Facile fabrication of polyelectrolyte complex / carbon nanotube nanocomposites with improved mechanical properties and ultra-high separation performance

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1. Effect of [HCl] on ionic complexation between CMCNa and PDDA.
2. FT-IR and $\zeta$ potential of MWCNT-COOH.
3. Dispersion of MWCNTs in the PEC/MWCNTs blending membrane and its mechanical property.
4. Comparison of pervaporation performance of PEC/MWCNTs nanocomposite membranes with other membranes.

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1. Effect of [HCl] on ionic complexation between CMCNa and PDDA.

Fig. 1 shows the light transmittance of CMCNa solutions (200 mL) with increasing PDDA dosage at different [HCl]. It is found that the light transmittance decreases with increasing PDDA dosage at each [HCl], especially for lower [HCl]. No turbidity happened in CMCNa when [HCl] is 0.015 M and PEC do not well precipitate out when [HCl] is 0.01 M. Moreover, when [HCl] is lower than 0.0025 M, the obtained PECs precipitate can hardly be dissolved in NaOH because less COOH groups are protonated. Thus, 0.004 M HCl was chosen to prepare CMCNa-PDDA PEC/MWCNT nanocomposites.

Fig. 1 Light transmittance of CMCNa solution (200 mL) added with different amount of PDDA solution at different [HCl]. The monomer mole concentration of both parent solutions of CMCNa and PDDA are 0.005 M

2. FT-IR and $\zeta$ potential of MWCNT-COOH.

FT-IR spectra of MWCNT-COOH and pristine MWCNT are given in Fig. 2(a). Compared with the pristine MWCNT, two new absorption bands at 1710 cm$^{-1}$ (-COOH group) and 1630 cm$^{-1}$ (-COONa group) rise for MWCNT-COOH sample. The presence of COONa is because partial ionization of COOH groups during the washing of MWCNT-COOH by de-ionized water. $\zeta$ potential of MWCNT-COOH aqueous dispersion is -5.1 mv (Fig. 2(b)) and this value is in accordance with FT-IR structure of MWCNT-COOH.
Fig. 2 (a) FT-IR of MWCNT-COOH and pristine MWCNT, (b) \( \zeta \) potential of MWCNT-COOH aqueous dispersion (0.016 wt%). MWCNT-COOH aqueous dispersion was filtered with a 5 \( \mu \)m microfiltration membrane before \( \zeta \) potential measurements.

3. Dispersion of MWCNTs in the PEC/MWCNTs blending membrane and its mechanical property.

Fig. 3 shows the dispersion of MWCNTs in the PEC/MWCNTs blend film. It can be seen from Fig. 3 that MWCNTs agglomerated in the PEC matrix. Moreover, cross-sectional examination (Fig. 3b) shows that MWCNTs are dispersed between PEC aggregates but not encapsulated in them.
Fig. 3 Dispersion of MWCNTs in the MWCNT/PEC blend film containing 5 wt% MWCNTs (a) surface, (b) cross-section.

Fig. 4 shows that the mechanical strength of the MWCNTs/PEC blend film is very poor and not improved as compared with pristine PEC film. This is due to the agglomeration of MWCNTs in the blend film.
Fig. 4 Stress–strain curve of PEC/MWCNT blend film (5 wt% MWCNTs) and pristine PEC film.

4. Comparison of pervaporation performance of PEC/MWCNTs nanocomposite membranes with other membranes.

Table 1 shows that the pervaporation performance of PEC/MWCNTs in dehydrating 10 wt% water-isopropanol. As compared with other recent reported membranes, it is seen that the pervaporation performance of PEC/MWCNT9505 nanocomposite membrane is superior, especially in flux.

Table 1. A comparison of pervaporation performance of PEC/MWCNT9505 nanocomposite membrane with other membranes in dehydrating water-isopropanol. J is permeation flux and $\alpha$ is separation factor.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Temp</th>
<th>Feed water</th>
<th>J (kg/m$^2$h)</th>
<th>$\alpha$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEC/MWCNT9505</td>
<td>70 °C</td>
<td>10 wt%</td>
<td>2.35</td>
<td>2562</td>
<td>This work</td>
</tr>
<tr>
<td>PERVAP 2510$^a$</td>
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<td>10 wt%</td>
<td>0.75</td>
<td>810</td>
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<td>PEC/MWCNT9505</td>
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<td>10 wt%</td>
<td>0.63</td>
<td>1991</td>
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</tr>
<tr>
<td>5 wt% APTEOS$^b$/PVA$^c$</td>
<td>30 °C</td>
<td>10 wt%</td>
<td>0.026</td>
<td>1580</td>
<td>2</td>
</tr>
<tr>
<td>5 wt% Na$^+$ MMAT$^d$-10/PVA</td>
<td>30 °C</td>
<td>10 wt%</td>
<td>0.051</td>
<td>1116</td>
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</tr>
<tr>
<td>10 wt% silicalite-1 / PVA</td>
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<td>10 wt%</td>
<td>0.069</td>
<td>2241</td>
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<tr>
<td>5 wt% NaY zeolite/SA$^e$</td>
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<td>10 wt%</td>
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<td>5</td>
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<tr>
<td>10 wt% NaY zeolite/CS$^f$</td>
<td>30 °C</td>
<td>10 wt%</td>
<td>0.062</td>
<td>254</td>
<td>6</td>
</tr>
</tbody>
</table>

$^a$ PERVAP 2510: Commercial membrane from Sulzer Chemtech, Germany.
$^b$ APEOS: $\gamma$-aminopropyl-triethoxysilane.
$^c$ Poly(vinyl alcohol)
$^d$ Sodium montmorillonite.
$^e$ Sodium alginate
$^f$ Chitosan
Ref for Table 1: