Preparation, characterization and performance of a novel PVDF/PMMA/TPU blend hollow fiber membrane for wastewater treatment
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ABSTRACT
Polyvinylidene fluoride (PVDF)/polymethylmethacrylate (PMMA)/thermoplastic polyurethane (TPU) blend hollow fiber membranes were successfully prepared by the wet-spinning method with the loading of PMMA and TPU in a range of polymer concentrations varying from 0 to 20 wt% and at a total polymer concentration of 16 wt%. The influence of the addition of PMMA and TPU on the morphologies and the properties of such prepared membranes was investigated through FTIR-ATR, SEM, viscosity measurements, UF experiments and mechanical strength tests. Based on the experimental results, the compatibility of the PVDF, PMMA and TPU blend was best under the conditions of the PVDF-rich phase. The elongation at break of the membrane increased to a maximum of 146% with increase in the TPU concentration to 20 wt% in dope solution. The addition of PMMA increased the water permeation flux from 120 to 195 L/(m² h) initially. The flux then decreased when PMMA concentration was increased to over 10 wt%. The membranes obtained at optimized blending ratio were applied to the dyeing process wastewater filtration. During continuous filtration for 8 h, the flux was stabilized at about 20 L/(m² h) at 0.1 MPa. The reduction in CODCr, turbidity and color were about 63, 84 and 63% respectively.

INTRODUCTION
Hollow fiber ultrafiltration membranes are widely used in wastewater treatment for their advantages of high specific surface, easy installation, simple processing and so on (Van Hoof et al. 2001; Hamada & Miyazaki 2004). However, the flux decline caused by membrane fouling and effluent quality decline caused by fiber breaking shorten the membrane life.

Polyvinylidene fluoride (PVDF) is the main polymeric membrane material because of its superior thermal, chemical and oxidation resistance (Jian & Pintauro 1997; Kong & Li 1999). Hydrophobic properties of PVDF lead easily to membrane contamination. To overcome this limitation, physical blending methods which could create a hydrophilic surface have been investigated. PMMA is attractive due to its good hydrophilicity and good compatibility with PVDF in the whole concentration range in a polymer blend (Elashmawi & Hakeem 2008). The miscibility of PVDF with PMMA depends on the tacticity of PMMA (Yoshida 1997). Several papers have reported the preparation and characterization of the PVDF/PMMA flat membrane (Ochoa et al. 2003; Ma et al. 2007). However, the reports on preparation of a hollow fiber membrane of PVDF/PMMA were few (Saeid et al. 2009). One of the reasons may be because PMMA is brittle (Lina et al. 2006), the addition of PMMA reduces membrane strength. Based on our early research, the PVDF/PMMA blend fiber membrane is not stiff enough to be used in wastewater treatment. In order to increase the breaking strength of PVDF/PMMA blend fiber membrane, thermoplastic polyurethane (TPU) was chosen as the third blending polymer, because of its extensively elastomeric property. It has been reported that at a low concentration of TPU (when PVDF/TPU was 8/2), the water flux of the PVDF/TPU blend fiber membrane was higher than the pure PVDF membrane. And with the use of hydrophilic additive PVP, the water flux of the PVDF/TPU membrane was further improved (Zhou & Xi 2008).
In this work, novel blending hollow fiber membranes based on PVDF were prepared with different weight fractions of PMMA and TPU. It was expected that PMMA may increase the membrane hydrophilicity which could effectively enhance the antifouling, and TPU may increase the membrane breaking strength which could be more suitable for wastewater treatment. The compatibility of PVDF, PMMA and TPU, and the mechanical and separating properties of the prepared membranes were studied. Generally the most suitable membranes for ultrafiltration were prepared for the membrane module. Dyeing process effluent from an anaerobic/anoxic/oxic (AAO) system was directly filtrated by this membrane module. The removals of CODCr, turbidity and color were investigated.

**MATERIALS AND METHODS**

**Materials**

PVDF (FR904) was purchased from Shanghai 3F New Materials Co., Ltd., China. PMMA (LX-40) and TPU (585A) were received from Heilongjiang Longxin Chemical Co., Ltd., China and Townsend Chemicals, Australia, respectively. N,N-dimethylacetamide (DMAc, >99% reagent, the product of Shanghai Chemical Agent Company, China) and distilled water were used as the solvent and nonsolvent, respectively. Bovine serum albumin (BSA) (Mw = 67,000) from Shanghai Bio Life Science and Tech Co., Ltd., China was obtained to characterize the separation performance of prepared membranes.

The dyeing process wastewater in our experiment was the effluent of an AAO system from another experiment. The CODCr values and dye concentration of the wastewater were 65–110 mg/L and 2–4.5 mg/L, respectively.

**Membrane preparation**

Firstly, the desired weights of PVDF, PMMA and TPU were dissolved into DMAc at 80 °C in a triangle flask with strong stirring to get a PVDF/PMMA/TPU solution for spinning at room temperature. The whole weight of solution was 400 g. The composition was 16 wt% polymers in 84 wt% DMAc as the solvent. The viscosity of the dope solutions was determined by a rotary viscometer (LVDV-C, Brookfield Engineering Laboratories, Inc., USA) at the constant temperature of 25 °C. Before spinning, the dope solutions were deposited in a dark place for 24 h to degas.

PVDF/PMMA/TPU blend hollow fiber UF membranes were spun at room temperature employing the wet-spinning method (Chung & Xu 1998). The difference in our experiment was that there were five inner tubes on the spinneret; the orifice and inner diameter of the spinneret are shown in Figure 1(a). The dope solution and bore fluid passed through the orifice and inner tubes at the pressure of N₂ and the constant-flow pump, respectively. The bore fluid and coagulant were both the distilled water. The nascent membranes were immersed in distilled water for at least 48 h to remove the traces of DMAc, and then kept in a 50 wt% glycerol aqueous solution for 24 h to prevent the collapse of porous structures. Finally, the membranes were dried in ambient air until ready to use.

**Membrane characterization**

**Compatibility study**

The FTIR-ATR (NEXUS670, Nicolet Instruments Corp., USA) sampling technique was used to estimate the compatibility of the blends. Pure PVDF, PMMA, TPU membranes and PVDF/PMMA/TPU blend membranes were analyzed after being dried in a vacuum. The FTIR spectra of the samples were recorded in the wave numbers ranging from 4,000 to 675 cm⁻¹ with a resolution of 4 cm⁻¹.

**Morphology examination**

The cross-sectional morphology of the membrane samples were observed with SEM (JSM-5600LV, JEOL, Japan). The fibers were firstly immersed into liquid nitrogen for a few minutes to expose the cross-section, then sputtered with gold under vacuum. All samples were obtained under 10 kV at 20 °C.

**Mechanical properties**

The tensile strength and elongation of the membrane samples were measured by a tensile apparatus (AG-1, Shimadzu, Japan). The sample was tested with a gauge length of 100 mm at an elongation velocity of 10 mm/min until it was broken.

**Permeation flux (J) and rejection (R) experiments**

The newly prepared membranes were pre-pressurized at 0.1 MPa using pure water for 50 min before measurement to ascertain that the steady state was obtained. Then the
pure water permeation \( (J_w) \) was measured at 0.1 MPa. The concentration of BSA in the permeation and feed were measured with a UV spectrophotometer (UVmini-1240, Shimadzu, Japan) at a wavelength of 280 nm. The permeation flux \( (J) \) and rejection \( (R) \) are calculated as in Equations (1) and (2), respectively.

\[
J = \frac{Q}{A} \tag{1}
\]

\[
R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \tag{2}
\]

where \( J \) is the permeation flux of the membrane for the BSA solution or water (L/(m² h)), \( Q \) is the volumetric permeation rate of the solute or pure water (L/h), \( A \) is the effective area of the membrane (m²). \( R \) is the rejection of the solute (%), \( C_P \) and \( C_F \) are the concentration of permeate and feed solution, respectively (wt%).

**Dyeing wastewater treatment**

A laboratory-made crossflow filtration unit was used in our experiments, as shown in Figure 1(b). The membrane module was coupled to a dyeing process wastewater tank via a pump-driven recycling loop. Ten hollow fibers with an effective length of 10 cm were installed into a module. The effective surface area and the packing density of the membrane module were 100.5 cm² and 854.2 m²/m³, respectively.

\( \text{COD}_{Cr} \) was measured by a Quick COD\textsubscript{Cr} Microwave-sealed Digestion Measuring Apparatus (DR/2500, Hach Co., USA). Color was measured by a spectrophotometer (UVmini-1240, Shimadzu, Japan) at a wavelength of 620 nm. A turbimeter (SGZ-2A, Shanghai Yuefeng Instruments & Meters Co Ltd., China) was used for the measurement of the turbidity.

**RESULTS AND DISCUSSION**

**Compatibility of PVDF/PMMA/TPU**

To investigate the compatibility of PVDF, PMMA and TPU, FTIR-ATR spectra are depicted in Figure 2. By comparison of the spectra of pure PVDF, PMMA and TPU, the strong absorption peak of PVDF at 1,182 cm\(^{-1}\) assigned to CF\(_2\) shifted to 1,179 cm\(^{-1}\), the peak of PMMA at 1,727 cm\(^{-1}\) assigned to –C=O shifted to 1,730 cm\(^{-1}\), and the peak of TPU at 1,530 cm\(^{-1}\) assigned to urethano group shifted to...
1,535 cm$^{-1}$ in the spectra of PVDF8/PMMA1/TPU1. This proved the existence of dipole interaction in the polymer molecules because of the strong polarity by the fluorides in PVDF (Canavate et al. 2000). With the concentration of PVDF decreased and that of PMMA, TPU increased, the strong absorption peaks of blend membranes shifted toward those of pure materials. Especially in the mixing ratio of 3/3.5/3.5, these three polymers showed their respective characteristics, but not the copolymer. The results indicated good compatibility when the mixing ratio of PVDF, PMMA, TPU was 8/1/1.

Membrane characterization

Mechanical properties

Due to breakage of the membranes under the high pressure process, the effect of filtration and membrane life are seriously affected. Tensile strength and elongation at break are the important mechanical properties of the fiber membrane in wastewater treatment. The mechanical strengths of the prepared fiber membranes are listed in Table 1. It is clear that the elongation at break increases with the increase of TPU concentration. Especially, in the case of the membrane containing 20 wt% TPU (M1), the elongation at break value is about five times more than that of the membrane without TPU (M8). These values illustrate that adding TPU to the dope solution can improve the membrane’s mechanical properties substantially (Zhou & Xi 2008). However, membrane elongation decreased by adding PMMA. In the case of M7 which contained 80 wt% PVDF and 20 wt% PMMA without TPU, the elongation value at break is the lowest.

The SEM micrographs reveal distinctly different morphological patterns for each of the membranes. The cross-sections of the membranes are shown in the SEM-micrographs of Figure 3. All the cross-sections of the prepared membranes are asymmetric and porous. General structures of membranes are very similar, consisting of macrovoids and sponge-structures. Because the compatibility of the PVDF-rich phase and TPU-poor phase is good (Zhou & Xi 2008), the TPU particle distribution pattern inside the membranes matrix was investigated to increase the elongation of the membrane (Figure 5(a)). With the increase of PMMA concentration, a porous structure started to form (Figure 5(b)). When the concentration of PMMA was higher than that of TPU, TPU particles became invisible, the sponge-like structure appeared in the cross-section. Figure 3(d) shows that PVDF blends well with PMMA (Ma et al. 2007).

On the other hand, PMMA and TPU addition change the dope solution viscosity obviously (as seen in Table 1). As the concentration of PMMA in the blends was increased, the viscosity of dope solution decreased, because increasing the PMMA content reduced the PVDF crystallization, this effect might be related to the variation in viscosity (Yoshida 1997; Gregorion & Chaves Pereira de Souza Nociti 1995). The decrease in the dope viscosity due to the addition of PMMA and the reduction of TPU enhanced the exchange rate of solvent (DMAc)/nonsolvent (water) and resulted in a further demixing process, with macrovoids formation (Yang & Wang 2006).

Separating properties

The water permeation flux (Jw) and rejection (R) of the prepared hollow fiber membranes are summarized in Table 1. The pure PVDF membrane (M8) exhibits the lowest Jw value as compared with the blend membrane, indicating that the addition of PMMA and TPU improve membrane performance.

<table>
<thead>
<tr>
<th>PVDF/PMMA/TPU (Membrane No.)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Jw (L/(m² h))</th>
<th>R (%)</th>
<th>Viscosity of dope solutions (mPa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/0/20(M1)</td>
<td>9.2</td>
<td>146</td>
<td>120.4</td>
<td>66.3</td>
<td>39,626</td>
</tr>
<tr>
<td>80/1/19(M2)</td>
<td>9.5</td>
<td>103</td>
<td>162.5</td>
<td>50.3</td>
<td>37,300</td>
</tr>
<tr>
<td>80/2/18(M3)</td>
<td>8.3</td>
<td>78</td>
<td>169.3</td>
<td>33.5</td>
<td>27,583</td>
</tr>
<tr>
<td>80/5/15(M4)</td>
<td>7.8</td>
<td>48</td>
<td>184.9</td>
<td>21.1</td>
<td>23,200</td>
</tr>
<tr>
<td>80/10/10(M5)</td>
<td>9.5</td>
<td>45</td>
<td>195.7</td>
<td>17.9</td>
<td>16,375</td>
</tr>
<tr>
<td>80/15/5(M6)</td>
<td>9.5</td>
<td>42</td>
<td>181.0</td>
<td>59.8</td>
<td>9,787</td>
</tr>
<tr>
<td>80/20/0(M7)</td>
<td>9.2</td>
<td>24</td>
<td>177.8</td>
<td>79.8</td>
<td>7,760</td>
</tr>
<tr>
<td>100/0/0(M8)</td>
<td>9.2</td>
<td>30</td>
<td>98.6</td>
<td>40.7</td>
<td>11,542</td>
</tr>
</tbody>
</table>
permeability properties. Generally, the water permeation flux is related to the porosity, interconnection of cavity, surface pore size and hydrophilic properties of the membrane. The addition of PMMA increased the hydrophilic property of the blend membranes. It resulted in an increase of $J_w$. However, as the concentration of PMMA was higher (M6 and M7), the amount of macrovoids increased, as was confirmed in Figure 3(c) and (d), which resulted in the decrease of $J_w$.

In order to evaluate the separation performance of PVDF/PMMA/TPU blend hollow fiber UF membranes, BSA was chosen as solute. The rejections are also shown in Table 1. As can be seen, the rejections were significantly affected by the different concentrations of PMMA and TPU.
Membrane application

The FTIR-ATR, SEM, pure water permeation flux and rejection of protein results revealed PVDF/PMMA/TPU blend hollow fiber membranes were suitable for wastewater filtration. To determine their filtration efficacy, dyeing wastewater from an AAO system effluent was used. The blend hollow fiber membranes of M2 were chosen to make the membrane module.

The filtering results run at 0.1 MPa in 8 h without backwash are shown in Figure 4. As seen in Figure 4, the flux was about 65 L m\(^{-2}\) h\(^{-1}\) at the beginning of the operation. Due to cake layer formation and fouling phenomena, the flux was reduced to about 30% of initial flux after 2 h filtration. With the flux decline, the transport of material to the membranes decreased and the effect of the crossflow velocity become more effective. Therefore the flux didn’t change obviously within the remaining 6 h (Ravazzini et al. 2005).

The COD\(_{\text{Cr}}\) values were reduced from 65–115 to 25–40 mg/L, corresponding to removal efficiencies between 46 and 77% (Figure 4). The color and turbidity removals were 46–75%, 63–93%, respectively. It can be seen that the ultrafiltration membrane was an efficient filtration material for particles, while being permeable for dissolved compounds. Therefore, the removal of turbidity was the highest. COD\(_{\text{Cr}}\) and color were associated with the removed particles. The removing behaviors of the studied pollution indices during the test period were quite similar, which were that they all increased at first for several hours and then became stable. This observation indicated that cake layer formation played an important role in filtration.

CONCLUSIONS

PVDF/PMMA/TPU blend hollow fiber membranes were prepared by a wet-spinning method and applied to dyeing wastewater filtration. The compatibility in the PVDF-rich phase was better than in the TPU-rich phase and the PMMA-rich phase. When the concentration of PVDF was 80 wt%, the compatibility of PVDF, PMMA and TPU was good. Blend membrane characteristics were varied with different concentrations of TPU and PMMA in the dope solution, with the elongation at break and water permeation flux increased to 146% and 195.7 L/(m\(^2\)h), respectively. The prepared membranes containing PVDF80/PMMA1/TPU19 with desired separation properties were proved by dyeing wastewater filtration. The flux was stable at about 20 L/(m\(^2\)h) at 0.1 MPa in 8 h. The removals of COD\(_{\text{Cr}}\), turbidity and color were about 63, 84 and 63%, respectively. The membrane showed good separation properties in advanced wastewater treatment.

ACKNOWLEDGEMENTS

This work was supported by the special S&T project on treatment and control of water pollution (No. 2009ZX07529-003) and the National Science and Technology Ministry (No. 2009BAC65B07) and the National Science Foundation of Shanghai (No. 11ZR1400800). China Postdoctoral Science Foundation (No. 20110490645).

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First received 12 May 2011; accepted in revised form 25 October 2011