Effect of PVP content on the quaternized polysulfone in blend membranes

Aibin Huang,1* Chaobo Xiao2

1*Hangzhou Dianzi University, Hangzhou 310018, China 1; fax: 086-571-81617830; e-mail: huangaibin436@yahoo.com.cn
2 Department of Chemistry, Wuhan University, Wuhan 430072, China 2; fax: 086-27-68766312; e-mail: cbxiao@163.com

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Abstract: A series of blend membranes of quaternized polysulfone (QPSF) and polyvinylpyrrolidone (PVP) were obtained by a novel method. The procedure of quaternization of chloromethylated polysulfone and the process of blend are synchronous. These blend membranes, prepared with quaternized polysulfone (QPSF) and polyvinylpyrrolidone (PVP), were characterized by FTIR, X-ray diffraction (XRD), tensile tests and scanning electron microscopy (SEM). The degrees of swelling of the membranes in some solvent were also measured. The ionic resistances of the membranes were measured too. With the increasing of PVP content, the properties of the membranes have changed. The tensile strength of blend membrane dropped while the degrees of swelling of the membranes in water increased. The ionic resistance of the membrane dropped with the PVP content increasing in blend membranes. The polyvinylpyrrolidone (PVP) has good compatibility with quaternized polysulfone in blend membranes.

Introduction

Polymeric membranes that function by the solution–diffusion mechanism are of great importance and have been developed for a variety of industrial applications like gas separations, reverse osmosis, pervaporation, etc [1-3]. Polysulfone is an excellent membrane material in terms of physical and chemical stability. Specifically, due to its hydrophobic nature, polysulfone membranes are susceptible to fouling by various mechanisms that reduces the application of polysulfone membranes in the treatment of food streams and biological separations. Furthermore, it is well-known that the incorporation of bulky pendant groups onto the polymer backbone bestows significant changes to the gas permeability, permselectivity, mechanical and surface properties of polysulfone membranes. Several reviews on the chemical modification of polysulfone by different chemical mechanisms to effect the introduction of functional groups onto the polysulfone backbone have been reported. Polysulfone was easily modified into charged material, such as sulphonated polysulfone and quaternized polysulfone, which have been widely used in the process of ultrafiltration, reverse osmosis and electrodialysis [4-8].

An ion exchange membrane is a typical functional polymer and has the potential to be utilized in new fields as new functional materials in addition to the separation of ionic materials. Several trials have been carried out for such purposes: sensors such as humidity sensors [9], carbon monoxide sensors [10], drug sensors [11], carriers for enzymes [12], solid polyelectrolytes [13] and carriers for functional materials [14].
PVP (polyvinylpyrrolidone, povidone, polyvidone) is made from the monomer \(N\)-vinyl pyrrolidone, PVP is soluble in water and other polar solvents. When dry it is a light flaky powder, which readily absorbs up to 18% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. The applications of PVP are widely used [15].

The process of blending has wide applications, as it is a versatile method to tailor materials for specific end uses. Blending techniques of immiscible polymers in this regard has received erstwhile emphasis; especially the membranes consisting of high molecular weight polymers. Blends comprising of water soluble and water insoluble polymers are known to give unique swelling properties to the membranes prepared, by solution casting technique or thermal gelation. Polymer blends having ternary systems comprising of the two polymers and the solvents are explored extensively to study the influence of their phase behavior on the properties of the blend [16] [17].

The blending of polysulfone and PVP was reported in some documents [18][19][20]. The blending films were applied as ultrafiltration membrane. The electricity properties of the blend membranes of modified polysulfone and PVP were rarely reported.

In the study, a series of blend membranes made of modified polysulfone and PVP were prepared. The blend membranes were characterized by FTIR, WXRD, SEM, and swelling tests. It was observed that the microcosmic structure of quaternized polysulfone membranes was changed with altering of PVP content. The membrane is more hydrophilic with the increase of PVP content too. The ionic resistance dropped both in 1.0mol/L NaOH and in deionized water. This investigation is more significant to widen the use of polysulfone and PVP. The addition of PVP can decrease the resistance of anion exchange membranes which is based on quaternized polysulfone. The blend membranes may be applied to redox flow battery.

**Results and discussion**

**FTIR Characteristics of the Membrane**

IR spectra were used to characterize the structure of the substances and investigate the interaction between the two polymers.

![FTIR of the blend membranes](image)

**Fig. 1.** FTIR of the blend membranes.
**Morphological Characteristics of the Membrane**

The SEM photographs of the various membranes are shown in Figure 2. In Figure 2, M1, M2, M3, M4, M5 stands for the SEM photographs of modified polysulfone: PVP = 100%:0%; 90%:10%; 70%:30%; 50%:50%; 30%:70%. “a” indicated the cross section of the membrane and “b” indicated the surface of the membrane.

![SEM photographs of the various membranes](image)

**Fig. 2.** The SEM results of the blend membranes.

In Figure 2, an obvious phenomenon can be observed; an acicular substance appeared in the SEM photographs of M1a, M2a, and M3a while not in M4a and M5a. They can be regarded as lamellar crystals that were formed by quarternized polysulfone. It is clear that there is layer structure in M1a. A high molecular orientation hints the large difference between the polarity of side groups and the polarity of polysulfone main chain. As is known to all, UDEL Polysulfone is an amorphous high performance polymer [22]. Obviously, quarternary ammonium groups linking with the polysulfone main chain is the reason that the lamellar crystals formed in the SEM of M1a. In the SEM of M2a, the reason that the compact structure
was formed may be attributed to the static exclusion effect between the quaternary ammonium groups [23]. In the photographs, from M1a— M2a—M3a—M4a—M5a, an interesting phenomenon can be observed, the crystalline form changed and disappeared gradually and pinhole appeared in M4a and M5a. The crystalline form structure of M3 is different from that of M2 and M1. The phenomenon can be explained that there is a strong interaction behavior between the carbonyl groups in PVP and the quaternary ammonium groups in quarternized polysulfone. On the other hand, PVP became continuous phase and quarternized polysulfone turned to dispersed phase with the increase of PVP content. Thus, the crystal disappeared in M4 and M5 because of the amorphous structure of PVP. Another reason is that during solvent evaporation, the QPSU in DMF may form crystalline phases. The presence of PVP changed the interaction between QPSF and DMF.

The crystallization of the membranes

The X-ray diffraction patterns of the membranes are shown in Figure 3.

As shown in Figure 3, the intensity of the diffraction peaks of the membranes descended gradually with increase of PVP content in the compounds, which implied that the degree of crystallization gradually decreased. It showed that the structures of the blend membranes tended to be amorphous as the PVP content increased. There are diffraction peaks at 2θ = 18° in M1, M2 and M3. The diffraction peak at 2θ = 12.2° in M1 and at 2θ = 9.3° in M3 hint that maybe different crystalline phase lies in M1 and M3 respectively.

![Fig. 3. The WXRD of the blend membranes.](image)

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The sharp peak has disappeared in M4 indicating that it tended to be amorphous. There is no diffraction peak in M5, which showed a thoroughly amorphous structure of M5. From Figure 3, the crystal phase changed and the degree of crystallization of the blend membranes gradually decreased with the increase of the PVP content. The phenomenon of the gradual decrease of degree of crystallization may be explained by that the PVP content is dispersed phase in quaternized polysulfone. It dispersed the static exclusion effect in quaternized polysulfone. With the increase of PVP content, it turned to continuous phase and led to a thoroughly amorphous structure of M5. The phenomenon of the crystal phase change from M1 to M3 hints that there are some kinds of interaction behavior between the PVP and the quarterized polysulfone.

**Water Swelling Properties**

The membrane was immersed in distilled water for 3 days; then its surface moisture was wiped and the wet membrane weighed. Then this weighed wet membrane $W_{\text{wet}}$ as dried at a fixed temperature (25 °C) until constant weight as dry membrane, $W_{\text{dry}}$, was achieved. The membrane swelling can be calculated from $\text{Swelling} = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100\%$. The degree of swelling of the blend membranes is shown in Figure 4.

![Figure 4](image)

**Fig. 4.** The degree of swelling of the blend membranes.

In Figure 4, with the increase of PVP content, the degree of swelling of the blend membranes became higher and higher. As is known to all, PVP is a kind of water-soluble polymer. With the increase of PVP content, the membranes became hydrophilic gradually and the degree of swelling of the blend membranes got higher, which is reasonable. In blend membranes, the PVP cannot be extracted to water thoroughly. The phenomenon hints that there is interaction between quaternized polysulfone and polyvinylpyrrolidone too. It swelled hardly of the blend membranes without PVP in H$_2$O, MeOH, EtOH, and acetone, for its high degree of crystallization. With the increasing of PVP content, the degree of swelling increased too. At the same PVP content, the order of the swelling degree of the membranes is
DMF>EtOH>MeOH>H2O>acetone. It hints that there was a strong interaction between QPSF and DMF too.

**Mechanical Properties of the Membranes**

The mechanical property of the membrane is very important to application. The mechanical performance of the membrane is shown in Fig. 5. In Fig.5, the tensile strengths of the blends change with an increase of PVP content, and the maximum value of 43.1 MPa is reached when the content of PVP is 30 wt%. When the content of PVP exceed 30 wt%, tensile strengths of the blends decreased with the addition of PVP. While the elongation at bleak are steady with the change of PVP content. The data of elongation at break show that blend membranes are brittle. It is related to the quality of quaternized polysulfone and PVP. But it did not affect the use of the membranes because PVP is prone to absorb water. They can be used in wet situation.

![Mechanical Performance of the Membranes](image)

**Resistance of the Membranes in deionzed water and in 0.1mol/L NaOH**

The resistances of the membranes were measured by electrochemistry workstation and the results are listed in Tab. 1.

**Tab. 1. Effect of PVP Content on the resistance of the membranes.**

<table>
<thead>
<tr>
<th>Samples/Testing condition</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0mol/LNaOH(Ω·cm²)</td>
<td></td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Deionzed water(Ω·cm²)</td>
<td>180.5</td>
<td>51.3</td>
<td>44.7</td>
<td>40.0</td>
<td></td>
</tr>
</tbody>
</table>

From Tab. 2, an obvious result can be found: The resistance of the membrane decreased step by step according to the order M2>M3>M5>M5 in deionized water. In 0.1mol/LNaOH, the resistances of the membranes were much lower than in deionized
For membrane A, its resistance is so high that it overruns the limiting of the electrochemistry workstation. Its hydrophobic property results in the same phenomenon in 0.1 mol/L NaOH. While the resistance of the membrane M2>M3>M4>M5 in deionized water hints that hydrophilic PVP may improve the conductivity of the membranes. Another explanation is that degree of crystallization decreased with the increasing of PVP content. As is known to all for the solid polymer electrolyte (SPE) of polyethylene oxide (PEO)-salt type, increasing chain flexibility by decreasing its degree of crystallization can be helpful in improving its ionic conductivities [25].

There were two possible reasons leading to low resistance in 0.1 mol/L NaOH: one is that the Cl\textsuperscript{−} was changed to OH\textsuperscript{−}, which conducts for its small ionic radius; the other is that Na\textsuperscript{+} and OH\textsuperscript{−} played a bridge role to improve the conductivity of the solid polymer electrolyte membranes. The small resistances of the membrane make it possible to apply to redox flow battery.

**Conclusions**

In the present study, a series of blend membranes were obtained by a special method. The process of blend membranes forming is synchronous with the process of quaternarization of chloromethyl polysulfone. The blend membranes were examined by FTIR, morphological characteristics, WXRD, swelling properties and mechanical properties. The structures of membranes changed with the increase of PVP content in blend membranes. The membranes turned hydrophilic gradually with the increase of PVP content in blend membranes. The results hint that there is a strong interaction behavior between PVP and quarternized polysulfone. The introduction of PVP improved the conductivity of the membranes. To add PVP may be a method for decreasing resistance of the anion exchange membrane.

**Experimental part**

**Materials**

Polysulfone (M\textsubscript{n}: 38000) used was Udel 1700 from Solvay. 1,2-Dichloroethane solvent and N,N'-dimethylformamide (DMF) solvent were purchased from Chemistry reagent factory, Shanghai. Chloromethyl methyl ether and N,N-diethylethanamine (triethylamine) were purchased from Chemistry reagent factory, Nanjing. The materials used in the preparation of blend membranes are polyvinyl pyrrolidone (PVP) from Aldrich and its M\textsubscript{w} is 50000

**Chloromethylation of polysulfone**

The process of chloromethylation of polysulfone is as follows: A polysulfone solution was prepared by dissolving 10 g of polysulfone into 100 ml of 1,2-dichloroethane placed into a glass separable flask equipped with a stirrer, a cooler and dropping funnel. Anhydrous stannic chloride (0.25g) was dissolved into 20 ml of chloromethylether. The zinc chloride solution in chloromethylether was dropped into the flask by the dropping funnel. Because chloromethylether is a toxic, carcinogenic agent, caution must be used to avoid any contact with or inhaling it. The resulting solution was heated to a temperature of 40 °C and further reflux for 12 h at 50-55 °C. After cooling, the solution was poured into methanol to precipitate the polymer. The polymer was further purified by redissolving in dimethylacetamide and precipitating in water. The crosslinking reactions and gelation can be avoided by controlling the reaction conditions [16]. The Substitution degree of chloromethyl content is 1.5 meq/g
measured by the Schöniger method [17]. The degree of substitution (DS) was calculated using the following equation:

$$DS = \frac{M_{PSF} \cdot C_{Cl}}{100 - M_{CH2Cl} \cdot C_{Cl}}$$

where, $M_{PSF}$, $M_{Cl}$, $M_{CH2Cl}$ and $C_{Cl}$, are referred to molecular weight of structural unit of PSF, atomic weight of chlorine, molecular weight of CH$_2$Cl group and concentration of chlorine analytically determined, respectively. The reaction is shown in Fig. 6.

**Fig. 6.** Synthesis of chloromethylated polysulfone and quaternized polysulfone.

**Preparation of the Membranes**

Because the last anion exchange membrane cannot be dissolved in DMF again, we have to mix the chloromethylated polysulfone and PVP. The process of quaternary ammonium halide and blend is synchronous. Some chloromethylated polysulfone (ClPSF) were dissolved in DMF at 80 °C and triethylamine added into it for half an hour. Some PVP was dissolved in DMF too. Two kinds of solutions were mixed for half an hour. The mixed solutions were cast on glass plate and allowed to evaporate the DMF at 80 °C. The membranes were dislodged carefully and then subjected to
further drying under vacuum for 2 days. A series of blend membranes of thickness ranging 55±5 μm were obtained. The ratio of different reagents is shown in Tab. 2.

Tab. 2. The ratio of chloromethylated polysulfone (CIPSF) and PVP and triethylamine.

<table>
<thead>
<tr>
<th>Blend membrane</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIPSF (g)</td>
<td>1.0</td>
<td>0.9</td>
<td>0.7</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>PVP (g)</td>
<td>0</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>triethylamine (mL)</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Characterization of Blend Membranes**

IR spectra of the films were recorded using a Fourier transform infrared (FTIR) spectrometer (Nicolet 170SX, USA) with attenuated total reflection instruments for investigation intermolecular interaction. The films were taken on the flat sheet and data were collected over 64 scans with a resolution of 4 cm⁻¹ at room temperature. The Wide-angle X-ray diffraction (XRD) patterns of the membranes of 55±5 μm thickness were recorded with a shibadzu XRD-6000 (Japan) diffractometer by using a Cu Kα target at 40 KV and 30 mA with a scan rate of 4º / min. The diffraction angle ranged from 5 to 45º. The tensile strength and breaking elongation of the membranes were measured on an electron tensile tester (XINSANSI-cmt6202, Shenzhen) with a tensile rate of 5 mm/min, at a gauge length of 50 mm and width of 10 mm. The temperature and relative humidity were 25 ºC and 50%, respectively. The morphology of membranes surfaces was examined by a Hitachi-570 scanning electron microscopy (Japan). The membranes were frozen under liquid nitrogen to fracture and were coated with gold under 13.3 Pa vacuum conditions before the SEM experiment. The resistances of the exchanged membranes are measured by electrochemistry workstation made by Chenhua Instrument Company (Shanghai, China). To measure the ionic conductivity of the blend membrane in deionzed water and in 0.1mol/L NaoH solutions, the membrane was sandwiched between two half-cells, each of which contained an electrolytic electrode made from Raney Ni mesh for electrolysis and a glass Luggin capillary connecting to a Hg/HgO reference electrode for potential measurement. The capillary tip was positioned close to the membrane, and the potential drop across the membrane was measured through the two reference electrodes. The ionic conductance was calculated from the slope of the linear relationship between the cross-membrane voltage and the electrolytic current.

**Acknowledgements**

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**References**