

# Poly(vinyl alcohol)-Based Polymeric Membrane: Preparation and Tensile Properties

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Received 24 September 2010; accepted 21 December 2010

DOI 10.1002/app.34014

Published online 23 May 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A series of poly(vinyl alcohol) (PVA)-based single-layer organic polymeric membranes were prepared via the crosslinking of PVA with different amounts of formaldehyde. Meanwhile, for comparison, both a three-layer organic polymeric membrane and a hybrid composite membrane were also prepared by the layer-upon-layer method. Their thermal stability and tensile properties were investigated to examine the effect of crosslinking on the membrane performances. Thermogravimetric analysis and differential scanning calorimetry thermal analyses showed that the thermal degradation temperature of the single-layer crosslinked membrane C reached up to 325°C. Tensile testing indicated that the three-layer organic polymeric membrane E had excellent tensile strength among these single-layer and three-layer membranes. The swelling

properties revealed that the swelling degree value of these membranes decreased with an increase in methanol concentration; this suggests that they were not easily swollen by the methanol solution, which is meaningful for the separation of organic mixtures. Field emission scanning electron microscopy images exhibited that the crosslinking of functional groups impacted their structures and confirmed that their mechanical properties were related to their structures. These findings suggest that the crosslinking of functional groups is an effective method for adjusting the tensile strength of PVA-based organic polymeric membranes and related hybrid composite membranes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1350–1357, 2011

**Key words:** crosslinking; membranes; tension

## INTRODUCTION

Poly(vinyl alcohol) (PVA) is an excellent biodegradable and water-soluble biopolymer. Because of their environmentally friendly properties, PVA and its derivatives have been widely used to fabricate PVA-based polymeric membranes or materials for various industrial applications.<sup>1,2</sup> Some typical application examples can be found in these fields: the recovery of acids and valuable metals from waste solutions,<sup>3–5</sup> direct methanol fuel cell applications,<sup>6</sup> and pervaporation separation of liquid mixtures.<sup>7</sup> Although these membranes reveal some advantageous properties—structural flexibility, excellent membrane-forming

properties, and so on—they also indicate such disadvantages as lower mechanical strength and thermal stability.<sup>8,9</sup> Thus, improving their mechanical strength and thermal stability has turned into a key consideration for membrane preparation. Presently, various innovative routes, such as free-radical polymerization,<sup>10</sup> crosslinking,<sup>11,12</sup> and hybridization,<sup>6,13,14</sup> have been developed for such purposes. Among these, crosslinking between polymeric matrices is regarded to be one of the most effective techniques for promoting the mechanical strength and thermal stability of PVA-based polymeric membranes. Consequently, the investigation of crosslinking effects on their mechanical strength and thermal stability so that the related membrane performances can be improved is significantly important and highly needed.

To increase the mechanical strength and thermal stability of polymeric membranes, an attempt was recently made to prepare and characterize functionalized polymeric membranes;<sup>10</sup> it was found that the thermal stability of the polymeric membranes produced could be obviously elevated up to a desired value. Our interest in such a type of polymeric membranes stimulated us to do further research. Therefore, to detect the impact of crosslinking on the thermal stability and tensile properties of polymeric membranes, herein, a novel route for synthesizing PVA-based polymeric membranes and corresponding

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Contract grant sponsor: Natural Science Foundation of China; contract grant number: 21076055.

Contract grant sponsor: Anhui Provincial Natural Science Foundation; contract grant number: 090415211.

Contract grant sponsor: Significant Foundation of Educational Committee of Anhui Province; contract grant number: ZD2008002-1.

Contract grant sponsor: Opening Project of Key Laboratory of Solid Waste Treatment and Resource Recycle, Ministry of Education; contract grant number: 09zxgk03.

TABLE I  
Composition of the PVA-Based Polymeric Membranes

Membrane	PVA (g)	Formaldehyde (mL)
A	30	5
B	30	10
C	30	15
D	30	20

hybrid composite membranes is proposed, in which a series of PVA-based single-layer organic polymeric membranes were prepared via the crosslinking of PVA with formaldehyde. Meanwhile, to further examine the effects of crosslinking on the tensile properties of the membranes, the single-layer membrane with a higher mechanical strength was selected as the base and upper layer to prepare the three-layer polymeric membrane. For comparison, a three-layer hybrid composite membrane was also prepared with a hybrid membrane as the intermediate layer. Such a preparation route provided the PVA-based organic polymeric membranes and the related hybrid composite membrane with high mechanical strength and demonstrated that the crosslinking of functional groups was an effective method for improving the mechanical strength of the PVA-based polymeric membranes.

## EXPERIMENTAL

### Materials

PVA (molecular weight = 1750), formaldehyde (37 wt % in aqueous medium), poly(ethylene glycol) (PEG; molecular weight = 1000), and other reagents were analytical grade and were used as received. 3-Aminopropyl trimethoxysilane (APTMS) was purchased from Silicone New Material Co., Ltd. of Wuhan University (Wuhan City, China) and was used without further purification.

### Membrane preparation

Preparation of PVA-based polymeric membranes

The preparation of PVA-based polymeric membranes was conducted as follows. First, 30 g of PVA was dissolved in deionized water to produce the aqueous PVA solution. Second, a proper amount of formaldehyde (the composition of the PVA-based polymeric membranes is listed in Table I) was added dropwise into the previously prepared aqueous PVA solution within 2 h. Subsequently, the mixed solution was stirred vigorously at room temperature (RT) for an additional 24 h at pH 2 to perform the crosslinking reaction. After the completion of this crosslinking reaction, the coating solution of the PVA-based polymeric membranes could thus be achieved. Finally, the previously synthesized coating

solution was aged for 24 h and then cast onto a Teflon plate, air-dried at RT for 2 h, and then kept at 50°C for 12 h to obtain the single-layer membrane. To increase the membrane thickness, this step could be repeated several times.

Therefore, a three-layer membrane (labeled as membrane E) was prepared by the layer-upon-layer method; that is, the previous preparation step of the single-layer membrane was repeated thrice by the layering of the single-layer membrane C upon the surface of another one to produce the resultant multilayer polymeric membrane.

### Preparation of the hybrid composite membrane

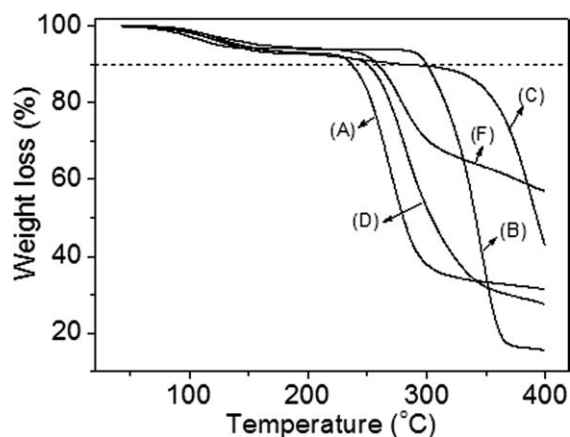
The fabrication of a three-layer hybrid composite membrane (labeled as membrane F) was prepared with the similar step as stated for membrane E and as described briefly as follows. The coating solution obtained from 30 g of PVA and 15 mL of formaldehyde (i.e., the composition of membrane C) was cast onto a Teflon plate, air-dried at RT for 2 h, and then kept at 50°C for 12 h to obtain the single-layer base membrane. Subsequently, the coating solution of the hybrid intermediate layer, which was produced by the dissolution of 20 mL APTMS into 5 g of PEG aqueous solution in the presence of acid as a catalyst (pH 2), was cast onto the surface of the previously prepared single-layer base membrane. Finally, the upper-layer membrane was produced by casting of the PVA-based coating solution onto the surface of the hybrid intermediate layer to obtain the desired three-layer hybrid composite membrane.

### Membrane characterizations

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermal degradation processes of the synthesized polymeric membranes were investigated with a Netzsch STA 409 PC/PG thermogravimetry analyzer (Selb, Germany) under a nitrogen flow with a heating rate of 20°C/min from 10 to 400°C.

The tensile test was measured with a universal tester (model CMT 4204, Shenzhen Sans Testing Machine Co., Ltd., Shenzhen, China) at a crosshead speed of 25 mm/min at RT, with an initial length of 10 cm and a breadth and thickness of 10 mm, respectively. The Young's modulus of the membranes was calculated on the basis of the line slope of the tensile strength versus elongation.

The swelling properties, that is, the swelling degree (SD), of the prepared polymeric membranes in water and aqueous methanol solution were determined by a conventional method, which was similar to that reported in previous articles<sup>6,15</sup> and described briefly as follows.



**Figure 1** TGA curves of membranes A, B, C, D, and F.

SD was calculated from the weight difference between the dried membrane and wet membrane. The effective membrane area was near 46.5 cm<sup>2</sup>. The wet membrane was prepared by dipping of the dried membrane into the solvent for 2 h; it was taken out, and we swept the surface solvent with filter paper and then weighed it instantly. The SD value was calculated by the following equation:

$$SD = (W_w - W_d)/W_d \quad (1)$$

where  $W_w$  and  $W_d$  are the wet and dry weight of the membrane, respectively.

Surface and cross-section field emission scanning electron microscopy (FE-SEM) images were observed with a field-emission scanning electron microscope (Sirion 200) operated with an accelerating voltage of 5.00 or 10.00 kV.

## RESULTS AND DISCUSSION

### Membrane preparation

The coating solution for the PVA-based polymeric membranes was prepared by the hydrolysis and condensation of an aqueous PVA solution in the presence of hydrochloric acid (HCl) as a catalyst at RT; this was followed by crosslinking with formaldehyde for 24 h. The single-layer membrane was thus obtained via casting of this coating solution on the Teflon plate and air drying.

For the preparation of the hybrid composite membrane, the coating solution of the hybrid intermediate layer was obtained by the hydrolysis and condensation of proper PEG with APTMS in the presence of HCl as a catalyst. Because membrane C had the highest thermal stability among membranes A–D (cf. Fig. 1, hereinafter), it was selected as the base- and upper-layer membrane to prepare the hybrid composite membrane. For comparison, a three-layer

PVA-based organic polymeric membrane from membrane C was also prepared by the same step.

### TGA

Thermal stability is a major concern for polymeric membranes. To obtain insight into the thermal degradation behavior of the single-layer PVA-based organic polymeric membranes, TGA was carried out and is shown in Figure 1. For the convenience of comparison, the TGA curve of the three-layer hybrid composite membrane (i.e., membrane F) is also presented in the same graph. Meanwhile, the thermal analysis data in the TGA curves are listed in Table II.

As shown in Figure 1, it could be noted that for membranes A–D that their change trends in weight loss (%) were similar, and three degradation steps were clearly found. However, the thermal degradation temperatures at 5 and 10% weight loss (i.e.,  $T_5$  and  $T_{10}$ , respectively) indicated different change trends. For example, for individual membranes,  $T_5$  and  $T_{10}$  improved with an increase in weight loss (%). As for different membranes,  $T_5$  increased from membranes B, C, D to F except that of membrane A. In contrast,  $T_{10}$  exhibited a zigzag change trend. Among them, membrane B had the lowest value of  $T_5$  and the highest value of  $T_{10}$ . Following was membrane C, which demonstrated a change in the thermal stability (cf. Table II).

In addition, it could be seen that the weight loss (%) of these membranes increased rapidly when the degradation temperature exceeded  $T_{10}$ , except that of membrane C; this suggested that the decomposition was accelerated. For membrane C, its degradation temperature could reach up to 325°C as the weight loss (%) arrived near 12%. Moreover, it could be observed that the residual weights at 400°C ( $R_{400}$ ) were 31.36, 15.59, 42.63, and 27.49% for membranes A, B, C, and D, respectively (cf. Table II); this implied that membrane C had the largest crosslinking degree among them, which was disagreement with the theoretical expectation (i.e., the residual weight decreased with an increase in the organic ingredient of a polymer). The reason could be ascribed to an increase in the crosslinking degree of

**TABLE II**  
Thermal Analysis Data of the Membranes Obtained from the TGA Curves

Membrane	$T_5$ (°C)	$T_{10}$ (°C)	$R_{400}$ (wt %)
A	141.55	233.88	31.36
B	125.26	297.73	15.59
C	136.04	282.38	42.63
D	143.81	250.45	27.49
F	162.61	255.26	56.86

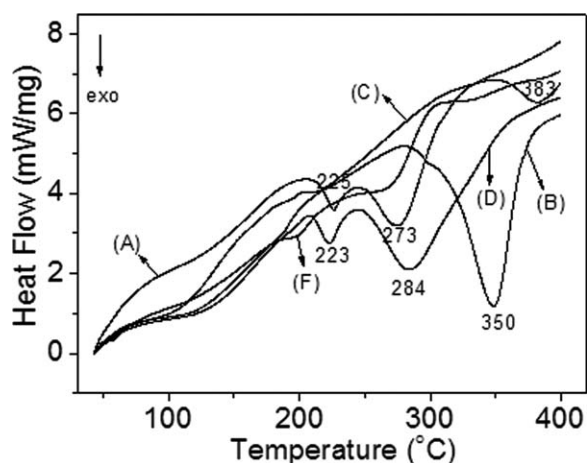


Figure 2 DSC curves of membranes A, B, C, D, and F.

functional groups in PVA and a decrease in the flexibility of membranes A–D; this led to increases in the degradation temperature and residual weight (%). This finding suggests that crosslinking between the polymeric matrices can be used to adjust the thermal stability of PVA-based membranes. With regard to the hybrid composite membrane F, it contained an inorganic ingredient, SiO<sub>2</sub>; its residual weight was, therefore, larger than that of the purely organic polymeric membranes, as observed.

The weight loss (%) below  $T_{10}$  was the removal of bonded water and solvent in the membranes, whereas the sharp weight loss above  $T_{10}$  could be assigned to the decomposition of organic ingredients and the breakage of functionalized groups in the polymer chains.

### DSC measurement

To inspect the glass-transition temperature ( $T_g$ ) of the prepared PVA-based organic polymeric membranes and the related hybrid composite membrane and to further recognize the crystallization transformation from rigid to flexible, DSC measurement was carried out, and the related curves are presented in Figure 2.

As shown in Figure 2, it could be seen that there existed two exothermic peaks for membranes A and D (the values were near 225 and 273 and 223 and 284°C, respectively). However, for membranes B and C, only one exothermic peak was detected (the values were near 350 and 383°C, respectively). In contrast, no larger endothermic or exothermic peak was found in the DSC curve of membrane F; this implied an improvement in the structural stability of the hybrid composite membrane.

It was reported<sup>16,17</sup> that in DSC curves, single or multiple endothermic peaks are the crystal melting, whereas the exothermic peak can be considered as

the crystallization. Consequently, it could be deduced that the crystallization temperatures of membranes A–D were near 225, 350, 383, and 223°C, respectively; this indicated an upward parabolic curve as the formaldehyde content increased. Moreover, it could be seen that the  $T_g$  values of membranes A–D were near 205.07, 279.40, 350.31, and 207.51°C, respectively, which revealed the same change trend as that of the crystallization temperature and suggested that the addition of formaldehyde into the aqueous PVA solution proportionally increased the crystallization temperature and  $T_g$  value of the single-layer membranes. However, further addition of formaldehyde into the aqueous PVA solution brought on an evident decrease in these values of single-layer membranes because of the crystallization transformation from rigid to flexible.

Note that the  $T_g$  value of the hybrid composite membrane, that is, membrane F, was centered near 268°C, which was clearly lower than that of membrane C and indicated that the addition of the hybrid intermediate layer decreased the interfacial interaction of membranes. Two factors were responsible for such a trend. One could be ascribed to the change of crystallization behavior due to the formation of a hybrid network and the crosslinking of molecular chains.<sup>18</sup> The other was related to the microphase separation between the interface layers<sup>19</sup> [cf. FE-SEM images in Fig. 4(f), shown later].

The previous findings clearly demonstrate that the crosslinking of functional groups in PVA-based polymeric membranes has some influence on their thermal degradation behaviors.

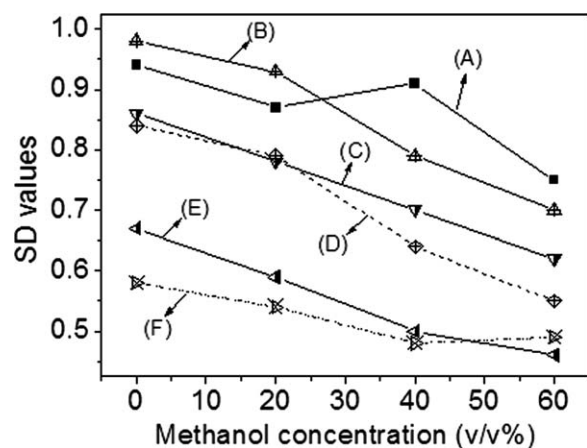
### Swelling properties

To investigate the swelling behaviors of the PVA-based polymeric membranes in pure water and organic solvent, as a typical example, the SDs of membranes A–F as a function of methanol concentration were measured and are presented in Figure 3.

As shown in Figure 3, it could be observed that for an individual membrane, its SD value decreased with an increase in the methanol concentration; this suggested that these membranes were easily swollen by pure water (i.e., 0% methanol concentration). However, for different membranes, the change trend of SD values in pure water followed such order as membrane B > membrane A > membrane C > membrane D > membrane E > membrane F; that is, membrane B had the largest SD value (or water uptake).

In contrast, the SD value of these membranes in aqueous methanol solution did not follow the same change trend as that in pure water. A complex change trend was observed. For example, at low

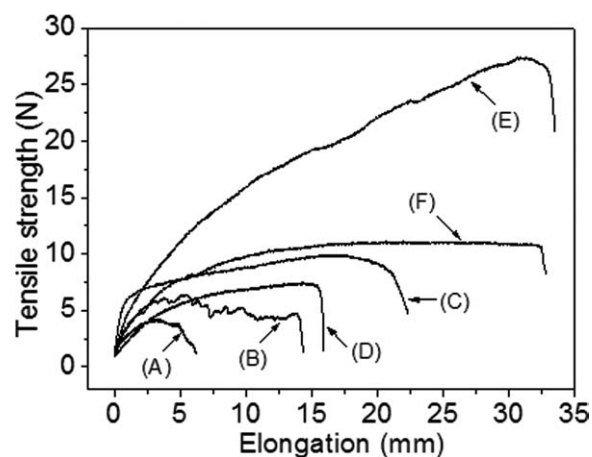




**Figure 3** Swelling values of the prepared membranes versus methanol concentration (v/v%).

methanol concentration (<20%), the SD value had a similar change trend as that in pure water if the experimental error was considered; this indicated that water was also the dominating swelling agent of the membranes. However, at high methanol concentration (>40%), the SD values decreased from membrane A to F; this implied that the swelling effect of water on the membranes was weakened as the concentration of methanol increased. These findings demonstrate that the swelling behaviors of polymeric membranes can be regulated via the addition of organic solvent in pure water.

To explain such phenomena, we considered the effect of crosslinking on both water and methanol uptake of polymeric membranes. Because PVA is a hydrophilic polymer and contains —OH groups in its polymer chain, it has an affinity for water. Consequently, a PVA-based polymeric membrane is easily swollen by pure water. With various membranes taken into account, the SD values indicated different change trends because of the existence of differences



**Figure 4** Tensile strength versus elongation of membranes A–F.

in the crosslinking degree and the amount of —OH groups in the polymer chains. Therefore, the change trend in pure water was logical. However, with an increase in methanol concentration, the effect of methanol on the solvent uptake of the membranes became the dominant factor. Especially, methanol also had an —OH group and could combine with the —OH groups in the PVA chains to produce hydrogen bonding between the —OH groups. Thus, it would block the accessibility of water to the —OH groups in the polymer chains of PVA-based membranes and influence their SD values. Consequently, the SD value of membranes A–F followed the following order as the concentration of aqueous methanol solution increased: A > B > C > D > E > F.

### Tensile testing

The mechanical properties are one of the chief parameters for polymeric membranes.<sup>2,20</sup> To examine the mechanical strength of the prepared PVA-based polymeric membranes, tensile testing was conducted, and the related curves are presented in Figure 4. The tensile properties are summarized in Table III.

As shown in Table III, it could be observed that for the single-layer membranes A–D, the ultimate stress, elongation, and elongation at break (%) increased from membranes A, B, to C and then decreased for membrane D. Such a change trend meant that the addition of formaldehyde to the aqueous PVA solution increased the tensile strength of the single-layer membranes; however, excess addition of formaldehyde caused a decrease in the tensile strength. In addition, it could also be observed that among the single-layer membranes A–D, membrane C had the highest values of ultimate stress, elongation, and elongation at break (%); this indicated that membrane C had a much higher mechanical strength and better toughness. This outcome revealed that the crosslinking of functional groups elevated the mechanical strength of the single-layer membrane to a relatively high level.

Furthermore, when we compared the tensile properties of three-layer membranes with those of

**TABLE III**  
Tensile Properties of the Prepared Membranes

Membrane	Ultimate stress (N)	Elongation (mm)	Young's modulus (N)	Elongation at break (%)
A	4.230	3.401	0.882	34.011
B	6.409	5.479	1.485	54.790
C	9.935	17.493	3.688	174.933
D	7.498	14.390	0.724	144.903
E	27.429	31.241	0.719	312.408
F	11.153	21.900	0.896	218.998

single-layer membranes, it could be found that the values of ultimate stress, elongation, and elongation at break (%) of three-layer membranes E and F were larger than those of single-layer membranes A–D, except that of Young's modulus. Especially, for membrane E, the value of ultimate stress was increased nearly 2.7 times, and the value of elongation at break (%) was increased nearly 1.8 times when compared with that of membrane C; this demonstrated that the tensile strength of the PVA-based membrane could be further elevated by multilayer superposition. Moreover, by comparison to the values of ultimate stress and elongation at break (%) of membranes E and F, it could be noted that these values decreased considerably from 27.429 and 312.408 to 11.153 and 218.998, that is, nearly 0.4 and 0.7 times, respectively; this confirmed that the addition of a hybrid intermediate layer reduced the tensile strength of hybrid composite membrane F. This result implies that the mechanical properties of the PVA-based polymeric membranes could be artificially controlled through the adjustment of the crosslinking degree or intermediate layer.

Several dominating factors were responsible for these trends. One was related to the change in the crosslinking degree of the functional groups. As stated in a previous article,<sup>2</sup> an increase in the crosslinking density of macromolecular chains would have led to an increase in the tensile strength and Young's modulus of the polymers. With single-layer membranes A–D taken into consideration, their crosslinking degrees increased with an increase in the formaldehyde content (cf. Table I); accordingly, their mechanical strengths increased. Another could be ascribed to the interfacial interaction. For single-layer membranes A–D, the interfacial interaction was relatively lower because of its weak linkage of bonds in the molecular matrix. However, the interfacial interaction between the multilayer membranes increased because of the formation of O—C—O bonds between —OH groups in the polymer chains of PVA; this led to a decrease in the interfacial tension of the surface layer and stronger interfacial bonds within the membranes.<sup>1,21</sup> Consequently, the tensile properties of three-layer membrane E were highly increased compared with those of single-layer membrane C.

Note that the mechanical strength of hybrid composite membrane F decreased a little by comparison with that of three-layer membrane E. The theoretical explanation is that the addition of hybrid intermediate layer resulted in the microphase separation among the interface layers (cf. Fig. 5). Such a type of microphase separation is unfavorable to an increase in the mechanical strength of membranes.<sup>3,20</sup> The mechanical strength of the hybrid composite membrane was, therefore, reduced. Furthermore, the

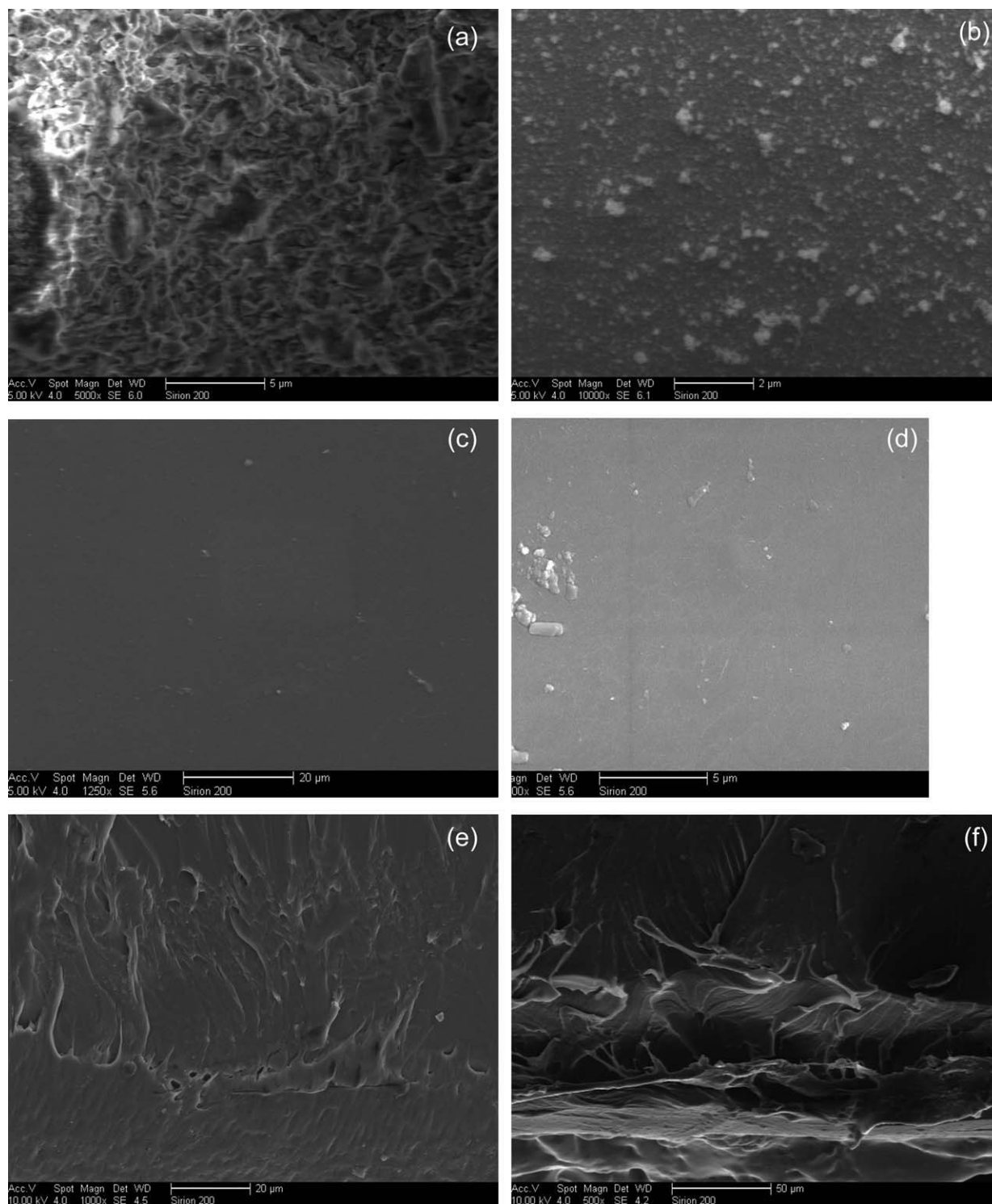
compatibility between the interface layers also made some contributions to the change in mechanical strength. This was because the incorporation of the hybrid intermediate layer increased the interfacial tension between the base membrane, intermediate layer, and upper-layer membrane. The covalent bonds between the interface layers would, thus, have been damaged. As a result, the damaged interface layers were a disadvantage to the increase in the mechanical strength of the examined membrane and led to a decrease in the ultimate stress, elongation, and elongation at break (%) of the hybrid composite membrane; this was further confirmed by the FE-SEM images, as presented in Figure 5.

In addition, it can be observed in Table III that with the addition of formaldehyde to single-layer membranes A–D, the Young's modulus went up and reached the highest value at membrane C; subsequently, it came down significantly for membrane D. Such a change trend seemed to be irregular. However, if the crosslinking degree of these membranes was considered, such a change trend was reasonable and consistent with that of the  $T_g$  value. This phenomenon could be explained as follows. As discussed in the section DSC Measurement, with the addition of formaldehyde to the aqueous PVA solution, both the crosslinking degree and  $T_g$  value of the single-layer membranes all increased; thus, the rigidity increased.<sup>2</sup> The Young's modulus of membranes A–C increased accordingly, whereas excess addition of formaldehyde to the aqueous PVA solution caused the further crosslinking of membrane D. Thus, this led to the crystallization transformation of the membrane from rigid to flexible. As a result, the Young's modulus of membrane D decreased remarkably.

### FE-SEM images

Figure 5 presents the FE-SEM images of single-layer membranes A, B, C, and D, and the cross-sectional FE-SEM images of three-layer membranes E and F, respectively.

As shown in Figure 5(a–d), it was interesting to find that the surface morphology of single-layer membranes A, B, C, and D was smoother and denser, and no obvious layered structure was detected, even when the amplification time of the membrane was increased up to 10,000 $\times$  [cf. Fig. 5(b)]. Meanwhile, it could also be found that the surface denseness of membranes A, B, C, and D increased with an increase in formaldehyde content [cf. Fig. 5(a,b)]; small pores were observed in membrane A, whereas no obvious pores were found in membrane B. This demonstrated an increase in the crosslinking of the membranes. The differences in the membrane surface could be ascribed to an increase in the crosslinking degree of



**Figure 5** FE-SEM images (a)–(d) denote the surface morphology of membranes A, B, C, and D, respectively. FE-SEM images (e) and (f) denote the cross-sectional morphology of membranes E and F, respectively.

the single-layer membranes, which resulted in these membranes becoming much tighter.

Moreover, it could be noted that a layered structure between the interface layers was detected in the cross section of three-layer membranes E and F, especially for membrane F; this indicated that micro-

phase separation occurred inside the multilayer membrane. This observation suggests that the addition of a hybrid intermediate layer decreased the compatibility between the interface layers. Consequently, the mechanical strength of the hybrid composite membrane decreased accordingly. This

result further confirmed that the mechanical properties of PVA-based polymeric membranes can be effectively adjusted by the change of membrane composition and structure.

### CONCLUSIONS

A novel route to the production of PVA-based organic polymeric membranes and the related hybrid composite membrane was proposed, in which single-layer PVA-based organic polymeric membranes were synthesized via the crosslinking of PVA with different amounts of formaldehyde. Meanwhile, a three-layer organic polymeric membrane and a hybrid composite membrane were prepared by the layer-upon-layer method. TGA and DSC thermal analysis showed that the thermal degradation temperature and crystallization temperature of single-layer crosslinked membrane C could reach up to 325 and 383°C, respectively. The swelling properties revealed that these membranes were unable to be swollen by methanol solution; this indicated an excellent resistance to organic solvent. Tensile testing demonstrated that the tensile strength of three-layer crosslinked membrane E could be highly increased by comparison with that of single-layer membrane C; this could be ascribed to the formation of stronger interfacial bonds within the membrane. FE-SEM images exhibited that the crosslinking of functional groups could impact their structures and confirmed that the mechanical properties of these PVA-based membranes were related to the difference of membrane structures. With their lower SD in aqueous methanol solution and higher mechanical strength considered, these PVA-based polymeric membranes can be potentially applied to the separation and recovery of methanol from wastewater.

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