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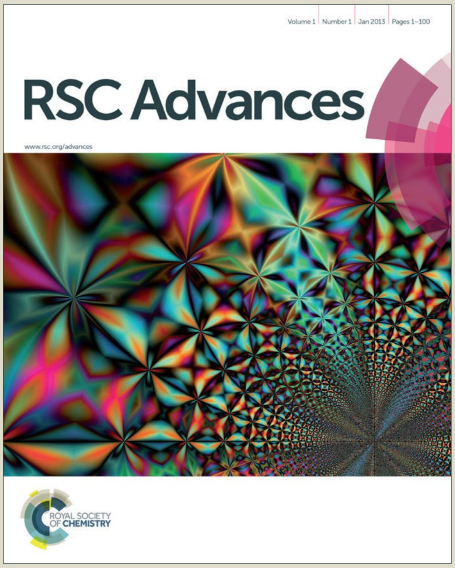

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TEA incorporated CS blend composite membrane for high CO_2 separation performance

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Triethanolamine (TEA) was incorporated into chitosan (CS) matrix to prepare a new blend composite membrane on polypropylene (PP) microporous substrate. Significant enhancements in mechanical properties, CO_2 permeation rate and CO_2/N_2 selectivity of thus obtained blend membrane were demonstrated compared with those of pristine CS membrane.

Global warming has become a more and more serious issue during last several decades because of its potential threats to economy and environment. Therefore, the emissions of carbon dioxide (CO_2), which is considered as one of the major contributors to the greenhouse effect, has attracted increasing attention.[1-5] To date, several techniques have been reported for CO_2 separation. Membrane processes in comparison with other methods have unique advantages such as less energy consumption, lower capital cost and ease of operation.[6-8] Among various kinds of membranes, facilitated transport membrane (FTM) is regarded as an approach to achieve both high permeability and selectivity.[9-12] The permeation of CO_2 through FTM follows facilitated transport mechanism with the help of carriers, which can react with CO_2 reversibly. These carriers are divided into fixed-site carriers (FSC) and mobile carriers. FSC membrane[13-17] has been paid more attention because the carriers are covalently bonded to the polymer matrix, which makes FTM no longer be restricted by instability problem.[18]

Chitosan (CS), as an abundant natural polymer produced by the deacetylation of chitin, is a promising FSC membrane material for high CO_2 separation performance due to its unique molecule structure.[19] In the repeating unit of CS, there are one amine group and two hydroxyl groups. The amine group can act as a carrier and the hydroxyl groups can help stabilize reaction products by forming intramolecular hydrogen bonds.[20] Bae SY et al.[21] firstly measured the steady-state permeation rates for CO_2 and N_2 in CS membranes. Their findings of the dual-mode sorption model of CO_2 could be interpreted by the interaction of sorbed CO_2 with the CS matrix, which was expressed as a reversible reaction. Feng et al.[22] used trimesoyl chloride crosslinked chitosan membranes for CO_2/N_2 separation. They observed that the membranes with higher degrees of crosslinking undergo more swelling. El-Azzami et al.[23] used arginine salt-chitosan membranes for the separation of CO_2 from H_2/N_2, and found that the presence of arginine salts in swollen chitosan membranes enhances the CO_2 permeability because the arginine salts increase the number of amine groups as well as the water levels in the membranes. Shen et al.[24] developed miscible carboxymethyl chitosan/polyethyleneimine blend membranes for CO_2/N_2 separation. It was observed that water vapour enhances the membrane performance.

However, most of these CS-related membranes were tested under swelling condition to enhance facilitated transportation, which leads to the decline of their mechanical properties. In this work, we prepared a novel FTM by incorporating triethanolamine (TEA), with both hydroxyl groups and amine groups, into CS matrix. Hydroxyl groups can benefit the mechanical properties by forming hydrogen bond interactions with corresponding groups in CS matrix. Moreover, amine groups can facilitate CO_2 transportation as mobile carriers, because though there may be hydrogen bonds between TEA and CS, such interactions are not strong enough to reduce the mobility of liquid TEA in the blend membrane. These two advantages make TEA a competitive additive to improve CO_2/N_2 separation performance and mechanical properties simultaneously. CO_2 permeation rate, CO_2/N_2 selectivity and mechanical performance of this membrane were studied.

Chitosan (deacetylation degree 91 %, molecule weight 20000Da) was purchased from Qingdao Haihui Bio-engineering Co., Ltd; triethanolamine and acetic acid (analytical pure) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd; polypropylene (PP) microporous membrane (thickness 40±2

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μm, porosity 73±5%) was purchased from Institute of Chemistry, Chinese Academy of Sciences; polyvinyl alcohol (average polymerization degree 1750±50) was purchased from Tianjin Damao Chemical Reagent Factory; gases for test (CO_2, N_2), purity 99.5 %, were purchased from Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Membrane solution was prepared by dissolving CS and TEA in 1 vol.% acetic acid aqueous solution and the total mass concentration was set as 1 wt.%. TEA content was defined as its mass fraction in both CS and TEA. PP microporous membrane was soaked in 0.5 wt.% polyvinyl alcohol (PVA) aqueous solution for 24 h and then washed by deionized water before use.

Composite membrane was prepared by coating the membrane solution homogeneously on hydrophilized PP microporous membrane with the help of coating wheel. And then, the membrane was put in constant temperature and humidity chamber (30 °C, 20 % RH) for 24 h to evaporate the solvent. Dense CS membrane for characterizations was prepared by pouring the membrane solution on glass plate directly. Drying method was the same as that of composite membrane.

Scanning electron microscopy (SEM, Hitachi-S-4800), Fourier transform infrared spectrometer (FTIR, Nexus) and X-ray diffractometer (XRD, Rigaku D/MAX-4200) were used to characterize the morphology, chemical and crystalline structure of the membrane. Microcomputer control electronic universal testing machine (CMT8502) was used to test the mechanical properties of the membranes.

Constant-pressure gas permeation device was used to test CO_2/N_2 separation performance of the membrane. Gas separation performance was studied via pure gas tests which were operated under room temperature. Gases were humidified via a humidifying can before entering the membrane module. Gas permeation rate and separation factor of the membrane were calculated by following equations:

$$J_i = \frac{Q_i}{\Delta p \cdot A} \quad (i = CO_2,\ N_2) \tag{1}$$

$$\alpha_{jk} = \frac{J_j}{J_k} \quad (j = CO_2;\ k = N_2) \tag{2}$$

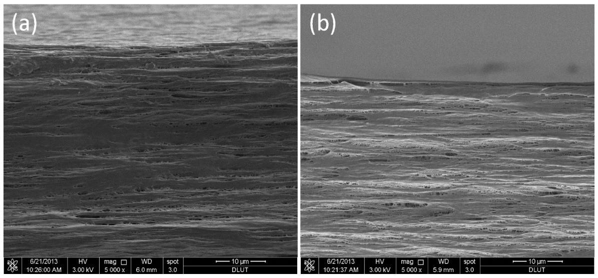

Fig. 2. SEM images of cross sectional morphologies for (a) PP supporting membrane; (b) TEA-CS/PP blend composite membrane (15 wt.%)

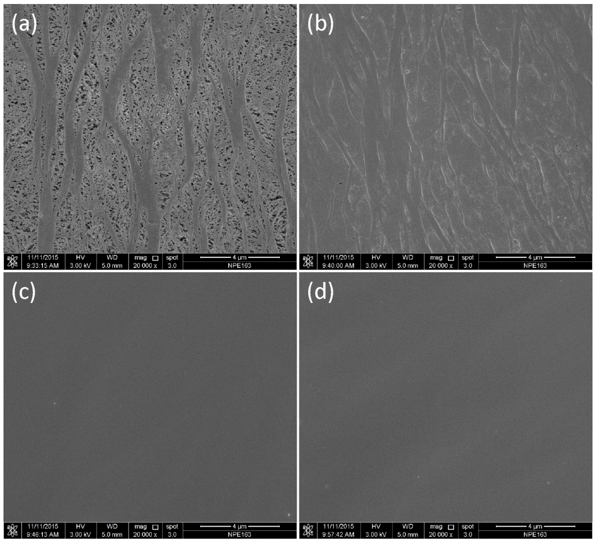

Fig. 1. SEM images of surface morphologies for (a) PP supporting membrane; (b) hydrophilized PP supporting membrane; (c) CS/PP blend composite membrane (d) TEA-CS/PP blend composite membrane (15 wt.%)

In above equations: J is gas permeation rate, GPU; α is separation factor; Q is gas flow rate; Δp is transmembrane pressure; A is effective membrane area, 9.61 cm^2.

SEM images of surface morphologies for supporting membranes and composite membranes are shown in Fig. 1. It can be seen that the surface of PP supporting membrane is porous, but most of the holes are occupied by PVA after hydrophilization process. The new surface increases its affinity with membrane solution. After coated by CS or TEA-CS, both of the surfaces become dense and flat without any defect, which explicates the great compatibility between CS and TEA. From the SEM images of cross sectional morphologies for PP supporting membrane and TEA-CS/PP blend composite membrane in Fig. 2, it is obvious that the composite layer and supporting layer bond tightly, verifying that TEA-CS layer has a great affinity with hydrophilized PP supporting membrane.

FTIR spectra of TEA-CS blend membranes are shown in Fig. 3(a). The peak corresponding to typical hydrogen bond interactions at 3100-3500 cm^{-1} becomes stronger and broader introduces more hydroxyl groups, which strengthen hydrogen bond interactions. Peaks at 1641 cm^{-1} and 1552 cm^{-1} are assigned to stretching vibration of C=O and bending vibration of N-H in CS molecule. With the increase of TEA content, the peak at 1552 cm^{-1} in TEA-CS blend membrane shifts to low-frequency region firstly and ends at 1530 cm^{-1}, indicating that new hydrogen bonds are formed between hydroxyl groups in TEA and CS. When TEA content reaches 30 wt.%, this peak shifts to high-frequency region contrarily, probably due to the occurrence of microscopic phase separation, which is demonstrated in the XRD patterns of TEA-CS blend membranes, as shown in Fig. 3(b).

XRD patterns of TEA-CS blend membranes are shown in Fig. 3(b) and three characteristic XRD diffraction peaks of pristine CS membrane can be seen at 2θ=10°, 13.5° and 21.3°, revealing the crystal form of CS.[25, 26] With the increase of TEA

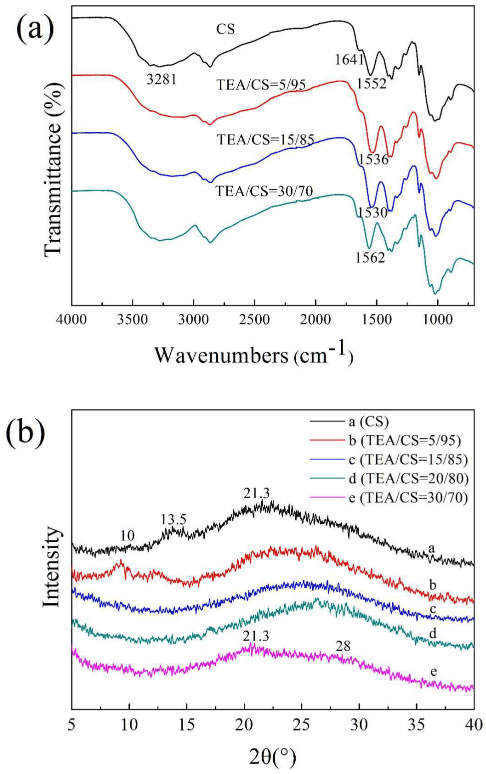

Fig. 3. (a) FTIR spectra of TEA-CS blend membranes; (b) XRD patterns of TEA-CS blend membranes

content, peaks at 2θ=10° and 13.5° disappear gradually, and the peak at 2θ=21.3° becomes broader and shifts to the wide-angle region. This is because the original hydrogen bonds are associated with the newly formed hydrogen bonds. Such associations can increase the regularity of CS molecular chains and the compactness of the molecular structure. According to Bragg Equation, more compact structure leads to the increase of diffraction angle. When TEA content reaches 30 wt.%, apart from the peak at 2θ=28°, which follows the above tendency, the peak at 2θ=21.3° which is assigned to pristine CS appears again. This indicates that when TEA content is too high, microscopic phase separation occurs owing to the aggregation of TEA. The cross-sectional morphologies of the corresponding TEA-CS dense blend membranes were also characterized and shown in Fig. S2. It can be seen from Fig. S2 that the homogeneity of CS matrix is obviously affected with the increase of TEA content, especially when TEA content is more than 20 wt.%, which could also verify the microscopic phase separation and the aggregation of TEA.

The mechanical properties of TEA-CS blend membranes are shown in Fig. 4. With the increase of TEA content, elongation at break of membrane increases significantly, which demonstrates the great enhancement of toughness of the membrane. This behavior is attributed largely to stronger hydrogen bond interactions formed after introducing more hydroxyl groups, and this has been verified by the FTIR spectra. When TEA content is 15 wt.%, the elongation at break and tensile strength increase from 15.05 to 52.50 % and 33.17 to 37.80 MPa, respectively. When TEA content is 30 wt.%, though tensile strength has a slight decrease, the elongation at break of the membrane reaches 87.45 %, which increases by more than 4 times than that of pristine CS membrane.

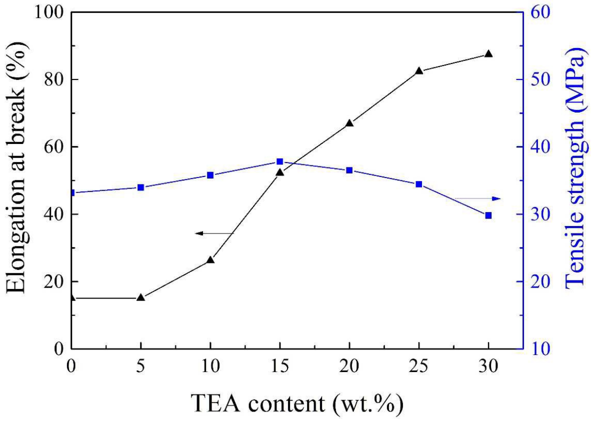

Fig. 4. Mechanical properties of TEA-CS blend membranes

The effect of TEA content on CO_2/N_2 separation performance of TEA-CS/PP blend composite membrane under 0.3 MPa is shown in Fig. 5(a). When TEA content increases from 0 wt.% to 15 wt.%, CO_2 permeation rate increases from

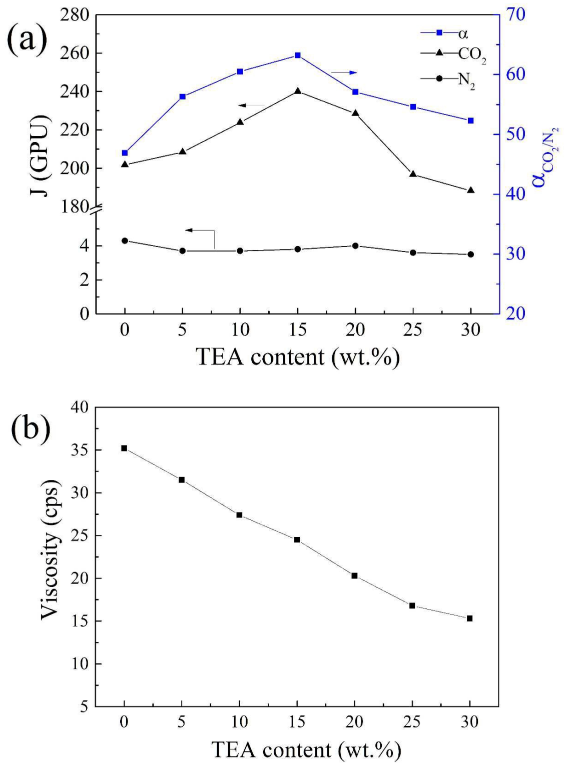

Fig. 5. (a) Effect of TEA content on CO_2/N_2 separation performance of TEA-CS/PP blend composite membrane; (b) Effect of TEA content on viscosity of membrane solution

201.8 GPU to 240 GPU, and CO_2/N_2 selectivity increases from 46.9 to 63.4, both of which reach the maximums. The increase of CO_2 permeation rate is because adding TEA increases the carrier content in the membrane, which can enhance the facilitated transportation of CO_2. Furthermore, compared with pristine CS, the solubility of CO_2 also increases with the help of liquid TEA. When TEA content increases from 15 wt.% to 30 wt.%, CO_2 permeation rate and CO_2/N_2 selectivity both decrease. This is mainly attributed to the microscopic phase separation in membrane matrix, which is verified in XRD analysis. TEA tends to aggregate in CS matrix with the increase of TEA content. So though the total number of carriers increases, the amount of effective carriers decreases contrarily. Moreover, the increase of TEA content decreases the viscosity of coating solution, as shown in Fig. 5(b). When TEA content is higher, more membrane solution intends to infiltrate into the cores of PP supporting layer during the preparation of membrane. This leads to thicker selective layer and higher mass transfer resistance of CO_2, which reduces CO_2 permeation rate. Among all the factors above, the permeation of N_2 is mainly affected by the thicker selective layer, so N_2 permeation rate has a slight decrease during the increase of TEA content. The long-term performance of the TEA-CS blend membranes were also investigated and shown in Fig. S3. It can be seen that CO_2 separation performance of the TEA-CS blend membrane has no significant change during the test, which verifies its good stability.

Conclusions

In this study, TEA was introduced into CS membrane for the first time. Compared with pristine CS membrane, CO_2/N_2 separation performance of blend composite membrane is enhanced by adding a certain amount of TEA. When TEA content is 15 wt.%, the blend composite membrane has excellent CO_2/N_2 separation performance with CO_2 permeation rate of 240 GPU and CO_2/N_2 selectivity of 63.4 (0.3 MPa), owing to the enhanced facilitated transportation and solubility of CO_2. In addition, TEA can improve the mechanical properties of CS membrane, especially the elongation at break, by forming new hydrogen bond interactions.

Acknowledgements

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A novel triethanolamine-chitosan blend membrane exhibits better CO_2/N_2 separation performance and mechanical properties than pristine chitosan membrane.