

# Organic solvent-resistant and thermally stable polymeric microfiltration membranes based on crosslinked polybenzoxazine for size-selective particle separation and gravity-driven separation on oil-water emulsions



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## ABSTRACT

Polymeric membranes, compared with their inorganic counterparts, usually suffer from insufficient solvent resistance and thermal stability. In this study, an organic solvent-resistant thermally stable polymeric microfiltration membrane is prepared with a self-crosslinkable polybenzoxazine as a precursor. The obtained membranes have pore sizes of approximately 3.4  $\mu\text{m}$  and superior antishrinkage stability in organic solvents; thus, they exhibit excellent performance in terms of size-selective particle separation in organic phases. The membranes are also effective in the gravity-driven separation of surfactant-stabilized water-in-oil emulsions. The water contents of the filtrate oil phases are close to the natural solubility of water in the solvents; for example, a water content of 350 ppm, which is comparable to the water solubility in toluene (330 ppm), has been found in the filtrate toluene from water-in-toluene emulsions. Moreover, the membrane demonstrates pH-induced changes in oil and water selectivity in oil–water separations. When treated with a strong base solution, the oil-selective membrane becomes water-selective and exhibits favorable performance in terms of separating organic solvents from surfactant-stabilized oil-in-water emulsions. These features effectively extend the application scope of the prepared membrane for oil–water separations.

## 1. Introduction

Microfiltration (MF) membranes with pore sizes of 0.1–10  $\mu\text{m}$  are used extensively for removing contaminants from mixed feed solutions and can isolate a targeted product from such solutions [1–4]. Commercial MF membranes made from various thermoplastic polymers such as polysulfone, polyethersulfone, poly(vinylidene difluoride) (PVDF), and polyacrylonitrile are used extensively for aqueous feed streams. However, because of membrane solubility in organic solvents, their application for solvent-phase separation is somewhat limited. Postcrosslinking these membranes with suitable chemical agents might prevent the membranes from dissolving in organic solvents [5–11]. Another concern is that the postcrosslinked membranes can become highly swollen in solvents, and this can result in them losing their separation function and performance. Therefore, organic solvent-resistant MF membranes are desired for specific applications such as solvent-phase filtration, oil–water separation, and porous support of composite membranes [12–18]; however, recent studies have focused on organic solvent nanofiltration.

For harsh separation conditions such as high polar solvents and high temperatures, filtration membranes made of polytetrafluoroethylene (PTFE) and polyimide (PI) fabric woven are commercially available. Because of their mechanical strength and thermal stability, organosoluble PIs may be the most studied polymers for organic solvent nanofiltration [19–21]. Organosoluble PI-based membranes are generally prepared through phase inversion processes. However, these membranes remain unsuitable for filtration with feed solution of high polar aprotic solvents. In one study, PI-based membranes were post-crosslinked to enhance their stability in filtration operations [22]. By contrast, conventional aromatic PI-based dense films, which are insoluble in organic solvents, are obtained by casting a poly(amic acid) (PAAc) solution into PAAc films and subsequently converting the films into corresponding PI films through thermal imidization. However, fabricating PI-based porous membranes through a nonsolvent phase separation process is impossible with a PAAc precursor because of the strong interaction between PAAc and water (the nonsolvent). To address this problem, Kang et al. [23] attempted to reduce the interaction between PAAc and water through partial imidization of the PAAc

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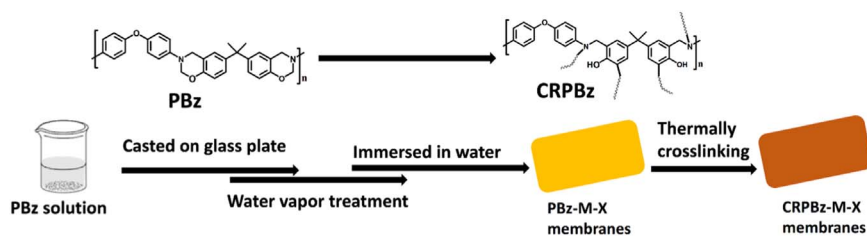


Fig. 1. Fabrication of crosslinked PBz based membranes.

precursor, and successfully prepared asymmetric PI membranes. In another such attempt, Chun et al. [24] added PAAc solvent (N,N-dimethylacetamide [DMAc]) into a coagulation solution to delay the demixing phase inversion. As not many successive works have been reported on preparation of solvent-resistant PI-based porous membranes, porous membranes made of thermosetting resins have been reported [25–30]. However, applying these membranes to filtration is rare because of the inconvenience of fabrication and unsatisfactory membrane properties.

As an alternative to postcrosslinking thermoplastic polymer-based membranes during fabrication processes, crosslinked membranes made of organosoluble self-crosslinkable polymers are relatively attractive because they can be fabricated through the conventional process. In the present study, a linear polybenzoxazine (PBz; Fig. 1) [31,32] was utilized because of its self-crosslinking ability, low cost, and processing property. Moreover, crosslinked PBz exhibits some attractive properties for membrane separation, including low-surface free energy [33,34], excellent solvent resistance, and high thermal stability. Crosslinked PBz-based dense membranes for pervaporation [35] and electrospun nanofiber mats [36] for oil–water separation [37] and separators for lithium-ion batteries [38] have been reported. In the present study, porous membranes of linear PBz were obtained through a conventional vapor-induced phase separation (VIPS) process and subsequently *in situ* thermally crosslinked through a simple thermal process (Fig. 1). Additionally, applications of the crosslinked PBz-based membranes for size-selective particle separation in organic solvents and for separating surfactant-stabilized oil–water emulsion were examined.

## 2. Experimental

### 2.1. Materials

Bisphenol-A (BPA; ECHO Chemicals), 4,4'-oxy-diphenylamine (ODA; Sigma-Aldrich), and paraformaldehyde (Acros) were used as received for preparing PBz in accordance with the reported method [32]. The preparation and characterization of PBz was reported in our previous paper [36]. The PBz sample utilized in the present study had a number-averaged molecular weight of  $6000 \text{ g mol}^{-1}$ , polydispersity index of 4.3, and inherent viscosity of approximately  $0.17 \text{ dL g}^{-1}$  (measured with N-methyl-2-pyrrolidone (NMP) at a concentration of  $0.5 \text{ g dL}^{-1}$ ) in. The surfactants, Span 80 and Tween 80, were purchased from Sigma-Aldrich and used as received. Silica particles were received from Chang Chun Petrochemical Company, Taiwan. Reagent-grade solvents were used for synthesis reactions and oil–water separation tests.

### 2.2. Instrumental characterization

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were collected using a Q20 differential scanning calorimeter and Q50 thermogravimetric analyzer (both purchased from Thermal Analysis Instruments), respectively, at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. Water contact angles (WCAs) were recorded using a surface analysis instrument from First Ten Ångströms Co. (model: FTA1000B). Morphology was observed using a scanning electron microscope (SEM; Hitachi SU8010 Field-

Emission SEM). Stress–strain curves of the membranes were recorded using an Instron 5543 mechanical tester with a sample size of  $1 \text{ cm} \times 4 \text{ cm}$  and an elongation rate of approximately  $0.5 \text{ mm min}^{-1}$ .

The pore sizes of the prepared membranes were determined using a capillary flow porometer purchased from Porous Materials Inc. (model: PMI CFP-1500). The mean pore size and error for each membrane was obtained with 3 measurements on independent samples. The gel fraction (GF) of each crosslinked membrane in the testing solvent was determined through a weight difference method. A dry membrane (weight:  $W_0$ ) was soaked in the solvent for 24 h, extracted, dried under a vacuum at room temperature, and weighed ( $W_r$ ). The GF of the sample was determined using the following formula:  $\text{GF} (\%) = W_r/W_0 \times 100\%$ . The water content in the organic solvent was measured using a C30 Karl Fischer coulometer from Mettler Toledo Co. The toluene content in water was measured through an absorption method involving ultraviolet-visible spectroscopy (PerkinElmer LAMBDA 850 UV/Vis Spectrophotometer). The sizes and size distribution of the droplets in oil–water emulsions were measured using a zeta potential analyzer (model: Malvern, zetasizer nano). Silica particles in tetrahydrofuran (THF) were analyzed using a laser diffraction particle size analyzer purchased from Beckman Coulter, Inc. (model: Coulter LS230) with an irradiation beam of 732 nm.

### 2.3. Preparation of crosslinked PBz-based microfiltration membranes

A PBz solution (20 wt% in NMP) was casted on a glass plate. The sample was placed into a chamber being continuously filled with a fully hydrated air stream (water vapor treatment). After a desired period, the sample was immersed in a deionized water bath for approximately 48 h. The obtained free-standing membrane was repeatedly washed with water and dried under a vacuum at  $60 \text{ }^\circ\text{C}$  for 48 h to yield the PBz-based membrane (PBz-M-X; X denotes the duration (min) of water vapor treatment). The thermally crosslinked analogues (CRPBz-M-X) were obtained by thermally treating the PBz-M-X membranes at 120, 180, and  $240 \text{ }^\circ\text{C}$  each for 1 h.

### 2.4. Basic and acidic solution treatments on CRPBz-M membrane

Basic treatment on CRPBz-M membrane was carried out with immersing the membrane in a NaOH aqueous solution ( $\text{pH} = 14$ ) for 4 h. The treated membrane was then washed with water. Acidic treatment was performed with the same manner using a sulfuric acid aqueous solution ( $\text{pH} = 1$ ).

### 2.5. Preparation of emulsified oil–water heterogeneous systems

For the water-in-oil emulsions, water (1 wt%) and Span 80 (0.3 wt%) were added to the oil phase. The mixtures were subsequently magnetically stirred and treated with an ultrasonic bath for 2 h. For the oil-in-water emulsions, oil (1 wt%) and Tween 80 (0.02 wt%) were added to water, and the mixtures were treated by following the procedure used for the water-in-oil emulsions. Toluene and chloroform were utilized as the oil phases in this study.

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