Structure and Pervaporation Performance of Novel Quaternized Poly(vinyl alcohol)/γ-aminopropyltriethoxysilane Hybrid Membranes

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ABSTRACT: Novel hybrid organic–inorganic membranes were prepared via sol–gel reactions of quaternized poly(vinyl alcohol) (q-PVA) and γ-aminopropyltriethoxysilane (APTEOS) for pervaporation dehydration of an 85 wt % ethanol solution. The physicochemical structure of the hybrid membranes was characterized by FTIR, XRD, SEM, TG, and TEM. Nanofractal objects originated from self-assembly of ammonium groups on the q-PVA chains and amino groups in APTEOS can be observed on the surface of the hybrid membranes. When APTEOS/PVA ratio is 5% (wt/wt), the hybrid membrane has specific nervate networks on its surface and exhibits the highest separation factor. The hybrid membranes have better pervaporation performance than pristine q-PVA membrane, and their permeation flux was found to increase linearly with increasing APTEOS content. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1121–1126, 2010

Key words: pervaporation; hybrid membranes; γ-aminopropyltriethoxysilane; self-assembly

INTRODUCTION

Organic–inorganic hybrid materials that favorably combine the important properties of organic and inorganic components are beginning to provide the opportunity for designing an almost unlimited range of new materials whose properties supersede those traditional materials. These hybrid membranes have been widely researched in many areas such as: optics, electronics, ionics, mechanics, energy, environment, biology, medicine.[1–4] For membrane-based separation processes, organic–inorganic hybrid membranes offer advantages with combining the specific transport properties from both organic and inorganic membranes and exhibit high separation performances.[5,6]

Polymers are widely used in separation science and account for 90% of all the membrane materials used. Unfortunately, they suffer from weak mechanical, chemical, and thermal resistance; and do not offer sufficient flux and selectivity for certain applications. Polymer membranes can be modified by silane precursors via sol–gel reaction into Si-O-Si networks, resulting in the formation of polymer-silica hybrid membranes at a molecular level. This type of hybrid membrane can have improved thermal and mechanical stabilities over traditional polymer membranes. Polyethyleneimine/3-glycidoxypropyltrimethoxysilane (GPTMS),[7] chitosan/GPTMS and poly (vinyl alcohol)/tetraethoxysilane (TEOS) hybrid membranes[8,9] are just a few such examples. Poly(ether imide)/TEOS hybrid membranes exhibit better stability under pressure than pristine poly (ether imide).[10] Furthermore, silica-hybrids can effectively depress swelling of polymer membranes in solution, especially for highly hydrophilic polymers in an aqueous solution. For example, it was reported that the introduction of silica precursors into the polymer matrix decreased the swelling of poly(vinyl alcohol), chitosan and quaternized chitosan membranes in an aqueous solution.[8,9,11–14] Most importantly, silica-hybrids can enhance application performance of polymer membranes, such as to solve the trade-off between permeability and selectivity of polymer membranes in pervaporation processes,[11,15–17] to improve selectivity and permeation in gas separation processes[18,19] and ion conductivity of membranes for fuel cells.[20,21]

In previous work, we successfully synthesized quaternized poly(vinyl alcohol) (q-PVA) membranes by grafting with (2,3-epoxypropyl) trimethylammonium chloride, and then by crosslinking with

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glutaraldehyde to reduce their swelling in an aqueous solution. These membranes were used for pervaporation dehydration of ethanol and anion exchange membrane for fuel cells.[22,23] The introduction of quaternary ammonium groups reduced the crystallinity of the q-PVA membranes, enhanced their hydrophilicity and simultaneously increased water permselectivity and permeation flux in pervaporation dehydration of ethanol.

In this study, γ-aminopropyltriethoxysilane (APTEOS) was used to modify q-PVA membranes via a sol–gel reaction with the aim to enhance their water permselectivity and stability. These new hybrid q-PVA membranes are expected to exhibit high permeability and selectivity in aqueous medium. Since the ammonium group on the q-PVA chains functions as an electron acceptor and the amino acid group on the APTEOS as an electron donator, both groups help to self-organize the molecules in aqueous solution. This may help to form a specific self-assembly structure in the hybrid membranes. Here, we focus on the physicochemical structure of the hybrid membranes and their pervaporation performance.

MATERIALS AND METHODS

Materials

Poly(vinyl alcohol) with polymerization degree of 1750 ± 50 and hydrolysis degree of 98% (Sinophatm Chemical Reagent Co., Shanghai, China), (2,3-epoxypropyl) trimethyl ammonium chloride with purity ≥ 95% (the Shandong Guofeng Fine Chemistry Factory, China), APTEOS (the Shanghai Yaohua Chemical Plant, China), were used without further purification. The other solvents and reagents, of analytical grade and used without further purification, were purchased from Sinophatm Chemical Reagent Co.

q-PVA was synthesized by grafting (2,3-epoxypropyl) trimethyl ammonium chloride onto poly(vinyl alcohol) according to the procedure and conditions previously described.[22] The degree of quaternization of the resulting q-PVA is 3.26% that was determined by elemental analysis (Vario EL III Elemental analyzer, Germany).[22]

Preparation of hybrid membranes

The hybrid membranes were prepared via sol–gel reaction between q-PVA and APTEOS. The q-PVA was dissolved in deionized water at 90°C for 1 h to form a solution with 4 wt % of q-PVA. The q-PVA solution was adjusted to pH 5 using HCl solution at 30°C, and then an amount of APTEOS added. The resulting mixture was stirred using a magnetic stirrer at 30°C for 10 h to form a homogeneous solution. The solution was cast onto a clean poly(methyl methacrylate) plate and dried at 30°C for 36 h to form membranes. The membranes were subsequently peeled off, and then heated at 80°C for another 6 h under vacuum. The membranes obtained were transparent with a thickness of 25 ± 1 μm. They are termed qPAH-*X*, where *X* is the percentage ratio of APTEOS to PVA, being set at 2.5, 5, 7.5, 10, and 15.

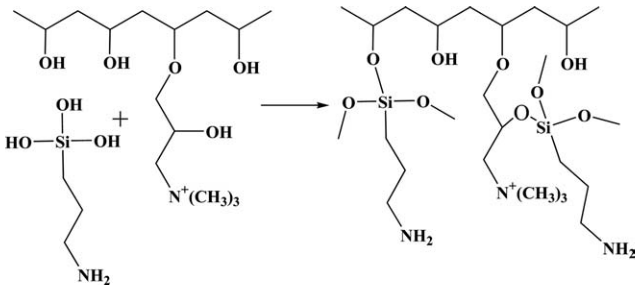
Characterization

The chemical structure of the hybrid membranes was measured using FTIR spectroscopy (Nicolet 740SX) in a transmission mode. The crystallinity of the membranes was investigated by X-ray powder diffraction (XRD, Panalytical Xpert, Enraf - Nonious Co., Holland) using Cu Kα radiation in a range from 5° to 45° at a step size of 0.0167° and a scan speed of 0.167°/s. The resulting XRD data was corrected for Lorenz and polarization factors. The surface morphologies and elemental composition of the hybrid membranes were also investigated by field emission SEM (LEO 1530, Germany) with energy-dispersive X-ray spectroscopy (EDS). The microstructure of the hybrid membranes was observed using high-resolution transmission electron microscopy (HRTEM, TECNAI F-30, Philips-PEI Co., Holland). Thermogravimetry (TG) were carried out using a TG209F1 (NETZSCH, Germany) analyzer, with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ from 30 to 600°C under a nitrogen atmosphere. Permeation experiments were carried out on the Pervaporation Bench Test Unit (Sulzer Chemtech., Germany) by pervaporation dehydration of 85 wt % ethanol solution at 50°C (under the same condition described in previous study[22]).

RESULTS AND DISCUSSION

Synthesis and characterization of the hybrid membranes

In preparing the hybrid membranes, APTEOS was first hydrolyzed in the presence of an acid catalyst to produce a silanol. Then, these silanol molecules would take condensation reaction with the hydroxyl groups on q-PVA chains to form the hybrid membranes at a molecular level (Scheme 1).[11] On the other hand, the silanol molecules may take self-condensation to form oligomer and polysesquisiloxanes, and then take condensation reaction with the q-PVA chains (Scheme 2). All of these will lead to the formation of a crosslinking network in the q-PVA matrix to restrict the mobility of q-PVA chains and enhance mechanical stability of the q-PVA membranes.

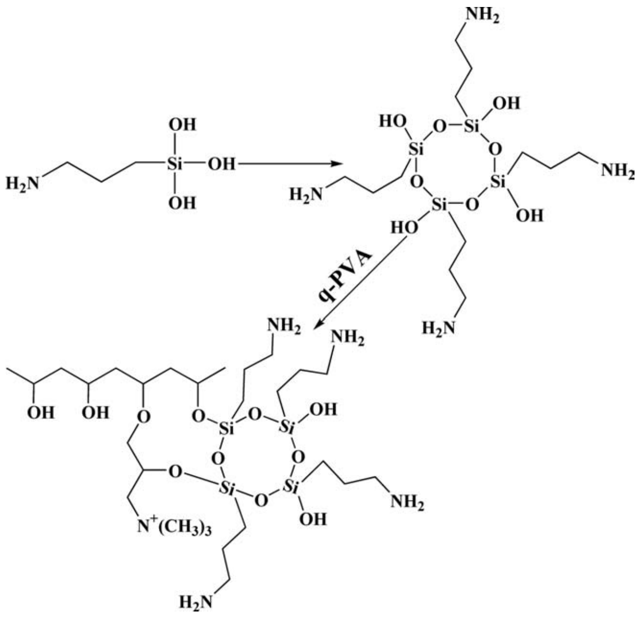


Scheme 1 Condensation reaction between q-PVA with APTEOS silanol.

Figure 1 shows FTIR spectra of the hybrid membranes in 600–1800 cm^{-1}. With increasing APTEOS content, the absorption at 1170 and 1030 cm^{-1} associated with the stretching of Si—O—C bonds increased.[15] This suggests that the condensation between q-PVA with APTEOS has occurred and the hybrid membranes were formed.

To investigate the self-condensation of APTEOS, a liquid film (the qPAH-15 casting solution) was formed on a copper net (300 mesh) and then rapidly dried to form a solid film. The copper net with sample was placed into F30 to observe the structure of the membranes. The results revealed that APTEOS took self-condensation to form silsesquioxane phases in the hybrid membranes [Fig. 2(a)].

Figure 3 shows XRD spectra of the hybrid membranes. The dispersion of APTEOS in the q-PVA matrix prevented the formation of crystalline regions in the hybrid membranes, leading to a decrease in the crystalline regions, which is favorable to enhancement of permeability. The intensity of the characteristic peak decreased with increasing APTEOS content, while increased slightly when the percentage ratio of APTEOS to PVA is 15. This may be owing to the condensation of most APTEOS to form silica phase [Fig. 2(a)].



Scheme 2 Formation of APTEOS oligomer and its condensation with q-PVA.

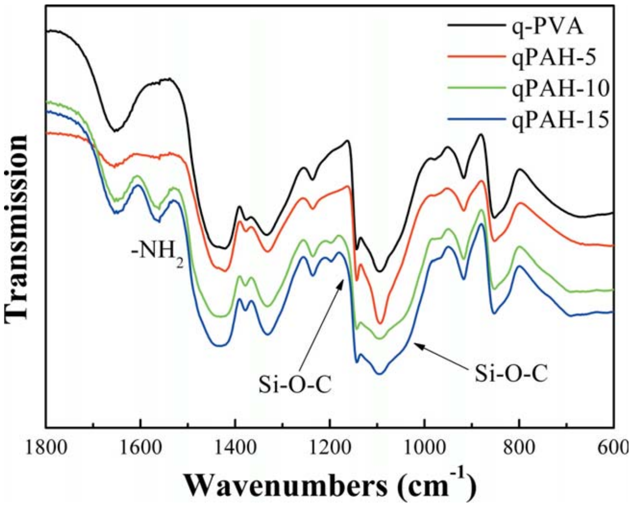


Figure 1 FTIR spectra of the hybrid membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 shows the TG and differential gravimetric analysis (DTG) thermographs of the hybrid membranes. Three principal weight loss regions and three peaks around 315, 370, and 440°C are found in the DTG curves originated from the degradation of C—N bonds, the rupture of C—O bond from q-PVA chains, and the cleavage of the backbone, respectively. With increasing APTEOS content, the first weight loss around 315°C increased owing to the degradation of C—N bonds [Fig. 4(a)]. And the residual mass (6.1, 7.8, 10.3, and 10.8 wt %) increased from q-PVA to qPAH-15 owing to an increase in silicon element [Fig. 4(a)]. On the other hand, the temperature of the second weight loss increased slightly owing to the incorporation of APTEOS into q-PVA matrix. This is because the C—O bonds in the C—O—Si groups are easier to rupture than those in the formation of C—O—H groups [Fig. 4(b)].

Nanofractal structure of the hybrid membranes

The topography of the membrane surfaces was observed by SEM, as displayed in Figure 5. The q-PVA membrane has a smooth surface, while the hybrid membranes have nanofractal blisters on their surfaces. Linear blisters gradually grow from qPAH-2.5 to qPAH-7.5, particularly for qPAH-5 with nervate network. Further, blisters change from linear shape into somewhat disorder on the surface of qPAH-10 and qPAH-15.

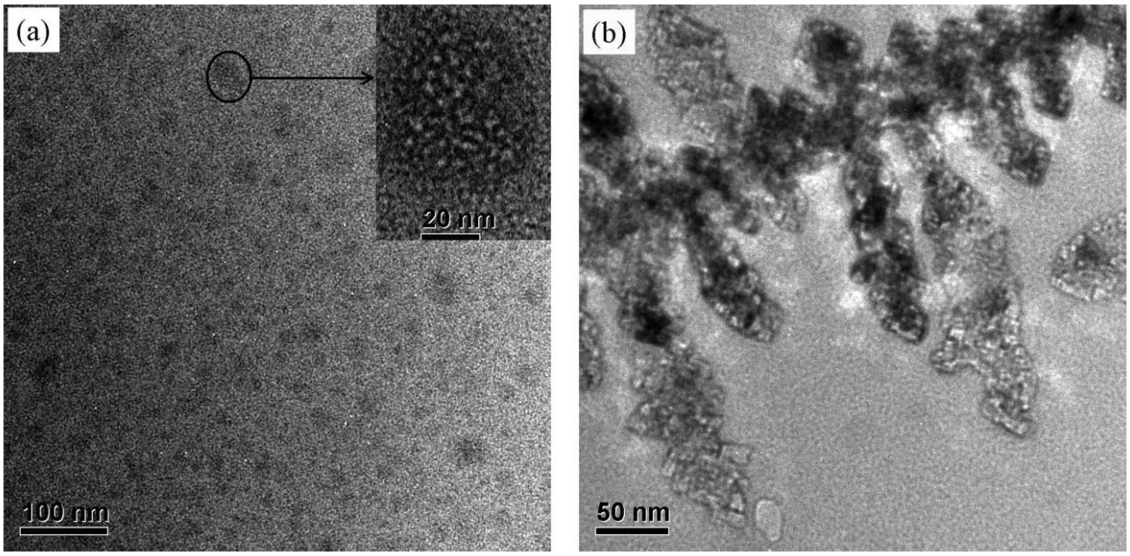


Figure 2 TEM micrograph of the qPAH-15(300 kV, point resolution of 0.20 nm and linear resolution of 0.1 nm).

These blisters originated from the self-assembly of ammonium groups on q-PVA chains and amino groups in APTEOS during preparation of the hybrid membranes, as shown in Scheme 3. The ammonium group is an electron acceptor, and the amino acid group an electron donator. They both self-assemble if brought together in an aqueous solution so that part of APTEOS concentrates around the ammonium groups to form a specific region containing abundant ammonium groups and APTEOS in the membrane casting solution. This is confirmed by TEM, spiniform phase formed in the solid film of qPAH-15, as shown in Figure 2(b).

During the formation of the hybrid membranes, the areas containing abundant ammonium group and APTEOS would entrap a small amount of water, resulting in the formation of blisters on the surfaces of the hybrid membranes. We used EDS to analyze elemental composition on the blisters and the other smooth areas of the qPAH-5 surface. As shown in Table I, the blisters were shown to contain more silicon element than the other areas. During the annealing process these blisters would split under tensile forces as observed on the surface of qPAH-7.5 and qPAH-15 (Fig. 5).

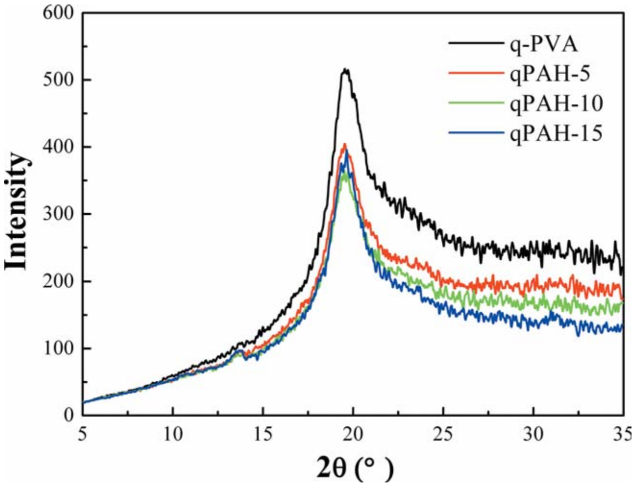


Figure 3 XRD spectra of the hybrid membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Pervaporation performance of the hybrid membranes

Pervaporation performances of the hybrid membranes in separation of an aqueous solution of 85 wt % ethanol at 50°C are shown in Figure 6. In this study, the q-PVA membrane was prepared under the same conditions as for preparing the hybrid membrane, —OH in ammonium groups were

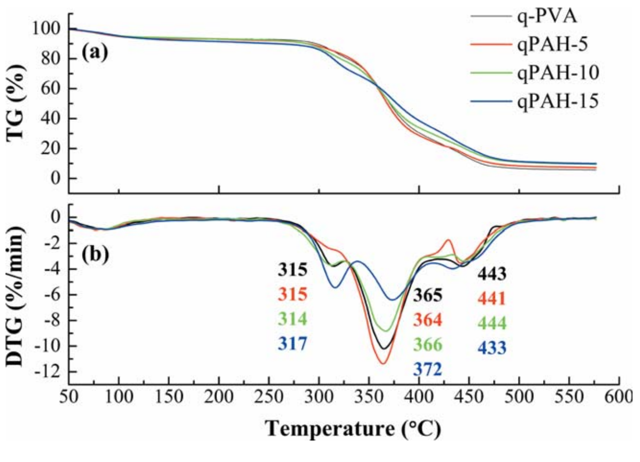


Figure 4 TGA curves of the hybrid membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

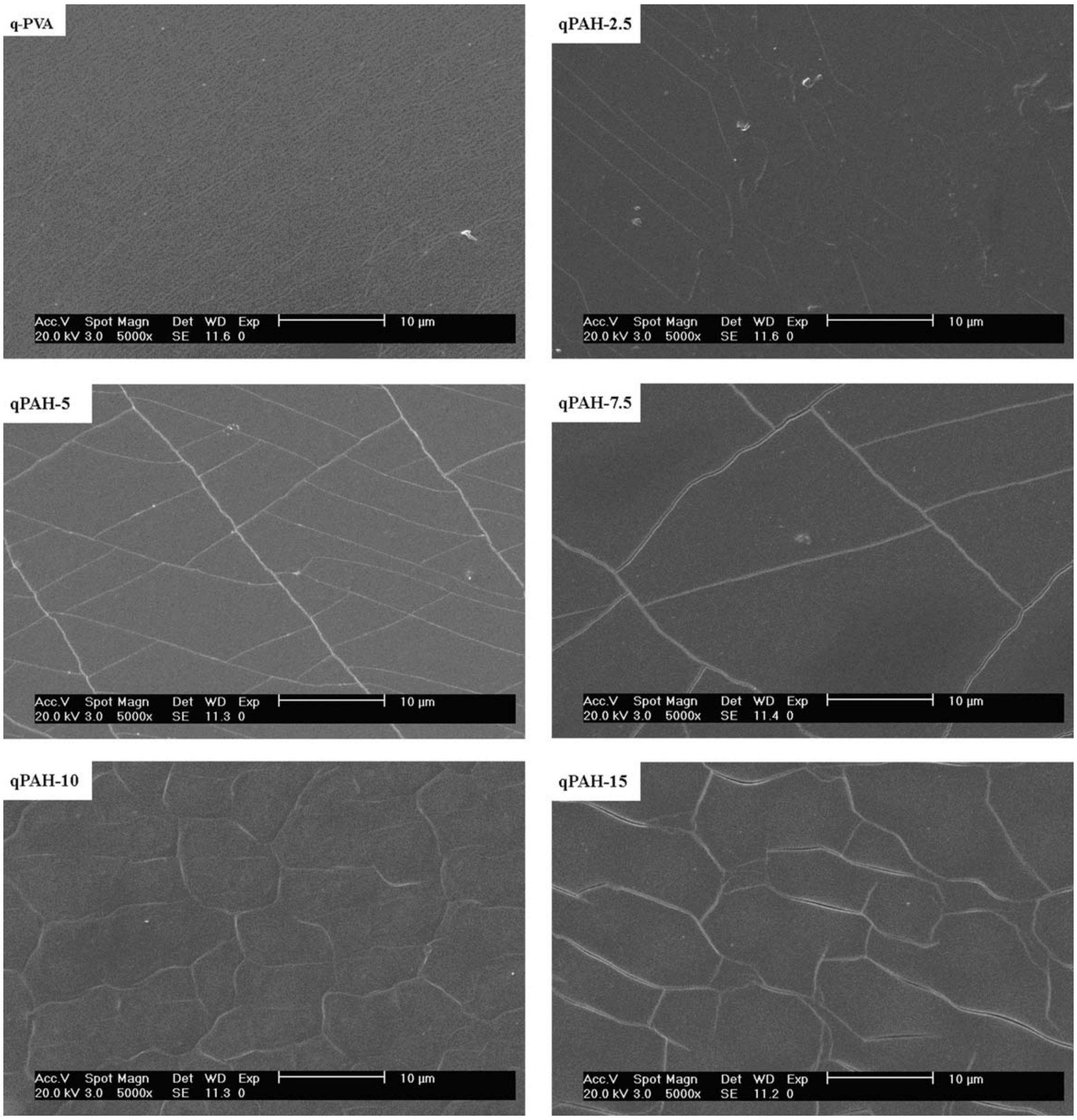
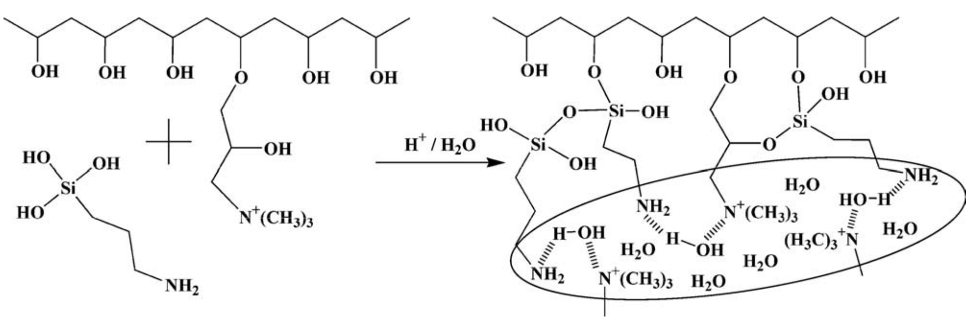


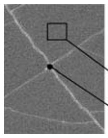
Figure 5 SEM images of the surfaces of the hybrid membranes.

therefore exchanged by Cl$^-$, resulting in a decrease in separation factor.[22] The separation factor sharply increased for the hybrid membranes up to qPAH-5 but decreased at a higher APTEOS content. This is similar to that for the PVA/APTEOS hybrid membranes.[11] An increase in separation factor may be due to the effect of APTEOS crosslinking, which compacts the amorphous region of the hybrid membranes and retards the mobility of q-PVA chains, resulting in an increase in water permselectivity



Scheme 3 Self-assembly structure of the hybrid membranes.

TABLE I
The Elemental Composition of the qPAH-5 Surface

Position	Elements content (At %) C	Si	O
 —	70.81	0.64	28.55
—	73.21	1.09	25.70

owing to its smaller size. On the other hand, an enlargement in the amorphous region in the hybrid membrane favors molecular diffusion of the desired species through the membranes, resulting in an increase of permeation flux. Further, the blisters with abundant ammonium and amino acid groups that are highly hydrophilic, swell excessively in aqueous solution, resulting in an increase in permeation flux and a decrease in water permselectivity when APTEOS/PVA ratio is above 5%, as shown in Figure 6.

SUMMARY

Novel organic–inorganic hybrid membranes composed of q-PVA and APTEOS were successfully prepared via a sol–gel process. Crosslinking networks between q-PVA chains and APTEOS were formed in the hybrid membranes. APTEOS took self-condensation to form silsesquioxane phases in the hybrid membranes. The incorporation of APTEOS into the q-PVA matrix resulted in an increase in the amorphous region of the hybrid membranes. Nanofractal blisters originated from self-assembly of ammonium groups on q-PVA chains and amino acid groups in APTEOS appeared on the surface of the hybrid membranes. The hybrid membrane of qPAH-5 that has nervate network on its surface has a highest water permselectivity. The hybrid membranes have improved pervaporation performance over pristine q-PVA membrane used for dehydration of 85 wt % ethanol solution, and their permeation flux linearly increased with increasing APTEOS content.

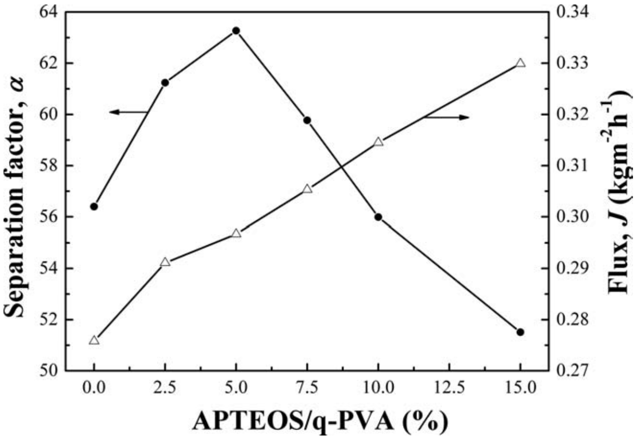


Figure 6 Pervaporation performances of the hybrid membranes for dehydration of 85 wt % ethanol.

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