Characteristics and separation efficiencies of PPSU/PEI/PEG blend membranes with different compositions for water treatment

Li-Luen Hwang, Ming-Yen Wey and Jyh-Cherng Chen

ABSTRACT
To overcome the problems and constraints in the application of single organic membranes in wastewater treatment or water reuse processes, different blend membranes were prepared and modified to improve the separation efficiency of humic acids (HAs) and mitigate the fouling problems occurring during water purification. This study extends the results of our previous research and further investigates the relationships between the composition of polyphenylsulfone/polyetherimide/polyethylene glycol (PPSU/PEI/PEG) blend membranes and membrane characteristics and performance. The experimental results showed that the PEI and PEG component ratios of PPSU could significantly affect the blend membrane structure, morphology, and properties. With the increase in PEG concentration, the pore volume, pore size distribution, and permeability of the blend membranes was enhanced. The hydrophilic or hydrophobic properties of the blend membranes can be modified by changing the PPSU/PEI ratios. The optimum composition of the PPSU/PEI/PEG blend membrane was 35/5/6 wt%, and the corresponding permeability and HAs separation efficiency was 127 Lm⁻²h⁻¹ and 83%, respectively.

Key words | blend membrane, humic acid, permeability, separation

INTRODUCTION
Because of increasing requirements for the quality of drinking and industrial water and the shortage in water resources, improvements in water treatment efficiency and reuse have become important issues. Currently, membrane filtration or membrane technology is extremely attractive among the existing or developing techniques of advanced water purification processes. In general, ultrafiltration (UF) combined with precoagulation or adsorption is widely applied to remove natural organic matter (NOM) because it can achieve high flux with low energy consumption (Meier et al. 2006). Although single organic membranes were developed early and applied in purification processes, fouling problems and constraints in their use still remain. The efficiency of water treatment with single organic membranes is not as good as expected. The rapid decline in filtration flux caused by fouling is the major challenge and problem in membrane systems. Humic substances (phosphoric acid, fulvic acid and humic acids (HAs)) and other organic matter which is indissoluble in water (Duan et al. 2005; Listiarini et al. 2009) may cause membrane fouling. Although membrane backwashing can mitigate the filtration flux decline, the effect is limited. The structures and properties of the membranes deteriorate and the valid period of a membrane is reduced by fouling (Listiarini et al. 2009).

To overcome these problems and constraints of single organic membranes, the membrane composition and properties can be modified (Buonomenna et al. 2007). Asymmetric membranes can be prepared by the coating method, porous membranes can be prepared by the polymerization method, and hydrophobic, porous, and multipurpose membranes can be prepared by the blending method (Lee & Wang 1998; Di Vona et al. 2006; Nagendran and Mohan 2008; Sikder et al. 2009). Therefore, the development of blend membranes has become mainstream in membrane technology. Blend membranes are prepared by mixing two polymer materials, and their properties can be modified by changing the solvents, additives, and pore-formation agents. Many studies have used cellulose acetate...
(CA) as the polymer for blending with other polymers (polyethersulfone (PES), polysulfone (PSU), polyethylenimine (PEI), and poly (vinyl acetate) (PVAc)) or additives to prepare the blend membranes. Such blend membranes are negatively charged and electrostatically repel the negative HAs, which can reduce the adsorption of HAs on the membrane surface, and thus reduce fouling (Sivakumar et al. 2006; Idris et al. 2007; Nagendran & Mohan 2008). Fu et al. (2008) indicated that the accumulation of HAs on the membrane typically affects the surface morphology of the membrane and causes serious fouling problems while decreasing the filtration flux. To improve the filtration flux and separation efficiency of HAs, we mixed hydrophobic or negatively charged polymers with hydrophilic or positively charged polymers to develop innovative, durable, and effective blend membranes.

The polyphenylsulfone (PPSU) polymer is especially suitable to prepare membranes for removing HAs because it is negative, hydrophobic, mechanically strong, ductile, and chemical resistant; furthermore, it has similar properties and morphology to that of polysulfone (PSF or PSU) (Bowen et al. 2002; Di Vona et al. 2006; Sivakumar et al. 2006). However, there have been few studies concerning the preparation of PPSU membranes and their application to wastewater treatment. To overcome the problem of low filtration flux caused by dense polymers in wastewater treatment, additional additives or pore-forming agents are required to increase the membrane porosity (Chakrabarty et al. 2008). Polyethylene glycol (PEG) is the most commonly used additive (pore-formation agent). Because PEG is hydrophilic and has different molecular weights (Idris et al. 2007; Chakrabarty et al. 2008), it has great influence on the pore size, pore distribution, and filtration flux of a membrane. The quantitative relation between PEG concentration and pore size distribution of the membrane is unclear and needs to be evaluated. PEI is one of the materials for the preparation of polymer membranes noted for its outstanding high chemical and thermal resistances, and mechanical strength. However, because of its macro-pore structure, PEI membranes commonly cannot achieve high removal efficiency of target pollutants. Therefore, blends of PEI with other polymers, such as CA, have been widely used in membrane preparation recently (Arthanareeswaran et al. 2007; Idris et al. 2007; Chakrabarty et al. 2008; Hwang et al. 2011).

To overcome the problems and constraints of the application of single organic membranes in wastewater treatment or water reuse processes, we have investigated the characteristics and performance of membranes with different PPSU/PEI ratios (Hwang et al. 2011). The results indicated that the membranes with increased negatively charged PPSU exhibited good resistance to HAs and thus membrane fouling decreased. However, we did not succeed in obtaining the optimal membrane composition, which exhibits good permeability and HAs separation efficiency. Therefore, we changed the contents of hydrophilic PEG and hydrophobic PPSU to increase the HAs separation efficiency and moderate membrane fouling. The surface morphology, hydrophilicity/hydrophobicity, and compatibility of each blend membrane were characterized by using a field emission scanning electron microscope (FE-SEM) and contact angle measurements. Finally, the performance of modified blend membranes was evaluated on the basis of pure water filtration flux (membrane permeability), hydraulic resistance, HAs separation efficiency, and antifouling properties.

**METHODS**

**Materials**

This study presents the characteristics of PPSU/PEI/PEG blend membranes with different component ratios and investigates the separation efficiency of HAs. The major membrane components were polyphenylsulfone (PPSU, \( M_W: 53,000-59,000 \) g/mol) and polyetherimide (PEI, \( M_W: 529 \) g/mol). Polyethylene glycol (PEG, \( M_W: 200 \) g/mol) and N-methyl-2-pyrrolidone (NMP) are used as the pore-formation agent and solvent, respectively. The HAs solutions for the blend membrane test were prepared by dissolving HAs powder in 1 L deionized water and filtering with a 0.45 \( \mu m \) membrane to remove the larger particulate matter (Yuan & Zydny 1999). Natural HAs can be roughly divided into dissolved organic matter (DOM) and particulate organic matter (POM) and they can be separated by the 0.45 \( \mu m \) membrane (Mao et al. 2007). The pH value of the HAs solution was controlled at 6.7 ± 0.1 by 0.1 M HCl or NaOH. The particle size distribution of the HAs solution was measured by a laser particle size analyzer (FRITSCH Analysette 22 COMPACT), and two peaks of particle size were found at 0.005–0.1 and 0.5–50 \( \mu m \).

**Membrane preparation**

All the PPSU/PEI/PEG blend membranes with different component ratios were fabricated using the wet phase inversion technique (Buonomenna et al. 2007). The weight ratios

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of the components in the different blend membranes are shown in Table 1. Different ratios of the PPSU and PEI polymers were mixed with 6 and 12 wt% PEG (pore-formation agent), respectively, and were dissolved in NMP solvent. The polymers were stirred at 500 rpm and heated at 60 °C for 2 h to become a completely mixed and homogeneous casting solution. Subsequently, the solution was uniformly spread on a glass plate using a casting knife. The solvent present in the cast film was allowed to slowly evaporate at room temperature overnight, next it was gently immersed in a water bath for 6 h, and the temperature of the water bath was controlled at 28 ± 2 °C to ensure complete precipitation and membrane formation. Then, the membrane was peeled off the plate glass and subsequently rinsed with deionized water to remove residual solvent and pore-forming agent (PEG). The finished membranes were stored in a mixed solution of deionized water/methanol (1:1) prior to the filtration test.

### Table 1 | Water contact angle and equilibrium water content (EWC) of different PPSU/PEI/PEG blend membranes

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Casting solution compositions (wt. %)</th>
<th>Contact angles (θ)</th>
<th>Contact angles (θ)</th>
<th>EWC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PPSU  PEI  PEG</td>
<td>Top</td>
<td>Bottom</td>
<td></td>
</tr>
<tr>
<td>S35P6</td>
<td>35      5    6</td>
<td>127.5 ± 0.1</td>
<td>107.7 ± 0.6</td>
<td>32.87</td>
</tr>
<tr>
<td>S35P12</td>
<td>35      5    12</td>
<td>82.4 ± 0.3</td>
<td>72.7 ± 0.1</td>
<td>41.56</td>
</tr>
<tr>
<td>S30P12</td>
<td>30      10   12</td>
<td>80.4 ± 0.4</td>
<td>77.7 ± 0.3</td>
<td>45.67</td>
</tr>
<tr>
<td>S20P12</td>
<td>20      20   12</td>
<td>76.7 ± 0.6</td>
<td>72.2 ± 0.7</td>
<td>53.84</td>
</tr>
<tr>
<td>S10P12</td>
<td>10      30   12</td>
<td>67.0 ± 0.4</td>
<td>67.9 ± 0.8</td>
<td>59.37</td>
</tr>
</tbody>
</table>

where $W_w$ and $W_d$ are the weights (g) of the wet sample and dry sample, respectively.

### Filtration test of blending membrane

#### Pure water flux (PWF)

An in-house membrane filtration system was designed and set up. As shown in Figure 1, the system is equipped with automatic filtration and backwash units and flow and pressure monitoring devices. The membrane test was conducted in a cross-flow filtration cell with an effective plate area of 105 cm². Each membrane was initially compacted with deionized water at pressures from 98.4 to 490.67 kPa and kept for 30 min at 490.67 kPa. Subsequently, the membrane filtration test was conducted at a water pressure of 294.4 kPa and a feed flow rate of 2,400 mL/min for 120 min (Arthanareeswaran & Thanikaivelan 2010). A big feed tank of ca. 20 L was used to avoid temperature variations of feed water due to the centrifugal pump. The temperature of the feed water was maintained constant at 28 ± 2 °C. The pure water flux (PWF, $J_{w1}$) through the membrane was measured using Equation (2):

$$J_{w1} = \frac{Q}{A \times \Delta T}$$

where $J_{w1}$ (kg m⁻² h⁻¹) is the PWF, $Q$ (kg) is the weight of the filtrate, $A$ (m²) is the membrane area, and $\Delta T$ (h) is the filtration time.

#### Membrane hydraulic resistance ($R_m$)

The membrane resistance is defined as the pressure drop from the permeation of pure water through the membrane. The membrane resistance is equal to
the tolerance of a membrane to the hydraulic pressure during the filtration process (Arthanareeswaran & Thanikaivelan 2010). It can be determined using Equation (3):

\[
R_m = \frac{\Delta P}{\mu \times J_{w1}}
\]  

(3)

where \(\Delta P\) is the trans-membrane pressure (294.4 kPa) and \(\mu\) is the viscosity of pure water.

HA removal efficiency \((R)\)

The performances of the blend membranes were tested by the filtration of HA. The HA removal efficiency was defined as the efficiency of the membrane to filter or separate HA from the test water (Arthanareeswaran & Thanikaivelan 2010). The HAs removal efficiency was calculated with Equation (4):

\[
R = 1 - \frac{C_p}{C_f} \times 100\%
\]  

(4)

where \(C_p\) and \(C_f\) (mg mL\(^{-1}\)) are the HAs concentration in the filtrate and feed water, respectively.

RESULTS AND DISCUSSION

Structure characteristic of the blend membranes

In this study, hydrophilic PEI was used to blend with the PPSU casting solution to improve the porous structure and hydrophilicity of the PPSU membrane. The surface and cross-section morphology of the PPSU/PEI blend membranes are shown in Figures 2 and 3, respectively. All the membranes exhibit similar asymmetric and sponge-like structures, which is typical of UF membranes. The pore size in the wall and the surface of the sponge-like structure changed as a function of the polymer content. The FE-SEM observations showed that the surface (Figures 2(a–d)) and cross-section (Figures 3(a–d)) structure of the S35P12 blend membrane were less porous than the other blend membranes (S30P12, S20P12, and S10P12), and all the blend membranes
exhibited typical sponge-like structures. Kim & Lee (1998) investigated the effect of adding different molecular weights ($M_w$) and PEG content on the formation mechanism of polysulfone (PSf) membrane (Kim & Lee 1998). They found that the polymerization of the membrane decreased as the molecular weight ($M_w$) and PEG content increased. The optimal PEG content in the PSf solution was 50 wt%, in which the pore size became bigger, the membrane surface became more porous, and all the membranes exhibited similar sponge-like structures. The effect of PEG 200 on the membrane structure and porosity is shown in Figure 3(a) and Figure 4(b). As the concentration of the pore-formation agent PEG 200 increased from 6 to 12 wt%, the FE-SEM cross-section pictures of the blend membranes showed the increase in the structure porosity.

Table 1 shows the water contact angle and EWC of different PPSU/PEI/PEG blend membranes. The results indicate that the EWC of the blend membranes increased with increasing PEI concentration. The EWCs of the blend membranes increased from 41.56 to 53.84% after blending with PEI from 5 to 20 wt%. The results of contact angle measurements indicate that the hydrophilicity of the blend membranes increased with increasing PEI concentration.

The hydrophilicity and hydrophobicity of the blend membranes

In this study, different concentrations of PEG were added in the PPSU/PEI blend membranes. The hydrophilicity and hydrophobicity of the membrane were analyzed by measuring the water contact angle. Figure 5 shows the water contact angles of PPSU/PEI membranes with different component ratios. As the PEI concentrations increased, the hydrophilicity, positive charge, and porosity of the blend membranes increased (Hwang et al. 2011). At the same time, the hydrophobicity, density, and negative charge of the PPSU polymer improved, and the PWF of the membrane increased (Singh et al. 2006; Srinivasa Rao et al. 2006). Table 1 shows the contact angles on the top layer (the surface between the membrane and air) and the bottom layer (the surface between the membrane and glass plate) of the membranes, as well as the hydrophilicity and hydrophobicity of the blend membrane with different concentrations of PEG and PPSU/PEI polymers. The results show that the contact angles on the top layer and bottom layer of the S35P12 blend membranes were more hydrophobic than that of S10P12. Comparing the dense top layer and porous bottom layer of the membranes, the pore size and pore structure of the
membrane surface were related to the exchange rate of the solvent and non-solvent and the contact surface of the membrane. The results indicate that the hydrophilicity and hydrophobicity of the top- and bottom-layer membrane are related to the pore size and distribution. Because PEG is highly hydrophilic, neutral, non-toxic, biodegradable, and non-repulsive (Ma et al. 2011), we can add different concentrations of PEG 200 in PPSU/PEI blend membranes to amend its hydrophilicity. The concentration of the PEG pore formation agent in the PPSU/PEI blend membranes affected the number of surface pores and the porous structure. As the PEG
concentration increased from 6 to 12 wt%, the FE-SEM observations showed that in the S35P6 and S35P12 blend membranes the number of surface pores increased, and the contact angles of the hydrophilic membranes increased from $82.4^\circ \pm 0.3^\circ$ to $127.5^\circ \pm 0.1^\circ$.

**Figure 4** | FE-SEM images for the surface and cross-section of S35P6 blend membrane.

**Figure 5** | Water contact angles of different PPSU/PEI/PEG 200 blend membranes.

**Pure water flux of the blend membranes**

The PWF and intrinsic membrane resistance ($R_m$) of PPSU/PEI/PEG blend membranes with different component ratios were measured by using the membrane filtration system.
Figure 6 shows the PWF and $R_m$ of different PPSU/PEI/PEG blending membranes. The pore size distribution of the membrane directly affected the filtration flux and HAs removal efficiency. The increased content of the PPSU polymer caused the pore size of the membrane to decrease and $R_m$ to increase. The increased content of the pore-formation agent PEG promoted the pore distribution, and the membrane resistance consequently decreased. Figure 6 shows the PWF and $R_m$ of different PPSU/PEI/PEG blend membranes. The results indicate that the membranes with higher PPSU content increase the $R_m$ and decrease the PWF. Conversely, the increased PEI and PEG content in blend membranes increases the PWF and decreases the $R_m$. Therefore, the modification of hydrophobic membranes by the hydrophilic polymers effectively increases the permeability of the hydrophobic membrane during filtration.

**HA removal efficiency of the blend membranes**

Figure 7 shows the relationships between the component concentrations in the blend membranes and PWF, EWC and HA separation efficiency. When PPSU/PEI blend membranes with different PEG concentrations were used, PWF and EWC increased but the HA separation efficiency decreased. When the PEG content was reduced to 6 wt%, the PWF and HA separation efficiency of the S35P6 blend membrane was 127 L m$^{-2}$ h$^{-1}$ and 83%,
respectively. Comparing the results of S35P6 and S35P12 blend membranes adding 6 wt% PEG in the membranes can change the membrane structure and reduce the porosity but increase the HA separation efficiency. Conversely, the blend membranes become more hydrophobic, so that the membrane fouling resulting from removal of hydrophobic HAs was mitigated. Comparing our results with other polymer blend membranes in the literature (Table 2), we find that the PWF of our membranes is higher and the separation efficiency of HAs is equally as good as the others.

**CONCLUSIONS**

To improve the separation efficiency of HAs and mitigate the fouling problems that occur during water purification, PPSU/PEI/PEG blend membranes with different component ratios were prepared. The membranes were asymmetric UF membranes with hydrophobic properties, which can prevent the fouling during the filtration of HAs, and hydrophilic properties, which can prevent the rapid decline in PWF. The component ratios of PPSU, the PEI polymers and PEG can affect the membrane structure, morphology, and properties of the blend membrane. The pore volume, pore size distribution, and permeability of the blend membrane increased with increasing PEG concentration. The optimum composition of the PPSU/PEI/PEG blend membrane was 35%/5%/6%, and the corresponding permeability and HAs separation efficiency was 127 Lm⁻² h⁻¹ and 83%, respectively.

**REFERENCES**


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