Highly swelling resistant membranes for model gasoline desulfurization

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ABSTRACT

The ubiquitous tradeoff relation between membrane separation performance and swelling resistance is another great challenge other than the tradeoff relation between membrane permeability and selectivity, which significantly restricts the application efficiency of all membrane processes. In this study, graphene nanosheets (GNS) were first functionalized by polydopamine (PDA) coating followed by silver nanoparticle (AgNP) loading to fabricate Ag-PDA/GNS composites, and were then incorporated into the polyether-block-amide, Pebax 2533, to fabricate the Pebax-Ag-PDA/GNS high-performance hybrid membranes. PDA can endow GNS with increased hydrophobicity and consequently increased interfacial compatibility between GNS and Pebax matrix. Ag-PDA/GNS can decrease the crystallinity, increase the fractional free volume, and enhance the swelling resistance of Pebax membrane via multiple interactions at the interface between Ag-PDA/GNS and Pebax. AgNPs were loaded onto the surface of Ag-PDA/GNS composites via the adhesive effect of PDA. AgNPs homogeneously dispersed on the surface of Ag-PDA/GNS, which could endow the membranes with facilitated transport function towards thiophenic components. Moreover, the desulfurization performance of the Pebax-Ag-PDA/GNS hybrid membranes was evaluated using the model gasoline as a separation system. When the filling content is 6 wt%, the separation performance of Pebax-Ag-PDA/GNS hybrid membrane reaches the optimal value, with a permeation flux of 4.42 kg/(m² h) and an enrichment factor of 8.76 at the operation temperature of 40 °C; when the operation temperature increases to 70 °C, the enrichment factor decreases to 6.07, however, the permeation flux significantly increases to 22.53 kg/(m² h), outperforming most of reported data in literature.

1. Introduction

Separation processes dealing with organic liquid mixtures have a significant and indispensable position in energy and environment areas. Unlike gas separation processes, organic liquid separation faces significant difficulties and challenges because of stronger interactions between different organic molecules. Distillation is widely applied for the organic liquid separation, however, distillation suffers from several inherent disadvantages: high energy consumption; difficult to deal with azeotropic and near azeotropic mixtures; uneconomic when the content of a main component is significantly higher or lower than other components in the mixture (known as asymmetric mixture). Pervaporation, as an energy-efficient, phase equilibrium-independent and environmentally friendly separation technology, holds great promise in overcoming those disadvantages of distillation, or even replaces distillation in some situations [1–6]. Usually, the pervaporation membranes can be categorized into polymer-based membranes and inorganic material-based membranes based on the essence of the membrane material. Compared with inorganic material-based membranes, polymer-based membranes are used more widely due to the intrinsic advantages, such as easy processability, facile large-scale production and relatively low cost [7,8]. Until now, various kinds of polymers including polydimethyl siloxane (PDMS), polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyimide (PI), polyamide (PA), ethyl cellulose (EC), polyaniline (PANI) and polyurethane (PU) have been applied for the pervaporation separation

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of organic liquid mixtures [1,4,5,9]. Besides high separation performance, high swelling resistance is also essential to the membranes used in pervaporation process. However, a tradeoff relation commonly exists between membrane separation performance and swelling resistance for polymer-based membranes, i.e. when the solubility parameters of the membrane material is close to that of organic mixtures, the separation performance becomes higher, while the swelling degree also becomes higher simultaneously [10]. For example, hydrophobic PDMS membranes have relatively high separation performances for organic liquid mixtures, whereas the excessive swelling restricts their long-term application [10,11]; although hydrophilic PEG and PVA membranes have relatively high swelling resistance against organic solvents, their separation performances are usually not as high as those of PDMS membranes [4,5]. Membranes with low swelling resistance would increase the cost of replacement, while membranes with low separation performance would increase the cost of equipment and operation. The tradeoff relation between separation performance and swelling resistance severely restricts the application efficiency of membrane processes.

Theoretically, copolymers should be a potent alternative to homogeneous polymers since copolymers can link polymer segments together and combine their advantages without undesirable macroscopic phase separation [10]. As a matter of fact, copolymers have been used as membrane matrix materials in pervaporation, gas separation and water treatment [12–14]. Among them, poly-ether-*block*-amide (known as Pebax or PEBA) is one of the most widely used copolymers in membrane separation [15–20], such as aromatic/aliphatic separation [18], ethanol recovery [19], and gasoline desulfurization [20]. The flexible polyether (PE) segments in Pebax can contribute to the membrane separation performance, while the rigid polyamide (PA) segments can contribute to the mechanical strength and prevent the excessive swelling, rendering Pebax an outstanding membrane material for organic mixture separation. Furthermore, the solubility parameter of Pebax can be conveniently tuned by altering the PE/PA ratio so as to become applicable to a variety of organic mixtures [21]. For example, the solubility parameters of PE, PA6 (nylon 6) and PA12 (nylon 12) are 20.1, 23.2 and 18.3 $MPa^{1/2}$, respectively [4,22,23]. Despite unique advantages, there is still much room for innovations and improvements, because at present the mechanism of Pebax-based membrane separation is merely based on preferential solution and diffusion, purely physical mechanism. If the reaction mechanism, especially facilitated transport is introduced, the membrane separation performance would be greatly elevated [24,25].

In general, the membrane selectivity can be improved by facilitated transport when specific interaction exists between preferred permeate molecules and the membranes, such as olefin/paraffin separation, benzene/cyclohexane separation and gasoline desulfurization. In these processes, π bonds often exist in the preferential components, and metal ions such as Ag^+, Cu^+ and Ni^{2+} are commonly used as carriers to facilitate the transport of these preferential components [24,25]. The mechanism of the interaction between metal ions and π bond-containing components is π-π stacking, as revealed by Dewar-Chatt model [26,27]. One of the key issues in the fabrication of membranes with the metal ions as carriers is the robust attachment of the certain amount of ions to the membrane to prevent the ions from being washed away. The common strategy is first to attach the ions on solid fillers such as solid particles and nanotubes, and then fabricate hybrid membranes (or mixed matrix membranes) using the functionalized fillers [28,29]. The loading amount of ions is usually low since the external surface area of particles and nanotubes are small, thereby in the efforts to increase the ion loading, the filling content of fillers is increased, leading to undesired agglomeration, voids at the interface between polymer matrix and fillers, and

consequently decreased membrane selectivity. Apparently, fillers with more external surface area would help to solve this problem well. Graphene, as a two-dimensional nanomaterial with relatively high external surface area and aspect ratio, can load and disperse metal ion-containing nanoparticles efficiently. To date, Ag, Au, TiO_2 and zeolitic imidazole framework ZIF-8 nanoparticles have been loaded on the graphene nanosheets (GNS) [30–33]. The nanoparticles can prevent GNS from agglomeration, and endow GNS with many other functions. However, if nanoparticles are only attached to graphene through the weak van der Waals force, they will be prone to fall off. To solve this problem, stronger interaction at the interface between nanoparticles and GNS is thus required. Dopamine-based adhesion should be an appropriate choice, since dopamine is an adhesive with wide application range and can attach well to both nanoparticles and GNS [34–37].

In this study, we used dopamine-coated GNS to load Ag nanoparticles, then fabricated hybrid membranes with Pebax 2533 as the polymer matrix and Ag-PDA/GNS as fillers. The hybrid membranes were applied for the pervaporative desulfurization of model gasoline, a mixture containing thiophene and octane as the representative components. Pebax 2533 is chosen because the solubility parameter of Pebax 2533 (19.5 $MPa^{1/2}$) is close to that of thiophene (20.0 $MPa^{1/2}$), while far from that of octane (15.5 $MPa^{1/2}$) [4,20]. Pebax 2533 contains 80 wt% polytetramethylene ether glycol (PTMG) soft segments and 20 wt% PA12 rigid segments (the molar ratio of PTMG to PA is 11:4). Dopamine coating and Ag nanoparticle (AgNP) loading can prevent GNS from agglomeration, meanwhile GNS can prevent AgNPs from agglomeration. AgNPs can perform facilitated transport function toward thiopheneic component in model gasoline and enhance the membrane separation performance. More importantly, the multiple interactions at the interface between Pebax matrix and Ag-PDA/GNS composites endow the membrane with enhanced swelling resistance.

2. Experimental section

2.1. Materials

Pebax 2533 was purchased from Arkema Group, Paris, France; graphene oxide (GO) nanosheets (1–10 layers) were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, Chengdu, China; dopamine hydrochloride (analytical grade) was purchased from Hubei Yuancheng Saichuang Technology Co., Ltd., Wuhan, China; tri-hydroxymethyl aminomethane (Trizma base or Tris, ≥ 99.8%) was purchased from Sigma Aldrich Co., LLC., Shanghai, China; silver nitrate (99.0%) was purchased from Jiangtian Technology Co., Ltd., Tianjin, China; hydrochloric acid (34–37%), ethanol (≥ 99.5%), *n*-butanol (≥ 99.4%) and *n*-octane (≥ 99.7%) were purchased from Guangfu Fine Chemical Research Institute, Tianjin, China; thiophene (≥ 99.0%) was purchased from Aladdin Industrial Corporation, Shanghai, China; PS-20 polysulfone (PSf) flat-sheet ultrafiltration membrane with molecular weight cutoff (MWCO) of 20 kDa was purchased from Zhejiang Meiyi Technology Co., Ltd., Hangzhou, China. All the chemicals were used without further purification. Deionized water (resistance over 18 MΩ/cm) was used throughout this study.

2.2. Fabrication of Ag-PDA/GNS

2.2.1. Fabrication of PDA/GNS

Polydopamine-coated GNS composites were fabricated through oxidative self-polymerization of dopamine. (1) A certain amount of GO were dispersed in water with the concentration of 0.5 g/L under ultrasound for 20 min; (2) Tris was dissolved in 0.4 L water