Pervaporation Dehydration of Water/Ethanol/Ethyl Acetate Mixtures Using Poly(vinyl alcohol)–Silica Hybrid Membranes

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ABSTRACT: The novel organic–inorganic hybrid membranes were prepared from poly(vinyl alcohol) (PVA) and vinyltriethoxysilane (VTES). They were characterized using Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), thermogravimetric analysis (TGA), and contact angle metering. The as-prepared membranes are formed at a molecular scale at a low VTES content. Aggregations in the surface of the as-prepared membranes were clearly evident above 18.43 wt % VTES loading. The introduction of VTES into the PVA matrix resulted in a decrease in the crystalline and an increase in compactness and thermal stability of the as-prepared membranes. Silica hybridization reduced the swelling of the as-prepared membranes in water/ethanol/ethyl acetate mixtures, decreased the permeation flux, and remarkably enhanced water permselectivity in pervaporation dehydration of ethanol/ethyl acetate aqueous solution. The hybrid membrane with 24.04 wt % VTES has the highest separation factor of 1079 and permeation flux of 540 g m^{-2} h^{-1}. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: poly(vinyl alcohol); vinyltriethoxysilane; pervaporation; ethyl acetate; dehydration

INTRODUCTION

Ethyl acetate, which has been widely used in industrial processes, such as organic intermediate of pharmacy, solvent of essence, rayon, paint, printing ink, etc., is attracting increasing attention.[1,2] And its demands are also increasing rapidly with the development of industry due to low toxicity. The industrial production of ethyl acetate is commonly based on a classical Fischer esterification process of acetic acid with excess ethanol.[3,4] The resultant ethyl acetate contains both water and residual ethanol, which can form binary and ternary azeotropes commonly separated by conventional distillation. Recently, azeotropic distillation and extractive distillation have

been thoroughly investigated and successfully used for the purification of ethyl acetate.[5] However, both processes suffer from high capital and operating costs because entraining is required.

Alternatively, pervaporation (PV) demonstrates a great advantage because of its mild operating conditions and no entraining is required.[6] PV-coupled distillation is considered to be a promising method for separating homogeneous azeotropic mixtures since it can reduce energy consumption and avoid the use of entrainer[7–11] and thus is an energy efficient process for separation of organic mixtures.[12,13] The separation mechanism in a PV process is based on difference in the sorption and diffusion of the liquid pairs through membranes rather than their relative volatility.[6,12,14–17] Thus, hydrophilic materials such as poly (vinyl alcohol) (PVA), chitosan (CS), and poly (acrylic acid) membranes should be used for dehydration of organic mixtures due to their strong interaction with water. For example, Xia et al. studied dehydration of ethyl acetate aqueous solution using a ceramic-PVA composite membrane.[18] Hasanoglu et al. investigated PV separation of ethyl acetate/ethanol mixtures using a polydimethylsiloxane membrane.[19]

PVA has been widely used in PV dehydration of organics because of its good membrane forming ability and high hydrophilicity, but its excessive

swelling in aqueous media tends to low water perm-selectivity.[20,21] To achieve an improved stability and selectivity, efforts have been made to modify PVA, such as blended with other polymers,[22,23] filled with inorganic particles,[24] crosslinked by organic chemi-cals,[25] and treated by metal salt agents.[26] Recently, the development of organic–inorganic hybrid mem-branes combining the advantages of both organic and inorganic components, provide an effective way to synthesize novel membrane materials and modify common polymers. For hydrophilic membranes, researchers have used silane precursors to prepare polymer–silica hybrid membranes, such as PVA/ tetraethylorthosilicate (TEOS), chitosan/γ-(glycidy-loxypropyl)trimethoxysilane, quaternized chitosan, and tetraethoxysilane hybrid membranes.[27–31] These membranes demonstrate low degree of swelling (DS) in aqueous solution and high separation perform-ance in dehydration of organic solutions. In previous work, we have used γ-aminopropyl-triethoxysilane (APTEOS) and 1,2-bis(triethoxysilyl)ethane to modify PVA, quaternized PVA, and CS membranes. The resulting hybrid membranes were used for dehydra-tion of alcohol solutions.[7,32–34] They exhibit low swelling in ethanol aqueous solution, and high per-meation flux and water permselectivity. To our knowledge, these efforts on the modification of PVA membranes have been focused on the separation of binary mixtures. However, there are practically many ternary aqueous azeotropes to be separated and purified to produce high- and ultra-pure chemi-cals. It is thus a very interesting topic to develop novel membranes and separation technology to dehydrate ternary aqueous azeotropes.

Vinyltriethoxysilane (VTES) was used in the pres-ent work to modify PVA to prepare PVA-silica or-ganic–inorganic hybrid membranes with high per-formance for PV dehydration of water/ethanol/ ethyl acetate mixtures. The physicochemical struc-ture and surface morphology were characterized. The effect of VTES content and feed composition on the structure and properties of the hybrid mem-branes were also investigated.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA), average molecular weight of 75,000 g mol^{-1}, polymerization degree of 1750 ± 50 and hydrolysis degree of 98% was supplied by Sinopharm Chemical Reagent (China). VTES, etha-nol, and ethyl acetate of analytical grade were all purchased from Sinopharm Chemical Reagent and used without further purification.

Membrane preparation

PVA (2 g) was dissolved in water (50 mL) with stir-ring at 90°C for 3 h to give a PVA solution, which was immediately filtered and cooled to room tem-perature. VTES with various amounts (0.1, 0.3, 0.5, and 0.7 mL corresponding to 4.32, 11.94, 18.43, and 24.04 wt %) was added into the PVA solution under stirring. NaOH (0.1 mL, 1 M) was added into the resulting solution after 2 min and stirred for 2 h. Af-ter static deaeration for 1.5 h, the resulting homoge-neous solution was cast onto clean poly(methyl methacrylate) plates to form membranes with the aid of a casting knife. The membranes were dried at 40°C for 5 h, subsequently peeled off, and then allowed the solvent to evaporate completely at 100°C in vacuum oven for another 4 h. The as-pre-pared PVA/VETS hybrid membranes were transpar-ent with a thickness of 20 ± 0.5 μm.

Membrane characterizations

IR spectra of membranes were recorded by Fourier transform infrared 740SX (FTIR, Nicolet) to analyze their chemical structure. Crystal structure characteri-zation was carried out using X-ray diffraction (XRD, Panalytical X'pert Philip, Holland) with Cu-Kα radi-ation. The diffraction was operated at 40 kV and 30 mA in a 2θ range 5–35°, using a step size of 0.0167° and a counting time of 10 s per step. Environmental scanning electron microscopy (ESEM, XL30ESEM-TMP, Philips, Holland) was used to characterize the surface and cross section of the membranes. The sample used to characterize the cross section was quenched by immersing the membrane in liquid nitrogen. Surface morphology of the membranes was also observed using atomic force microscopy (AFM, Nanoscope IIIa, Digital Instruments) in a tapping mode at 25°C. Water static contact angles of the membranes were measured by the pendant drop method using a contact angle meter (SL200B, SOLON TECH, Shanghai, China) at 26 ± 1°C with 67 ± 2% relative humidity. The thermal stability of the membranes was analyzed using a TG209F1 (Netzsch, Germany) system with heating from 30 to 990°C at a constant rate of 10°C·min^{-1} under nitro-gen atmosphere.

Swelling measurements

Before each swelling test, the PVA/VTES hybrid membranes were completely dried at 80°C in vac-uum oven to evacuate the moisture and weighed im-mediately. They were then immersed in water/etha-nol/ethyl acetate mixtures until equilibrium was achieved. The swollen membranes were taken out, quickly wiped with filter paper, and weighed. This

process was repeated several times until the weight of the swollen membrane was constant. The DS is calculated by

$$DS = \frac{W_w - W_d}{W_d} \times 100\%$$ (1)

where W_w is the weight of the swollen membrane (g), and W_d the weight of the dry membrane (g).

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

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

where C_i^a and C_i^L are the concentration of species i in the adsorbed solution and the liquid mixture, respectively.

In this work, we investigated the effect of VTES, ethanol, and water contents on sorption and PV. The ethanol concentration was fixed a constant of 8.4 wt %, while feed water concentration was changed. Similarly, the water concentration was fixed a constant of 9 wt %, while feed ethanol concentration was changed.

Pervaporation experiments

PV experiments were carried out in laboratory scale apparatus with the effective membrane area of 71 cm^2. The feed solution was an azeotrope of water (9 wt %)/ethanol (8.4 wt %)/ethyl acetate. A vacuum pump was used to maintain the permeate side pressure at 650 Pa. The permeate was collected using a liquid nitrogen cold trap and analyzed by gas chromatography (GC-950). The total permeation flux (J) including all components in the permeate and the separation factor (α) are calculated from

$$J = \frac{\Delta G}{A \times \Delta t}$$ (3)

$$\alpha = \frac{y_i/(1 - y_i)}{x_i/(1 - x_i)}$$ (4)

where ΔG refers to the amount of the permeate (g) including water, ethanol, and ethyl acetate, A is the effective area (m^2) of the membrane used in PV, and Δt is the time (h) used to collect the permeate. In eq. (4), x_i and y_i are the concentration of species i in the feed and the permeate, respectively.
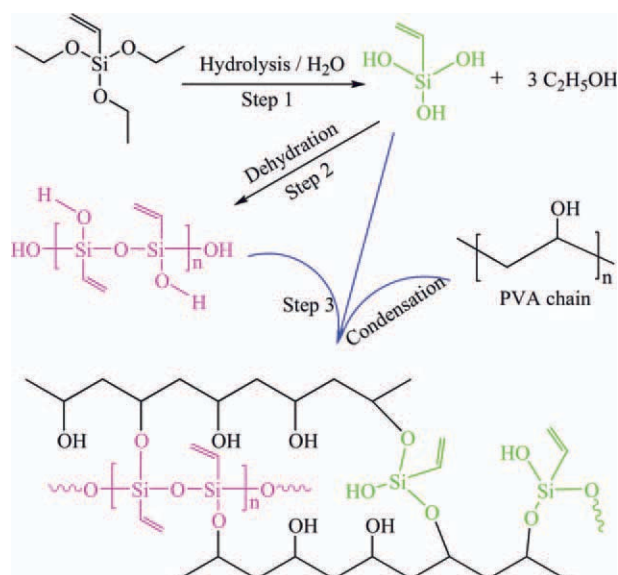
Scheme 1 The proposed reaction of the PVA/VTES hybrid membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Based on the Fick's first law, the diffusion coefficient of permeants across the membranes can be calculated using

$$J_i = -D_i \frac{dC_i^M}{dz}$$ (5)

where J_i is the diffusion flux of species i (kmol m^{-2}·s^{-1}), dC_i^M/dz the concentration gradient along the diffusion direction (kmol m^{-3} m^{-1}), and D_i the diffusion coefficient of species i in the membrane. dC_i^M/dz can be approximately replaced by $\Delta C_i^M/\Delta z$, where Δz is the thickness of the membrane, ΔC_i^M is the concentration difference of species i in membrane between the feed side and the permeate side. With considering the concentration of species i in the membrane adjacent to the permeate side approaching zero due to vacuum atmosphere exerted on the permeate side, ΔC_i^M can be approximately taken as the concentration of species i (C_i^a) in the swollen membrane. eq. (5) can thus be roughly expressed by
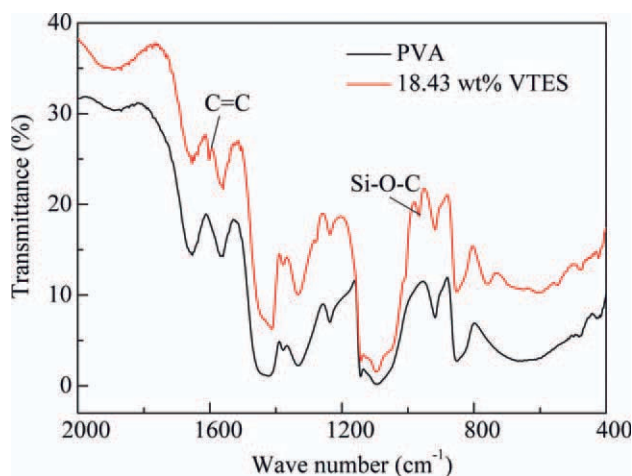
$$\overline{D_i} = J_i \frac{\Delta z}{C_i^\alpha}$$ (6)

RESULTS AND DISCUSSION

Membrane characterizations

FTIR spectra

The reaction between PVA and VTES is proposed as follows (Scheme 1). VTES is first hydrolyzed in the

Figure 1 FTIR spectra of PVA membrane and PVA/VTES hybrid membrane containing 18.43 wt % VTES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presence of water to produce a transitional VTES silanol (Step 1), which is unstable and tends to form a kind of multicondensed silanol (Step 2). The VTES silanols and the resulting condensed silanols would take condensation reaction with PVA chains to form

the crosslinking bridges of Si—O—C, resulting in the formation of PVA/VTES hybrid membranes at a molecular scale (Step 3).

The proposed reaction scheme was confirmed via FTIR spectra that allow for a qualitative and quantitative determination of functional groups of polymers. Figure 1 shows the spectra of PVA membrane and PVA/VTES hybrid membrane containing 18.43 wt % VTES. The peak around 1595 cm^{-1} is characteristic of C=C groups of VTES. And the peak at 962 cm^{-1} originated from the stretching of Si—O—C bonds confirms the formation of Si—O—C crosslinking network between PVA chains and VTES.[32,33]

SEM and AFM observations

Figure 2 shows SEM images of the PVA/VTES hybrid membranes containing 4.32 and 18.43 wt % VTES. The former has a smooth surface and uniform inner structure from cross-sectional image, while the latter has particulates formed on the membrane surface and in the inner matrix. This indicates that the compatibility between PVA and VTES was quite good at a low VTES content, possibly because chemical bonds were formed between the PVA and the
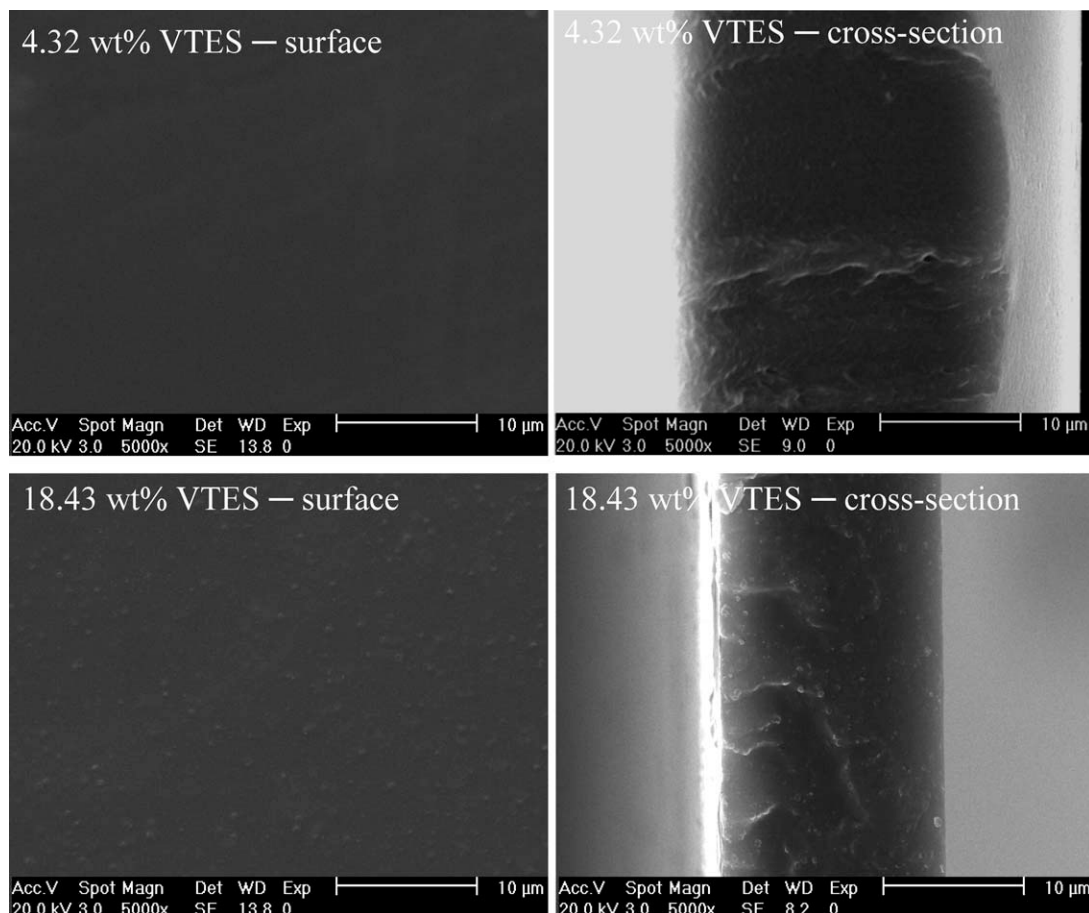
Figure 2 SEM images of surface and cross section of the PVA/VTES hybrid membranes with 4.32 and 18.43 wt % VTES.
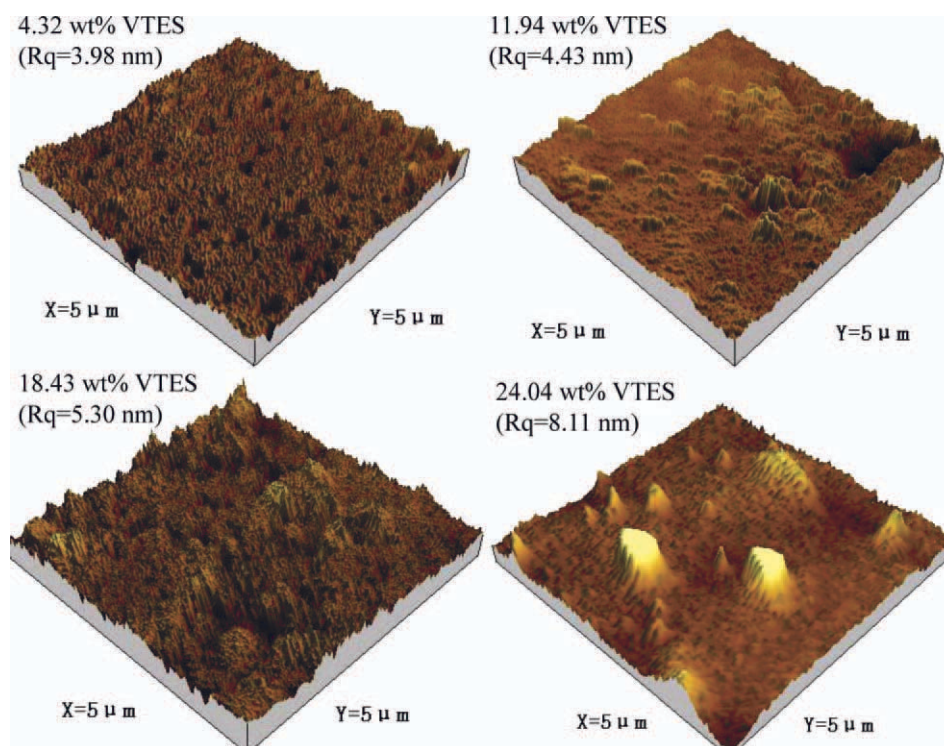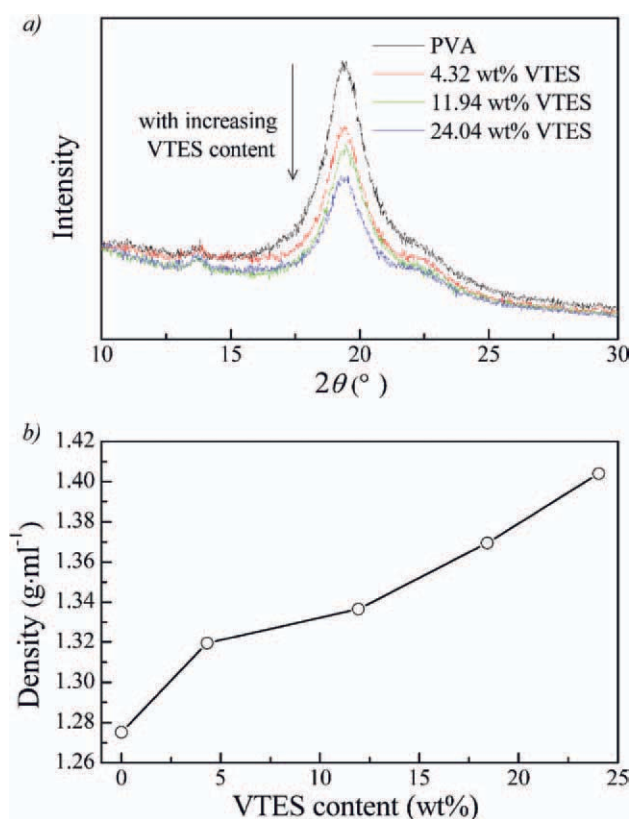
Figure 3 AFM images of the PVA/VTES hybrid membranes with 4.32, 11.94, 18.43, and 24.04 wt % VTES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

VTES. However, particulates would form on the surface and inner matrix of the hybrid membranes at a high VTES content. It is probably that part of the VTES silanols self-condensed to form cubic products and thus aggregated to particulates at a high VTES content. AFM observations also agree with this, i.e., particulates would form above 11.94 wt % VTES content (Fig. 3). The similar membrane structure can be observed in the TEOS and APTEOS hybridized PVA membranes.[27,32] The thickness of the hybrid membranes was 20 ± 0.5 μm, as shown in Figure 2.

The roughness of the as-prepared membranes with VTES content of 4.32, 11.94, 18.43, and 24.04 wt % was 3.98, 4.43, 5.30, and 8.11 nm, respectively (Fig. 3). This suggests that the roughness of surface of the membranes increased with increasing VTES content due to the potential aggregation of VTES at a high VTES content. The remarkable roughness of the hybrid membranes above 18.43 wt % VTES content should affect the hydrophilicity of the membranes and will be discussed later.

XRD characterization and density measurement

The physical structure of the PVA/VTES hybrid membranes was characterized using XRD, as shown in Figure 4(a). A sharp diffraction peak was observed at about 20° for the membranes, and its intensity decreased with introduction of VTES into the

Figure 4 XRD pattern (a) and density (b) of the PVA/VTES hybrid membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
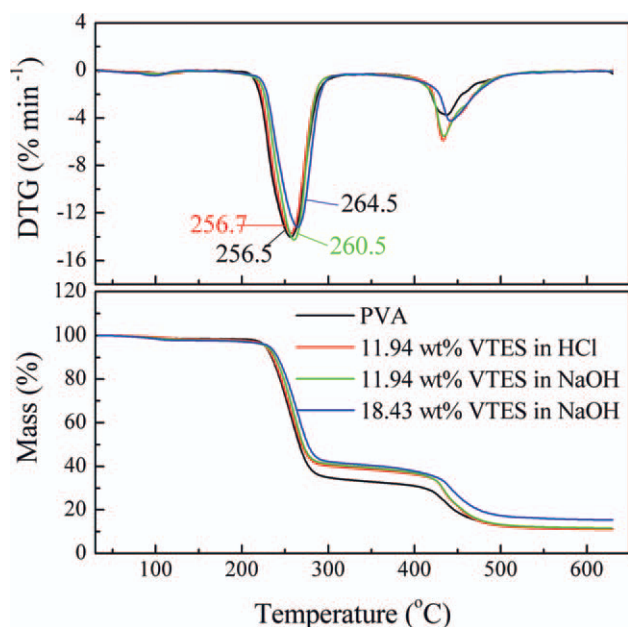
Figure 5 TG and DTG curves of the PVA/VTES hybrid membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PVA. PVA hybridized by VTES is found to exhibit less crystalline domains than the pristine PVA in bulk phase. As the Si—O—C bonds formed between the linear PVA chains and VTES molecules that dispersed in the membranes exhibit a size-exclusive effect. They play a role in preventing the formation of crystalline region in preparing the hybrid membranes. Therefore, the amorphous region increased with increasing VTES content. Figure 4(b) shows that density of the hybrid membranes increased with increasing VTES content. This is because the density of siloxane is greater than that of PVA and crosslinking density increases with increasing VTES content. An increase of the crosslinking spots in the PVA matrix makes the membrane matrix more compact since the VTES molecules may inhabit the big free volume cavies in amorphous region. As a result, water permselectivity increases owing to the size-exclusive effect.

Derivative thermogravimetric analysis (DTG)

The thermal stability of the PVA/VTES hybrid membranes was studied by TG and DTG, as shown in Figure 5. Two weight loss regions and two peaks around 260 and 450°C are found in DTG curves originated from the degradation of C—O bonds and the cleavage of the backbones of PVA chains, respectively.[34] And the introduction of VTES improved the thermal stability of PVA membranes from the peak top temperature of DTG curves around 260°C.

The effect of medium in which PVA hybridized was also investigated. PVA hybridized by VTES in a

basic medium exhibits a better thermal stability than that formed in an acidic medium (Fig. 5). This is probably that significant fractions of hydrolyzed molecules are formed, and then condensation proceeds in solution to form cubic structure oligomers. The rate constant of oligomerization has the same order of magnitude as that of hydrolysis and is highest in basic medium. Therefore, there is a greater tendency to form cubic structure oligomers in basic solutions than in acidic ones. As a result, the PVA/VTES hybrid membranes exhibit an improved thermal stability when PVA was treated by VTES in basic solutions. The thermal stability of the PVA/VTES hybrid membranes was found to increase with increasing VTES content. This is probably because an increase in the condensation of higher content VTES leads to an increase in oligomer formation.

### Contact angle measurements

According to the results from AFM, the as-prepared membranes have relatively smooth surfaces below 11.94 wt % VTES content and rough surfaces above 18.43 wt % VTES content. This suggests that the influence of the roughness of PVA/VTES hybrid membranes on the contact angle is negligible below 11.94 wt % VTES content, and considerable above 18.43 wt % VTES content. The contact angle reveals the outermost surface characteristics. Figure 6 shows the influence of VTES content on the wetability of the surface of membranes.

The hydrophilicity first increased with increasing VTES content, and then decreased above 4.32 wt % VTES. This is probably that introducing VTES into PVA matrix increased the dissociative hydroxyl groups on PVA chains due to the decrease of the crystallinity of PVA. As a result, the hydrophilicity
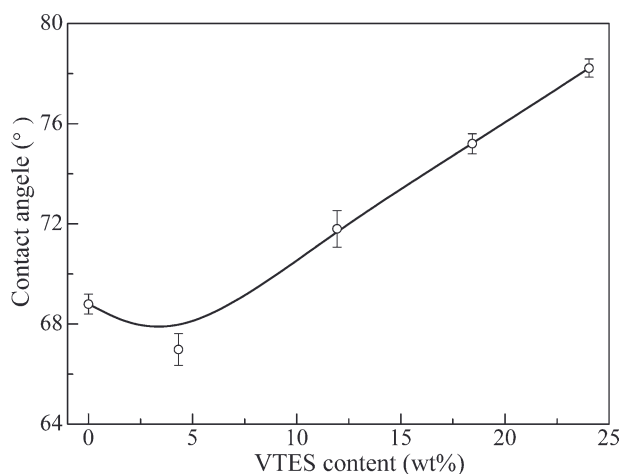
Figure 6 Contact angle of the PVA/VTES hybrid membranes.
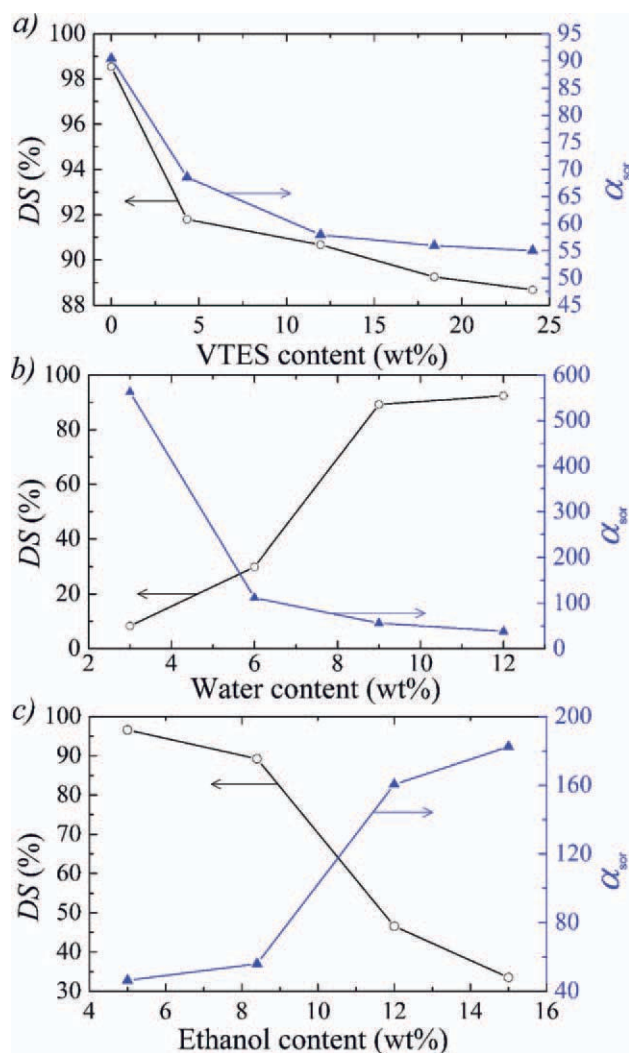
Figure 7 The swelling properties of the hybrid membranes: (a) effect of VTES content, (b) effect of feed water content, and (c) effect of feed ethanol content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the surface and bulk of the hybrid membranes increases accordingly. However, the membrane surface would be less hydrophilic because abundant hydroxyl groups take condensation with VTES above 4.32 wt % VTES. On the other hand, the roughness of surface above 18.43 wt % VTES content would decrease the contact angle; therefore increase in the contact angle with increasing VTES content above 18.43 wt % decelerates accordingly.

Swelling studies

In terms of the solution–diffusion mechanism widely used in PV, the swelling of a membrane in the feed plays a significant role in PV and affects both the permselectivity and the permeation flux of the membrane. The effects of water and ethanol contents in the feed and VTES content on the swelling

behavior of the PVA/VTES hybrid membranes in a ternary mixture of water/ethanol/ethyl acetate are shown in Figure 7.

The DS of the PVA/VTES hybrid membranes decreased gradually with increasing VTES content [Fig. 7(a)]. This is owing to the formation of siloxane bonds and depletion of hydroxyl groups in the PVA matrix. VTES crosslinking with PVA chains would restrict the mobility of PVA chains and decrease the hydrophilicity of the hybrid membrane. These are responsible for the decrease of DS of the hybrid membranes in water/ethanol/ethyl acetate mixture. On the other hand, water sorption selectivity (α_{sor}) of the hybrid membranes decreased slightly with increasing VTES content since the membranes become less hydrophilic [Fig. 7(a)].

The effects of feed water and ethanol contents on the swelling of the hybrid membranes were also
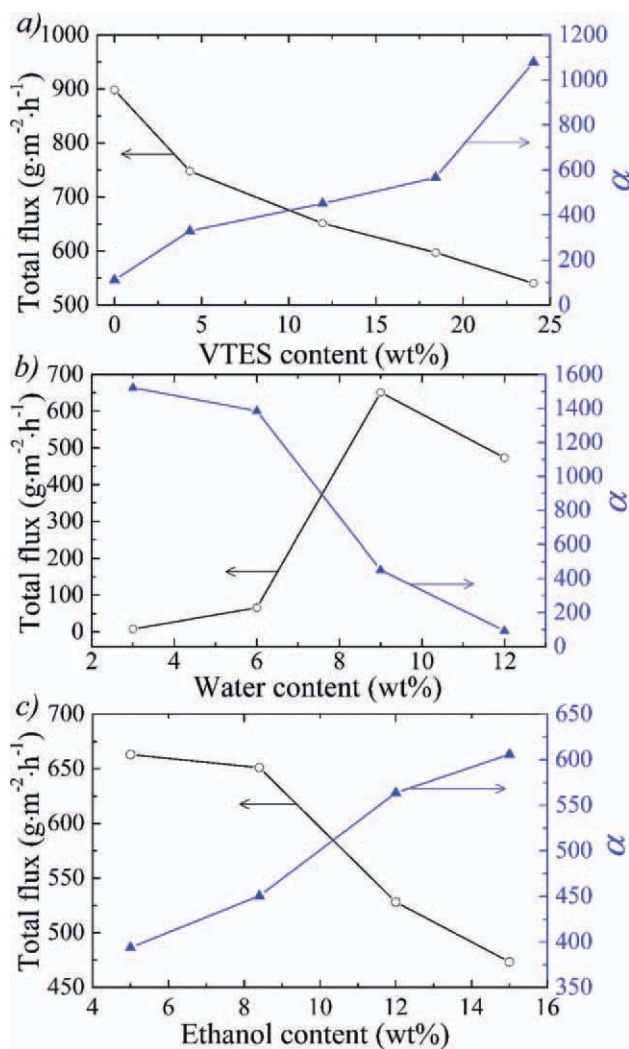
Figure 8 The pervaporation performance of the hybrid membranes: (a) effect of VTES content, (b) effect of feed water content, and (c) effect of feed ethanol content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
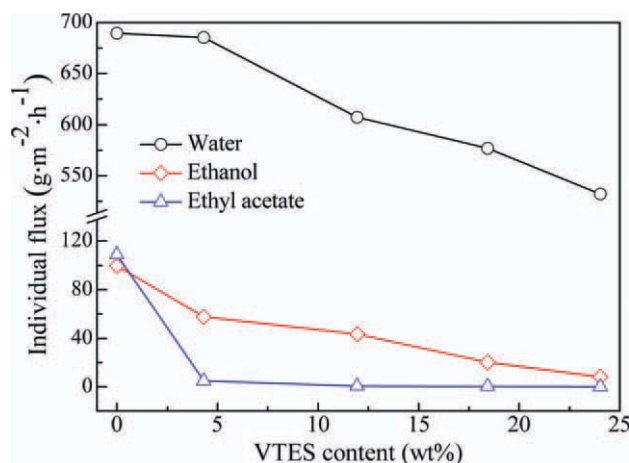
Figure 9 The individual fluxes of water, ethanol, and ethyl acetate through the PVA/VTES hybrid membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

investigated. The DS increased remarkably with increasing feed water content owing to inherent hydrophilicity of PVA-based membranes, while the α_{sor} decreased with increasing feed water content since the DS increased [Fig. 7(b)]. By contrast, the DS decreased with increasing feed ethanol content and the water sorption selectivity increased accordingly [Fig. 7(c)].

Pervaporation performance

The effect of VTES content on the separation performance of the as-prepared membranes was studied. Total permeation flux was found to decrease rapidly with increasing VTES content, whereas water permselectivity (α) increased remarkably [Fig. 8(a)]. And the hybrid membranes with 24.04 wt % VTES have highest α of 1079 and total flux of 540 g m^{-2}h^{-1}. This can be attributed to the efficiency of condensation between silanol groups and hydroxyl groups on PVA chains. The size and quantity of diffusion channels in the hybrid membranes would decrease since the membrane swelling decreased and the crosslinked bridges of Si—O—C restricted the mobility of PVA chains. As a result, the flux decreased and water permselectivity increased.

Membrane performance in PV separation is influenced not only by membrane and characteristic of permeant, but also by process operating parameters such as feed concentration. The effect of feed concentration on permeation flux and separation factor is shown in Figure 8(b). The permeation flux was found to increase and the separation factor to decrease with increasing feed water content. This is because the DS, the mobility of PVA chains, and the free volume of the membranes increased with increasing water content leading to an increase in

the diffusion of water, ethanol, and ethyl acetate. On the other hand, the sorption selectivity decreased and the diffusion of ethanol and ethyl acetate increased resulting in a decrease in water permselectivity with increasing water content.

By contrast, the ternary permeation flux is found to decrease and the separation factor to increase with increasing feed ethanol content. The reason is that the DS, the mobility of PVA chains, and the free volume of the membranes decreased with increasing ethanol content leading to a decrease in the diffusion of water, ethanol, and ethyl acetate [Fig. 8(c)]. On the other hand, the sorption selectivity increased and the diffusion of ethanol and ethyl acetate decreased resulting in an increase in water permselectivity with increasing ethanol content. Figure 9 shows individual flux of water, ethanol, and ethyl acetate. They were decreased with increasing VTES content.

Diffusivity analysis

Diffusion coefficients of permeants in the hybrid membranes were estimated by Fick's diffusion equation. The diffusivity of water decreased and tended to a constant value and the diffusivity of ethanol and ethyl acetate also decreased with increasing VTES content (Fig. 10). This is because the decrease of membrane hydrophilicity influenced the sorption and diffusion of water, and the aggregation of excessive VTES blocked the diffusion of larger molecules such as ethanol and ethyl acetate. The diffusivity of permeants relies not only on the morphology of the membranes but also on their concentration in the membranes. With increasing VTES content, the DS decreased, and water content in the membranes decreased. Therefore, the diffusivity of water
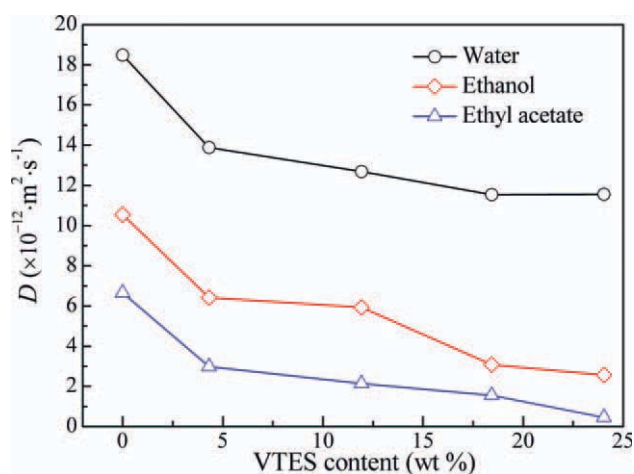
Figure 10 Diffusion coefficients of water, ethanol, and ethyl acetate through the PVA/VTES hybrid membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased. By contrast, the diffusivity of ethanol and ethyl acetate decreased accordingly.

CONCLUSIONS

The novel organic–inorganic hybrid membranes consisting of PVA and VTES were prepared via a conventional sol–gel route. The hybrid membranes were formed at a molecular scale at a low VTES content. And particulates were observed on the surface and inner matrix of the hybrid membranes above 11.94 wt % VTES. The crystalline of the hybrid membranes decreased gradually with increasing VTES content, while the density increased slightly. The hybrid membranes formed in a basic medium exhibit better thermal stability than those formed in an acidic medium. And the thermal stability of the hybrid membranes improved accordingly with increasing VTES content.

VTES hybridization reduced the swelling of the hybrid membranes in water/ethanol/ethyl acetate mixtures. The DS decreased with increasing VTES content and feed ethanol content, while increased with increasing feed water content. On the other hand, sorption selectivity increased with increasing feed ethanol content, and decreased with increasing VTES content and feed water content. The hybrid membranes have good performance in PV dehydration of water/ethanol/ethyl acetate mixtures. The permeation flux decreased with increasing VTES content, while the separation factor increased accordingly. And the hybrid membrane with 24.04 wt % VTES has the highest separation factor of 1079 and permeation flux of 540 g m^{-2}h^{-1}.

NOMENCLATURE

A	effective area of the membrane (m^2)
C_i^L	concentration of species i in the liquid mixture
C_i^a	concentration of species i in the adsorbate (evacuated from the swollen membrane)
dC_i^M/dz	concentration gradient along the diffusion direction (kmol m^{-3} m^{-1})
ΔC_i^M	concentration difference between the feed side and the permeate side of the membrane
D_i	diffusion coefficient of species i in the membrane
$\overline{D_i}$	average diffusivity of species i in the membrane
ΔG	amount of the permeate (g)
i	component i in the solution: 1 referring to water, 2 to ethanol, and 3 to ethyl acetate
J	the total permeation flux (g m^{-2} h^{-1})
J_i	diffusion flux of species i (kmol m^{-2} s^{-1})
Δt	time used to collect the permeate (h)
W_w	weight of wet membrane (g)
W_d	weight of dry membrane (g)
x_i	concentration of species i in the feed
y_i	concentration of species i in the permeate
Δz	thickness of the membrane

Greek letter

α_{sor}	sorption selectivity
α	separation factor

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