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Development of high performance nanofibrous composite membranes by optimizing polydimethylsiloxane architectures for phenol transport

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ABSTRACT

Phenol removal and recovery from wastewaters are highly demanded in industries due to its high toxicity and industrial importance. It can transport through the silicon-based rubber polydimethylsiloxane (PDMS) via the solution-diffusion mechanism. To improve the phenol removal efficiency in extractive processes, dense PDMS membranes with different macromolecular structures have been developed and evaluated in this work. The condensation-cured PDMS membranes (PA) with network architecture exhibited higher phenol partition coefficients (*K*) than the hydrosilylation-cured PDMS membranes with linear and branch architectures. This was attributed to the four-armed quaternary-siloxy linkages formed in the three-dimensional network structure, increasing the free volume for phenol passage and hydrogen bonding between phenol and PDMS matrix. The *K* of PA was further enhanced by optimizing the PDMS precursor chain length and cross-linker amount, and the corresponding membrane mechanical properties and phenol overall mass transfer coefficients (k_O) were examined. The optimal PA formulation was utilized to fabricate a highly effective nanofibrous composite membrane via spray coating. The resultant composite membrane exhibited a k_O of $18.3 \pm 1.3 \times 10^{-7}$ m/s in an aqueous-aqueous extractive process, significantly outperforming the commercial counterpart with 45% increment. This is the first demonstration of the importance of PDMS macromolecular structures on phenol extraction. The newly-developed condensation-cured PDMS could contribute to the fabrication of highly effective composite membranes for various extractive processes.

1. Introduction

Phenol and phenolic compounds exist widely in the effluents of many industries such as petrochemicals, textile, gas and coke manufactures, which are highly toxic to human and ecosystem due to their protein-degenerating effects and the formation of phenoxyl radicals [1,2]. On the other hand, they are considered as valuable chemicals for producing polycarbonates, epoxies, nylon, detergents, herbicides and numerous pharmaceutical drugs [3]. Therefore, utilizing economically feasible and reliable technologies for efficient separation and recovery of phenol and phenolic compounds from wastewater streams before discharge is highly demanded. The technologies currently available for phenol treatment include: (1) traditional methods such as extraction [4], distillation [5], adsorption [6], biodegradation [7] and chemical oxidation [8]; (2) advanced methods such as photo oxidation processes [9] and membrane separation technologies [10]; and (3) hybrid systems which combine traditional and advanced techniques including reverse osmosis coupled with adsorption process [11], extractive membrane bioreactor (EMBR) [12–14], membrane aromatic recovery system (MARS) [15] and membrane pervaporation [16]. Among them, the hybrid systems employing membrane-based extractive processes, such as EMBR, have emerged as promising techniques [13,14].

In the membrane-based aqueous-aqueous extractive processes, the target organic contaminants transport from the feed wastewaters to the receiving solutions through a dense membrane driven by the concentration gradient. As the feed and receiving solutions are separated by the membrane, the receiving solutions can have numerous options regardless of harsh conditions in the feed wastewaters. Additionally, the aqueous-aqueous extractive processe exhibits advantages including low energy consumption, low operating costs and easy scalability [17,18]. However, one of the main challenges in the aqueous-aqueous extractive processe is the shortage of specially designed membranes capable to

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extract the target organic compounds into the aqueous receiving medium with high efficiencies and excellent stabilities.

Owing to its organophilicity and hydrophobicity that allow preferential transfer of organics while rejecting water and inorganics, polydimethylsiloxane (PDMS) has been employed as the most commonly used membrane material in such configurations as silicone rubber tubes [17] and the selective layer of composite membranes [13,14]. Small molecules can transport through the free volume of PDMS by the solution-diffusion mechanism, which involves three steps: adsorption at the upstream boundary, diffusion through the bulk membrane and desorption away from the downstream boundary [19]. The control of the adsorption, diffusion and desorption of the small molecules by engineering the polymer macromolecular structures, free volumes and functional groups to optimize mass transfer efficiency is of great value.

Generally, two types of cross-linking reaction pathways exist for PDMS preparation [20–22]. In the pathway of hydrosilylation reaction, a linear PDMS polymer structure can be formed by reacting vinyl-terminated PDMS precursors with hydrosilyl-containing cross-linkers under Pt catalysis; while in the condensation reaction pathway, hydroxyl-terminated PDMS precursors react with multi-functional cross-linkers under catalysis to generate a three-dimensional network [20–22]. Both methods have been adopted to fabricate PDMS-based membranes for applications such as gas separation [20], pervaporation [21] and solvent-resistant nanofiltration [22]. However, to the best of our knowledge, the effects of PDMS cross-linking conditions and resultant polymer architectures on phenol transport behavior have not yet been studied systematically.

Additionally, the mechanical properties of the PDMS membrane are critical for practical applications, especially for the development of composite membranes. Although PDMS membranes have high organic affinity, they usually display unsatisfactory mechanical strength resulting from the intrinsic weak intermolecular interactions among the polymer chains [23] as well as the thin PDMS thickness (< 10 μm) for reducing the membrane resistance [14,24]. Moreover, if the PDMS membranes are developed for pressure-driven processes such as gas separation, the mechanical strength needs to be further boosted so as to withstand the elevated pressure (> 100 bar) [25]. For the purpose of preparing high strength PDMS, a number of reinforcing fillers such as fumed silica and montmorillonite clays have been incorporated into the PDMS matrix [26–29]. However, pre-treatments such as surface modification of fillers [26,28,29] and functionalization of PDMS [27] are usually required in order to achieve adequate interfacial interactions between the fillers and PDMS matrix [29]. Alternatively, PDMS mechanical strength could be enhanced by optimizing the cross-linking methods and thus controlling the polymer architectures, which is considered to be more promising, convenient, economically valuable and practical [30]. However, the consequences of the architecture changes on the membrane separation performance, particularly, the phenol removal efficiency in extractive processes, have not been studied in details. Therefore, it is of high importance to systematically investigate the correlations among the cross-linking regimes, mechanical strength and phenol extractive performance of dense PDMS membranes.

Moreover, to meet the requirements of practical operations and enhance membrane permeability, an alternative option is to develop PDMS-based composite membranes by means of coating a thin PDMS skin layer onto a highly porous substrate, which is capable of reducing the overall membrane resistance significantly [13,14]. So far, the widely used membrane substrates are fabricated via phase inversion techniques, typically producing an asymmetric porous structure [31]. Our group has developed a series of electrospun nanofibrous membranes which exhibit highly porous and interconnected open structures, large surface area to volume ratio, controllable pore sizes and excellent tensile strengths, making them promising membrane substrates [13,32]. Nevertheless, it is still challenging to directly form a thin and defect-free PDMS layer on the nanofibrous scaffolds as they usually possess large surface pore sizes (> 0.4 μm) [32].

To ensure the formation of defect-free selective layers, a stable and reproducible method to coat the PDMS layers on the nanofibrous substrates is essential [32]. Several coating methods have been reported in literatures to fabricate PDMS-based composite membranes: (1) dip coating is the most common approach to prepare the selective layer, but it is hard to produce a thin and uniform skin layer [33]; (2) spin coating is advanced to fabricate an ultrathin top selective layer, however the scalability of the process is limited [34]; (3) knife-coating (casting) method is a facile coating technique, and the membrane thickness could be controlled by adjusting the gap setting of the coating knife [35]; (4) spray coating has emerged as a versatile technique to produce a thin and uniform coating layer in a simple, fast and reproducible way [36]. In addition, the whole spray coating process can be conducted in an automatic manner which ensures the high reproducibility of this technique [36]. Thus, in this work, a spray coating technique was utilized to fabricate PDMS-coated nanofibrous composite membranes with high phenol mass transfer efficiency in an aqueous-aqueous extractive process.

In summary, both condensation and hydrosilylation reactions were adopted to prepare dense PDMS membranes with various polymer architectures. The corresponding PDMS structures were confirmed by ATR-FTIR and XPS analyses. Phenol partition coefficients of resultant dense PDMS membranes were examined. Moreover, PDMS precursor molecular weights as well as cross-linker amounts were varied to investigate their impacts on phenol partition efficiencies and mechanical strengths. Aqueous-aqueous phenol extractive tests were conducted to examine the phenol mass transfer efficiencies of selected dense PDMS membranes, from which the optimum conditions were identified to prepare the final composite membrane. An electrospun dual-layer polyvinylidene fluoride (PVDF) nanofibrous membrane with a tiered structure was utilized as the substrate to prepare PDMS-coated nanofibrous composite membranes. The morphologies of the resultant nanofibrous composite membranes were confirmed by FESEM and EDX. The phenol extractive performances of the composite membranes were examined in aqueous-aqueous phenol extractive tests.

2. Experimental

2.1. Materials and chemicals

Polyvinylidene fluoride (PVDF) (Kynar HSV900) supplied by Arkema was used as the substrate material. Anhydrous lithium chloride (LiCl, Merck chemicals) was added in polymer dope solutions as an additive. Vinyl-terminated polydimethylsiloxane (VPDMS, average molecular weight: 25,000, viscosity: 850–1150 cSt), hydroxyl-terminated polydimethylsiloxane (HPDMS, viscosity: 750 cSt, 3500 cSt and 18,000–22,000 cSt, respectively), tetraethyl orthosilicate (TEOS), dibutyltin dilaurate (DBTDL), trimethylsilyl terminated poly(dimethylsiloxane-*co*-methylhydrosiloxane) (PDMS-MHS) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Pt. catalyst, 0.05 M in vinyl terminated PDMS) were supplied by Sigma Aldrich. A two-component Sylgard® 184 silicone elastomer kit was supplied by Dow Corning. Acetone (Fisher Scientific), *n*-hexane (Merck chemicals) and N,N-dimethyl formamide (DMF, Merck chemicals) were used as solvents. Glycerol (85% aqueous solution, Merck chemicals) was mixed with deionized water (DI water, purified by a Milli-Q system, Millipore Co. Singapore) to prepare the substrate pre-wetting agent. Sodium chloride (Merck chemicals) and phenol ($\geq 99\%$, Sigma Aldrich) were employed to prepare the feed solution. All the reagents were used directly without further treatment.

2.2. Preparation of dense PDMS membranes

To investigate the effect of polymer architectures on phenol extractive performances of dense PDMS membranes, three methods were