on the change of pore morphology on membrane surface because most works focused on ultrafiltration membrane and in this case the surface pore was not visible in SEM images.

In this study, the first method was used to prepare PES–TiO₂ composite membranes combined with immersion precipitation and vapor induced phase separation (VIPS). It was found that TiO₂ nanoparticles affect the surface morphology greatly for its specific surface properties. The interface mass transfer in VIPS stage would change largely by the addition of TiO₂ nanoparticles and different surface morphologies were obtained. The modified surface morphology induced by the addition of TiO₂ nanoparticles led to better hydrophilicity and permeation properties. This phenomenon has not been mentioned in the past reports. The contact angle, permeation, pore size, thermal stability and mechanical properties of the composite membranes were investigated. The effect of TiO₂ nanoparticles on the precipitation kinetics especially in VIPS process was discussed. The special interaction between TiO₂ nanoparticles and PES was also mentioned.

2. Experiment

2.1. Materials

The membrane-forming polymer, polyethersulfone [Characteristic Viscosity: $\eta = 0.48$ dL/g, density = 1.370 g cm⁻³] was produced by Jilin Jida High Performance Materials Co. Ltd. (China). The polymer was dried at 90 °C for 3–4 h prior to the used. Nano-sized anatase titanium dioxide (AEROXIDE® TiO₂ P25, mean particle size: 21 nm) was purchased from Degussa (Germany). *N,N*-dimethylacetamide (DMAc) was purchased from Shanghai Xiang-Yang Chemical Reagent Corporation (China). Diethylene glycol (DegOH) was purchased from Shanghai Lingfeng chemical reagent Corporation (PR China). All the water used in this work was deionized water.

2.2. Preparation of membrane

The flat membranes were prepared by combined vapor induced phase separation/immersion precipitation process. The casting solutions consisted of 15 wt.% PES, 0–5 wt.% TiO₂, and mixed solvent (DegOH:DMAc = 1:1). First DMAc and DegOH were mixed and then TiO₂ powders were added and stirred at a low speed for 30 min with ultrasonic vibration to avoid the serious aggregation of particles. Finally the casting solutions were prepared by dissolving PES powders in the above solutions. After stirred for 72 h, the casting solution was degassed at 20 °C for at least 24 h to remove air bubbles, and then cast on a glass plate using a casting knife with a gap of 380 μ m at 20 °C. The casting solution was firstly exposed in an air environment with relative humidity (RH) of 50% for 30 s and then immersed in a non-solvent coagulation bath (deionized water). The prepared membranes were washed with deionized water every 4 h in the first days and kept in deionized water till used.

2.3. XRD analysis

X-ray diffraction patterns were obtained with an X-ray diffractometer (D/max-rB 12 kW Rigaku, Japan; 45 kV, 40 mA) operated at 50 mA and 50 kV from 10° to 80°.

2.4. Thermal analysis

Differential thermal analysis (DSC) and thermal gravitational analysis (TGA) were used to investigate the glass transition

temperature (T_g) of membranes and their thermal property. In DSC measurement (PerkinElmer Pyris Diamond), the sample was first heated to 300 °C at a speed of 10 °C/min and kept for 5 min under nitrogen atmosphere to eliminate the effect of the thermal history, then the sample was cooled down to 50 °C and the second scan started from 50 °C to 300 °C. The onset of the transition in the heat capacity was defined as glass transition temperature (T_g). The thermal stability of the PES membrane and PES–TiO₂ membranes was evaluated by TGA (TGA, TA SDT-Q600). The TGA measurements were carried out under nitrogen atmosphere at a heating rate of 10 °C/min from 25 °C to 900 °C. The decomposition temperature (T_d) was defined as the temperature at 3% weight loss.

2.5. SEM and EDX analysis

The wet membranes were immersed in ethanol for 24 h and then dried in air at room temperature. Samples of the membranes were frozen in liquid nitrogen and then fractured. Cross section and surface of the membranes were sputtered with gold and then transferred to the microscope. The morphology of the cross section and surface of the membranes were inspected by SEM using a JEOL Model JSM-6360LV scanning electron microscope (Tokyo, Japan). For the same sample for SEM, the linescan of spectrum of energy dispersion of X-ray (EDX, S250, EDAX) was used to investigate the nanoparticle distribution on top surface of the composite membrane.

2.6. Water contact angles

Water contact angles (θ) were measured at 25 °C and 50% RH on a contact angle system (OCA20, Dataphysics Instruments, Germany). 1 μ L water was carefully dropped on the top surface and the dynamic contact angles were determined using the high speed optimum video analysis system.

2.7. Permeation properties

A self-made dead-end stirred cell (effective area 19.63 cm²) was used to measure the pure water flux of the PES membranes. The pure water penetration flux is defined as:

$$\text{PWP} = \frac{Q}{A \times T} \quad (1)$$

where Q is the volume of the permeate pure water (L), A is the effective area of the membrane (m²), and T is the permeation time (h).

2.8. Porosity and pore size

The porosity was determined by gravimetric method, defined as:

$$\varepsilon = \frac{m_1 - m_2}{\rho_w \cdot A \cdot l} \quad (2)$$

where m_1 is the weight of the wet membrane; m_2 is the weight of the dry membrane; ρ_w is the water density (0.998 g cm⁻³); A is the effective area of the membrane (m²), l is the membrane thickness (m).

Mean pore radius was determined by filtration velocity method. According to Guerout–Elford–Ferry equation, r_m could be calculated [27]:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \cdot A \cdot \Delta P}} \quad (3)$$

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