

Chitosan/Polyvinylpyrrolidone-Silica Hybrid Membranes for Pervaporation Separation of Methanol/Ethylene Glycol Azeotrope

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ABSTRACT: Chitosan (CS)/polyvinylpyrrolidone (PVP)-silica hybrid membranes are prepared to separate the methanol/ethylene glycol (EG) azeotrope. These hybrid membranes are formed in semi-interpenetrating network structure at the molecular scale via sol-gel reactions between CS and tetraethoxysilane (TEOS). The physico-chemical property and morphology of the as-prepared membranes are investigated in detail. They have lower crystallinity, higher thermal stability, and denser structure than the pristine CS membrane and its blending counterpart. The as-prepared hybrid membranes demonstrate excellent performances and a great potential in pervaporation separation of methanol/EG. Silica-hybridization depressed the swelling degree of membranes in the azeotrope, and remarkably enhanced methanol sorption selectivity. The membrane containing 7.77 wt % PVP and 14.52 wt % TEOS has a permeation flux of $0.119 \text{ m}^{-2} \text{ h}^{-1}$ and separation factor of 1899. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Ethylene glycol (EG) is an important organic chemical widely used as a precursor to polyester and an automotive antifreeze. Their demand rapidly increases with the current development of the world polyester production. In the past, most of EG was produced from ethylene oxide via petroleum route. However, this process is generally accompanied by high cost and environmental pollution. And excessive water is consumed as well to increase EG yield and to inhibit the formation of diethylene glycol and triethylene glycol by-products. By contrast, nonpetroleum routes have great prospects for synthesis of EG due to the limited oil resources. Direct synthesis of EG from syngas is one of the easiest and the most effective nonpetroleum routes, and can produce EG in high purity after removal of methanol by-product from the system.¹ However, methanol easily forms an azeotrope with EG. Pressure swing distillation is the conventional method for separation of this azeotrope, but consumes a huge amount of energy. Therefore, exploring for alternative methods of distillation to separate the methanol/EG solution is growing a core issue.

As a novel green separation technology, pervaporation has attracted great attention owing to its advantages of high efficiency, simple process and environmental friendliness.^{2,3} Recently, there has been a growing interest in pervaporation

dehydration of EG solution. Various pervaporation membranes with good performances were successfully fabricated to dehydrate EG solution, such as CS coated zeolite filled regenerated cellulose membranes, poly (*N,N*-dimethylaminoethyl methacrylate)/polysulfone composite membranes, CS-poly(acrylic acid) polyelectrolyte complex membranes, and polybenzimidazole-based membranes.^{4–7} As aforementioned, removal of methanol from EG solution is also an important separation process in EG production. Pervaporation should have a great potential in separation of methanol/EG azeotrope.

Membrane with high selectivity and large permeation flux is the core of pervaporation technique.^{8–11} As a typical cationic polyelectrolyte with good hydrophilicity, good film-forming characteristics and chemical stability, CS is widely used as pervaporation membrane material.^{12–14} However, CS can be dissolved into some organic solvents and easily swelled in the aqueous solutions, and thus cannot provide sufficient selectivity and permeation flux in pervaporation. Great efforts are therefore taking to improve the stability and mechanical properties of CS-based membranes, such as CS blended with other polymers, filled with inorganic particles and hybridized by inorganic components.^{15–19} Surprisingly, silica-hybridization significantly improved water permselectivity and reduced swelling of CS membranes in aqueous organic solutions.^{19–22} However, silica hybridization remarkably depressed their permeation flux that

Table I. Composition of the CS/PVP-TEOS Organic–Inorganic Hybrid Membranes

No.	CS (wt)	PVP (wt)	TEOS (wt)	CS/PVP (wt/wt)
1	100	-	-	
2	85.48	0	14.52	-
3	81.41	4.07	14.52	20/1
4	80.14	5.34	14.52	15/1
5	77.71	7.77	14.52	10/1
6	71.23	14.25	14.52	5/1
7	90.91	9.09	0	10/1
8	86.04	8.60	5.36	10/1
9	70.86	7.09	22.05	10/1
10	65.09	6.51	28.40	10/1

decreased with increasing silica content. Recently, CS was blended with PVP to prepare novel pervaporation membranes.^{15,23,24} As a nonionic water soluble polymer with excellent adsorption, adhesion capacity, biocompatibility, and good thermal stability, PVP exhibits good miscibility with other polymers. The as-prepared CS/PVP blending membranes have high permeation flux. Unfavorably, the incorporation of PVP reduced mechanical stability of the CS membrane and simultaneously increased its swelling in aqueous methanol solution.

In this work, we fabricated novel CS/PVP-TEOS organic–inorganic hybrid membranes for removal of methanol from the EG azeotrope. PVP was incorporated to adjust the CS/PVP blending membrane microstructure at the molecular level to enhance permeation flux. Hybridization of the CS/PVP blend using TEOS will form semi-interpenetrating network in the hybrid membranes, resulting in an increase in the mechanical stability of the membranes and a decrease in the mobility of CS and PVP chains. Thus, the as-prepared CS/PVP-TEOS hybrid membranes should have large permeation flux and high separation factor in pervaporation separation of methanol/EG azeotrope. The influences of PVP and TEOS contents on the physico-chemical properties and pervaporation performance were studied in detail. And the feed temperature dependence was also investigated as one of important operating conditions.

EXPERIMENTAL

Materials

CS, with average molecular weight of 200 kD and deacetylation degree of 95%, was obtained from *Golden Shell Marine Biological Chemical Co. Ltd.* (Zhejiang, China). PVP with average molecular weight of 70 kD was purchased from *Xi Long Chemical Co. Ltd.* (Shantou, China). Deionized water was produced from a Milli-Q reagent grade system (RiOs™ 50, *Millipore*). All the other reagents of analytical grade were purchased from *Sino-pharm Chemical Reagent Co. Ltd.* (Shanghai, China) and used without further purification.

Membrane Preparation

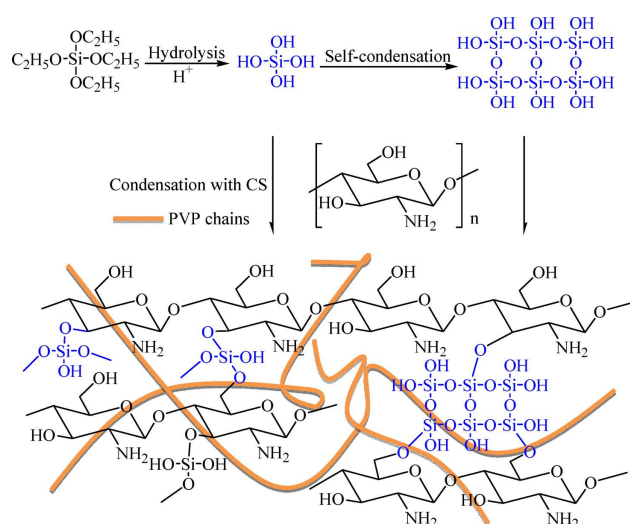
As shown in Table I, a given amount of CS and PVP under various ratios was dissolved in 1 wt % acetic acid solution at 60°C for 2 h to obtain 1.5 wt % CS/PVP mixtures.²⁵ Then, TEOS

and 0.2 mL of 1M HCl solution were added to form a mixture of pH 4. The former was used as a silica precursor and the latter a catalyst. Subsequently, the mixture was stirred at 60°C for 1 h to take hydrolysis-condensation of TEOS molecules with CS chains. The resulting solution was cast on a clean plastic plate and placed in an oven at 35°C for 24 h to form a membrane. The membrane was peeled off and heated in a vacuum oven at 100°C for another 4 h to get the CS/PVP-TEOS hybrid membrane.

In preparing CS/PVP-TEOS hybrid membrane, CS took a dehydration-condensation reaction with TEOS to form organic–inorganic hybrid membranes at the molecular scale (Scheme 1). TEOS was first hydrolyzed under acidic conditions to form TEOS silanol. The hydroxyl groups in one silanol and in the CS chains took a condensation reaction to form siloxane bonds as crosslinking bridges in the hybrid membranes. The inter-silanol self-condensation took place simultaneously to form oligomers that took a condensation reaction with the CS chains. All of these led to the formation of the semi-interpenetrating network in the hybrid membranes. This would restrict the mobility of CS and PVP chains and enhance the mechanical stability of the membranes.

Membrane Characterizations

The chemical structure of the hybrid membranes was analyzed using Fourier transform infrared 740SX (FTIR, Nicolet). The physical structure was characterized using X-ray powder diffraction (XRD, *Panalytical X'pert, Enraf Nonious*, Holland) at 25°C. The static water contact angles were measured by the sessile drop method using a contact angle meter (SL200B, *Shanghai Solon Tech*, China) at 25°C with relative humidity of 65%. The thermal stabilities were analyzed by a STA 409EP analyzer (*Netsch*, Germany) with a heating rate of 10°C min⁻¹ in the temperature range 25–900°C under nitrogen atmosphere. And the densities were measured by a digital microbalance (AB204-S, *Mettler Toledo*, MT) with density kit at 25°C.



Scheme 1. The formation process and chemical structure of the CS/PVP-TEOS hybrid membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

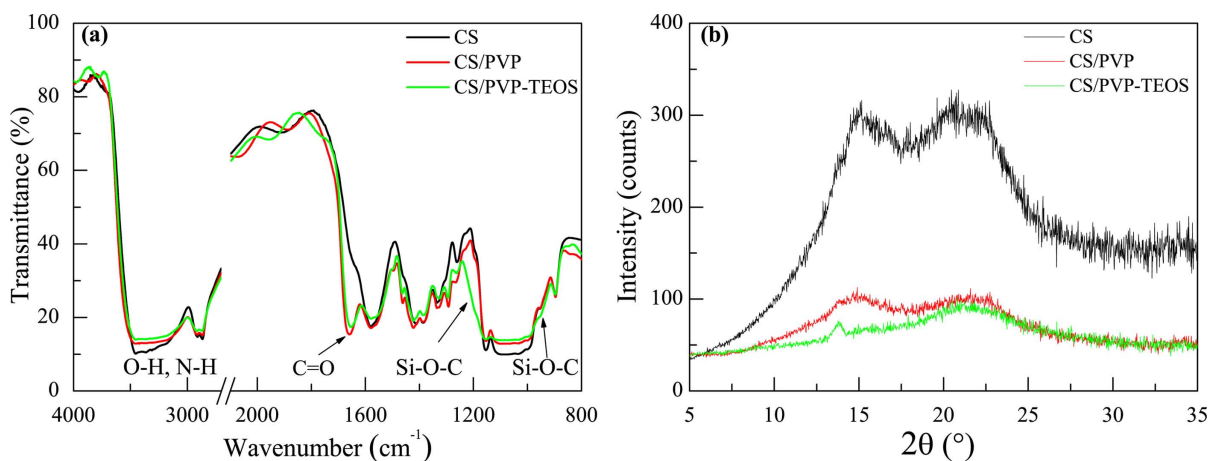


Figure 1. (a) FTIR and (b) XRD spectra of the CS membrane, the blending membrane with CS/PVP mass ratio of 10 : 1, and the hybrid membrane with CS/PVP mass ratio of 10 : 1 and 14.52 wt % TEOS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The morphology was observed using field emission scanning electron microscopy (SEM) (LEO 1530, LEO, Germany) and transmission electron microscopy (TEM) (JEM 2100, JEOL, Japan). Before SEM observation, a 5 nm-thick Pt layer was deposited on the samples to prevent electric charging. The samples for cross-sectional observation were prepared by freeze fracturing in liquid nitrogen. A copper grid was immersed into the membrane solution and then dried to prepare the sample for TEM characterization.

Swelling Studies

The membranes were heated in a vacuum oven at 80°C for 12 h to get the dry weight (W_d , g) before swelling testing. They were then immersed in the methanol/EG azeotrope (6 wt % methanol) for 48 h. Afterwards, the wetted membranes were taken out, wiped with tissue and weighed immediately. After that, the swollen membranes were immersed in the azeotrope again for 6 h. These steps were repeated until a constant weight (W_s , g) of the swollen membranes. The degree of swelling (DS) can be calculated by:

$$DS (\%) = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (1)$$

The adsorbate was completely desorbed from the swollen membrane at 90°C under vacuum and collected in a liquid nitrogen cold trap. The concentration of the adsorbate was determined by gas chromatography (GC-950). The sorption selectivity (α_{sor}) can be calculated by:

$$\alpha_{\text{sor}} = \frac{C_i^a / (1 - C_i^a)}{C_i^L / (1 - C_i^L)} \quad (2)$$

where C_i^a (wt %) and C_i^L (wt %) are the concentration of species i in the adsorbate and the azeotrope, respectively.

Pervaporation Experiments

Pervaporation experiment was carried out on a laboratory scale apparatus (Sulzer Chemtech, Germany) with the effective membrane area of 71 cm². The methanol/EG azeotrope (6 wt %

methanol) was used as feed. The pressure on the permeate side of 10 mbar and the feed flow rate of 80 L h⁻¹ were maintained. The permeate was collected in liquid nitrogen cold traps and measured by gas chromatography. The total permeation flux (J) and the separation factor (α) are calculated by:

$$J = \Delta M / (A \cdot \Delta t) \quad (3)$$

$$\alpha = \frac{y / (1 - y)}{x / (1 - x)} \quad (4)$$

where ΔM is the mass of the permeate (kg); A is the effective area of the membrane (m²); Δt is the permeation time (h); y and x are the concentration of methanol in the permeate and the feed, respectively.

RESULTS AND DISCUSSION

The Chemical Structure of the Hybrid Membranes

Figure 1(A) shows the FTIR spectra of the CS, CS/PVP blending, and CS/PVP-TEOS hybrid membranes. The characteristic peak around 1660 cm⁻¹ in the blending and the hybrid membranes is associated with stretching vibrations of C=O in PVP chains. The adsorption band at 970–1180 cm⁻¹ broadened in the hybrid membranes. This reveals the formation of Si—O—C bond with two characteristic peaks around 1170 and 990–945 cm⁻¹.²⁶ As shown in Scheme 1, the Si—O—C bonds are formed by the dehydration-condensation reaction between TEOS and CS chains. These formed bonds tethered the crosslinked CS chains and bridged CS chains into TEOS oligomers resulting in the formation of a crosslinking network in the hybrid membranes. On the other hand, a strong and broad peak around 3300 cm⁻¹ attributed to stretching vibrations of O—H and N—H in the pristine CS membrane decreased with the addition of PVP. However, this peak is the lowest in the hybrid membrane due to a decrease of the hydroxyl groups resulting from the condensation reaction between CS and TEOS.

The Physical Structure of the Hybrid Membranes

The crystalline structure of the hybrid membranes was studied by XRD. The resulting XRD data was corrected for Lorenz and

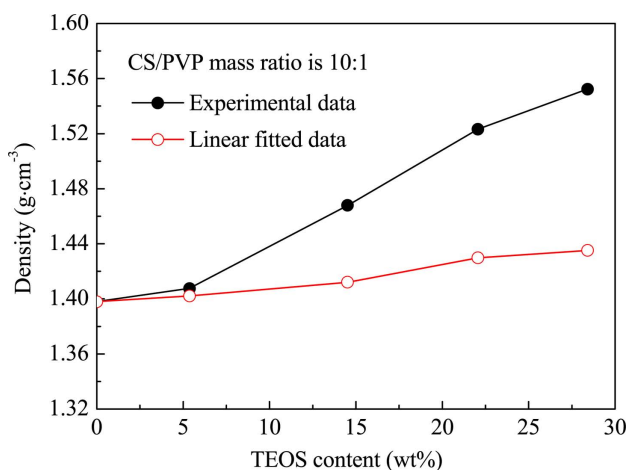


Figure 2. The experimental density and fitted density of the hybrid membranes with CS/PVP mass ratio of 10 : 1 at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polarization. The characteristic band of CS around 15°–22° depressed remarkably in the CS/PVP blending membrane owing to a decrease in CS content and their blending at the molecular level, as shown in Figure 1(B). When compared to the blending membrane, the intensity of the characteristic peak reduced slightly in the hybrid membranes because the introduction of TEOS dramatically interfered with the ordered packing of the CS chains. Both of them are almost amorphous, which is favorable to enhance the permeation flux of small molecules through the membranes.

Figure 2 shows that experimental density of the hybrid membranes increased with TEOS content. The hybrid membranes have higher density than their fitted data from linear addition of the CS/PVP blending membrane and the SiO₂ formed from TEOS. This sug-

gests that crosslinking of CS chain with TEOS reduced the free volume of membranes and made CS/PVP matrix denser.

Morphology and Microstructure of the Hybrid Membranes

Surface morphology and microstructure of the hybrid membranes were characterized by SEM and TEM. Figure 3 shows surface and cross-sectional images of the CS, CS/PVP blending and CS/PVP-TEOS hybrid membranes. Both the CS and CS/PVP blending membranes have smooth surfaces and uniform inner-structure from the SEM observations.²⁷ This confirms that CS and PVP blended uniformly with a good compatibility without phase separation. As described above, TEOS took self-condensation reaction to produce TEOS oligomers that possibly formed silica particles in the hybrid membranes at high TEOS content. The hybrid membranes are found to have a smooth surface below 14.52 wt % TEOS and a rough surface above 22.05 wt % TEOS. The hybrid membrane of 28.40 wt % TEOS has rough surface and silica particles were formed on its surface and cross-section due to the self-condensation of TEOS [Figure 3(C)]. By the way, all the as-prepared membranes in this work have thickness of 11–20 μm from the SEM observations.

Figure 4 shows the TEM microphotograph of the hybrid membranes. Silica nanoparticles of 1–3 nm in size are found to disperse uniformly in the hybrid membrane of 14.52 wt % TEOS [Figure 4(A)]. And with increasing TEOS content, big silica nanoparticles of 30–40 nm in size were formed in the hybrid membrane of 28.40 wt % TEOS [Figure 4(B)]. This suggests that TEOS took self-condensation reaction in the preparation of the hybrid membranes with abundant TEOS.

Thermal Stability and Hydrophilicity of the Hybrid Membranes

The thermal stability of the membranes is illustrated by DTG curves measured under nitrogen atmosphere. The peak-top temperature of

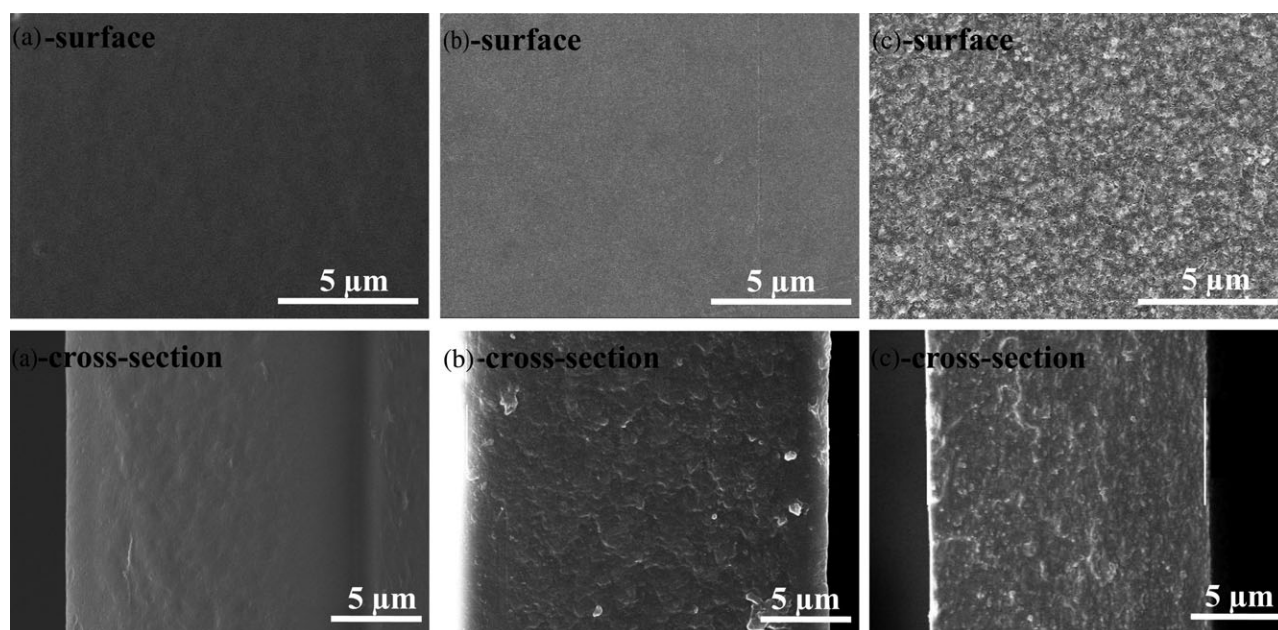


Figure 3. SEM images of membrane surface and cross section: (a) the CS membrane, (b) the hybrid membrane with CS/PVP mass ratio of 10 : 1 and 5.36 wt % TEOS, and (c) the hybrid membrane with CS/PVP mass ratio of 10 : 1 and 28.40 wt % TEOS.

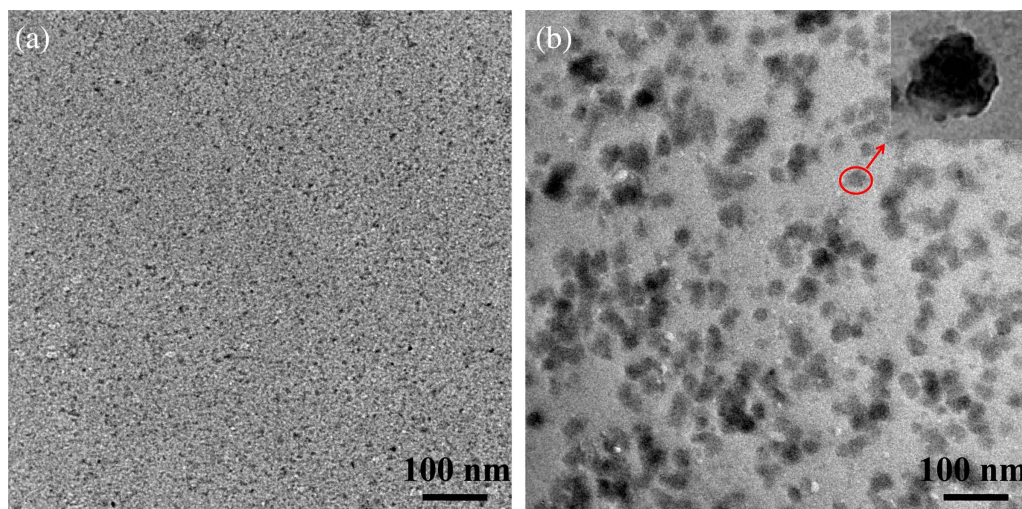


Figure 4. TEM images of the hybrid membranes: (a) CS/PVP mass ratio of 10 : 1 and 14.52 wt % TEOS, and (b) CS/PVP mass ratio of 10 : 1 and 28.40 wt % TEOS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the CS, CS/PVP blending, and CS/PVP-TEOS hybrid membranes was 301.7, 300.2, and 303.4°C, respectively (Figure 5). The addition of PVP disordered the arrangement of the CS chains, and thus reduced the crystalline regions of CS, resulting in a slight decrease in the thermal stability of the blending membranes. Since the incorporation of TEOS inhibited the mobility of the polymer chain, the thermal stability of the hybrid membrane increased accordingly.

In the hybrid membranes, TEOS molecules disordered the CS chains leading to an increase of the dissociative hydroxyl groups and amino groups on the CS chains, resulting in an increase in membrane hydrophilicity. Whereas, the number of hydroxyl groups decreased because of condensation between the hydroxyl groups of CS chains and TEOS silanols, particularly when TEOS content is above 14.52 wt %. As a result, the contact angle slightly increased below 14.52 wt % TEOS, and then rapidly enhanced at higher TEOS content [Figure 6(A)]. It reveals

the hydrophilicity of the hybrid membranes decreased with increasing TEOS content.

Swelling Properties of the Hybrid Membranes

Solubility of the membranes is a thermodynamic property and affects permselectivity in pervaporation, and is generally evaluated by swelling testing. Figure 6(B) shows the effect of TEOS content on the swelling of the hybrid membranes in the methanol/EG azeotrope at 25°C. Silica hybridization yielded the semi-interpenetrating network of crosslinked CS chains. This confined the mobility of CS and PVP chains, shortened the interchain spacing and made the membranes dense. Thus, the swelling of the hybrid membranes decreased with increasing TEOS content.

Sorption selectivity (α_{sor}) is an important factor in describing the sorption properties of a membrane in liquid mixtures. Methanol sorption selectivity of the membranes increased with TEOS content [Figure 6(B)]. This is owing to the crosslinking induced dense structure of the membrane treated by TEOS. The increase in the compactness of the hybrid membranes is favorable to adsorption of methanol molecules into the membrane and unfavorable for EG molecules. As a result, absorption of large molecules onto the membrane surface and diffusion through the membranes are found to be difficult.

Pervaporation Performances of the Hybrid Membranes

The effects of PVP and TEOS contents and feed temperature on pervaporation performance of the CS/PVP-TEOS hybrid membranes were investigated in detail. Figure 7(A) shows the effect of PVP content on pervaporation performance of the hybrid membranes of 14.52 wt % TEOS for separation of the methanol/EG azeotrope at 60°C. With the introduction of PVP into the membrane matrix, the disordered packing of CS chains and the increase of amorphous region in the hybrid membrane [Figure 1(B)] are favorable to diffusion of penetrant through the membrane, and thus result in an increase in permeation flux and a decrease in separation factor. On the other hand, the pervaporation separation index [$\text{PSI} = J \times (\alpha - 1)$] first increased with PVP content, and then decreased when PVP content is

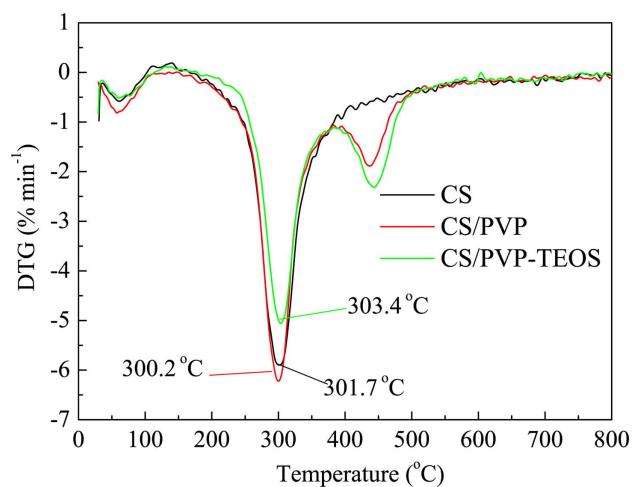


Figure 5. DTG curves of the CS membrane, the blending membrane with CS/PVP mass ratio of 10 : 1, and the hybrid membrane with CS/PVP mass ratio of 10 : 1 and 14.52 wt % TEOS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

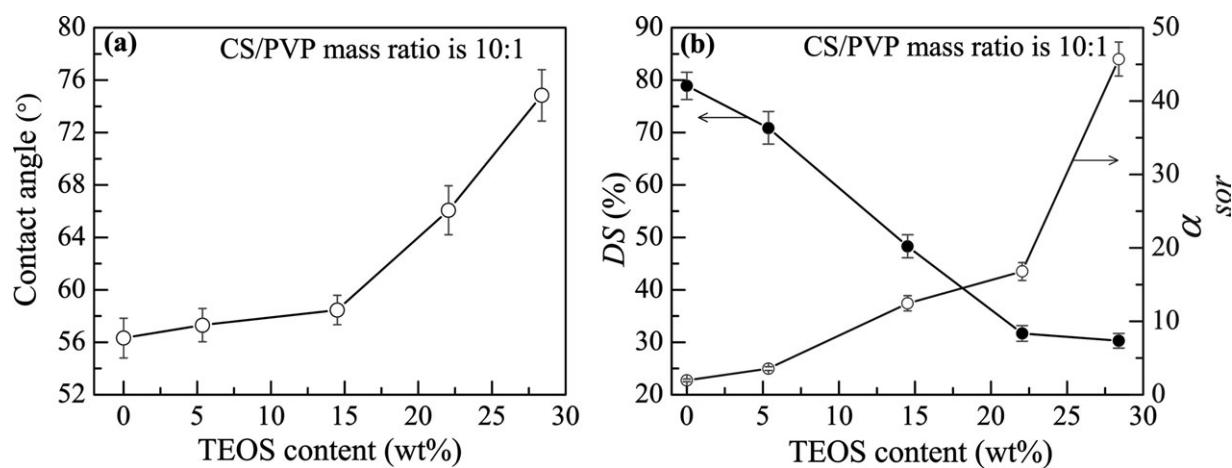


Figure 6. Effect of TEOS content on (a) the static water contact angle and (b) the degree of swelling in methanol/EG azeotrope of the hybrid membranes with CS/PVP mass ratio of 10 : 1 at 25°C.

above 5.34 wt %. The membrane (No. 6) with 14.25 wt % PVP has the smallest *PSI* of 14.0 being less than the pristine CS membrane. This reveals that Nos. 5 and 6 have an appropriate ratio of CS/PVP, and excess PVP content will lead to low permeation selectivity.

The crosslinking of the polymers by TEOS reduced the mobility of the polymer chains (Figure 2). Methanol and EG molecules thus have difficulty in permeating through the membranes. Larger EG molecules are found to have more difficulty in passing through the membranes than methanol. Further, methanol sorption selectivity increased with increasing TEOS content [Figure 6(B)]. Consequently, permeation flux of the hybrid membrane decreased rapidly whereas separation factor increased with increasing TEOS content, as shown in Figure 7(B). The *PSI* almost increased with TOES content associated with the

crosslinking degree of the hybrid membranes. Though the membrane with 28.40 wt % TEOS has the highest *PSI*, but too low flux. Therefore, we believe that membrane No. 5 with 14.25 wt % TEOS has the greatest potential in pervaporation separation of methanol/EG azeotrope.

Figure 7(C) shows the temperature dependence of pervaporation performance of the hybrid membrane No. 5 with 7.8 wt % PVP and 14.52 wt % TEOS. The permeation flux increased with feed temperature while the separation factor first increased and then decreased. With increasing temperature, the swelling degree of the hybrid membranes increased leading to an increase in the mobility of penetrant molecules and polymer chains. This results in an increase in the permeation flux. Meanwhile, the number of dissociative hydroxyl and amino groups increased due to the increase in the amorphous area of CS with increasing

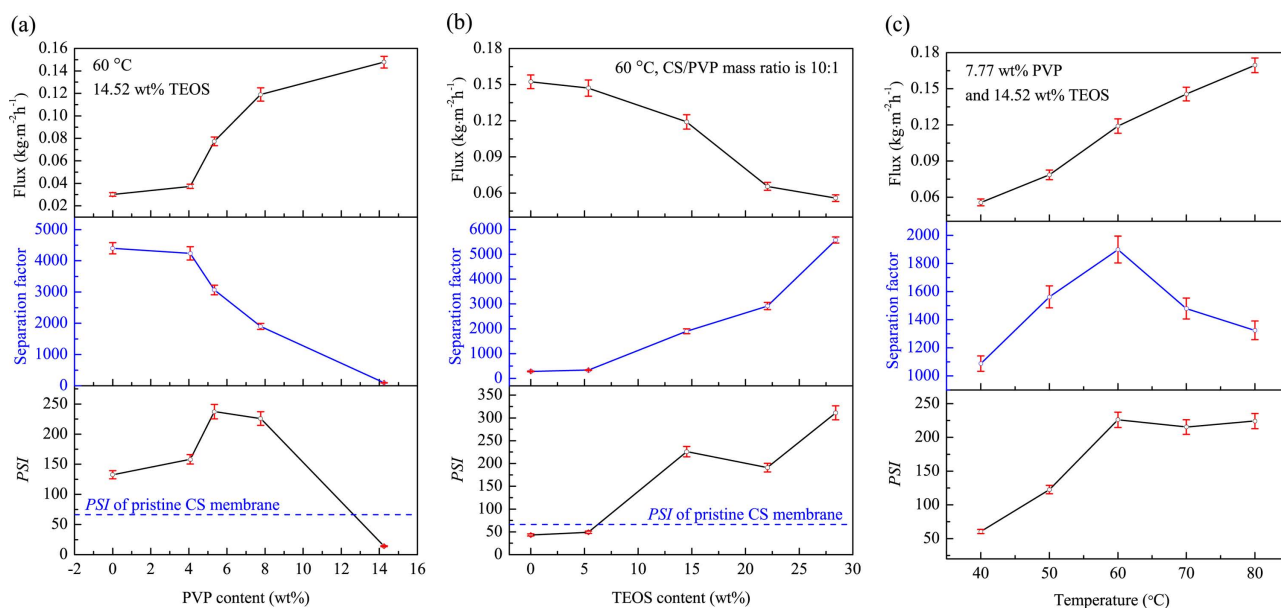


Figure 7. Pervaporation performance of the hybrid membranes: (a) effect of PVP content (14.52 wt % TEOS), (b) effect of TEOS content (CS/PVP mass ratio of 10 : 1), and (c) effect of temperature (CS/PVP mass ratio of 10 : 1 and 14.52 wt % TEOS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature, leading to an increase in both flux and separation factors when feed temperature is below 60°C. However, over-swelling would lead to a decrease in separation factor when feed temperature is above 60°C. The separation factor has the highest value of 1899 at 60°C.

CONCLUSIONS

The CS/PVP-TEOS organic–inorganic hybrid membranes are prepared successfully. The physico–chemical structures, morphology, microstructure, hydrophilicity, and thermal stability are characterized using FTIR, XRD, SEM, and TGA. The Si–O–C bonds from the condensation between CS and TEOS silanol are confirmed by FTIR, leading to the formation of the hybrid membranes in semi-interpenetrating network structure at the molecular scale. The hybrid membranes have lower crystallinity, higher thermal stability, and denser structure than the pristine CS membranes and CS/PVP blending counterpart.

The hybrid membranes are used for pervaporation separation of methanol/EG azeotrope. The swelling degree of the hybrid membranes decreased whereas sorption selectivity increased with TEOS content. Separation factor of the hybrid membranes remarkably increased with TEOS content, while permeation flux decreased. The hybrid membrane with 6.51 wt % PVP and 28.40 wt % TEOS has the highest separation factor of 5579. The newly developed CS/PVP-TEOS hybrid membranes have a great potential in pervaporation process.

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