Journal of Membrane Science 467 (2014) 253–261

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Thermally stable and solvent resistant self-crosslinked TiO_2/PAN hybrid hollow fiber membrane fabricated by mutual supporting method

Wanbin Li [a], Zhihong Yang [a], Qin Meng [b], Chong Shen [b], Guoliang Zhang [a,*]

[a] Institute of Oceanic and Environmental Chemical Engineering, College of Chemical Engineering and Material Science, Zhejiang University of Technology, Hangzhou 310014, PR China
[b] Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 3 August 2013
Received in revised form
20 April 2014
Accepted 14 May 2014
Available online 21 May 2014

Keywords:
Hybrid membrane
Titanium dioxide
Self-crosslink
Solvent resistance
Thermal stability

ABSTRACT

Organic/inorganic blend and self-crosslink reaction are elaborately incorporated to fabricate thermally stable and solvent resistant self-crosslinked TiO_2/PAN hybrid membranes. This new fabrication method is a kind of mutual supporting technique which does not require a separate crosslinker or a catalyst. The prepared TPAN membrane shows excellent thermal stability which can persist up to 400 °C without any large mass loss and has good solvent resistance in various boiling systems including N,N-dimethylacetamide. The hybrid membrane also holds a very big BET surface area of 8.36 m^2/g at 250 °C and can be successfully used as structured packing for distillation to separate IPA/water mixture. An extremely low mass transfer time $1/(K_G a)$ of 0.1 s indicates that the hybrid membrane has excellent mass transfer performance. Similarly, for gas separation, because formed TiO_2 can effectively reduce the pore size of membrane dense layer, the hybrid membrane also presents a good prospect in application under harsh environments.

1. Introduction

As an important energy-efficient and environmentally friendly separation medium, membranes have been successfully applied in many fields [1]. In some important processes (such as distillation in hollow fibers [2–5], gas separation [6–9], organic solvent filtration [10–14], fuel cell [15–18] and catalytic reactor [19,20], etc.), the thermal stability and solvent resistance of the membranes are urgent requirements. Polymers are the most widely used membrane materials, but their thermal stability and solvent resistance are tender due to their natural properties. Ceramic membranes can practice in some aggressive solvents and high temperature system, but the fragility in materials, shaping and relative high prices limited the application of the ceramic membranes. Meanwhile, their upscaling is less straightforward [20].

Therefore, more and more attentions are being drawn on the new types of thermally and solvent stable membranes in recent years. They are mainly divided into two research directions: first; hybrid membrane, inorganic nanoparticles as fillers are introduced into polymer membrane to reduce the swelling of membrane in some solvents. Vanherck et al. used the hollow spheres with silicalite-1 shell as filler into PDMS to fabricate mixed matrix membranes, and found that swelling in toluene, dichloromethane and ethyl acetate can be decreased [21]. In general, the fillers in polymers lead to the reinforcement of membranes and consequently decrease swelling, enhancing their chemical stability. This strategy can just reduce the amount of swelling in some solvents to a certain extent but the chemical structure has not been changed. Moreover, the inorganic nanoparticles is in the polymer, so which cannot protect the membrane from high temperature that higher than the distortion temperature. As a result, if the polymer cannot stand some solvents and high temperature, the mixed matrix membrane also cannot stand those solvents and temperature. Second; crosslinked membrane, by using of intermolecular crosslinking materials, the bonding force between the molecules is strengthened and tends to form a three-dimensional mesh structure. In this case, covalent crosslinking has been used for various membranes to improve their dimensional stability and solvent resistance successfully [22]. For example, crosslinked polyimides PI-membranes have been used for gas separation [23], pervaporation [24,25] and solvent resistant nanofiltration [26] due to their strong organic solvent resistance and thermal stability. Li et al. proposed the use of photochemical crosslinking to improve the thermal stability and organic solvents resistance of polystyrene membranes [27]. All these facts show that self-crosslinking is a commendable method to improve the solvent

* Corresponding author. Tel./fax: +86 571 88320863.
E-mail address: guoliangz@zjut.edu.cn (G. Zhang).

http://dx.doi.org/10.1016/j.memsci.2014.05.019
0376-7388/

resistance and thermal stability. But the solvent resistance tests in these previous studies were just carried out at room temperature, the solvent resistance and the thermal stability at higher temperatures should be more investigated. Meanwhile, the crosslinking techniques often require the introduction of separate crosslinker molecule and catalyst. It often takes at least two reaction-steps for the crosslinker molecules to fulfill crosslinking, thus the process complexity and uncontrollability will obviously increase. In addition, those self-crosslink reactions have too many strict requirements on the catalyst and reaction conditions [22].

To produce a membrane with strong solvent resistance and thermal stability, the density of self-crosslinking should be increased and the self-crosslink reaction should be simplified. By analysis, we notice that the polyacrylonitrile (PAN) membrane can meet this challenge very well. PAN has a chain of carbon connected to one another. It is horn-like, hard and high-melting material with limited solvent solubility. It has been formed consensus that PAN-based carbon fiber is stronger than other polymers-based carbon fiber [28]. PAN membranes are also widely used in ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and pervaporation (PV). It has high thermal stability and no obvious heat distortion temperature [29–33]. Most importantly, if the PAN is heated, the reactions between two nitrile groups will occur, thus the macromolecules will crosslink together through the chemical bonds and make PAN membranes with good chemical stability. In our previous study [34], the PAN hollow fiber membrane was directly heat-treated, the solvent resistance and thermal stability of the membrane is improved obviously, and the membrane can be used for distillation successfully. According to the observation of SEM, it has shows that the morphology of heat-treated PAN hollow fiber membranes is denser with increasing the heat-treatment temperature. If we want to obtain a membrane that maintain an intact pore structure as the original membrane, we should introduce a high thermally stable material that can prevent the tiny deformation.

Herein, we present a new way named mutual supporting method to fabricate self-crosslinked TiO_2/PAN hybrid membrane that does not require a separate crosslinker or a catalyst and combine the hybrid and crosslinking. The PAN and TiO_2 will support each other when the membrane is fabricated. Thus the obtained hybrid membrane keeps an original porous bulk structure as the results of the produced TiO_2 to prevent collapse of the pore as a scaffold. The membrane exhibits both excellent thermal stability and solvent resistance. When the TiO_2/PAN hybrid membranes are used as structured packing for distillation that requires good thermal stability and high solvent resistance, they show excellent performance in separation. Similarly, for gas separation, the TiO_2/PAN hybrid membranes also present a good prospect in application under harsh environments.

2. Experimental

2.1. Materials

All solvents used are of analytical reagents (A.R. grade) including tetrabutyl titanate (Meixing Chem., China), ethanol, isopropanol and cyclohexane acetic acid and acetone (Sinopharm Chemical Co., China), N,N-dimethylacetamide (DMAc), ammonia water and toluene (Changzheng Chemical Reagent, China). Deionized water was obtained from a self-made RO-EDI system, in which ion concentration was analyzed by IRIS Intrepid ICP and Metrohm 861 Compact IC and controlled to meet the experimental requirement of conductivity $\sigma \leq 0.5\ \mu S\ cm^{-1}$. PAN membranes were self-made membranes with molecular weight cut-off 60,000 Da. The membranes were prepared by a wet-spinning process and the molecular weight cutoff of the membranes was determined by bovine serum albumin (BSA).

2.2. Preparation of TiO_2/PAN hollow fibers

Titania sol–gel tetrabutyl titanate (TBT) was dissolved into a mixture solvent containing ethanol and acetic acid at ambient temperature under continuous stir. Deionized water was added to the above solution. The final ratios (v/v) were TBT: CH_3COOH: C_2H_5OH:H_2O=1:0.3:5:0.15. Then the PAN hollow fiber membranes with a length of 14 cm were immersed in the titania sol–gel for 10 min under ultrasonic treatment. When these fibers were taken out, the residual solution in tube was removed by blowing with compressed N_2 and fibers were dried at 50 °C. The dipping–drying process was repeated 3 times for soaking thoroughly. The fibers coated with TBT sol–gel were calcined in air with a heating rate of 2 °C/min at different temperatures for different time. After thermal treatment, hollow fiber membranes were cooled naturally to room temperature. The membranes processing heat-treatment were labeled as "TiO_2/PAN-temperature-duration (hour)", for example, TPAN-250-6.

2.3. Membrane characterization

Thermal field emission scanning electron microscopy (SIRION-100, FEI, USA) and scanning electron microscopy (TM-1000, Hitachi, Japan) were used to observe the morphology of hollow fiber membranes. The radial distribution of titania in the cross section was analyzed by an X-ray energy dispersion spectroscopy (EDS) (GENESIS4000, EDAX, USA). X-ray diffraction (XRD) patterns were collected on a X'Pert PRO (PNAlytical, Netherlands) diffractometer in the reflection mode with CuKα radiation (40 kV, 40 mA, λ=0.154056 nm). The Brunauer–Emmett–Teller surface area (a_{BET}) was measured by Micromeritics-Accelerated Surface Area and Porosimetry system (ASAP 2020M+C, Micromeritics Instrument Co., USA). N_2 was used as an adsorbent. Samples were degassed at 363 K (10 °C→90 °C, 10 °C/min) for 90 min before the isothermal adsorption measurements which were conducted at 250 °C (10 °C→250 °C, 10 K/min) and at relative pressures in the range of 0.001–0.994. Thermal gravimetric analysis (TGA) (PERKIN ELMER, Model TGA 7) was carried out at a rate of 20 °C /min in the temperature ranges of 30–700 °C under air atmospheres. The chemical structure change of PAN was studied using Fourier Transform Infrared Spectrometer (Nicolet 6700, Thermo Scientific, USA). The tensile strength and elongation of hybrid TiO_2/PAN membranes were evaluated by using a tensile test instrument (HS-3000A, ShangHai Heson Instrument Co., China). Membrane porosity was obtained by mercury porosimetry (AutoPore IV 9500, Micromeritics, USA) and determinated repeatedly by the pycnometer method.

2.4. Distillation and gas permeation experiments

For distillation, the membrane PAN and TPAN-250-6 were chosen as structured packing for preparing membrane modules. All distillation experiments were run at total reflux. The experimental setup and the manufacture of membrane modules as well as detailed distillation process are similar to those in former reports [2–5].

The permeances of H_2, CO_2 and N_2 through the hybrid membranes were measured using pure cylinder gases. Testing modules were prepared by potting the fibers with epoxy in metal plugs. The target gas was used to rinse the tube before measurement to exclude other gases. The gas permeation rates were recorded using a bubble tube technique at room temperature (20 °C). The downstream pressure was 101 kPa.