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Fabrication and characterization of micro-patterned PDMS composite membranes for enhanced ethanol recovery

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ABSTRACT

Bio-ethanol recovery via pervaporation process has drawn growing attention in the past few decades, however, its large-scale industry application remains limited due to the relatively low separation efficiency, especially in flux. In view of this, surface patterned nonporous PDMS (Polydimethylsiloxane) composite membranes with enhanced ethanol recovery efficiency were fabricated in this work. Line and space pattern was first printed on two-layer PVDF (Polyvinylidene fluoride) substrate using phase separation micromolding followed by modified immersion precipitation. And then PDMS solution prepared with three kinds of crosslinking agents (TEOS, Tetraethyl orthosilicate; VTES, Triethoxyvinylsilane; p-TTES, p-tolyltriethoxysilane) were cast atop the as-prepared patterned substrate as selective layer. Morphology, topography and surface chemistry were thoroughly characterized and results indicated that PDMS cross linked with TEOS showed the largest pattern size, while for membranes prepared with VTES and p-TTES, pattern size appeared to be smoothed. This can be mainly ascribed to the higher steric effect introduced by vinyl and phenmethyl groups, which increased the rigidity of polymer and thereby reduced the pattern size. Pervaporation performance for both patterned and non-patterned composite membranes under varied feed concentration and temperature were also evaluated. Evidence supported that permeate flux of patterned membranes cross linked with TEOS reached 977.73 g m^{-2} h^{-1} (45 °C, 2 wt% ethanol concentration) and are generally 2.11 times as high as that of non-patterned one. In addition, although increased the permeate flux, surface patterning exerted no adverse effect on membrane selectivity. The overall findings of this work provide a promising platform for nonporous composite membrane preparation to achieve high permeate flux without losing selectivity.

1. Introduction

Bio-ethanol has been recognized as one of the most promising alternative fuels in the 21st century. Based on its relatively high octane number and heat of vaporization, bio-ethanol is wildly used by blending with petrol and has great potential for future use in hybrid fuel vehicles [1]. Compared with fossil fuel, bio-ethanol not only emits less greenhouse gas but also produces no nitrogen and sulfur oxides. During the past few years, governments around the world have already focused on the development of this novel renewable fuel to deal with increasing energy crisis and environmental pollution [2]. The “Advanced Energy Initiative” of USA has planned to replace more than 75% foreign oil with biofuels (mainly bio-ethanol) by 2025 [3], and for China, the third major producer of bio-ethanol in the world, annual production was 1.7 million tons in 2009 and was predicted to reach 10 million tons at 2020 [4]. Considering all the environmental and energy supply factors, there is certainly an urgent need for both efficient and large-scale production of bio-ethanol.

Currently, bio-ethanol is mainly produced by fermentation of the second-generation feedstock (agricultural residues and forest biomass). And to ensure continuous fermentation, ethanol has to be removed from fermentation broth to maintain the activity of fermenting microorganisms which would stop reacting at high ethanol concentration (around 13 wt%). To date, a variety of methods have been applied to recover ethanol from fermentation broth, such as pervaporation [5–7], membrane distillation [8,9], vacuum distillation [10] and solvent extraction [11,12]. Among them, pervaporation shows superiority as cost-effective, less energy consumption and exerting little unpleasant effect on fermenting microorganisms [13]. However, its further application in biofuel industry is still limited by the low efficiency, especially in flux.

To improve the separation efficiency for organic liquid (ethanol) recovery, many optimizations have been applied to hydrophobic membranes used in pervaporation. Generally, separation performance can be optimized by the following two methods: modifying the intrinsic membrane materials and introducing hydrophobic additives like inorganic nano-fillers. For membrane materials, PDMS is one of the most

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Nomenclature

PDMS	poly dimethylsiloxane
PVDF	poly vinylidene fluoride
TEOS	tetraethyl orthosilicate
VTES	triethoxyvinylsilane
p-TTES	p-tolyltriethoxysilane
PTMSP	poly [1-(trimethylsilyl)-1-propyne]
ZIF	zeolitic imidazolate framework
MOF	metal–organic framework
MBR	membrane bioreactor
PES	poly ethersulfone
DBTL	dibutyltin dilaurate
DMF	N,N-dimethylformamide
TEP	triethyl phosphate
wt	weight(%)
P	gas pressure (bar)
γ	surface tension of liquid (dyn cm^{-1})
θ	contact angle between liquid and capillary wall (o)
D	pore size diameter (nm)
$\alpha_{i/j}$	separation factor
$C_{i,P}$	concentrations of component i in permeate (wt%)
$C_{i,F}$	concentrations of component i in feed solution (wt%)
J	total flux (g m^{-2} h^{-1})
m	mass of permeating mixture (g)
A	membrane effective surface area (m^2)
Δt	collecting time (h)

widely studied polymers and played a dominant role in organic solvent recovery [14] due to its easy processability, chemical stability and hydrocarbon affinity. Apart from pure PDMS, researchers have also tried to optimize the PDMS pervaporation efficiency by grafting or copolymerizing with other polymers [15]and changing the crosslinking agents [16]. Another big category of hydrophobic membrane material is PTMSP (poly[1-(trimethylsilyl)-1-propyne]), a high free-volume glassy polymer showing both remarkable permeability and selectivity [6,17], however, lower durability (caused by packing into dense layer in a few weeks) [18]. To mitigate this age-old limitation, Cher et al. [19] introduced aromatic framework (ultraporous additives) into PTMSP to make glassy polymer remain at its initial porous (high free-volume) stage, which ultimately helped maintain the superior permeability of PTMSP. In addition, Nikos et al. has recently demonstrated the possibility to increase the free-volume for rubbery polymer (like PDMS) by block copolymer self-assembly, which extraordinarily improved ethanol/butanol (biofuel) permeability [20]. As for optimizations using inorganic nano-fillers (silica [21,22], ZIFs [23,24],MOFs [25], etc.), which has drawn great attention in the recent years, performance promotion can be mainly ascribed to enhanced resistance towards aqueous molecules and/or newly built pathways for target hydrocarbon molecules.

Apart from conventional improving methods based on polymer synthesis or nano-filler introduction, surface patterning has been an emerging and effective method to break through the trade-off effect and optimize separation efficiency for various membrane processes [26]. For microfiltration, Won et al. [27] successfully prepared patterned (pyramid and prism) PVDF membrane using lithographic method followed by modified immersion precipitation. Results of membrane bioreactor (MBR) testing showed higher water flux for patterned membrane, which was in proportion with increased surface area. In ultrafiltration, micro-patterned surface was introduced to hollow fiber membranes by patterned spinneret and have been extensively studied by Culfaz et al. [28–32]. Compared with conventional round fiber, micro-patterned membranes showed higher fouling resistance resulting from looser deposition of particles in the pattern grooves. Maruf et al. [33] prepared flat polyethersulfone (PES) ultrafiltration membranes by hot embossing and results indicated that presence of patterned surface obviously increased the critical flux (flux at which particles begin to deposit). In theory, Maruf explained this anti-fouling character with shear-induced diffusion. Specifically, the increased local shear rate near membrane surface (caused by patterning) prevented the particle deposition. On the basis of patterned PES ultrafiltration membrane, interfacial polymerization was then introduced atop to prepare surface patterned thin film composite membrane [34–36]. In nanofiltration and reverse osmosis testing [37], patterned thin film composite membranes displayed both higher flux and rejection values than non-patterned ones due to reduced concentration polarization. As for gas separation, Peters et al. [38] reported that micro-patterned membrane was able to increase gas flux by 59% compared with flat one. Combining all these works, surface patterning is certainly an efficient way to increase surface area and modify the local flow behavior [39–41], which as a result lead to higher flux and anti-fouling property. However, up to now, the effect of surface patterning on pervaporation process has not been a subject of much investigation.

In view of the above research deficiency and growing significance of bio-ethanol recovery via pervaporation, we for the first time fabricate micro-patterned PDMS composite membranes to enhance the ethanol separation efficiency. The three-layer composite membrane consists of a two-layer micro-patterned PVDF substrate, which fabricated by phase separation micro-molding [42] and modified immersion precipitation methods [27], and a selective PDMS layer on top cross linked with three kinds of crosslinking agents. Morphology, topography and chemical property of composite membranes were comprehensively characterized. Ethanol recovery performance was also evaluated for both patterned and non-patterned composite membranes under varied feed concentration and temperature, and results indicated that surface patterning is definitely a potential method to improve membrane permeability by increasing effective membrane surface area.

2. Experimental

2.1. Materials

The photoresist master mold made by photolithography process was fabricated by micro systems engineering lab of Capitalbio Co., Ltd. Silicon elastomer and cross-linking agent (PDMS, Sylgard 184), used for replica mold preparation, were supplied by Dow Corning Corporation. For selective layer preparation, PDMS (kinetic viscosity, 20,000 mPa s) was obtained from Beijing Dingye Co., Ltd (Beijing, China), and catalyst Dibutyltin dilaurate (DBTL, 95%) was from TCI (Shanghai) Development Co., Ltd. The tetra-functional cross-linking agent Tetraethyl orthosilicate (TEOS, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). For tri-functional cross-linking agents: Triethoxyvinylsilane (VTES, 98%) was obtained from TCI (Shanghai) Development Co., Ltd. and cast) and p-tolyltriethoxysilane (p-TTES, 98%) from Tianjin Heowns Biochem Co., Ltd. To fabricate porous substrate, polyvinylidene fluoride (PVDF-6020) was purchased from Solvay (Shanghai) Co., Ltd. N,N-dimethylformamide (DMF,AR), heptane (AR), triethyl phosphate (TEP, AR) and ethanol (AR) were used as solvent and supplied by Modern Oriental Technology development Co., Ltd.(Beijing, China).

2.2. Fabrication of patterned and non-patterned PDMS/PVDF composite membranes

2.2.1. Preparation of patterned replica mold

The photoresist master mold with line and space pattern (100 μm in