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Poly(vinyl alcohol)–graphene oxide nanohybrid “pore-filling” membrane for pervaporation of toluene/*n*-heptane mixtures

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ARTICLE INFO

Article history:

Received 1 March 2013

Received in revised form

9 December 2013

Accepted 10 December 2013

Available online 2 January 2014

Keywords:

Dynamic pressure-driven assembly
Nanohybrid “pore-filling” membrane
Toluene/*n*-heptane separation
Graphene oxide

ABSTRACT

The stability of the membrane for pervaporation separation of aromatic/aliphatic mixtures is critical for industrial applications. To improve the stability of the membrane, a “pore-filling” membrane was prepared by dynamic pressure-driven assembly of a poly(vinyl alcohol)–graphene oxide (PVA–GO) nanohybrid layer onto an asymmetric polyacrylonitrile ultrafiltration membrane. The results of the swelling experiment suggest that the pore-filling structure could effectively reduce swelling of the nanohybrid membrane. Assembly of the nanohybrid membrane by molecular-level dispersion of GO in PVA led to enhanced affinity of the membrane to aromatic compounds and thus improved performance in the pervaporation of toluene/*n*-heptane mixtures. Moreover, the dynamic assembly process could easily be used to adjust the separation performance by controlling the pressure, filtration time, polymer, and GO concentration.

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1. Introduction

Separation of aromatic/aliphatic mixtures is one of the most important and difficult processes in the chemical industry. Traditional azeotropic distillation and extractive distillation are two techniques of choice for carrying out the separation. However, these techniques have many problems such as process complexity, large equipment investment, and high energy consumption. In recent years, there has been much interest on pervaporation as a separation technique for aromatic/aliphatic mixtures. This interest is due to its economy, simplicity, and minimal environmental impact. Pervaporation is based on the various sorption and diffusion properties of the mixture components in the membrane. Therefore, pervaporation has strict requirements for membrane material and membrane structure. Many studies have demonstrated that in pervaporation, the sorption selectivity plays a more important role than does diffusion selectivity of the membrane [1,2]. However, in order to obtain high selectivity for efficient separation of aromatic/aliphatic mixtures, the membrane must have both affinity to aromatic components and a rigid structure to resist excessive swelling. Aromatic compounds have a π electron cloud that usually has stronger affinity to polar polymers. Poly(vinyl alcohol) (PVA) has proved to be an ideal material for membranes used in separating aromatic/aliphatic mixtures because of its polar, hydrophilic and good membrane-forming

properties [3,4]. However, PVA is a semicrystalline compound whose polymer chains are closely packed because of intermolecular and intramolecular hydrogen bonding [5]. Homogeneous PVA membranes often perform poorly in pervaporation [6] because PVA molecules lack π electron acceptors; this leads to weak interactions between the membrane and the aromatic compounds. On the other hand, the affinity of the membrane material to aromatic compounds is also critical, as excessive affinity could damage the integrity of the membrane structure and reduce the separation performance. In this respect, improvement in the pervaporation performance has been achieved by adding inorganic particles to the polymer solution to form organic–inorganic hybrid materials. Such hybrid membranes have both membrane-forming properties of the polymer and physicochemical stability of the inorganic particles [4,7–9]. Recently, Jiang et al. [10] reported a novel graphite-filled PVA/chitosan hybrid membrane for pervaporation of benzene/cyclohexane mixtures. They found that both the permeation flux and separation factor increased by incorporating graphite into the polymer matrix. These improvements are due to the structure of graphite, which consists of repetitions of the hexagonal carbon ring similar to the benzene structure. The σ - and π -bond interactions between graphite and benzene could improve the separation performance.

Graphene oxide (GO), a compound with structure and physicochemical properties resembling those of graphite, has been similarly used to form hybrid membranes. GO may be integrated with other functional materials at a molecular/nanometer scale to create multifunctional GO-based composites because of its numerous oxygen-containing functional groups (e.g., hydroxyl, epoxide,

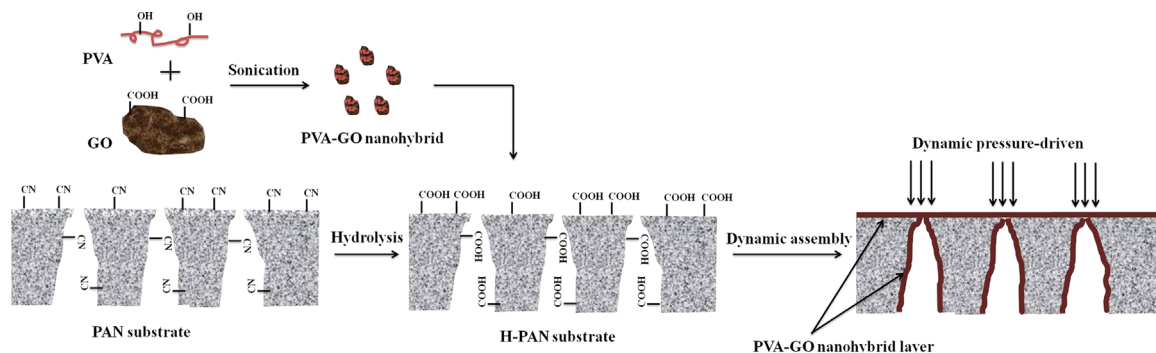
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and carboxyl groups). Moreover, it is possible to achieve a truly molecular-level dispersion of GO because GO can be dispersed at the individual-sheet level in aqueous solution [11]. Recently, small amounts of GO have been found to effectively reinforce PVA films. This reinforcement is ascribed to the molecular-level dispersion of GO sheets in the PVA matrix and the strong interfacial interaction between these two components [12,13]. Likewise, in the present study, the doping of GO into PVA membrane was hypothesized to improve the affinity of aromatic compounds through the interaction between σ and π bonds. This interaction enhances the selectivity of the membrane toward aromatic compounds, and thereby improves its performance in the separation of aromatic/aliphatic mixtures.

Besides membrane material, membrane structure is an important factor influencing membrane stability. The “pore-filling” membrane is a composite membrane with the separation layer formed onto the surface of porous substrates and into the sublayer pores. Pore-filling membranes have high affinities toward aromatic compounds and the ability to resist excessive swelling. Li et al. [14] grafted copolymers in the sublayer pores and onto the surface of an asymmetric polyacrylonitrile (PAN) ultrafiltration membrane, using the atmospheric dielectric-barrier-discharge plasma graft-filling technique. The synthesized pore-filling membrane suppressed swelling and enhanced selectivity. Dynamically formed membranes are prepared by filtration of a dilute solution containing specific membrane materials through a porous support [15,16]. Dynamic pressure-driven assembly is a useful process for filling defects in porous substrates, especially polymeric porous substrates with a wide pore diameter distribution. In the present study, specific dynamic transmembrane pressures were considered for fabricating pore-filling membranes by assembling the PVA–GO nanohybrid onto the surface of porous substrates and into the sublayer pores.

The PVA–GO nanohybrid membrane for pervaporation separation of toluene/*n*-heptane mixtures in this study was dynamically assembled onto a PAN substrate. As shown in Scheme 1, a stable nanoscale dispersion of the PVA–GO nanohybrid solution was obtained by simultaneously sonicating PVA and GO in solution. Afterward, the PVA–GO nanohybrid was assembled onto hydrolyzed PAN substrate by dynamically filtering the nanohybrid solution. Under the effects of transmembrane pressure, some of the PVA–GO nanohybrids in this process enter the sublayer pores to form the pore-filling structure. The pore-filling nanohybrid membrane was systematically characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and nanoindentation. The pore-filling nanohybrid membrane was used for separating toluene/*n*-heptane mixtures. The effects of dynamic pressure, filtration time, polymer, and GO concentration on the pervaporation performance of the membrane were investigated.



Scheme 1. Schematic illustration of the preparation of PVA–GO nanohybrid membranes by dynamic pressure-driven assembly.

2. Experimental

2.1. Chemicals and materials

Flat-sheet polyacrylonitrile ultrafiltration membranes were supplied by Sepro Membranes (MWCO, 20,000). Graphene oxide (GO) was obtained from Nanjing XFNANO Materials Tech Co. Ltd. (China). Poly(vinyl alcohol) (Mw 80,000), sodium hydroxide, toluene, and *n*-heptane were provided by the Beijing Chemical Factory (China). All chemicals were used as received without further purification.

2.2. Dynamic assembly of the PVA–GO nanohybrid membrane

First, specific concentrations of PVA solution and GO solutions were prepared. The PVA solution was blended with the solution of GO sheets, and the resulting mixture was subjected to intense sonication for 30 min. The PAN ultrafiltration membranes were hydrolyzed by immersing them in 2 mol/L sodium hydroxide aqueous solutions at 65 °C for 30 min [17]. The hydrolyzed membranes were rinsed with deionized water until the pH of the washings reached about 7.0. The membranes were loaded in a dead-ended filtration cell for the dynamic assembly (Scheme 2). The PVA–GO solutions were poured into the loaded dead-ended filtration cell, and filtration was carried out under a certain pressure. Afterward, the membranes were removed and dried in an oven at 75 °C for about 2 h. The PVA–GO nanohybrid membranes were subsequently stored for pervaporation tests.

2.3. Pervaporation experiments

The PVA–GO nanohybrid membranes had an effective area of 21 cm². They were evaluated using a pervaporation cell fabricated in our laboratory [18]. The permeate vapor was trapped in liquid nitrogen. For each pervaporation run, the membrane was subjected to 2 h conditioning to ensure that the membrane reached a steady state before sample collection. The permeate was collected at 2 h intervals. Three samples were collected for measurements. The experiments were carried out at a downstream pressure of 100 Pa, which was maintained by a vacuum pump. Fluxes were determined by measuring the weight of the liquid collected in the cold traps at specific times under steady-state conditions. The composition of the collected permeate was determined by gas chromatography (FULI 979011, China). The separation factor was calculated according to the following equation:

$$\alpha = \frac{Y_i/Y_j}{X_i/X_j} \quad (1)$$

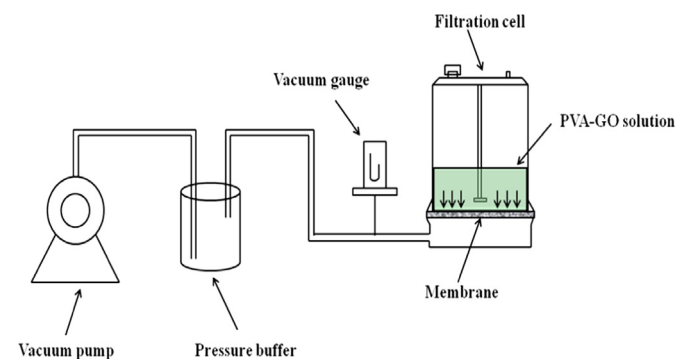
where Y_i and Y_j represent the mass fraction of toluene and *n*-heptane in the permeate, respectively; X_i and X_j represent the mass fraction of toluene and *n*-heptane in the feed, respectively.

2.4. Swelling experiments

The degree of swelling (DS) of the membranes was measured by immersing the membrane in 50 wt% toluene/*n*-heptane solutions at room temperature. After 30 h, the membrane was removed and quickly wiped with filter paper to remove the solvents. The membranes were weighted on an accuracy balance. The DS was calculated as follows:

$$DS = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s and W_d are the weights of the solvent-swollen and dry membranes, respectively.



Scheme 2. Dynamic pressure-driven assembly system for preparation of PVA-GO nanohybrid membrane.

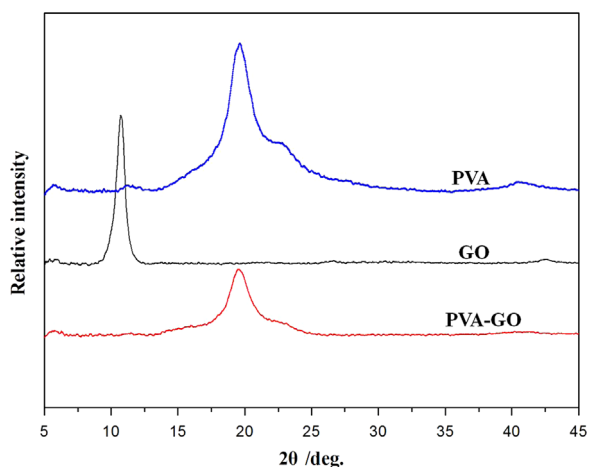


Fig. 1. XRD patterns of pure PVA, GO and PVA-GO nanohybrid. (Preparative conditions: 2.5 wt% PVA aqueous solutions with 0.1 g/L GO.)

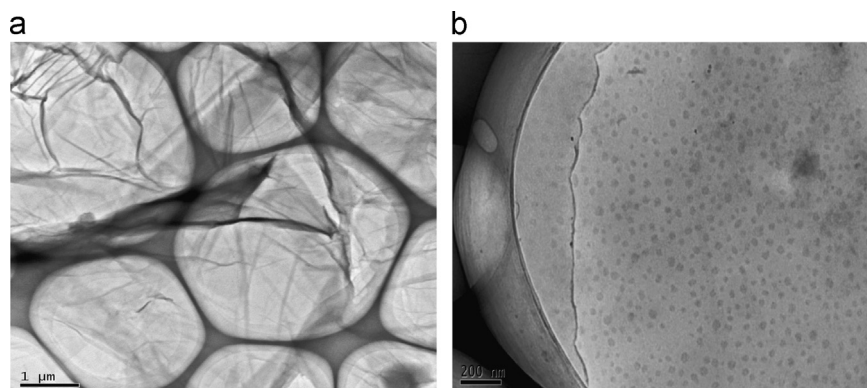


Fig. 2. TEM images of GO sheets before and after sonication. (a) GO sheets before sonication and (b) GO sheets after sonication in PVA solutions.

2.5. Characterization

The surface and cross-section morphologies of the composite membranes were observed by SEM (Model S-4800, Hitachi, Japan). All membrane samples were dried under vacuum. Transmission electron microscopy (TEM) measurements were carried out on a JEM-2010 microscope (JEOL, Ltd., Japan). Attenuated total reflection FTIR spectroscopy was performed on a Vertex-70 spectrophotometer (Bruker, Germany) to characterize the morphological changes of the nanohybrid assembled on the PAN substrate. Young's modulus and hardness were characterized using a Nano Indenter G200 (Agilent Technologies). Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) experiments were carried out at a heating rate of 10 °C/min under nitrogen atmosphere, using a TGA/DTA 6300 thermogravimetric analyzer. Differential scanning calorimetry (DSC) experiments were performed using a differential scanning calorimeter (DSC 60, Shimadzu, Japan). Measurements were done at room temperature.

3. Results and discussion

3.1. Characterization of the PVA-GO nanohybrids and nanohybrid membrane

It is well recognized that a stable dispersion at the nanoscale level is critical to achieving high-quality nanohybrid coatings [19,20]. X-ray diffraction (XRD) was used to determine whether the graphene oxide sheets were indeed present as individual graphene sheets in the nanohybrids [11]. The XRD patterns of PVA, GO, and PVA-GO nanohybrids are shown in Fig. 1. The typical diffraction peaks of GO and PVA were observed at about $2\theta = 10.7^\circ$ and $2\theta = 19.6^\circ$, respectively. However, when GO was dispersed in the PVA matrix, the diffraction peak of GO disappeared. This result clearly demonstrates that GO was fully exfoliated into individual graphene sheets in the PVA matrix [21–24]. To further verify the stable nanoscale dispersion of GO in PVA solution, TEM was used to characterize the GO sheets before and after sonication. The GO sheets before sonication were dozens of micrometers wide and overlapped with each other (Fig. 2(a)). After sufficient sonication in PVA solution, the size of the GO sheets sharply decreased to about 20 nm (Fig. 2(b)). These results suggest that the PVA-GO nanohybrid sheets were well dispersed in the nanoscale range. The PVA-GO nanohybrid sheets were thereafter deposited onto the PAN ultrafiltration membrane to form a uniform, dense nanohybrid membrane.

The PVA-GO nanohybrid membrane was characterized by FTIR spectroscopy. As shown in Fig. 3, the peaks at around 2243 and 1451 cm^{-1} , which are due to the $-\text{CN}$ group on the PAN substrate, disappeared after assembly with the PVA-GO nanohybrid sheets.

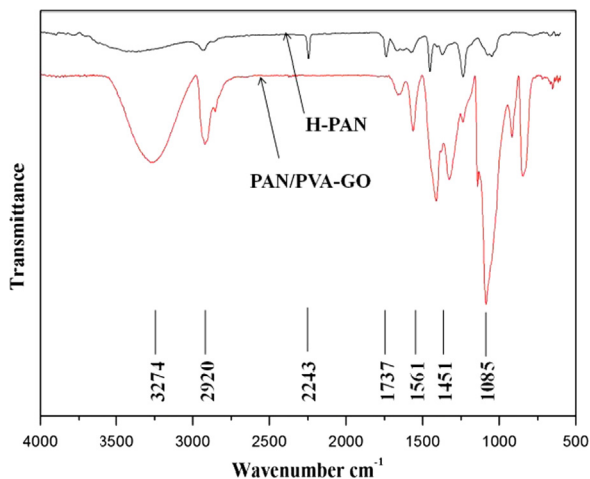


Fig. 3. FTIR spectra of hydrolyzed PAN substrate and PAN/PVA-GO nanohybrid membrane. (Preparative conditions: 10 min filtration time, 2.5 wt% PVA aqueous solutions with 0.1 g/L GO, dynamic pressure -0.08 MPa.)

Simultaneously, the peak at 3274 cm^{-1} attributed to the $-\text{OH}$ group sharply increased. These changes suggest that the surface of the PAN substrate was sufficiently covered by the PVA-GO nanohybrid sheets.

The surface and cross-sectional morphologies of the composite membrane are presented in Fig. 4. As shown in Fig. 4(a), the PAN substrate had many nanoscale pores on the surface. After pressure-driven assembly of the PVA-GO nanohybrid sheets, all pores on the surface were completely covered by PVA-GO nanohybrid sheets (Fig. 4(b)). This indicates that a defect-free, dense separation layer was formed on the top layer of the PAN substrate. The cross-section of the PAN substrate before and after assembly are shown in Fig. 4(c) and (e). Magnified images are shown in Fig. 4(d) and (f). The cross-sectional structure of the PAN substrate was finger-like (Fig. 4(c) and (d)). After assembly of the PAN substrate with the PVA-GO nanohybrid sheets (Fig. 4(e) and (f)), the top layer and sublayer of the PAN substrate was filled with the sheets.

The match between the size of the building blocks and the pore size of the supporting membrane strongly influence the morphologies

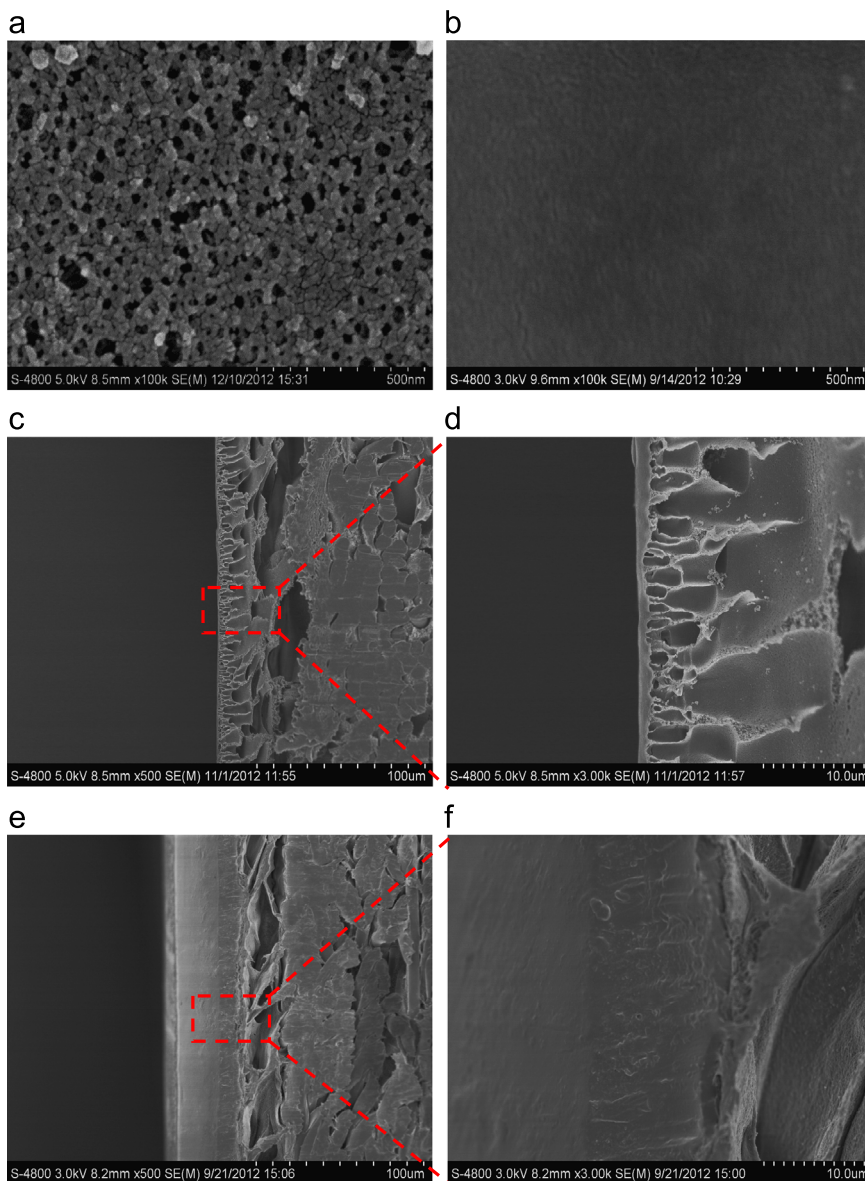


Fig. 4. SEM images of (a) surface of PAN substrate ($\times 100\text{k}$), (b) surface of PAN/PVA-GO membrane ($\times 100\text{k}$), (c) cross-section of PAN substrate ($\times 500$), (d) cross-section of PAN substrate ($\times 3\text{k}$), (e) cross-section of PAN/PVA-GO membrane ($\times 500$), and (f) cross-section of PAN substrate ($\times 3\text{k}$). (Preparative conditions: 10 min filtration time, 2.5 wt% PVA aqueous solutions with 0.1 g/L GO, dynamic pressure -0.08 MPa.)

and separation performance of the composite membranes [18]. Comparing Fig. 2(b) with Fig. 4(a), it can be observed that the pore size of the PAN substrate was about 30–50 nm, whereas the PVA–GO nanohybrid sheets after sonication had dimensions of about 20 nm. Therefore, under the transmembrane pressure, the PVA–GO nanohybrids could enter into the nanopores of the PAN substrate to form the pore-filling nanohybrid membrane.

3.2. Analyses of mechanical strength and thermal properties

Nanoindentation was used to determine Young's modulus and the hardness of the selective layer of the composite membranes. As shown in Fig. 5(a) and (b), Young's modulus and hardness of the PAN substrate membrane were 0.5 and 0.04 GPa, respectively. The values increased after assembly of PVA. A further increase occurred when PVA–GO was deposited on the membrane. For example, with the incorporation of GO, Young's modulus and hardness increased from 4.1 and 0.39 GPa to 5.3 and 0.45 GPa, respectively. These results provide evidence that the mechanical behavior of the composite membrane was improved by the addition of GO.

DSC was used to measure the melting enthalpy of pure PVA and the PVA–GO nanohybrid. As shown in Fig. 6, the melting point of the PVA–GO nanohybrid was 211.14 °C, only 1.3 °C higher than that

of pure PVA (209.84 °C). The melting peaks of both materials had similar patterns. This indicates that both samples had similar crystallinity (χ_c , which is calculated as follows).

$$\chi_c = \frac{\Delta H_m}{\Delta H_0} \quad (3)$$

where ΔH_m is the measured melting enthalpy (from DSC) and ΔH_0 is the enthalpy of pure PVA crystal (138.6 J/g) [11]. According to the above formula, the crystallinity of the PVA–GO nanohybrid was 17.3, which was slightly higher than that of pure PVA (16.4). PVA is a semicrystalline polymer and its mechanical properties strongly depend on the degree of its crystallinity [25]. The results provide evidence that the significant increase in the strength and Young's modulus are attributed to the addition of the GO sheets.

The TGA/DTG results for pure PVA and PVA–GO nanohybrid are shown in Fig. 7. As shown in Fig. 7(a), both pure PVA and PVA–GO nanohybrid decomposed in a two-step process. The TGA curve of the PVA–GO nanohybrid shifted toward a temperature higher than the curve of pure PVA. The degradation temperature for the nanohybrid was about 5 °C higher than that of pure PVA. The peak degradation temperature, which represents the temperature at which the maximum weight loss rate is reached, is shown in the DTG curves in Fig. 7(b). The peak degradation temperature of the PVA–GO nanohybrid complex was about 8 °C higher than that of pure PVA. Furthermore, the decomposition rate of the PVA–GO nanohybrid complex was lower than that of pure PVA. The TGA and DTG results suggest that addition of GO resulted in enhanced thermal stability of the polymer nanohybrid complex.

3.3. Effects of assembly conditions on the pervaporation of toluene/*n*-heptane

The correlation of pervaporation performance with GO content of the PVA–GO nanohybrid membrane is shown in Fig. 8. The separation factor of PVA membrane was 3.8 with the permeate flux of 47.4 g/m² h for separating 50 wt% toluene/*n*-heptane mixtures. After incorporation of GO nanosheets, the separation factor of the nanohybrid membranes increased, and the permeate flux decreased. When the GO contents was increased from 0.05 to 0.1 g/L, the separation factor increased from 7.0 to 11.4 (toluene content in permeate=91.9 wt%). Clearly, the incorporation of GO increased the interaction between GO and toluene. This enhancement may be attributed to the large number of carbon hexagonal rings in the structure of GO. This also increases the selectivity. However, when the GO content was increased from 0.1 to 0.4 g/L, the separation factor decreased from 11.4 to 8.0. The poor compatibility between

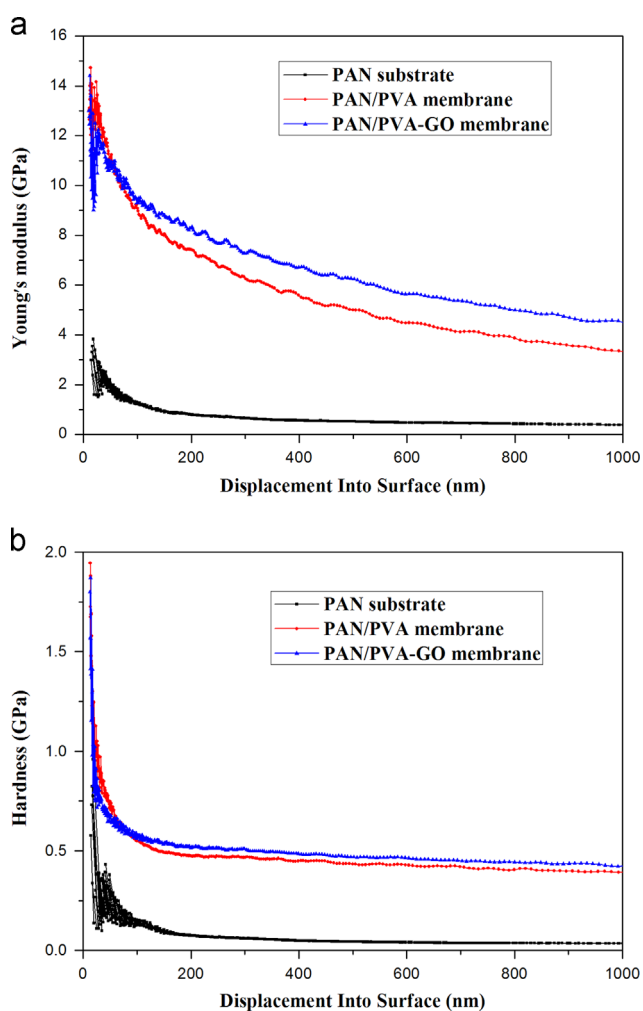


Fig. 5. Young's modulus and hardness–displacement curves before and after assembly. (a) Young's modulus–displacement curves before and after assembly, (b) hardness–displacement curves before and after assembly. (Preparative conditions: 10 min filtration time, 2.5 wt% PVA aqueous solutions with 0.1 g/L GO, dynamic pressure –0.08 MPa.)

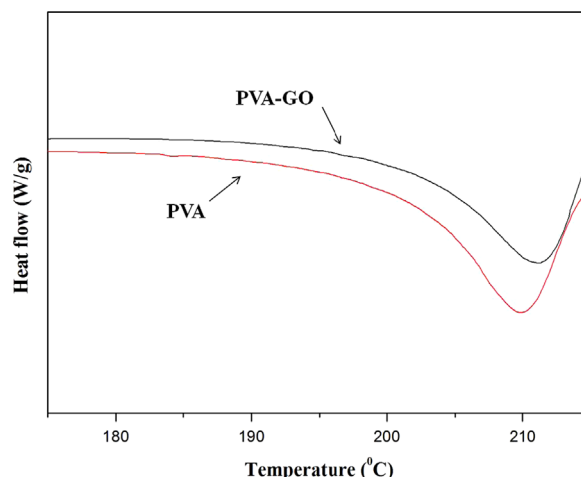


Fig. 6. DSC curves of pure PVA and PVA–GO nanohybrid. (Preparative conditions: 2.5 wt% PVA aqueous solutions with 0.1 g/L GO.)

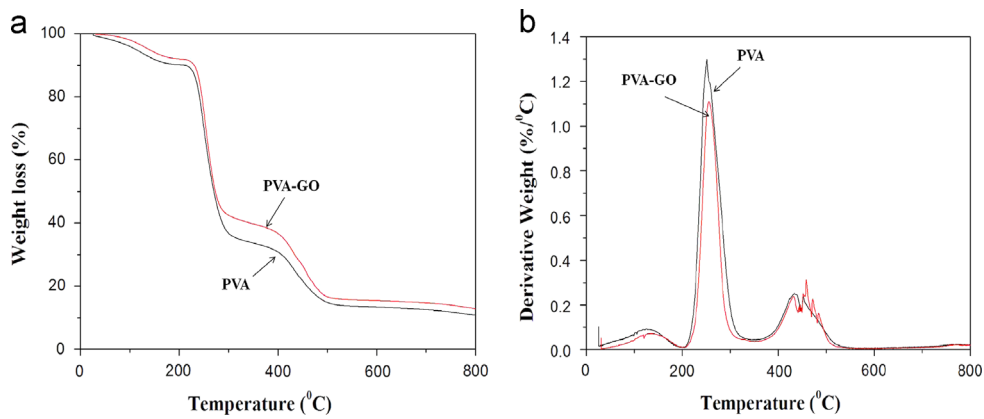


Fig. 7. TGA (a) and DTG (b) curves of pure PVA and PVA-GO nanohybrid. (Preparative conditions: 2.5 wt% PVA aqueous solutions with 0.1 g/L GO.)

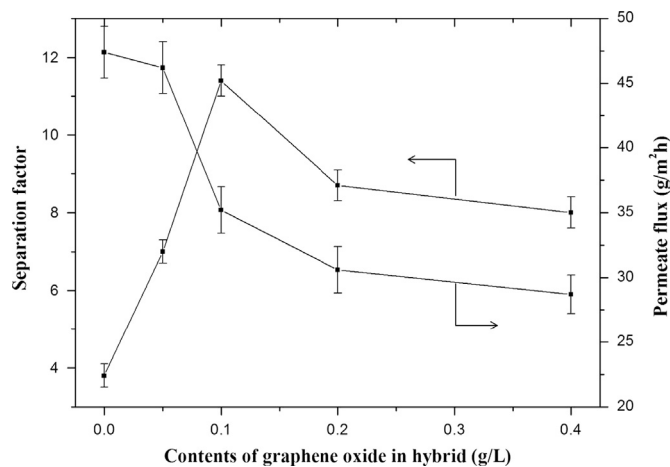


Fig. 8. Effect of contents of GO in nanohybrid on pervaporation performance. (Preparative conditions: 10 min filtration time, 2.5 wt% PVA aqueous solutions with GO, dynamic pressure -0.08 MPa.)

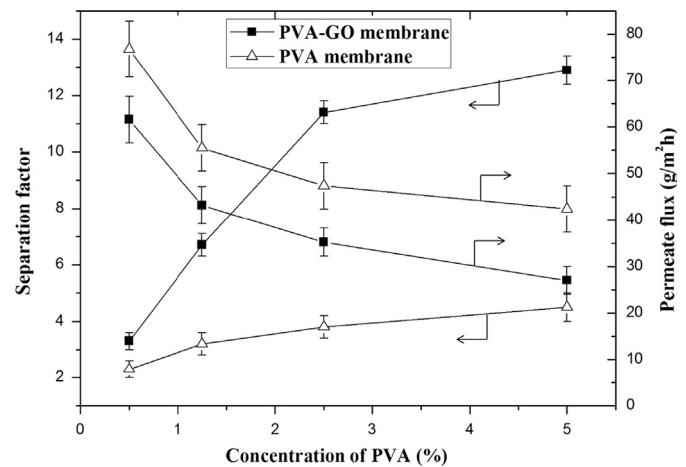


Fig. 9. Effect of PVA concentrations on pervaporation performance. (Preparative conditions: 10 min filtration time, PVA aqueous solutions with 0.1 g/L GO, dynamic pressure -0.08 MPa.)

GO and PVA at excess GO loading might not improve selectivity. Moreover, increasing the GO led to a decrease in the permeate flux. This reduction may be explained by the impeded diffusion of toluene adsorbed on GO due to the interaction between toluene and GO. The nonporous GO particles act as barriers to diffusion of the components in the solution [10].

As shown in Fig. 9, the separation factor increased whereas the permeate flux sharply decreased with increasing the PVA concentration. For example, for PVA-GO nanohybrid membrane, the separation factor increased from 3.3 to 12.9 as the PVA concentration was increased from 0.5 to 5 wt%. Meanwhile, the permeate flux declined from 61.6 to 27.0 g/m²h. Compared to pure PVA membrane, the PVA concentration has apparently influence on separation performance for PVA-GO nanohybrid membrane. High concentrations of PVA made the composite membrane much denser and thicker, so that the permeate flux quickly dropped.

The recently developed technique in our laboratory, dynamic negative adsorption, provides a particularly effective method for fabricating a dense nonporous layer on the substrate surface [26,27]. Since the nonporous selective layer in the present study was formed under a pressure-driven process, the effects of negative pressure on membrane performance were investigated at -0.02 to -0.08 MPa. As shown in Fig. 10, the separation factor improved whereas the permeation flux decreased with increasing negative pressure. For example, the separation factor of the PVA-GO nanohybrid membrane increased from 5.8 to 11.4 when the negative pressure was increased from -0.02 to -0.08 MPa. Meanwhile, the

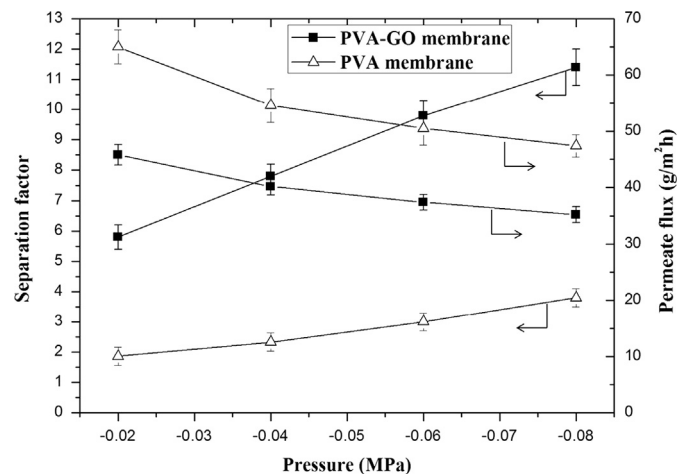


Fig. 10. Effect of dynamic pressure on pervaporation performance. (Preparative conditions: 10 min filtration time, 2.5 wt% PVA aqueous solutions with 0.1 g/L GO.)

permeate flux decreased from 45.8 to 35.2 g/m²h. The separation performance of pure PVA membrane was also investigated. The results indicated that, although the separation factor was lower than nanohybrid membrane, the effect of pressure on separation performance for pure PVA membrane has the same trend. Under higher negative pressure, more nanohybrid molecules enter the pores of

the sublayer. Furthermore, the separation layer becomes thicker and denser; this leads to a much higher separation factor and lower permeate flux.

The effects of dynamic coating time on the pervaporation performance of the PVA–GO nanohybrid membrane and pure PVA membrane are shown in Fig. 11. With increasing dynamic coating time, the separation factor increased whereas the permeate flux decreased. For example, the separation factors of the PVA–GO nanohybrid membrane obtained from dynamic coating times of 10 and 30 min were 11.4 and 12.3, respectively. This change suggests that the surface pores of the PAN support could be completely covered with PVA–GO nanohybrid within 10 min, at which point a defect-free PVA–GO nanohybrid selective layer could be formed. The similar results can be also observed from pure PVA membrane. Therefore, 10 min was selected as the optimal coating time.

The pervaporation performance of membranes prepared with different materials and preparation methods was also examined. As shown in Table 1, the composite membrane prepared using PVA–GO nanohybrid had better separation performance compared with the membrane prepared using pure PVA. The pure PVA membrane had a separation factor of 4.5 for the separation of 50 wt% toluene/*n*-heptane mixtures. In contrast, the separation factor was 12.9 when the membrane consisted of the PVA–GO nanohybrid. Although the testing conditions are different, to some extent, the results in this manuscript have demonstrated that the separation capacity of PVA–GO membrane is comparable with reference data [14,28–30]. It is noteworthy that the recovery and

purity are both important for an economical separation in industry. More efforts are still needed to improve the permeate flux of the membrane.

3.4. Stability of the PVA–GO composite membrane

The membrane stability is one of the most important factors for the performance of commercial separation applications. The DS of the pure PVA membrane prepared by the dip-coating method was 47.3%. In contrast, the DS of the PVA–GO membrane was 57.0%. This difference indicates that doping with GO enhanced adsorption of the solvents. However, the DS of dynamically assembled PVA–GO membrane decreased to 51.9% due to the pore-filling structure. These results suggest that the pore-filling composite membrane could effectively control excessive swelling of the polymer. To further understand the solvent-tolerance capacities of the PVA membrane and PVA–GO nanohybrid membrane, the membranes were directly immersed in 50 wt% toluene/*n*-heptane solutions for 480 h. The pervaporation performance was recorded before and after immersion for a certain time. As shown in Fig. 12, we can see that the separation factor of PVA membrane had a little decrease, but the PVA–GO membrane showed no obvious change after immersion. The possible reason for this result was the interaction between GO and PVA make the nanohybrid membrane more stable. Therefore, the pore-filling nanohybrid membrane had long-term stability in its performance in separating aromatic/aliphatic mixtures.

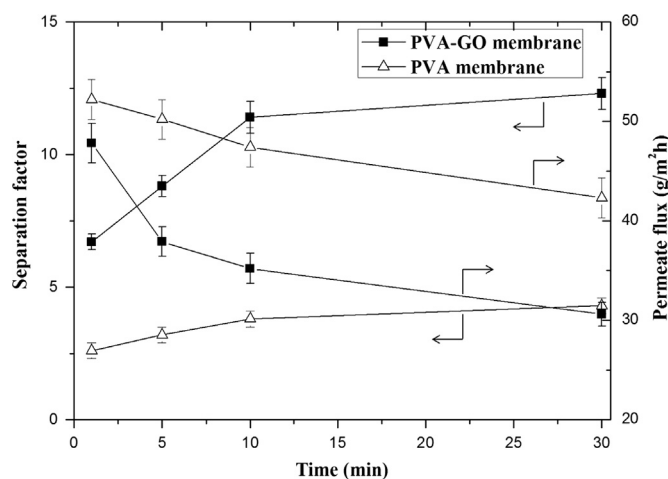


Fig. 11. Effect of filtration time on pervaporation performance. (Preparative conditions: 2.5 wt% PVA aqueous solutions with 0.1 g/L GO, dynamic pressure –0.08 MPa.)

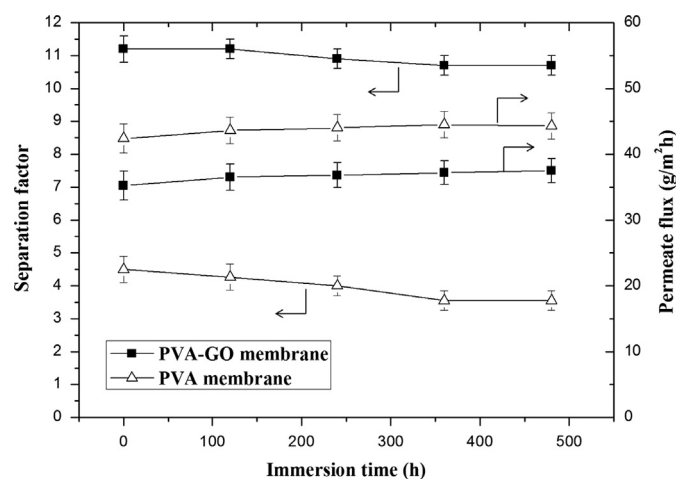


Fig. 12. Effect of immersion time on pervaporation performance. (Preparative conditions: 10 min filtration time, 2.5 wt% PVA aqueous solutions with 0.1 g/L GO, dynamic pressure –0.08 MPa.)

Table 1
Pervaporation performance of membrane prepared by different materials and method.

Membrane	Preparation method	Feed solution	Temperature (°C)	Permeate flux (g/m ² h)	Separation factor	Reference
Polyethylene glycol dimethacrylate/acrylated cyclodextrins	Solution casting method	10% toluene/cyclohexane	60	4.3–7.5	14	[28]
Aromatic polyimide and polybenzoxazole	Solution casting method	40% toluene/ <i>n</i> -heptane	80	15–46	4.7	[29]
PAN/poly(ethylene glycol) methacrylate	Plasma graft-filling technique	25% toluene/ <i>n</i> -heptane	80	1620	7.8	[14]
PAN/p-(MMA-co-MASPE)/BDDDMAC	Dip-coating	20% toluene/ <i>n</i> -heptane	80	1070	4.7	[30]
PAN/PVA ^a	Dynamic assembly	50% toluene/ <i>n</i> -heptane	40	42.4	4.5	This study
PAN/PVA–GO ^b	Dynamic assembly	50% toluene/ <i>n</i> -heptane	40	27.0	12.9	This study

PAN: polyacrylonitrile; MMA: methyl methacrylate; MASPE: methacrylic acid (3-sulfopropyl ester) potassium salt; BDDDMAC: benzyl dodecyl dimethyl ammonium chloride; PVA: poly(vinyl alcohol); GO: graphene oxide.

^a Preparative conditions: 10 min filtration time, 5 wt% PVA aqueous solutions, dynamic pressure –0.08 MPa.

^b Preparative conditions: 10 min filtration time, 5 wt% PVA aqueous solutions with 0.1 g/L GO, dynamic pressure –0.08 MPa.

4. Conclusions

A PVA–GO nanohybrid membrane was successfully prepared for the pervaporation separation of toluene/*n*-heptane mixtures. The PVA–GO nanohybrid molecules could easily enter substrate pores to form the pore-filling structure during dynamic pressure-driven assembly. The PVA–GO nanohybrid membrane was rigorously characterized through FTIR, SEM, TGA and nanoindentation. The results demonstrate that the mechanical and thermal properties of the PVA–GO composite membranes were significantly improved after incorporating GO into PVA. With respect to the separation factor of pure PVA membrane, an improvement in the separation factor (from 4.5 to 12.9) in the pervaporation of 50 wt% toluene/*n*-heptane mixture (40 °C) was observed after doping of PVA with GO. The pervaporation performance of the composite membrane was relatively stable even after immersion of the membrane in 50 wt% toluene/*n*-heptane solution for 480 h. These results strongly suggest that the PVA–GO composite membranes deposited by dynamic pressure-driven assembly have much potential in applications for the pervaporation separation of aromatic/aliphatic mixtures.

Acknowledgments

This work was financially supported by the National Natural Science Foundation (No. 21176007), the National High Technology Research and Development Program of China (No. 2012AA03A607), the State Key Laboratory of Materials-Oriented Chemical Engineering (No. KL11-10) and Fok Ying Tung Education Foundation (No. 131068).

Nomenclature

α	separation factor
Y_i	mass fraction of the toluene in the permeate
Y_j	mass fraction of the <i>n</i> -heptane in the permeate
X_i	mass fraction of the toluene in the feed
X_j	mass fraction of <i>n</i> -heptane in the feed
W_s	weights of solvent swollen membrane
W_d	weights of dry membrane
χ_c	crystallinity
ΔH_m	measured melting enthalpy
ΔH_0	enthalpy of pure PVA crystal

Abbreviations

GO	graphene oxide
PAN	polyacrylonitrile
PVA	polyvinyl alcohol
DS	degree of swelling
SEM	scanning electron microscopy
FTIR	Fourier transform infrared
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
DTG	derivative thermogravimetry analysis
DSC	differential scanning calorimetry
XRD	X-ray diffraction

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