

Sol-gel derived hybrid polymer-inorganic membranes for pervaporation desalination process

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Abstract

Application of pervaporation to desalination involves the evaporation of water through hydrophilic non-porous membranes. Transport through the membrane is driven by a vapour pressure difference between the feed solution and the permeate vapour. It has the advantage that high salt rejection and potential low energy consumption. However, the low flux is still remained as the major technical challenge for commercial application of pervaporation processes for desalination.

In this study, a hybrid polymer-inorganic membrane based on poly-(vinyl alcohol) (PVA) and inorganic silica was developed via a sol-gel method for desalination by pervaporation. Maleic acid was used as an additional crosslinking agent to improve the dense packing of polymer chains and also to improve the compatibility between the polymer and silica network. Results revealed that an uniform dispersion of silica nanoparticles less than 50 nm in the polymer matrix could be achieved. The swelling of PVA in water has been greatly suppressed by the addition of silica. Pervaporation testing of fabricated thin film composite membranes for brackish water desalination achieved high salt rejection (>99.5%). The flux was generally increasing with the feed temperature and a high flux of 9.84 kg/m²·hr was achieved at a feed temperature 65°C and 6 Torr vacuum.

Keywords

Poly(vinyl alcohol); hybrid polymer-inorganic membrane; desalination

1. INTRODUCTION

Poly(vinyl alcohol) (PVA) has been studied extensively as membrane material in various applications due to its excellent film-forming and highly hydrophilic properties. PVA membranes are known to exhibit high degrees of swelling in aqueous solutions due to the presence of hydroxyl groups [1, 2]. To improve the performance and stability of PVA membranes in aqueous solutions, it is necessary to insolubilise or modify the membrane by crosslinking or addition of hydrophobic groups to achieve a stable membrane with good mechanical properties and selective permeability to water. Incorporation of inorganic particles in PVA membranes to form hybrid polymer-inorganic membranes has been one such technique to improve the stability and separation performance of PVA membranes, which has been studied intensively due to their extraordinary properties[3-5]. A defining feature of polymer nanocomposites is that the small size of the inorganic fillers leads to a dramatic increase in interfacial area as compared with traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings [6]. This is especially important for enhancing the permeation property of membrane in water separation application.

Although pervaporation is widely used for separation or concentration of mixtures of aqueous-organic or organic liquids, there are only limited studies on application of this technology for water desalination [7, 8]. Application of pervaporation to desalination involves the evaporation of water through hydrophilic non-porous membranes. Transport through the membrane is driven by a vapour pressure difference between the feed solution and the permeate vapour [1]. In desalination applications, pervaporation has the advantage of near 100% of salt rejection and potential low energy consumption. The pervaporation of an aqueous salt solution can be regarded as separation of a pseudo-liquid mixture containing free water molecules and bulkier hydrated ions formed in solution upon dissociation of the salt in water [7]. A major limitation for commercial application of pervaporation processes for desalination is the water flux, as in existing systems the flux is generally quite low. One major reason for this is due to lack of high performance membranes with both high water flux and high salt rejection [9, 10].

The objective of this study is to fabricate a novel hybrid polymer-inorganic membrane based on PVA, MA and silica and evaluate its pervaporation performance for desalination application. The hybrid membrane was synthesised via a sol-gel route by using tetraethoxy-silane (TEOS) as the silica precursor with maleic acid (MA) as an additional crosslinking agent. A supported composite membrane consisting above mentioned PVA/MA/silica layer on cellulose acetate porous support was also fabricated and its pervaporation performance was also tested.

2. EXPERIMENTAL

2.1 *Hybrid membrane synthesis and characterisation*

PVA (98+% hydrolysed, molecular weight of 130,000g/mol), TEOS (98%), MA, p-toluene sulfonic acid and sodium chloride (NaCl) were obtained from Sigma-Aldrich and used without further purification. Milli-Q deionised water (18.1 M Ω ·cm@25°C) was used to prepare PVA solution.

The PVA/MA/silica hybrid membranes were synthesised via an aqueous route. A 0.75wt% PVA solution was obtained by dissolving 0.75 g of PVA polymer powder in 100 mL of deionised water at 90°C. The obtained 0.75wt% PVA solution was cooled to room temperature and the pH was adjusted by HCl or p-toluene sulfonic acid (pH=1.7 \pm 0.1). Then

predetermined amount of MA (the weight content of MA with respect to PVA = 5-20 wt%) was added into the PVA solution and stirred till fully dissolved. Under steady stirring, a predetermined TEOS and ethanol mixture (mass ratio of TEOS: ethanol = 1:9) was added drop wise to the above solution and kept stirring for 2 hr (The weight content of SiO₂ with respect to PVA = 10-25 wt%). For unsupported membranes, the resulting homogeneous mixture was filtered and casted on Perspex Petri dishes to the desired thickness and dried in air. For supported composite membrane, an 8 wt% PVA solution was used instead and the final solution was filtered and coated on a cellulose acetate membrane (0.2 μm pore size) using a Revco control multi coater system. Finally, the obtained membrane samples were heated to 140°C for 2 hr. Pure PVA membrane samples were also prepared as a reference for comparison. The thickness of unsupported membranes was measured at different points using a Fowler electronic digital micrometer (accuracy ±1 μm). The thickness of supported membrane was measured from the cross section by SEM.

The functional groups of the hybrid membrane were assessed using a Perkin-Elmer Spectrum 2000 FTIR instrument. FTIR spectra of thin films were obtained with an 8 cm⁻¹ resolution, from 400 to 4000 cm⁻¹ wavelength. The morphology of the hybrid membrane samples were imaged using a Philips XL30 scanning electronic microscope (SEM). All samples were coated by sputtering with iridium for imaging. For cross section imaging, membrane samples were fractured in liquid nitrogen.

The water uptake of PVA and PVA/MA/silica hybrid membrane was measured by the following procedures: (1) Immersing the dried membrane in deionised water at room temperature for 48 h to reach the absorption equilibrium. (2) Blotting surface of wet membrane with the cleansing tissue to remove surface water and quickly weighing the wet membrane within 10 sec (W_s). (3) Drying the membrane in a vacuum oven at 50°C for overnight and then weighing again to obtain the mass of dried membrane (W_d). The water uptake of membrane was then calculated according to:

$$\text{Water uptake} = (W_s - W_d)/W_d \times 100\% \quad (1)$$

2.2 Pervaporation testing

The pervaporation experiments were carried out on a laboratory scale pervaporation unit. The membrane was placed in the middle of a pervaporation cell and the effective surface area of the membrane was 12.6 cm². The feed solution containing 2000 ppm NaCl was pumped to the feed side of the membrane. The pressure on the permeate side of the pervaporation cell was maintained at 6 torr with a vacuum pump. The permeate was collected in a cold trap immersed in dry-ice. The salt concentration of the feed and permeate were derived from measured conductivity with an Oakton[®] Con 110 conductivity meter.

The pervaporation performance of hybrid membranes treating aqueous salt solutions were characterised by water flux and salt rejection. The water flux (J) was determined from the mass (M) of permeate collected in the cold trap, the effective membrane area (A) and the experimental time (t).

$$J = M/At \quad (2)$$

The salt rejection (R) was determined by the following equation:

$$R = (C_f - C_p)/C_f \quad (3)$$

where C_f and C_p are NaCl concentration in the feed and permeate, respectively.

The overall mass transfer coefficient (K_{ov}) was determined using the following equation as explained in [11, 12].

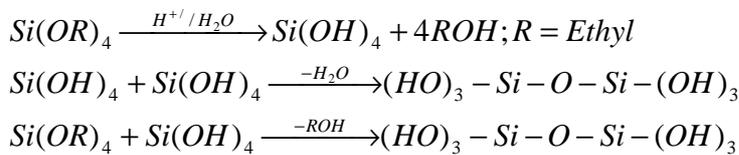
$$K_{ov} = \frac{V}{At} \ln\left(\frac{C_0}{C}\right) \quad (4)$$

where V is the initial liquid volume of the feed solution, A is the membrane area, C_0 is the initial feed concentration and C is the feed concentration at time t.

3. RESULTS & DISCUSSION

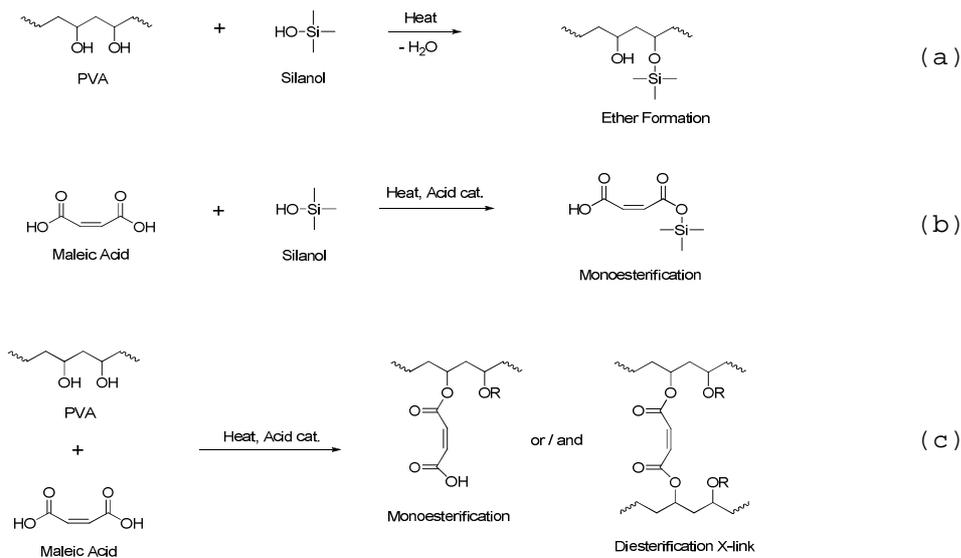
3.1 Synthesis of hybrid membranes

The sol-gel process using TEOS is one of the most efficient methods for preparing silica containing composite materials. The method comprises initial hydrolysis to form silanol groups and subsequent condensation and removal of water and solvents, resulting in silica oxide network, as shown in scheme 1 [5, 13]. Under acid conditions, the hydrolysis reaction is more rapid than condensation reactions and linear or random branches of silica network tend to be formed [14].



Scheme 1: hydrolysis and condensation reaction of TEOS [5, 13].

In fabricating the hybrid PVA/MA/silica membranes, the hydroxyl groups in the repeating units of PVA and the carboxylic groups in MA were expected to produce strong secondary interactions with the residual silanol groups generated from acid catalysed hydrolysis and polycondensation of TEOS to form hydrogen and covalent bonds. In addition, PVA and MA would go through esterification reaction via grafting or crosslinking under heat treatment to form the ester group. Main reaction routes for the hybrid PVA/MA/silica membrane are presented in scheme 2. Resulting hybrid PVA/MA/silica membrane would form a compact structure with network crosslinking due to above mentioned reactions among PVA, MA and TEOS.



Scheme 2: Reaction scheme for the hybrid PVA/MA/silica membrane.

3.2 Characterisation of hybrid membranes

Figure 1 shows the FTIR spectra of PVA/MA and PVA/MA/silica membrane with a pure PVA sample as a reference. FTIR spectra confirmed the formation of PVA/MA and PVA/MA/silica hybrid with network crosslinking. The pure PVA sample (Figure 1-a) shows the typical C-H broad alkyl stretching band (2800-3000 cm^{-1}) and the hydrogen bonded hydroxyl band (3200-3570 cm^{-1}) [15]. The peak at 1000-1100 cm^{-1} was assigned to the C-O stretching vibration of the secondary alcohol (-CH-OH) of PVA. For the hybrid PVA/MA/silica membrane (Figure 1c), it was noticed there was an increase in the peak intensity at this range. The increase in peak intensity at 1000-1100 cm^{-1} could be explained by the formation of Si-O-Si bonds (1080 cm^{-1}) resulting from the self condensation reaction between the Si-OH groups of the hydrolysed TEOS, and also covalent Si-O-C bonds resulting from the reaction (or crosslinking) of PVA/TEOS. There was another increase in peak intensity at $\sim 1170\text{cm}^{-1}$. This could be an ether(C-O-C) or ester (-CO-O-) formation which resulted from the reaction between MA/TEOS and/or PVA/MA (scheme 1 and scheme 2b, 2c). There were also three new peaks observed at 950 cm^{-1} (figure1-c) assigned to Si-OH bonds, $\sim 1715\text{-}1725\text{cm}^{-1}$ and $\sim 1640\text{ cm}^{-1}$ (figure1-b&c) assigned to the ester (-CO-O-) or acid (-CO-OH) and C=C group, respectively [16]. Si-OH bonds at $\sim 950\text{ cm}^{-1}$ was resulted from the hydrolysis reaction of TEOS and the hydrogen bonds between the organic groups and the silica. The ester and acid groups at 1715-1725 cm^{-1} were attributed to the esterification reaction (by grafting or crosslinking) between PVA and MA (scheme 2c) or MA and TEOS (scheme 2b).

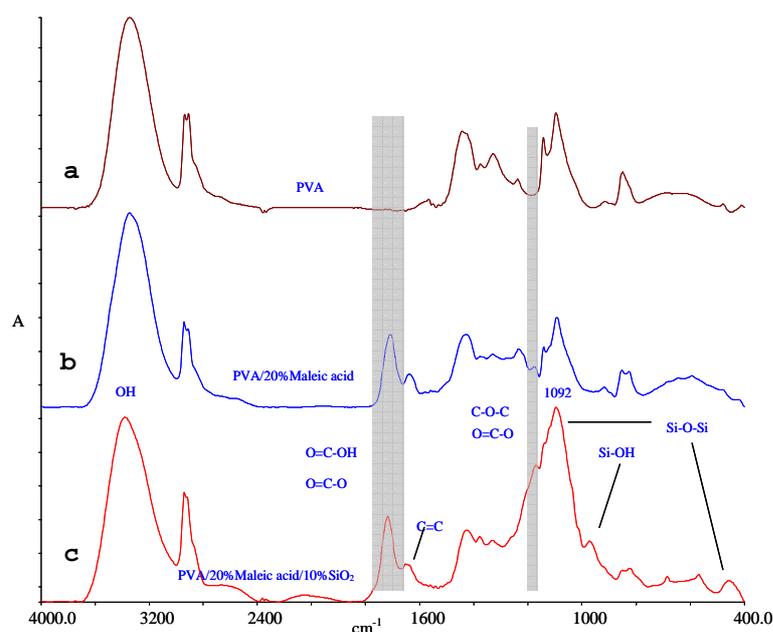


Figure 1. FTIR spectra of pure PVA and hybrid membranes.

In the hybrid PVA/MA/silica membrane, MA is also believed to act as an organic-inorganic coupling agent, as resulted from reaction scheme 2b&2c. This idea is supported by comparing the optical properties of hybrid PVA/MA/silica and PVA/silica membranes. Figure 2 shows the optical images of PVA/silica and PVA/MA/silica membranes. The membrane sample with MA (PVA/MA/silica) was clear and transparent. On the other hand, the membrane sample in the absence of MA (PVA/silica) was brown in colour and not transparent.

Figure 2: Optical image of hybrid PVA/MA/silica and PVA/silica membranes.

The morphology of hybrid membranes was studied by SEM, cross section images of both unsupported and supported composite membranes are shown in Figure 3. The cross section image of unsupported membrane shows a smooth surface. No particles or agglomeration greater than 50 nm was observed (Fig. 3a), indicating that the silica nanoparticles were well dispersed in the polymer matrix. The cross section image of supported composite membrane shows a selective skin layer on top of a porous support layer. The average thickness of the active membrane layer was about 17 μm and the thickness of the support layer was 135 μm .

Figure 3: SEM images of unsupported and supported hybrid PVA/MA/silica membrane (a: unsupported membrane, b: supported composite membrane).

Table 1: Water uptake of PVA and its hybrid membranes.

Sample details	Water uptake, %
PVA	301%
PVA, 20%MA	61%
PVA, 20%MA, 10%SiO ₂	22%
PVA, 20%MA, 25%SiO ₂	11%

Table 1 shows the water uptake of pure PVA and hybrid membranes. Pure PVA membrane showed a very high degree of swelling in cold water. For the PVA/MA membrane, the swelling was greatly suppressed. This could be explained by the grafting or crosslinking of the PVA polymer chains via an ester linkage between PVA and MA (Scheme 2c). For PVA/MA/silica membranes, the swelling was further suppressed with the addition of silica. This could be explained by the further formation of chemical bonds between polymer and silica (Scheme 2a and 2b), which resulted in a dense and rigid hybrid structure. Therefore, the water uptake was greatly suppressed.

3.3 Pervaporation testing

Table 2 shows the pervaporation desalination performance of unsupported PVA/MA/silica hybrid membranes with same thickness (5 μm) at a feed temperature of 22°C and a vacuum of 6 Torr. Pure PVA membrane was not stable and PVA was gradually dissolved in the aqueous solution. Therefore, only pervaporation results on hybrid membranes are shown in Table 2. Overall, the PVA based hybrid membranes demonstrated good desalination performance with high flux (>3.65 kg/m²·hr) while maintaining a high salt rejection (up to 99.6%). The PVA/MA/silica membrane containing 20 wt% MA and 10 wt% silica gave the highest flux of 5.51 kg/m²·hr (sample c). The high flux may be contributed to the size and quantum effect of silica nanoparticles dispersed in the polymer matrix. The incorporation of silica particles in the polymer chain at the nano-scale may disrupt the polymer chain packing and increase free volume, resulting in an increase in water flux. Further increase of the silica content from 10 to 25% led to a further increase of the crosslinking density, resulting in less water solubility capacity (ie. lower water uptake rates) during the diffusion process. Therefore, the water flux decreased. This is also supported by the results on overall mass transfer coefficients (Table 2).

Table 2: Pervaporation testing results of unsupported hybrid membranes (membrane thickness 5 μm , feed flowrate 30 mL/min, feed temperature 22°C, vacuum 6 Torr).

Sample details	Water flux, kg/m ² ·hr	Salt rejection	Overall mass transfer coefficient, 10 ⁻⁹ m/s
a) PVA, 10% SiO ₂	2.99	95.2%	1.71
b) PVA, 20% MA	4.29	95.1%	2.55
c) PVA, 20% MA, 10% SiO ₂	5.51	99.6%	3.53
d) PVA, 20% MA, 25% SiO ₂	3.65	99.6%	2.22

The solution-diffusion model is usually used to describe the transport mechanism of the pervaporation process which involves three steps: sorption at the membrane surface, diffusion through the dense membrane and desorption into the vacuum [17]. That is, there are three mass transfer resistances which exist on the feed side, the membrane and on the permeate side. Under the high vacuum used in the study, the resistance to mass transport at the permeate side of the membrane is eliminated in pervaporation, as occurred also in vacuum membrane distillation. Thus, the overall mass transfer resistance could be either controlled by the feed side boundary layer or by the membrane itself [11, 12]. Overall mass transfer coefficients of hybrid membranes were estimated by using equation 4. The trend in change of overall mass transfer coefficient is in consistent with the trend in the water flux. The highest mass transfer coefficient was found for hybrid PVA/MA/silica membrane containing 20 wt% MA and 10 wt% silica (sample c). With further increase of silica content (sample d), the mass transfer coefficient decreased. This indicates that an optimum balance of MA and silica in the hybrid membrane is required to achieve the best performance.

The high salt rejection could be attributed to non-volatile nature of NaCl and compact structure of hybrid membranes. Firstly, NaCl is a non-volatile compound and it is unlikely to enter the vapour stream on the permeate side, which will lead to high salt rejection in the pervaporation process. On the other hand, the water molecules which are smaller in size will preferentially diffuse through the membrane due to the hydrophilic nature of the membrane [10, 18]. Secondly, the crosslinking among PVA, MA and silica reduced the swelling of the PVA membranes (Table 1), which led to a more rigid and compact structure, lowering the salt diffusivity. In particular, the degree of crosslinking increased with the increasing silica content (Table 1). Therefore, the salt rejection increased to >99.5%.

From the commercial aspect, one of challenges is to develop technology for making supported ultra-thin membranes to compensate for reduced membrane productivity [19]. Previous studies have shown multilayer-structured thin film composite membrane with a thin dense selective skin of PVA are more suitable for the alcohol dehydration by pervaporation due to excellent mechanical stability and process durability enhanced by the porous neighbouring layer [20-22]. In this work, supported composite hybrid PVA/MA/silica membrane was successfully prepared by a solution casting method, with the cross section image shown in Figure 3b. A series of experiments were carried out to test the pervaporation performance of this supported composite hybrid membrane for separation of aqueous salt solution, with the results shown in Figure 4. The pervaporation experiment was carried out at various feed temperatures (22-65°C). The salt rejection remained high (>99.5) under all temperatures. The water flux increased significantly with the feed temperature and a high flux of 9.84 kg/m²·hr was achieved at a feed temperature 65°C and 6 Torr vacuum. The result is in good agreement with that of the unsupported membranes [18]. The positive impact of feed temperature on water flux is mainly due to the increased vapour pressure on the feed side resulted from increasing temperature. This leads to the increase of the driving force for the mass transport, therefore the water flux increased. In addition, increasing in the water vapour pressure reduced the interactions between water molecules, which increased the motion energy and diffusion coefficient of the water molecules and made it easier for the transport of the water

molecules. This also contributed to the increase of water flux.

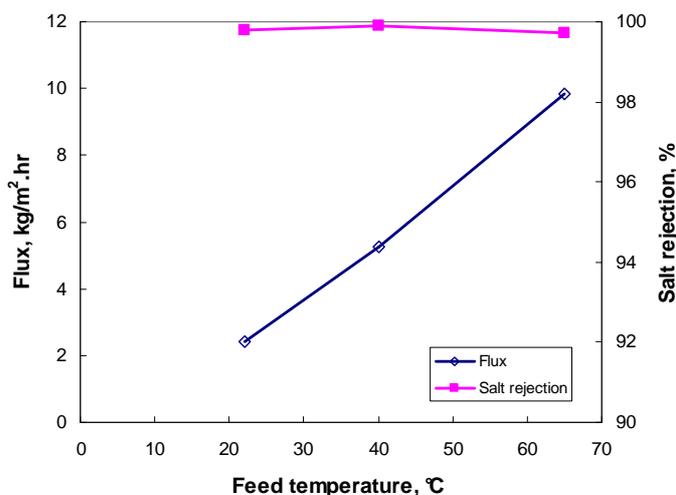


Figure 4. Pervaporation performance of supported hybrid PVA/MA/silica membrane (active layer thickness 17 μm , feed flowrate 30 mL/min, vacuum 6 Torr)

4. CONCLUSIONS

In this study, a hybrid polymer-inorganic membrane based on PVA, MA and silica was developed via a sol-gel method. Maleic acid was used as an additional crosslinking agent to improve the dense packing of polymer chains and also to improve the compatibility between the polymer and silica network. Results revealed that uniform dispersion of silica nanoparticles less than 50 nm in the polymer matrix could be achieved. The swelling of PVA in water has been greatly suppressed by the addition of silica. Pervaporation testing of unsupported hybrid PVA/MA/silica for brackish water desalination process shows very promising results with high salt rejection ($>99.5\%$) and good water flux ($5.51 \text{ kg/m}^2\cdot\text{hr}$). Addition of MA and silica in the right amount will enhance both water flux and salt rejection. A supported composite membrane was also successfully fabricated by the solution casting method. Preliminary results showed a potential for application the composite hybrid membrane for pervaporation desalination process. The flux was generally increasing with the feed temperature and a high flux of $9.84 \text{ kg/m}^2\cdot\text{hr}$ was achieved at a feed temperature 65°C and 6 torr vacuum. Future work will be focusing on the reduction of the thin skin layer to improve the water flux while maintaining high salt rejection.

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