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

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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.

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.

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

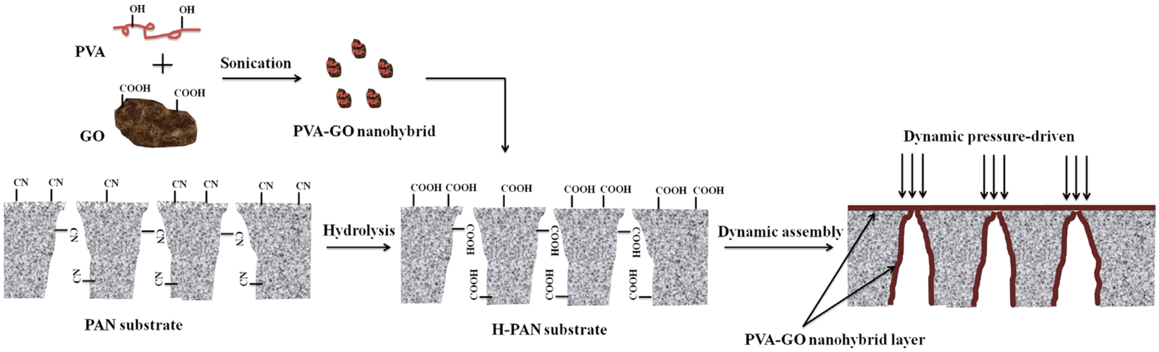
First, specific concentrations of PVA solution and GO solutions were prepared. The PVA solution was blended with the solution of GO sheets, and the resulting mixture was subjected to intense sonication for 30 min. The PAN ultrafiltration membranes were hydrolyzed by immersing them in 2 mol/L sodium hydroxide 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 cm^2. 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:

$$\alpha = \frac{Y_i/Y_j}{X_i/X_j} \tag{1}$$

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.



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