

Study on the interfacial micro-voids of poly(vinylidene difluoride)/polyurethane blend membrane

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Abstract The poly(vinylidene difluoride)/polyurethane (PVDF/PU) blend membrane was prepared using the method of immersion-precipitation process. The influence of the miscibility of the two polymers on the formation of the interfacial micro-voids (IFMs) of the blend membranes was analyzed by the theory of thermodynamics and discussed with DMA, DSC and SEM. The effect of working pressure on the pure water flux (PWF) of the IFMs was also studied using membrane instrument. Results show that the IFMs are formed due to the miscibility of PVDF and PU. The existence of IFMs attributes much to the PWF of the PVDF/PU blend membrane, and the PWF of the IFMs is related not only to the miscibility of PVDF and PU but also to the deformation of IFMs under working pressure.

Introduction

Blending has become a useful method to get novel membranes with the development of membrane technology [1]. The blend polymer membranes have now been an attractive field and several such membranes have been studied, manufactured and used [2, 3]. PVDF is usually used to prepare different kinds of membranes due to its excellent chemical resistance and thermal stability [4–6], and because of PU's good elasticity, good physical and

chemical properties such as high tensile strength, abrasion and oil resistance, PU membranes have also received wide attentions from researchers [7–9]. However, researches on PVDF/PU blend membranes are relatively few and studies on the IFMs of the two polymers are also so far unreported. In this article, the PVDF/PU blend membranes were prepared using the immersion-precipitation process [10] and the relationship between the composition of the blend membranes and their IFMs was discussed. The effect of working pressure on the PWF of the IFMs was also studied.

Experimental

Materials and method

Poly(vinylidene difluoride) (W#1300 powder, from Kureha chemical industrial Co.Ltd, Tokyo, Japan), polyurethane [polyether-type, the molecular weight of polyether is 1000, fiber grade, polyether/diisocyanate (MDI)/butanediol (BDO) = 1/2/1] was purchased from Tianjin Daqiu Zhuang foamy factory] (Tianjin, China). *N,N*-dimethylacetimide (DMAc, >99%) was obtained from Institute of Membrane Science and Technique, Tianjin Polytechnic University.

PVDF/PU blend membranes with mass ratio of 1/4, 1/1 and 4/1 were prepared at 20 °C using the direct immersion-precipitation method. First of all, PVDF, PU and DMAc were mixed well in a mixer for 3 h at 2000 r/min to get the casting dope. After deposited in a vacuum oven for 2 h for removing air bubbles from it, the casting dope was cast on a horizontal glass plate with a glass blade at 20 °C. Then the glass plate with the casting solution was immersed immediately in a bath which consisted of distilled water. The sheet membranes were laboratory prepared and would be kept in a 5 wt% formaldehyde solution for use.

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Measurements

The morphology of the membranes was observed with FEI Quanta 200 (Netherlands) scanning electron microscope. The samples were broken by dipping in liquid nitrogen and sputtered with gold.

The dynamic mechanical analysis (DMA) curves of the membranes were obtained by Netzsch DMA242. The temperature range covered in this analysis was -180–100 °C at a heating rate of 5 °C/min and the stress frequency was 1.670 Hz.

The differential scanning calorimetric (DSC) curves were obtained using Perkin Elmer DSC-7. The temperature range covered in this analysis was 140–190 °C at a heating rate of 10 °C/min.

The PWF of the membranes was determined by the following equation

$$J = V/(A \times t) \tag{1}$$

where J is PWF ($L\ m^{-2}\ h^{-1}$), V is the quantity of the permeate (L), A is the membrane area (m^2) and t is the sampling time (h). The PWF measurement apparatus was showed in Fig. 1 where the place left for the deformation of the membranes under pressure could be seen.

Results and discussion

The miscibility of PVDF/PU and the formation of the IFMs

According to the solution theory, the miscibility of two polymers is mainly governed by the solubility parameter in

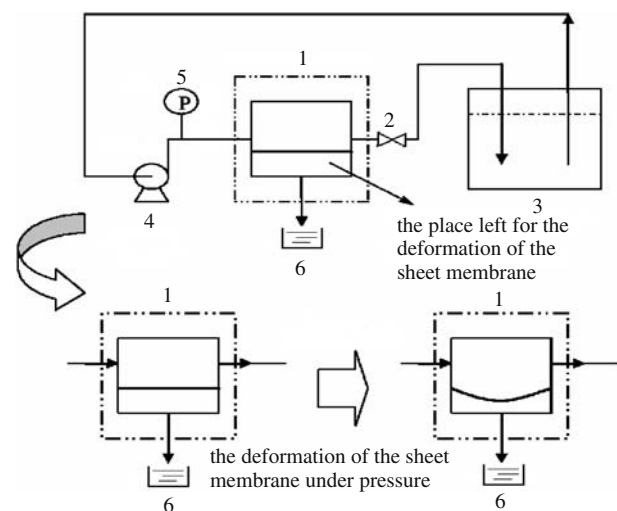


Fig. 1 Schematic diagram of the measurement apparatus: (1) module; (2) valve; (3) feed tank; (4) pump; (5) manometer; (6) permeate through

a system without polar interaction and hydrogen bonding. From the theory of thermodynamics, the molar free enthalpy is given by Eq. 2

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2}$$

where ΔH_m is the molar enthalpy of mixing and ΔS_m is the molar entropy of mixing. The lower the value of ΔG_m is, the better miscibility the two polymers will have. For polymeric system, ΔS_m is small enough to omit [11]. Thus the miscibility of the two polymers is mainly determined by the sign and the magnitude of ΔH_m , and the lower the value of ΔH_m is, the better miscibility of the two polymers will have. ΔH_m here can be given by Eq. 3 [11].

$$\Delta H_m = V_m (\delta_1 - \delta_2)^2 \Phi_1 \Phi_2 \tag{3}$$

where δ_1, δ_2 are the solubility parameter of PVDF and PU respectively, V_m is the molar volumes of the mixture, and Φ_1, Φ_2 are volume fraction of PVDF and PU respectively. V_m assumed to be constant, ΔH_m is then related to $|\delta_1 - \delta_2|, \Phi_1$ and Φ_2 . Generally, if $|\delta_1 - \delta_2| > 1.0[(J/cm^3)^{1/2}]$, the compatibility of the two polymer would be bad, and the chains of the two polymer would exclude each other. The solubility parameter of PVDF and PU is δ_1 equal to $30.95(J/cm^3)^{1/2}$ and δ_2 equal to $20.49(J/cm^3)^{1/2}$, respectively. Therefore, PVDF and PU can not be entirely miscible in any proportion directly. Analyzing the structure of PVDF and PU, both of them are polar polymers, and one having F atoms and the other containing carbonyls. Moreover, there must be specific interaction between dipole in PVDF and the carbonyl in PU. DMAc is a polar non-proton solvent and proper one for polar substances. In this study, DMAc helped us well mix the two polymers together. However, during the solvent removing process, the system would be unstable and the IFMs would be formed due to the far difference between δ_1 and δ_2 of the two polymers.

Because $\Phi_2 = 1 - \Phi_1$, Eq. 3 can be easily changed to Eq. 4 as below

$$\Delta H_m / [V_m (\delta_1 - \delta_2)^2] = -\Phi_1^2 + \Phi_1 \tag{4}$$

According to the analysis above, the $V_m (\delta_1 - \delta_2)^2$ here can be considered to be constant. Therefore, ΔH_m is only determined by the change in Φ_1 and Φ_2 . Figure 2 showed the correspondent value of the left side of Eq. 4 to Φ_1 . Along with the change in Φ_1 , the ΔH_m of PVDF and PU would reach its maximum (see Fig. 2). With Eq. 2 and the analysis above, the changing in the value of ΔG_m would be direct proportion to the value of ΔH_m . And when ΔH_m becomes higher, ΔG_m would become higher and the miscibility of PVDF and PU would become worse, thus the

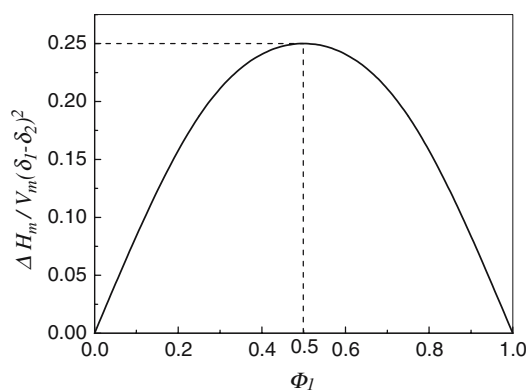


Fig. 2 Schematic diagram of $\Delta H_m/V_m(\delta_1 - \delta_2)^2$ to Φ_1

extent of the separation between PVDF and PU during the formation of the blend membranes would be higher, then more IFMs would be formed.

As is known that ρ_{PVDF} is equal to $1.7 \times 10^3 \text{ kg/m}^3$ and ρ_{PU} is equal to $1.2 \times 10^3 \text{ kg/cm}^3$, the correspondence Φ_1 to the mass ratio of PVDF to PU was given in Table 1. From Fig. 2 and Table 1, the conclusion can be drawn that the blend membrane with m_{PVDF}/m_{PU} equal to 1/1 would have more IFMs than the other two, and that the amount of the IFMs in the membrane with m_{PVDF}/m_{PU} equal to 4/1 would be more than that in the membrane with m_{PVDF}/m_{PU} equal to 1/4.

The change in T_g is shown in Fig. 3. In DMA curves, T_g can be denoted by the X-coordinate of the $\tan\delta$ peak. Figure 3 shows that the T_g of the blend membrane with m_{PVDF}/m_{PU} equal to 1/4 is higher than the T_g of PU membrane and than that of the other two blend membranes and the peak of T_g becomes weaker and weaker with the increase in PVDF amount. The former is due to the better miscibility of PVDF and PU in this mass ratio, and the latter may be due to the crystallization of PVDF.

Since T_g of PU membrane is equal to -46.5°C and that of PVDF membrane is equal to -35.1°C (see Fig. 3), the T_g of the blend membrane, if entirely compatible, can be predicted by the Fox equation [12].

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (5)$$

where T_g , T_{g1} and T_{g2} are the glass transition of the blend membrane, PVDF membrane and PU membrane, respectively, and the mass fraction of PVDF and PU in the blend membranes are respectively represented by W_1 and W_2 . Figure 4 shows the difference between the calculated

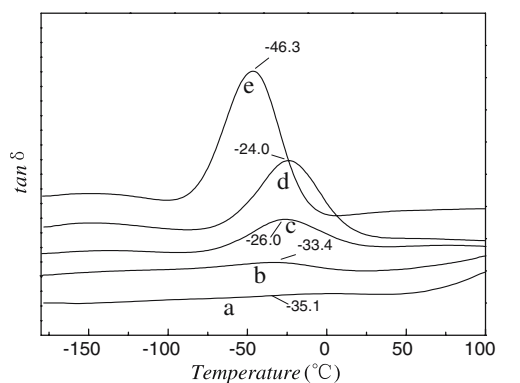
Table 1 The correspondence Φ_1 to the mass ratio of PVDF to PU

m_{PVDF}/m_{PU}	1/4	1/1	4/1
Φ_1	0.15	0.42	0.74

values and the experimental ones with the change in the amount of PVDF.

It can be seen in Fig. 4 that the membrane with m_{PVDF}/m_{PU} equal to 1/4 shows much more difference between the experimental T_g value and the calculated one. In this study, since PVDF and PU were mixed well by DMAc first, the δ difference between PVDF and PU would be demonstrated during the solvent removing and the extent of separation between PVDF and PU of the membranes with m_{PVDF}/m_{PU} equal to 1/4 would be relatively lower than that of the other two membranes due to the better miscibility, thus the interaction of the two polymer chains of this kind of membrane would be stronger and the PVDF chains would constrain more the movement of the PU chains during the glass transition, which in the end results in the highest T_g and the lowest IFM quantity.

Figure 4 also shows that the membrane with m_{PVDF}/m_{PU} equal to 1/1 shows much more difference between the experimental T_g value and the calculated one than the membrane with m_{PVDF}/m_{PU} equal to 4/1. This seems to be



a. PVDF; b. $m_{PVDF}/m_{PU} = 4/1$; c. $m_{PVDF}/m_{PU} = 1/1$; d. $m_{PVDF}/m_{PU} = 1/4$; e. PU

Fig. 3 $\tan\delta$ curves from DMA of the membranes. (a) PVDF; (b) $m_{PVDF}/m_{PU} = 4/1$; (c) $m_{PVDF}/m_{PU} = 1/1$; (d) $m_{PVDF}/m_{PU} = 1/4$; (e) PU

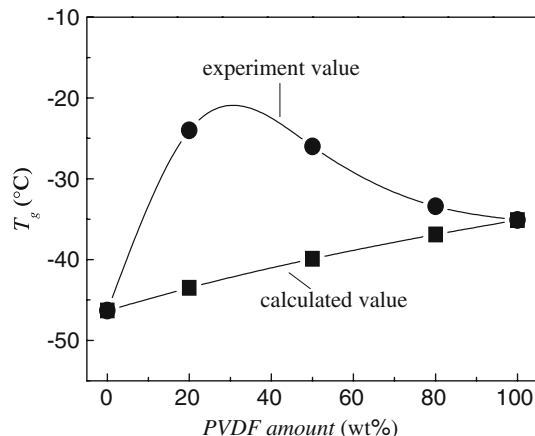


Fig. 4 The effect of the amount of PVDF on T_g

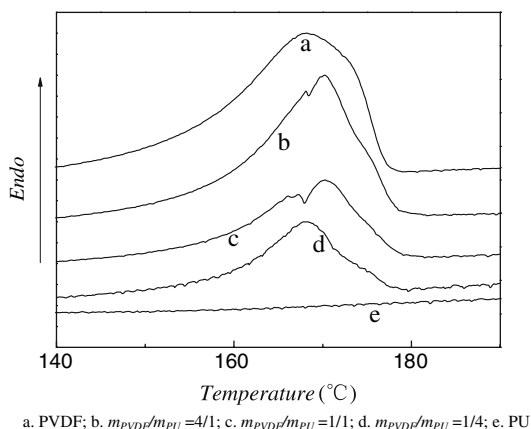


Fig. 5 DSC curves of the membranes. (a) PVDF; (b) $m_{PVDF}/m_{PU}=4/1$; (c) $m_{PVDF}/m_{PU}=1/1$; (d) $m_{PVDF}/m_{PU}=1/4$; (e) PU

inconsistent with the results of the theory of thermodynamics and may be due to the crystallization of PVDF with the increase in its amount. DSC curves were obtained in Fig. 5 for further study of the relationship between crys-

tallization and the miscibility of PVDF and PU. Figure 5 indicates that, as the miscibility of the two polymers becomes worse and worse, the crystallization peak of the mixture changes gradually from one to two, but the reasons for this phenomenon are still unclear.

The morphology of the membranes

Figure 6a–c represent the morphologies of membrane with m_{PVDF}/m_{PU} equal to 4/1, 1/1 and 1/4, respectively. It can be clearly seen that the pore size of the top surface is much smaller than that of the bottom. Because the top surface contacted water directly during the formation of the membrane and experienced much shorter coarsening time during coagulation, the compact structure could be easily formed.

Contracting the top surfaces of the three compositions in Fig. 6, the uniformity of the pore size from good to bad is the membrane with m_{PVDF}/m_{PU} equal to 1/4, 4/1 and 1/1 orderly. Seen from the bottom surfaces in Fig. 6, the quantity of the IFMs of membrane with m_{PVDF}/m_{PU} equal

Fig. 6 Morphologies of the PVDF/PU blend membranes. (a) $m_{PVDF}/m_{PU}=1/4$ (b) $m_{PVDF}/m_{PU}=1/1$ (c) $m_{PVDF}/m_{PU}=4/1$

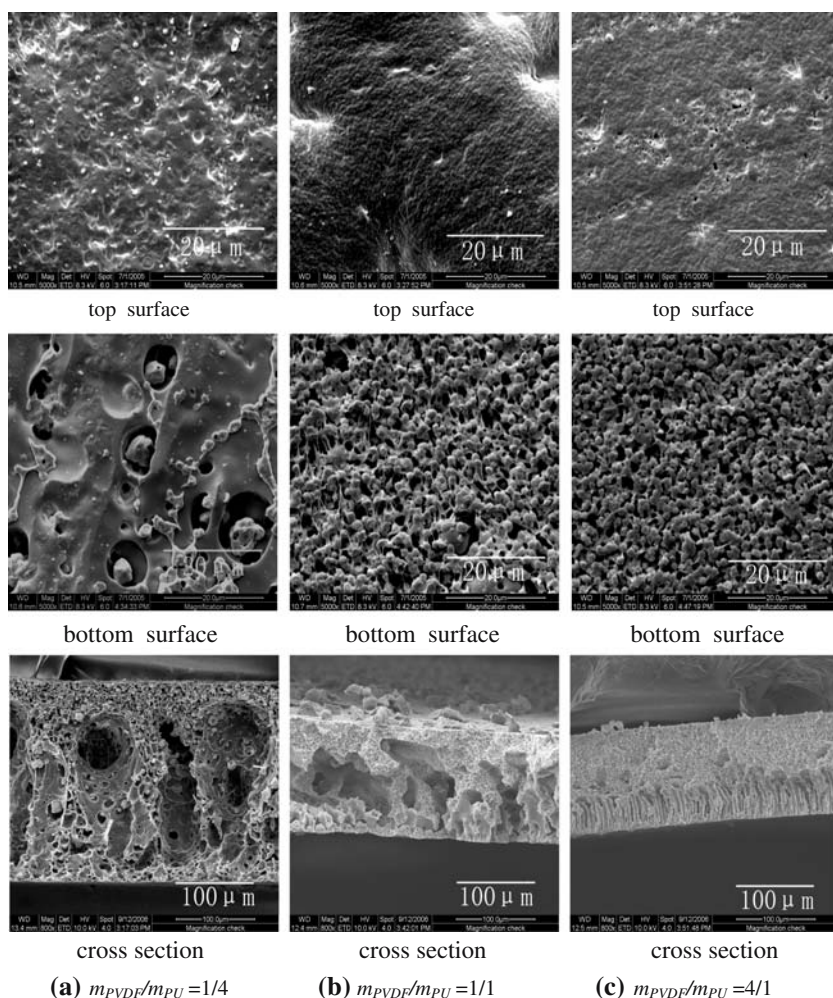


Fig. 7 Effect of working pressure on the PWF of membranes (a) PVDF (b) PU

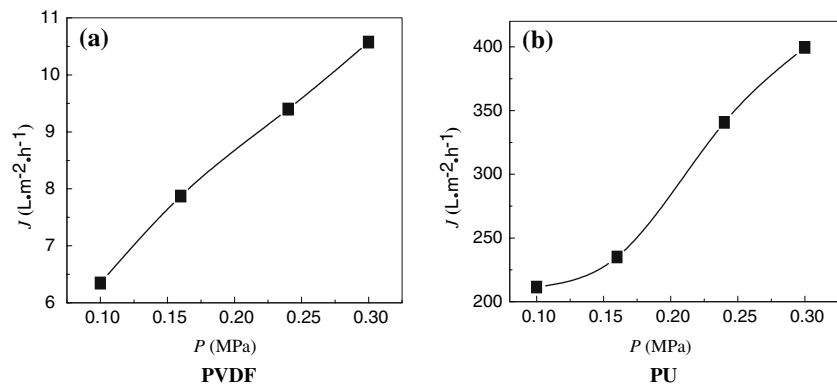


Table 2 Effect of working pressure on the PWF of blend membranes

		PWF of the blend membrane J ($L \cdot m^{-2} \cdot h^{-1}$)			
		0.10Pa	0.16Pa	0.24Pa	0.30Pa
$m_{PVDF}/m_{PU} = 1/4$	Weighted average	180.7	200.9	291.1	341.2
	Experimental value	352.5	634.5	940.0	3102.0
$m_{PVDF}/m_{PU} = 1/1$	Weighted average	125.3	139.6	201.6	236.2
	Experimental value	320.4	846.0	1551.0	2021.0
$m_{PVDF}/m_{PU} = 4/1$	Weighted average	59.7	66.9	95.6	111.7
	Experimental value	126.9	155.1	216.2	364.3

to 1/4 is much lower than that of the other two membranes, and seen from the cross sections in Fig. 6, the pores of the membrane with m_{PVDF}/m_{PU} equal to 1/1 penetrated each other more than that of the other two membranes. All these results are consistent well with the thermodynamic analysis above in 3.1.

Effect of the IFMs on the PWF of blend membranes

The changes in the PWF of PVDF membrane and in that of PU membrane with working pressure are shown in Fig. 7, and by contrast, the PWF of the PVDF membrane is much lower than that of the PU membrane. This may be due to the hydrophile and good elasticity of PU.

The changes in the PWF of the PVDF/PU blend membranes with working pressure are shown in Table 2. The weighted averages were obtained using the PWF shown in Fig. 7 and the volume fractions of PVDF and PU shown in Table 1. Obviously, the experimental values are all much higher than that of the two pure membranes and also than the weighted averages. This may prove that the IFMs attribute much to the PWF of the blend membranes.

The effect of working pressure on the IFM PWF

In Table 2, the change in IFM PWF with working pressure was obtained after the experimental value subtracted the weighted average (see Fig. 8). The IFM PWF of the

membrane with m_{PVDF}/m_{PU} equal to 1/1 shows higher value than that of the other two membranes incipiently, which is due to the worst miscibility of this composition and consistent with the results analyzed with the theory of thermodynamics. However, with the increase in working pressure, the IFM PWF of the membrane with m_{PVDF}/m_{PU} equal to 1/4 shows higher value than that of the membrane with m_{PVDF}/m_{PU} equal to 4/1 and even gradually exceeds that of the membrane with m_{PVDF}/m_{PU} equal to 1/1. This may be related to the better elasticity of PU at 20 °C, and the IFM deformation ability of the membrane with m_{PVDF}/m_{PU} equal to 1/4 is better than that of the other two

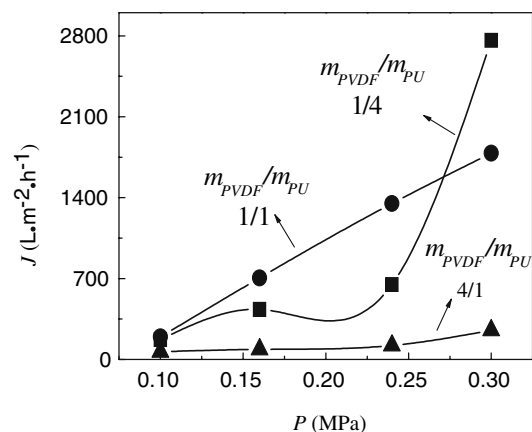


Fig. 8 Effect of working pressure on the PWF of the IFMs

membranes under the same working pressure, which would cause the pore size to become much larger under certain working pressure and increase the PWF. Therefore, the attribution of PWF from IFMs is related not only to the miscibility but also to the IFM deformation ability under working pressure.

Conclusion

The miscibility of PVDF and PU depends on the ratio of the two polymers. The IFMs are formed due to the far δ difference between PVDF and PU, and the IFM quantity depends on the miscibility of PVDF and PU. Because of the existence of IFMs, the PWF of the blend membranes is much more than the weighted averages and also much more than the PWF of the two pure membranes. The IFM PWF of the membrane increases as the working pressure increases and is influenced not only by the miscibility of the two polymers but also by the IFM deformation ability under working pressure.

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