



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Improvement in the permeation performance of hybrid membranes by the incorporation of functional multi-walled carbon nanotubes

Ting Wang^a, Jiang-nan Shen^b, Li-guang Wu^{a,*}, Bart Van der Bruggen^c

^a School of Environment Science & Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

^b Center for Membrane and Water Science, Ocean College, Zhejiang University of Technology, Hangzhou 310014, China

^c Department of Chemical Engineering, Process Engineering for Sustainable Systems (ProcESS), KU Leuven, W. de Croylaan 46, B-3001 Leuven, Belgium

ARTICLE INFO

Article history:

Received 29 November 2013

Received in revised form

30 March 2014

Accepted 28 April 2014

Available online 14 May 2014

Keywords:

Hybrid membranes

Multi-walled carbon nanotubes

Surface modification

Swelling absorption

Pervaporation

ABSTRACT

The morphology and swelling performance of poly(methyl methacrylate) (PMMA) and polyurethane (PU) membranes containing pristine multi-walled carbon nanotubes (P-MWCNTs) was investigated. Next, amino (NH₂) groups were introduced into the MWCNTs by chemical modification for improving their affinity to the membranes, thereby resulting in a better distribution of the MWCNTs in the membranes. The performance of the hybrid membranes was evaluated by swelling and pervaporation experiments. The Fourier transform infrared and transmission electron microscopy analyses showed that the addition of both the pristine and functionalized MWCNTs to the membranes improved their permeation performance. The dispersion of the P-MWCNTs and MWCNTs-NH₂ in the PU hybrid membranes was better than that in the corresponding PMMA hybrid membranes because of the rapid polymerization rate of the monomers and the elasticity of the membranes. Thus, the P-MWCNTs/PU and MWCNTs-NH₂/PU hybrid membranes performed better than the corresponding P-MWCNTs/PMMA and MWCNTs-NH₂/PMMA hybrid membranes. The surface functionalization promoted the affinity of the MWCNTs to the monomer solution and the polymer membranes. Compared to the P-MWCNTs, the MWCNTs-NH₂ showed an improved distribution in the PU and PMMA hybrid membranes, and the membranes containing the MWCNTs-NH₂ performed better than those containing the P-MWCNTs.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Because of their low power consumption, high separation performance and stability, membrane separation processes have a great potential for the environmental applications and energy production [1–4]. Membrane technology is a rapidly developing separation process in diverse fields such as chemical and environmental engineering, production of pharmaceuticals, and process intensification. However, there is a lot of potential in this technology that still needs to be explored or optimized. The development of new membrane materials is the key factor that enhances the application of the separation technology [5]. The separation properties of common organic polymer and inorganic membrane materials are difficult to determine because of the “trade-off” phenomenon [6,7]. In recent years, the development of nanomaterials and their use in membranes has provided a novel way to solve this problem. The preparation of organic–inorganic hybrid membranes containing inorganic nanomaterials can effectively overcome the trade-off phenomenon and significantly improve

the membrane performance [8,9]. For example, the hybrid polymer membranes containing AgCl nanoparticles did not only increase the separation performance by combining the Ag⁺ ions and the double bonds in the aromatic or olefinic molecules, but also decreased the effect of the Ag⁺ ions on the polymer–silver salt complex membranes [10,11]. In previous studies [12–14], hybrid membranes containing AgCl nanoparticles were prepared via *in situ* microemulsion polymerization. These hybrid membranes showed a high separation performance for benzene/cyclohexane mixtures. Hybrid membranes containing other inorganic particles, such as TiO₂ [15] and SiO₂ [16], have also been prepared and are commonly used for the CO₂ separation and wastewater treatment processes. However, these membranes are mainly used to separate only certain types of substances, such as aromatic hydrocarbons or CO₂ gas, indicating that they have a narrow application range. Therefore, the development of novel hybrid membranes with wider applications is an important research area in membrane technology. Among the many new inorganic nanomaterials suggested, carbon nanotube (CNT) is the most promising material because of its unique one-dimensional tubular structure and hydrophobic properties [17–20].

Since their discovery in 1991, CNTs, including single-walled and multi-walled CNTs (MWCNTs), have attracted significant research

* Corresponding author. Tel.: +86 571 88071024 7017; fax: +86 571 88865762.

E-mail address: wulug64@hotmail.com (L.-g. Wu).

attention because of their unique structure and outstanding physical, electronic, and thermal properties [21]. MWCNTs are of particular interest because of their relatively low cost and more advanced stage in commercial production. Recently, the addition of CNTs into the intermediate and final polymer products, as the CNT/polymer composites, has been studied. These composites significantly increase the separation performance of the hybrid membranes. Hinds et al. [18] reported that the aligned MWCNT membranes showed potential for application in chemical separation and sensing. Peng et al. [19] reported the preparation of novel nanocomposite membranes composed of polyvinyl alcohol (PVA) and chitosan-wrapped CNTs. Compared to pure PVA membranes, these PVA–CNT membranes showed both higher permeation flux and separation factor in the pervaporation (PV) for the separation of benzene/cyclohexane mixtures. Qiu et al. [20] reported the preparation of functionalized MWCNTs incorporated in a chitosan membrane for the separation of ethanol/water mixtures by PV. The CNT-filled membranes were easier to penetrate and exhibited a higher flux performance than the pristine membranes.

Similar to the preparation and application of most nanocomposite membranes, the dispersion and alignment of CNTs is crucial in improving the quality and properties of the resulting hybrid membranes. However, it is difficult to achieve a homogeneous distribution of CNTs in the polymer matrices because of the chemical inertness of CNTs and their tendency to form bundles, which significantly compromises the membrane performance. This challenge must be overcome in the preparation of CNT/polymer membranes. In particular, it is important to ensure an adequate interfacial adhesion between the CNTs and polymers to facilitate the uniform distribution of CNTs in the polymers and avoid agglomeration. To date, the improvements in the distribution of CNTs in membranes have only focused on the CNT surface modification.

The properties of the monomer and polymer are also key factors that affect the CNT distribution in a membrane. The characteristics of the dispersion of the same type of CNTs in different monomer and polymer materials are expected to vary; however, this topic has been rarely studied. In this study, polymethyl methacrylate (PMMA) and polyurethane (PU) membranes were used as the substrates for the preparation of the corresponding hybrid membranes containing different MWCNTs. This study aims to investigate the effect of different polymer materials on the distribution of pristine and functionalized MWCNTs in the corresponding hybrid membranes.

2. Experimental

2.1. Materials

Pristine MWCNTs with diameters ranging from 20 to 40 nm, inner diameter of ~5 nm, and 95% purity were manufactured by Nanotech Port Co., Ltd. (Shenzhen, China). H_2SO_4 and HNO_3 acids were purchased from Shanghai Reagent Factory (Shanghai, China). 2-Azobisisobutyronitrile (AIBN), methyl methacrylate (MMA), *N,N*-dimethylformamide (DMF), phenyl isocyanate (MDI), 1,4-butanediol (BDO), and dibutyltin dilaurate (DBTDL) were purchased from Reagent Chemical Manufacturing (Shanghai, China) and used as received without further purification. The polysulfone film used in this manuscript with a molecular weight cutoff of 20,000 was obtained from Hangzhou Development Center of Water Treatment Technology (Hangzhou, China).

2.2. Functionalization of MWCNTS

Carboxylic MWCNTs (MWCNTS–COOH) were prepared according to the method reported elsewhere [19]. First, the pristine MWCNTs

were treated with a mixed acid solution ($H_2SO_4/HNO_3=3/1$) at 80 °C for 6 h and then diluted with deionized water. The minor nanotube residues and impurities were removed via a reduced pressure distillation, and the bulk MWCNTs were washed with deionized water repeatedly to remove the traces of the acid completely. The MWCNTs were dried in a vacuum drying oven at 70 °C prior to further treatment.

The oxidized MWCNTs were dispersed in DMF and then refluxed in diisobutryl peroxide, which was synthesized from butanedioic anhydride and oxydol placed in an ice bath for several hours, at 80 °C for 10 d. The resulting mixture was washed with an excess of DMF, and the MWCNTs–COOH was obtained after the reduced pressure distillation and drying in an oven.

The MWCNTs–COOH were treated with 4,4-diaminodiphenylmethane dissolved in a mixture of pyridine and acetone at 140 °C for 48 h, diluted with deionized water, and then dried in a vacuum drying oven at 70 °C to afford the aminated MWCNTs (MWCNTs–NH₂).

2.3. Preparation of hybrid membranes containing MWCNTs

2.3.1. Preparation of MWCNTs–NH₂/PMMA

Certain amounts of different MWCNTs were added to 30 mL of MMA. The mixed solution was stirred for ~24 h and then placed in an ultrasonic bath at a fixed frequency for ~30 min in order to improve the MWCNT dispersion in the MMA and achieve a homogeneous mixture. Next, AIBN was added to this homogeneous mixture while stirring from 60 to 65 °C to initiate the polymerization reaction. When the viscosity of the reaction system reached ~300 mPa s, the reaction mixture was used to coat a polysulfone film (molecular weight cut-off (MWCO)=20,000). The hybrid membranes with different MWCNTs on the polysulfone film were incubated and obtained by continuing the polymerization reaction in a vacuum oven at 60–65 °C for another 12 h to allow the evaporation of the solvent.

2.3.2. Preparation of MWCNTs–NH₂/PU

Different MWCNTs were dispersed in 15 mL DMF using an ultrasonic probe (VC750, 150 W, 20 Hz) for 5 min and then stirred in a water bath at 45 °C for 10 min. MDI (5.75 g) was dissolved in 15 mL DMF using an ultrasonic bath (70 W, 42 Hz) and then added to the DMF containing the MWCNTs under stirring at 45 °C. After 30 min of constant stirring, 4.7 mL BDO and 50 μL DBTDL were sequentially added to the mixture while stirring vigorously at 45 °C to initiate the polymerization reaction. When the viscosity of the reaction system reached about 300 mPa s, the reaction mixture was used to coat a polysulfone film (MWCO=20,000). The hybrid membranes with different MWCNTs on the polysulfone film were incubated and obtained by continuing the polymerization reaction in a vacuum oven at 45 °C for another 10 h to allow the evaporation of the solvent.

2.4. Swelling and sorption measurements

The pre-weighed membranes were immersed in benzene or cyclohexane in a closed bottle at room temperature for > 48 h for achieving the swelling equilibrium state after dehydration in a desiccator. The membranes were periodically weighed until a constant mass was obtained. The membrane sample was then taken out from the liquid bath; the surface solution was wiped off carefully with a tissue paper; and then weighed in a tightly closed bottle. The amount of sorbed liquid in the membranes was expressed as the degree of swelling (DS), which was calculated

Download English Version:

<https://daneshyari.com/en/article/7022171>

Download Persian Version:

<https://daneshyari.com/article/7022171>

[Daneshyari.com](https://daneshyari.com)