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Non-charged PVA–SiO_2 hybrid membranes for potential application in diffusion dialysis

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ABSTRACT

Non-charged PVA–SiO_2 hybrid membranes are prepared from the sol–gel reaction of polyvinyl alcohol (PVA) and methacryloxypropyl trimethoxy silane (γ-MPS) or poly(γ-MPS). As the polymerization degree increases from γ-MPS to poly(γ-MPS), the sol–gel solution becomes turbid or generates precipitation, while the formed silica particles in the hybrid membranes become smaller from 1.0–3.4 μm to 0.1–0.2 μm or disappear. The membrane tensile strength (TS) generally increases from 35 MPa to 44 MPa, while the elongation at break (E_b) decreases from 318% to 141%.

Three deductions are proposed according to the structure of poly(γ-MPS), membrane swelling behaviors in 65–85 °C water and 65 °C alkaline solution, and the diffusion dialysis (DD) performance. (1) As poly(γ-MPS) contains no ion-exchange groups like the multisilicon copolymer [1], it tends to become inhomogeneous during sol–gel process, which reduces its crosslinking ability. (2) The membrane structure is generally stable in 65 °C water with the swelling degrees of 140–347%, but is damaged in 85 °C water or 65 °C alkaline solution. (3) Non-charged hybrid membranes can be potentially applied in DD process. The dialysis coefficient of NaOH (U_{OH}) is in the range of 0.0069–0.0127 m/h, and the separation factor (S) is in the range of 19–92. The OH^- ions may be transferred in the hybrid membranes through PVA-OH groups and interstices between organic and inorganic phases, according to the mechanisms of adsorption–desorption and free diffusion, correspondingly.

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1. Introduction

Diffusion dialysis (DD) is a membrane separation process driven by concentration gradient [2], and can be applied for the recovery of acid [3,4] or alkali [5] from the waste solutions. During DD process, the membrane is fixed in a two-compartment cell. One compartment is filled with waste solution such as $HCl/FeCl_2$ [4] or $NaOH/Na_2WO_4$ [6], which is signed as dialysate solution. The other compartment is filled with water or solution with low concentration, which is signed as diffusate solution. As the acid (HCl) or alkali (NaOH) transfers faster than other components, it will pass through the membrane firstly from the dialysate side to the diffusate side. Hence, the membrane is the key factor during DD process. Generally, anion exchange membranes are used to separate acid waste such as $HCl/FeCl_2$. The Cl^- ions can transfer through the membrane freely, and the H^+ ions, due to their low valence state and small volume and thus high activity, are more likely to follow with Cl^- ions to keep the neutrality of solution. Similarly, cation exchange membranes can be used for the alkali recovery such as NaOH.

Cation exchange membranes used in DD process, though are less frequently reported, are attempted recently in our research group. Cation exchange membranes based on different polymers are developed and investigated with the water uptake (W_R), ion exchange capacity (IEC) and DD performance including dialysis coefficient of NaOH (U_{OH}) and separation factor (S). For example, hybrid membranes based on sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) has the W_R of 23–51%, IEC of 1.4–2.1 mmol/g, U_{OH} of 0.0017–0.0022 m/h and S of 62–300 at 25 °C [7]. Hybrid membranes based on polyvinyl alcohol (PVA) and multisilicon copolymers are also developed for DD process. Multisilicon copolymer has a long main chain and many branched chains, with plenty of $-Si(OCH_3)_3$ and ion exchange groups [1]. Membranes from the multisilicon copolymer containing acryl acid has the W_R of 70–81%, IEC of 0.76–0.90 mmol/g, U_{OH} of 0.010–0.016 m/h and S of 52–95 at 35 °C [6]. Membranes from the multisilicon copolymer containing maleic anhydride has the W_R of 34–67%, IEC of 1.4–1.8 mmol/g, U_{OH} of 0.0095–0.0123 m/h and S of 28–54 at 20 °C [8]. Comparisons among different membranes can show two deductions. (1) The U_{OH} values of PVA based membranes are

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Nomenclature

Codes	Full name or meaning
PVA	polyvinyl alcohol
γ-MPS	methacryloxypropyl trimethoxy silane
TS	tensile strength
E_b	elongation at break
DD	diffusion dialysis
multisilicon copolymer	copolymer contains multi –Si(OR)$_3$ groups and plenty of ion-exchange groups
U_H	dialysis coefficient of HCl
U_{OH}	dialysis coefficient of NaOH
S	separation factor
W_R	water uptake
IEC	ion exchange capacity
SPPO	sulfonated poly(2,6-dimethyl-1,4-phenylene oxide), a type of cation exchange material
DMF	dimethyl formamide
AIBN	azobisisobutyronitrile
SEM	scanning electron microscopy
IDT	initial decomposition temperature

five times higher than those of membranes based on SPPO. (2) The IEC values, though are always important for other applications [9], have insignificant effect on U_{OH}. Hence, an idea is proposed naturally, i.e., can non-charged PVA based hybrid membranes be used in DD process?

Therefore in this work, non-charged hybrid membranes based on PVA will be developed. The PVA will be crosslinked with methacryloxypropyl trimethoxy silane (γ-MPS) or poly(γ-MPS) through sol–gel reaction. Poly(γ-MPS) can be obtained from the polymerization of γ-MPS prior to or during the sol–gel reaction. As the poly(γ-MPS) contains plenty of –Si(OCH$_3$)$_3$ groups but without ion exchange groups, it may have higher crosslinking ability but lower polarity as compared with multisilicon copolymers [1], which will affect the sol–gel reaction and thus membrane structure. Membrane structure, such as supramolecular interactions and organic–inorganic phase separation, would dominate membrane hydrophilicity, swelling and alkaline resistances, and thus the DD performance.

This work has two main purposes. One is that poly(γ-MPS) will be primarily used as a new type of crosslinking agent to develop PVA–SiO$_2$ hybrid membranes. Poly(γ-MPS) should have high crosslinking ability, but may be difficult to show out at present due to its low polarity. The other purpose is that the non charged PVA–SiO$_2$ hybrid membranes will be attempted for potential application in DD process.

2. Experimentals

2.1. Materials

Polyvinyl alcohol (PVA), toluene, n-hexane and N,N-dimethyl formamide (DMF) were supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd. (China). The average degree of polymerization of PVA was 1750 ± 50. γ-methacryloxypropyl trimethoxy silane (γ-MPS) was supplied by Liyang Tomorrow Chemical Co., Ltd. (China). Distilled water was used throughout the experiments. Azobisisobutyronitrile (AIBN, 10 g) was dissolved in 100 mL ethanol at 50 °C, recrystallized in an ice bath, and then dried at room temperature under ventilated circumstance for 2 days.

PVA (5 wt%) aqueous solution was prepared through dissolving. As PVA had contained some water and alcohols (5.7 wt% [10]) before dissolving, 42.4 g PVA was immersed in 760 mL water at room temperature for 1 day, then heated to 102 °C at the rate of 8 °C/h and kept at 102 °C for around 2.5 h.

2.2. Preparation of hybrid membranes A–C

Membranes A was prepared from the sol–gel solution of PVA and γ-MPS, as shown in Table 1. PVA solution (120 mL, 6 g) was kept at 60 °C with continuous stirring, then added with the mixture of 3 g γ-MPS and 20 mL DMF within 0.25 h, and continued to react for 12 h. Finally, generally homogeneous solution was obtained.

Table 1
The dosages of different materials for preparing hybrid membranes A–C.

Sample	PVA (g)	γ-MPS (g)	Poly(γ-MPS) (g)	AIBN (g)	DMF (mL)
Membrane A	6	3			20
Membrane B	6	3		0.2	20
Membrane C[a] Precipitation	6		3		50

[a] Membrane C and precipitation were prepared from the same sol–gel solution of PVA and poly(γ-MPS), which contained homogeneous solution and precipitation.

Membrane B was prepared from the sol–gel solution of PVA, γ-MPS and AIBN. PVA solution (120 mL) was kept at 60 °C with continuous stirring, then added with the mixture of 3 g γ-MPS, 0.2 g AIBN and 20 mL DMF within 0.25 h, and continued to react for 12 h. The solution gradually became turbid, and. finally, light white but homogeneous solution was obtained.

For the preparation of membrane C, poly(γ-MPS) was prepared prior to the sol–gel reaction with PVA. γ-MPS (0.2 mol) was mixed with 280 mL toluene, then heated to 70 °C and added with 4.8 mmol AIBN. The solution was stirred for 24 h, and then concentrated by rotary evaporation to remove 3/4 volume of the solvent (toluene). The concentrated solution was purified twice by the method of hexane precipitation/toluene dissolution. The volume of hexane was about 3–4 times higher than that of toluene. After the precipitation, some viscous liquid was obtained with the yield of 28.8%. The viscous liquid, namely poly(γ-MPS), was dissolved in DMF to form 0.06 g/mL solution. Poly(γ-MPS) solution (50 mL) was dropped into 120 mL PVA at 60 °C within 0.25 h, and then stirred at 60 °C for 12 h. Finally, totally homogeneous and transparent solution, together with a cluster of white flocculent precipitation, was obtained. The homogeneous solution was taken for membrane formation. The cluster of precipitation, which was adsorbed at the bottom of the flask, was taken out, dried at 130 °C for 4 h, weighed and taken for the measurement of TGA and swelling in 85 °C water. The weight percent of the precipitation with respect to the PVA and poly(γ-MPS) was 31%. The digital photographs of poly(γ-MPS), poly(γ-MPS)/DMF solution, and the mixture of poly(γ-MPS) and PVA are shown in Fig. 1. It should be noted that: (1) in our primary work, different methods were attempted to avoid the formation of the precipitation, including the addition of HCl as catalyst (0.012 mol), prolongation of the dropping time (3 h), increasing the reaction temperature (70 °C), and decreasing the concentration of poly(γ-MPS) (0.03–0.15 g/mL). However, the precipitation can hardly be avoided, and thus these methods were not

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