Journal of Membrane Science 326 (2009) 117–129

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Preparation of porous PMMA/Na$^+$–montmorillonite cation-exchange membranes for cationic dye adsorption

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ARTICLE INFO

Article history:
Received 4 June 2008
Received in revised form 29 August 2008
Accepted 19 September 2008
Available online 30 September 2008

Keywords:
PMMA/Na$^+$–MMT composite membrane
Cation-exchange membrane
Cationic dye
Adsorption

ABSTRACT

Porous PMMA/Na$^+$–montmorillonite (MMT) cation-exchange membranes were successfully prepared by entrapment method in this study. One approach (simple mixing) was to mix commercial PMMA polymer with Na$^+$–MMT clays in solvent for membrane preparation (Membrane A). The other approach (emulsion polymerization) was to synthesize the PMMA/Na$^+$–MMT polymer composite via emulsion polymerization first, followed by membrane casting (Membrane B for Kunipia F clays and Membrane C for PK-802 clays). Membrane morphology and properties were characterized. The thermogravimetric analysis (TGA) verified the near complete incorporation of feed Na$^+$–MMT clays in the PMMA/Na$^+$–MMT composite membranes, while X-ray diffractograms (WXRD) exhibited the slightly enlarged interlayer spacing of Na$^+$–MMT. The range of cation-exchange capacity (CEC) was 9–32 μequiv./47 mm disc. For batch cationic dye adsorption, the best performance was achieved by Membrane B with feed Na$^+$–MMT/MMA (M/P) ratio (w/w) = 0.5 and Membrane C with feed M/P = 0.6, where about 95% Methyl violet adsorption was attained in 2 h. The optimal desorption solution was 1 M KSCN in 80% methanol and its related dye desorption efficiency was 92%. In the flow process using one piece of 47 mm disc of Membrane B (M/P = 0.5), dye solution was recirculated for 6 h and ≥85% dye could be removed. Higher than 94% of dye was desorbed at 1 or 4 mL/min, and the membrane regenerability was proved by successfully performing three consecutive cycles.

1. Introduction

In recent years, inorganic nanoparticle-filled composite membranes have received great attention due to their improved mechanical and thermal properties [1–7]. The popular inorganic nanoparticles adopted in the literature included silica, titania, zeolites, montmorillonite (MMT), silver, etc., while the base polymers investigated were polyvinyl alcohol (PVA), polyamide (PA), polymethyl methacrylate (PMMA), polypropylene (PP), sulfonated polyether ether ketone (SPEEK), polybenzimidazole (PBI), polyethersulfone (PES), polysulfone (PSf), poly(*n*-butyl acrylate-co-glycidyl methacrylate-iminodiacetic acid) (poly(BA-co-GMA-IDA)), etc. [1–16]. A brief summary for these inorganic nanoparticle-filled hybrid membranes is presented in Table 1. There are several methods to immobilize the inorganic nanoparticles on polymeric membranes, such as deposition, self-assembly, coating, entrapment, and so on [1–17]. The deposition method is to filtrate the aqueous nanoparticle suspension through porous membrane support and deposit a cake layer of nanoparticles on the support [13,14]. The self-assembly method employs the membranes with terminal functional groups to react with (or adsorb to) the nanoparticles such as TiO_2, Ag^+, etc. [15,16]. As for the coating method, a gel of nanoparticles is formed and directly coated on the base membrane, followed by drying at room temperature [17]. The entrapment method can be conducted by various approaches. A simple approach is to add the nanoparticles into polymer casting solution, mix, and then cast to prepare the composite membrane [1,5–14]. Another approach is called compression molding, which has to melt the polymer, add nanoparticles for mixing, and finally compress the membrane with a high shear roller-type rotor [4]. In situ or emulsion polymerization is to use monomer and synthesize the nanoparticle-filled polymer composite first, followed by mixing the polymer composite in solvent for forming casting solution, and then prepare the composite membrane [2,3].

The applications of most inorganic nanoparticle-filled composite membranes were focused on pervaporation, filtration, packaging, membrane reactor, direct methanol fuel cell, etc. [1–17]. Some nanoparticles, e.g. zeolites, could play the role of molecular sieving in the composite membranes. The gas permeability for zeolite-filled membranes usually decreases with an increase in zeolite loading, due to either the polymer chain rigidification near zeolites or the partial pore blockage by zeolites; but increases with an increase in zeolite pore size, which is consistent with the molecular sieving mechanism [9–12]. The presence of MMT or silica in the

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doi:10.1016/j.memsci.2008.09.038

Table 1
Inorganic particle-filled hybrid membranes in literature.

Inorganic particle	Membrane matrix	Method	Application	Ref.
Na^+–MMT	PVA (poly(vinyl alcohol))	Entrapment	Pervaporation	[1]
SDS–MMT	PA (polyamide)	Entrapment	Pervaporation	[2]
C18DMB–MMT	PMMA (poly(methyl methacrylate))	Entrapment	Gas storage or packaging	[3]
Na^+–MMT, 2M2HT–MMT	PP (polypropylene)	Entrapment	Beverage and food packaging	[4]
HSO_3–MMT	Nafion	Entrapment	Direct methanol fuel cell	[5]
DOA–MMT	PBI (polybenzimidazole)	Entrapment	Direct methanol fuel cell	[6]
CTAC–MMT	SPEEK (sulfonated poly(ether ether ketone))	Entrapment	Direct methanol fuel cell	[7]
TEOS	PBI (polybenzimidazole)	Entrapment	Direct methanol fuel cell	[8]
Zeolite	PES (polyethersulfone)	Entrapment	Gas separation	[9]
Zeolite modified with APDEMS	PES (polyethersulfone)	Entrapment	Gas separation	[10]
Zeolite, zeolite modified with TMOPMA	PMMA (poly(methyl methacrylate))	Entrapment	Gas separation	[11]
Zeolite	PMMA (poly(methyl methacrylate))	Entrapment	Gas separation	[12]
TiO_2	PES (polyethersulfone), PSf (polysulfone), PA (polyamide)	Deposition, entrapment	Photocatalytic membrane reactor	[13]
TiO_2	PSf (polysulfone), PAN (polyacrylonitrile), PVDF (polyvinylidenefluoride)	Deposition, entrapment	Activated sludge filtration (membrane bioreactor)	[14]
TiO_2	Aromatic polyamide	Self-assembly	Anti-biofouling reactor membrane	[15]
TiO_2	Glass fiber cloth	Coating	Photocatalytic degradation	[17]
Ag	Poly(BA-co-GMA-IDA) (poly(*n*-butyl acrylate-co-glycidyl methacrylate-iminodiacetic acid))	Self-assembly	Polymer thin film containing noble metal nanoparticles	[16]

SDS: sodium dodecyl sulfate; C18DMB: octadecyl-dimethyl betaine; 2M2HT: dimethyl, dihydrogenatedtallow with quaternary ammonium; HSO_3: including 1,4-butane sultone, 1,3-propane sultone and 1,2,2-tri-fluoro-hydroxy-L-trifluomethylethane sulfonic acid sultone; DOA: dodecylamine; CTAC: hexadecyltrimethylammonium chloride; TEOS: tetraethoxysilane; APDEMS: (3-aminopropyl)-diethoxymethyl silane; TMOPMA: 3-(trimethoxysilyl) propylmethacrylate.

composite membranes for direct methanol fuel cells improves the thermal stability and mechanical properties of membranes, as well as decreases the methanol permeation [5–8]. The addition of clays in polymer composites could also elongate the diffusion distance by creating a tortuous path and hence reduce the gas permeability in polymer matrix for packaging or storage tank application [3]. On the other hand, introducing titania nanoparticles into membranes could take advantage of their photocatalysis function by decomposing organic compounds and killing bacteria to decrease membrane fouling [13–15,17], while introducing silver nanoparticles into polymer films may be superior in electrical conductivity, antielectrostatic, oxidative catalysis, and antimicrobial effects [16].

Although inorganic nanoparticle-filled composite membranes have been extensively investigated, their application in adsorption separation process has thus far been overlooked. It is well known that there are plenty of negative charges on MMT clays which are balanced by natural inorganic cations such as Na^+ and Ca^{2+}. Some studies [18–20] indicated that MMT clay has been accepted as one of the low-cost adsorbents with large cation-exchange capacity (CEC) and adopted for cationic dye adsorption. However, the practical applications of clay nanoparticles as adsorbents may suffer certain serious problems such as difficulties in solid–liquid separation for batch process and packing complexity or high pressure drop for column process. The membrane system not only has the ability of overcoming the technical limitations of packed-bed operations (solid–liquid separation or bed packing) but also exhibit the advantage of simple scale-up by either stacking more membranes together or using a larger membrane area. Thereby, the purpose of this work is to prepare porous MMT clay-filled composite membranes and apply them in cation-exchange process.

In this study, PMMA was chosen as the base polymer because it has been widely used and well investigated in many membrane applications owing to its advantages in excellent processibility and low cost [3,11,12,21–23]. In this work, two approaches were adopted to prepare the PMMA/Na^+–MMT composite membranes by entrapping MMT clays inside the membrane matrix. One is to mix Na^+–MMT clay particles with polymer (simple mixing approach) and then cast the membrane via phase inversion. This approach has been employed in most studies [1,5–14]. The other one is to stir MMA monomer with Na^+–MMT, surfactant, and initiator together and synthesize the PMMA/Na^+–MMT polymer composite (emulsion polymerization approach). By this way, polymer chain may be able to intercalate into the interlamellar structure of clay and lead to a firmer entrapment of clay nanoparticles with polymer [24–26]. The composite membrane was then prepared from the polymer composite solution via phase inversion. The properties of the composite membranes obtained from these two approaches were characterized and compared. In addition, the prepared membranes were applied in adsorption and desorption of cationic dye (Methyl violet) and the effect by varying the feed Na^+–MMT/MMA (M/P) ratio was investigated.

2. Experimental

2.1. Materials

Two Na^+–MMT clay products were employed in this study. Na^+–MMT (Kunipia F) with cation-exchange capacity (CEC) of 119 mequiv./100 g was supplied by Kunimine (Tokyo, Japan), while Na^+–MMT (PK-802) with CEC of 115 mequiv./100 g was from Pai-Kong (Taoyuan, Taiwan). Poly(methyl methacrylate) (PMMA, CM 205, $Mw \approx 90{,}400$ g/mol and PDI = 1.71 (measured by gel permeation chromatography using polystyrene as standard)) was a kind gift from Chi-Mei (Tainan, Taiwan). Methyl methacrylate (MMA) was bought from SHOWA (Tokyo, Japan) and used as supplied without further purification. Sodium dodecyl sulfate (SDS) was purchased from Angus Buffers and Biochemicals (Niagara Falls, NY, USA). Methyl violet (75%, Mw = 408) was purchased from Sigma–Aldrich (Milwaukee, WI, USA). Other reagents were of HPLC or analytical grade.

2.2. Preparation of PMMA/Na^+–MMT composite membranes

Three kinds of PMMA/Na^+–MMT composite membranes were prepared in this study. Membrane A was made by mixing commercial PMMA and Na^+–MMT in NMP as casting solution. For Membrane B and Membrane C, emulsion polymerization of MMA/Na^+–MMT mixture was conducted, followed by dissolving the polymer composite in NMP/THF = 1 (w/w) as casting solution.