Carbohydrate Polymers 106 (2014) 403–409

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Preparation and properties of PEC nanocomposite membranes with carboxymethyl cellulose and modified silica

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ARTICLE INFO

Article history:
Received 19 August 2013
Received in revised form 10 January 2014
Accepted 12 January 2014
Available online 21 January 2014

Keywords:
Polyelectrolyte complex
Silica nanoparticles
Carboxymethyl cellulose
Nanocomposite membranes

ABSTRACT

Carboxymethyl cellulose (CMC)-modified silica nanocomposites were prepared via in situ incorporation of modified silica during the ionic complexation between CMC and poly(2-methacryloyloxy ethyl trimethylammonium chloride) (PDMC). Ionic bonds were introduced between the poly(2-acrylamido-2-methylproanesulfonic acid) modified silica (SiO_2-PAMPS) and the polyelectrolyte complex (PEC) matrix. The PEC nanocomposites (PECNs) and their membranes (PECNMs) were characterized with Fourier transform-infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and tensile testing. PECNM containing 5 wt.% SiO_2-PAMPS showed a tensile strength of 68 MPa and elongation at break of 7.1%, which were 1.9 and 2.6 times as high as those of pristine PEC membranes, respectively. Moreover, the pervaporation performance of as-prepared PECNMs was evaluated with dehydration of 10 wt.% aqueous isopropanol mixtures, and the PECNMs exhibited a flux of 2400 g m^{-2} h^{-1} with a high separation factor of 4491 at 70 °C.

1. Introduction

Carboxymethyl cellulose (CMC) is an important polysaccharide with a wide range of applications in flocculation, paper, foods, and drugs (Biswal & Singh, 2004; Rokhade et al., 2006). Sodium carboxymethyl groups (CH_2COONa) of the cellulose molecule impart the desired characteristic of water solubility. CMC is an ideal alternative material for the preparation of polyelectrolyte complexes (PECs) owing to its cheap price, stable structure and charged feature. PECs are formed by mixing oppositely charged polyelectrolytes via electrostatic force (Gucht, Spruijt, Lemmers, & Cohen Stuart, 2011; Thünemann, Müller, Dautzenberg, Joanny, & Löwen, 2004). Since the 1940s, PECs have attracted tremendous attention for their wide range of applications in drug delivery, biomaterials, flocculation, papermaking processes and membrane materials (Hartig, Greene, Dikov, Prokop, & Davidson, 2007; Juntapram, Praphairaksit, Siraleartmukul, & Muangsin, 2012; Nam & Lee, 1997; Petzold, Mende, Lunkwitz, Schwarz, & Buchhammer, 2003; Wu et al., 2011). Recently, CMC has been used to prepare various PECs that have been used in papermaking, wound dressings and separation membranes (Dhar, Akhlaghi, & Tam, 2012; Hebeish, Higazy, El-Shafei, & Sharaf, 2010; Rosca, Popa, Lisa, & Chitanu, 2005).

PECs are promising candidates for pervaporation dehydration of alcohol due to their high hydrophilicity and ionic cross-linked structure. A facile "protection–deprotection" method for achieving solution processable PECs has been reported that utilized CMC as polyanion and other polysaccharides as polycation, such as chitosan and cationic cellulose (Zhao, An, Ji, Qian, & Gao, 2011). The resultant CMC-based membranes derived from PECs for pervaporation dehydration of aqueous alcohol have demonstrated excellent performance, viz., high permeate flux and high separation selectivity (Jin, An, Zhao, Qian, & Zhu, 2010; Liu et al., 2013; Zhao, Qian, An, Yang, & Gui, 2009).

However, the mechanical property of the PEC membrane is the key factor for long time operation in industrial applications. This means that a key challenge for PEC membranes is to improve their mechanical property. The mechanical property of PEC membranes was enhanced by the incorporation of unmodified SiO_2 nanoparticles in our previous work (Zhao, Qian, Zhu, An, et al., 2009). It is noteworthy that the mechanical property of the hybrid material is intensively affected by the dispersion of inorganic nanoparticles and interfacial interaction between the polymer matrix and nanoparticles (Fu, Feng, Lauke, & Mai, 2008; Rong, Zhang, & Ruan, 2006). However, in the above-mentioned work, the enhancement efficiency of the mechanical property was inhibited by the aggregation of unmodified nanoparticles and poor interfacial adhesion between the organic and inorganic phases. A method of surface modification by polyelectrolyte is proposed to settle this issue.

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0144-8617/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2014.01.040

On the one hand, nanoparticles modified by polyelectrolyte can be dispersed homogenously due to good hydrophilicity. While, on the other hand, the ionic groups of nanoparticles could take part in complexation with the oppositely charged polyelectrolytes of the PEC matrix, which leads to robust interfacial adhesion at the interface.

In this work, CMC-modified silica nanocomposites composed of CMC and poly (2-methacryloyloxy ethyl trimethylammonium chloride) (PDMC) incorporating the SiO_2-PAMPS nanoparticles was prepared. The polyelectrolyte for modification of SiO_2 was poly (2-acrylamido-2-methylproanesulfonic acid) (PAMPS). Strong ionic interactions were achieved between the sulfonic groups derived from the SiO_2-PAMPS nanoparticles and the quaternary ammonium groups of PDMC. The PEC nanocomposites (PECNs) and their membranes (PECNMs) were characterized with Fourier transform-infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and tensile tests. Covalently modified SiO_2-PAMPS nanoparticles showed reduced aggregations and improved interfacial interactions with the PEC matrix through electrostatic interaction. The aim of this work was to optimize the performance of PECNMs in the mechanical testing and separation process. The pervaporation dehydration performance of PECNMs in dehydrating 10 wt.% water/isopropanol was investigated.

2. Experiment

2.1. Materials

CMC, with an intrinsic viscosity of 625.1 mL g^{-1} in 0.1 M aqueous sodium hydroxide (NaOH) at 30 °C, was obtained from Sinapharm Chemical Reagent Co., Ltd., Shanghai, China. PDMC (M_w = 30 0000 g mol^{-1}) was purchased from Henyi Chemical Plant. Tetraethoxysilane (TEOS) and vinyltriethoxysilane (VTEOS) were obtained from Nanjing Capatue Chemical Co., Ltd., Nanjing, China. 2-Acrylamido-2-methylproanesulfonic acid (AMPS) was supplied by Shouguang Runde Chemical Co., Ltd., Shandong, China. Potassium persulfate ($K_2S_2O_8$) and sodium bisulfite ($NaHSO_3$) were purified by recrystallization before use. All the chemical reagents, including, ethanol, isopropanol, sodium hydroxide and hydrochloric acid (HCl), were analytical reagent grade. Polysulfone ultrafiltration (PSF-UF)-supporting membranes (MWCO = 35,000 Da) were provided by the Development Center of Water Treatment Technology, Hangzhou, China. The water used in all experiments was deionized water that had a resistivity of 18 MΩ·cm.

2.2. Synthesis of SiO_2-PAMPS and preparation of PECNs

The synthesis route of the SiO_2-PAMPS nanoparticles was according to our previous report (Zhang et al., 2012). The schematic diagram is shown in Fig. 1. In detail, TEOS (20.8 g), VTEOS (19 g), deionized water (5.4 g), ethanol (40 ml) and HCl (37%, 0.15 ml) were added into a 250 ml three-neck flask and stirred at 50 °C for 4 h. AMPS monomer (20.7 g) and $K_2S_2O_8$/$NaHSO_3$ (1:1, 40 mg), as redox initiators, were added. The reaction was continuous for 4 h to obtain the resultant nanoparticles. Deionized water was poured into the flask and stirred for 1 h. Then the precipitates were obtained by centrifugation at 3000 rpm. To prepare the unmodified SiO_2 nanoparticles, the same method was used only without the presence of the AMPS monomer.

The PECNs were fabricated by the protection–deprotection method as reported previously (Zhao et al., 2011). Firstly, a 0.4×10^3 g L^{-1} dispersion solution of SiO_2-PAMPS was obtained by ultrasonication treatment (40 kHz, 100 W) for 30 min. Subsequently, a certain dosage of SiO_2-PAMPS was mixed with 0.01 M PDMC solution (0.1 L). The total polycation solution (PDMC@SiO_2-PAMPS) was added dropwise into a 0.01 M CMC solution (0.2 L). Both the PDMC@SiO_2-PAMPS and CMC solution contained the same concentration of HCl (0.007 M). Finally, the precipitates were collected after phase separation when the endpoint of complexation was reached. The weight content of SiO_2-PAMPS in the nanocomposite was calculated from the dosage of the SiO_2-PAMPS dispersion solution on the assumption that the nanoparticles in the polycation solution were entirely incorporated into the PEC. The corresponding equation is as follows:

$$W(\mathrm{SiO_2\text{-}PAMPS}) = \frac{C_{\mathrm{SiO_2\text{-}PAMPS}} \times V_{\mathrm{SiO_2\text{-}PAMPS}}}{M_{\mathrm{PEC}}} \times 100\% \quad (1)$$

where $C_{SiO_2\text{-}PAMPS}$ (g L^{-1}) is the concentration of the as-prepared SiO_2-PAMPS dispersion solution, $V_{SiO_2\text{-}PAMPS}$ (L) is the volume of the SiO_2-PAMPS dispersion solution added into the PDMC solution and M_{PEC} (g) is the dried weight of pristine PEC without SiO_2-PAMPS. A series of PECNs were prepared with different $V_{SiO_2\text{-}PAMPS}$ contents. In addition, to enable a comparison, unmodified SiO_2 nanoparticles were added to the PEC matrix.

2.3. Mechanical property of PECNMs

PECNMs were prepared as follows: PECN was dissolved in 0.1 M NaOH to obtain a 2 wt.% homogenous dispersion solution with a pH at ca. 8. The PECN solution was then cast onto a clean glass slide and dried at 40 °C for 12 h. The free-standing membranes were directly cut into 10 mm × 60 mm strips. The thickness of PECNMs for testing was maintained at 20 ± 2 μm. The mechanical property of the PECNMs was examined on a universal testing machine (SANS, CTM4204, Shenzhen, China) under a crosshead speed of 2 mm min^{-1}. Each value was obtained from an average of five measurements. The humidity of the environment for the tensile tests was maintained at 40 ± 5%.

Five PECNMs specimens were prepared with the designation PECNM-X, where X represents the weight percentage of SiO_2-PAMPS nanoparticles. That is, PECNM-0 stands for pristine PEC membrane and PECNM-1 represents PECNM containing 1 wt.% SiO_2-PAMPS nanoparticles.

2.4. Pervaporation performance of PECNMs

A 2 wt.% homogenous dispersion solution of PECN was cast onto a polysulfone ultrafiltration membrane and dried at 60 °C for 4 h. Pervaporation experiments were carried out using the apparatus described in our previous report (Zhao, Qian, et al., 2009). The effective area of PENMs in contact with the feed was 16.02 cm^2, and the downstream pressure was maintained at 300 Pa. The stirring rate in the cell was 500 rpm. Normally, the separation performance in pervaporation dehydration of 10 wt.% H_2O/isopropanol is evaluated in terms of the total flux (J), separation factor (α) and pervaporation separation index (PSI), according to the following equation:

$$J = \frac{\Delta g}{A \times t}$$
$$\alpha = \frac{P_W/P_{IPA}}{F_W/F_{IPA}} \quad (2)$$
$$PSI = J \times (\alpha - 1)$$

where Δg is the weight of the permeate collected in an operation time t and A is the effective membrane area; P_W and P_{IPA} are the weight percentage of the water and isopropanol in the permeate, respectively; and F_W and F_{IPA} are the respective weight percentage of the water and isopropanol in the feed, respectively. A GC-1690A gas chromatographer was used to determine the water content in the permeate.

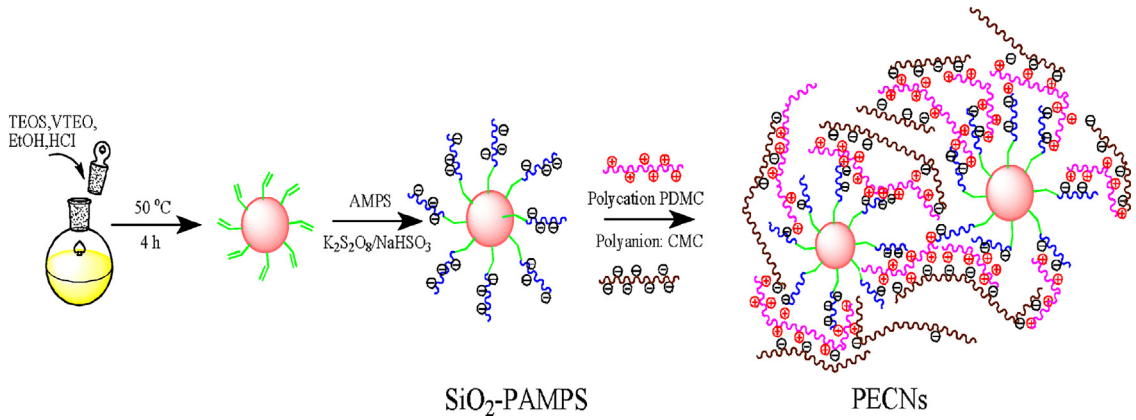

Fig. 1. Schematic diagram of fabrication for PECNs.

2.5. Characterization

FT-IR spectra were collected on a FT-IR spectrometer (Bruker Vector 22, Germany). Samples were ground with KBr to prepare pellets and scanned over a range from 400 to 4000 cm^{-1}. The morphology of the specimen was examined by a field emission SEM (FESEM, Hitachi S4800, Japan). The specimens were coated with gold prior to SEM examination. Thermogravimetric analysis (TGA) was conducted on a thermal analyzer (PE Pyris 1, USA) at a scanning rate of 20 °C min^{-1} in nitrogen with a temperature range of 50–800 °C.

3. Results and discussion

3.1. Fabrication and characterization of PECNMs

The chemical structure of the as-prepared SiO_2-PAMPS nanoparticles has been identified by FT-IR spectra in a previous work (Zhang et al., 2012). SEM was used to determine the nanoparticles' size and morphology. As seen from Fig. 2, the size of the nanoparticles increased from 200 nm to 250 nm after modification. Moreover, the surface of the SiO_2-PAMPS nanoparticles became rough compared with the pristine smooth surface.

Fig. 3 shows the FT-IR spectra of the SiO_2-PAMPS nanoparticles and their corresponding PECNMs. The peak at 1730 cm^{-1} was ascribed to the stretching vibration of the carbonyl group of PECs (Zhao et al., 2011), while the characteristic absorption at 1640 cm^{-1} was assigned to the amide group of SiO_2-PAMPS nanoparticles. The absorption at 1045 cm^{-1} was associated with a condensed siloxane network (Si—O—Si) (Wan, Tai, Leck, & Ying, 2006), which shows that the SiO_2-PAMPS nanoparticles were indeed incorporated into the PECNMs.

The content of the SiO_2-PAMPS in the PECNMs was measured with a thermo gravimetric analyzer, where the residual weight of the PECNMs included nanoparticles and residue of the polymer (Zhao, Qian, Zhu, & An, 2009). It can also be observed from Fig. 4 that the PECNM-7 contained ca. 3.2 wt.% nanoparticles. Moreover, the percentage of grafting polymer on SiO_2-PAMPS was 42 wt.% from the TGA, as shown in Fig. 4. Actually, the result is reasonable considering that the total 7 wt.% SiO_2-PAMPS nanoparticles were comprised of a 42 wt.% organic component and 58 wt.% inorganic component, i.e. 3.8 wt.% inorganic moieties incorporated into the PEC matrix. The values obtained from Eq. (1) and the TGA were within a reasonable error range of each other.

3.2. Mechanical property of PECNMs

Stress–strain curves of PECNMs with varying SiO_2-PAMPS nanoparticle contents are shown in Fig. 5(a). It can be observed that both the tensile strength and elongation at break of the PECNMs were remarkably improved with an increase in the SiO_2-PAMPS content up to 5 wt.% and then they decreased slightly. In detail, the tensile strength and elongation at break of the PECNM reached a maximum of 68 MPa and 7.1%, up to 1.9 and 2.6 times as high as those of the pristine PEC membrane, respectively. On the one hand, the improved mechanical property of PECNMs is attributed to a uniform dispersion of nanoparticles. Polyelectrolyte modified nanoparticles are capable of high hydrophilicity, which benefits the dispersion of nanoparticles. On the other hand, SiO_2-PAMPS nanoparticles containing a sulfonic group afford ionic complexation with the PDMC of the PEC matrix through electrostatic interaction (Fig. 1). Robust interfacial adhesion is acquired at the interface naturally. Therefore, when the stress was loaded on the polymer matrix it transferred from the matrix to the nanoparticles (Wu, Zhang, Rong, & Friedrich, 2002). Loading of excessive SiO_2-PAMPS

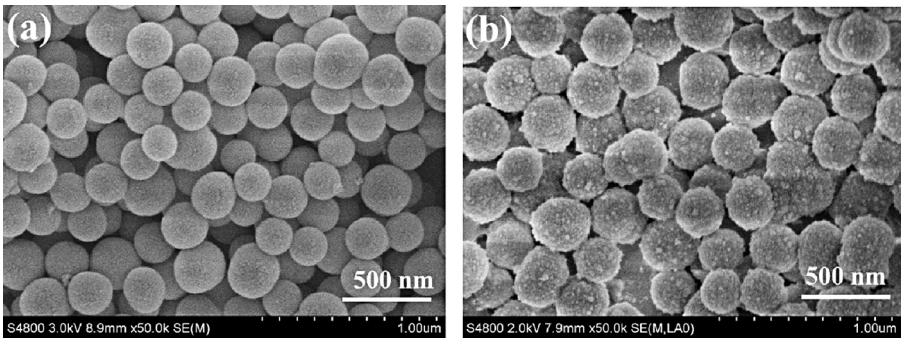

Fig. 2. SEM images of (a) SiO_2 and (b) SiO_2-PAMPS.

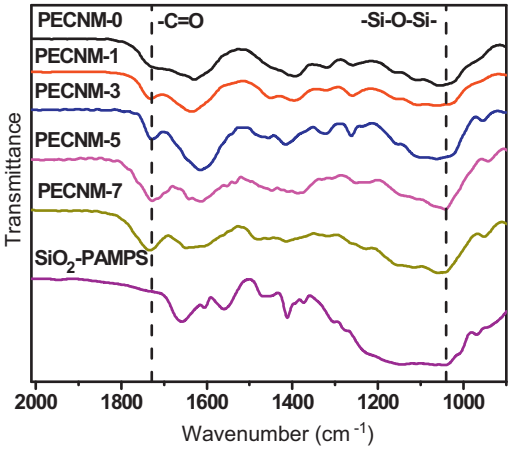

Fig. 3. FT-IR spectra of SiO_2-PAMPS and their PECNMs.

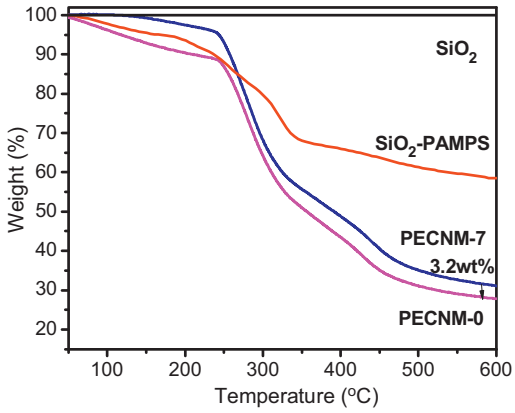

Fig. 4. TGA curves of SiO_2, SiO_2-PAMPS and PECNMs.

nanoparticles usually could result in agglomeration and deterioration of the mechanical property.

To enable comparisons, the PEC matrix also had unmodified SiO_2 nanoparticles introduced. The effect of the nanoparticle content, including SiO_2-PAMPS and unmodified SiO_2 on the tensile property of PECNMs is shown in Fig. 5(b–d). Although unmodified SiO_2 nanoparticles could enhance the mechanical property of PECNMs to a certain extent, SiO_2-PAMPS nanoparticles loaded in the PEC matrix suggested a great advantage over the former due to their good dispersion and strong interfacial adhesion.

It was observed that the Young's modulus of the PECNMs increased significantly with the addition of SiO_2-PAMPS nanoparticles compared with the unmodified SiO_2. The Young's modulus of the PECNMs containing SiO_2-PAMPS nanoparticles increased constantly with increasing nanoparticle content, while the modulus of the PECNMs containing unmodified SiO_2 nanoparticles decreased at nanoparticle contents over 3 wt.%. A linear relationship between the nanoparticle content and Young's modulus has been predicted by previous research (Einstein, 1956). The experimental data derived from PECNMs containing SiO_2-PAMPS nanoparticles was in accordance with the theoretical model. This is attributed to the fact that SiO_2-PAMPS nanoparticles are dispersed uniformly and have strong interfacial adhesion to the PEC matrix through ionic complexation (Ou, Yang, & Yu, 1998). In general, as the nanoparticle loading increases, the stiffness and strength of the nanocomposites increase but the toughness fails to decreases (Tjong, 2006). Both SiO_2-PAMPS and unmodified SiO_2 nanoparticles could enhance the strength and toughness of the PECNMs, which reached the maximum values at 3 wt.% and 5 wt.% content, respectively, and then decreased as shown in Fig. 5(c) and (d). Since the unmodified SiO_2 nanoparticles were prone to aggregate, PECNMs reached the optimized value at a low content. In fact, the surface modification

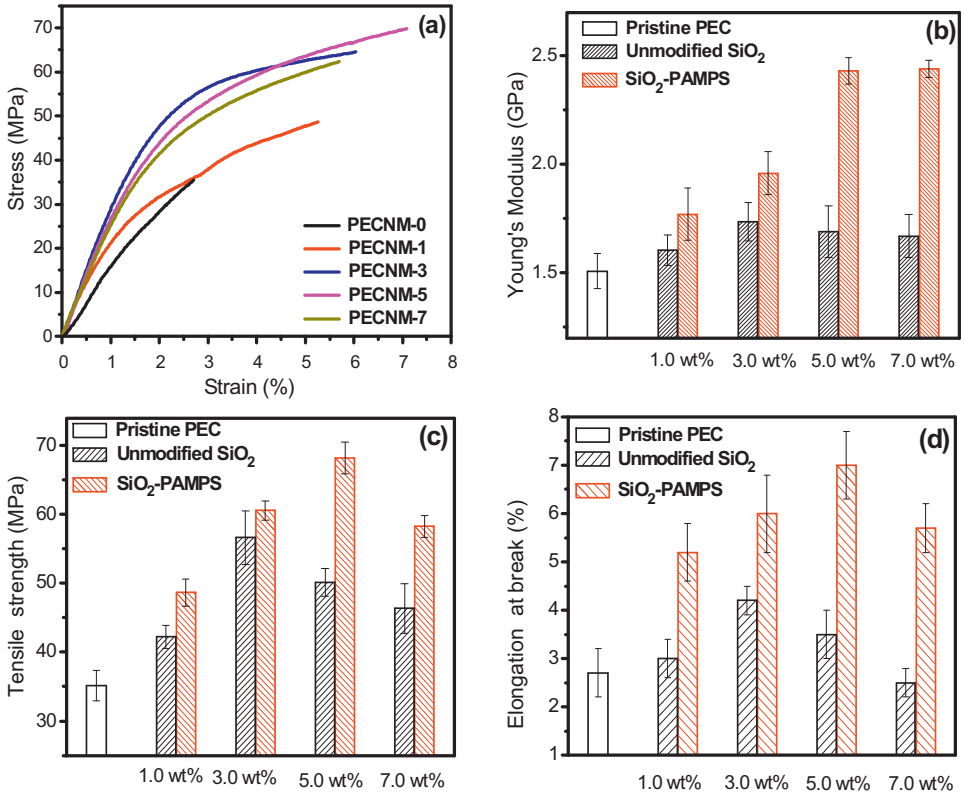

Fig. 5. (a) Stress–strain curves of PECNMs, (b) Young's modulus, (c) tensile strength and (d) elongation at break of PECNMs versus SiO_2-PAMPS and unmodified SiO_2.

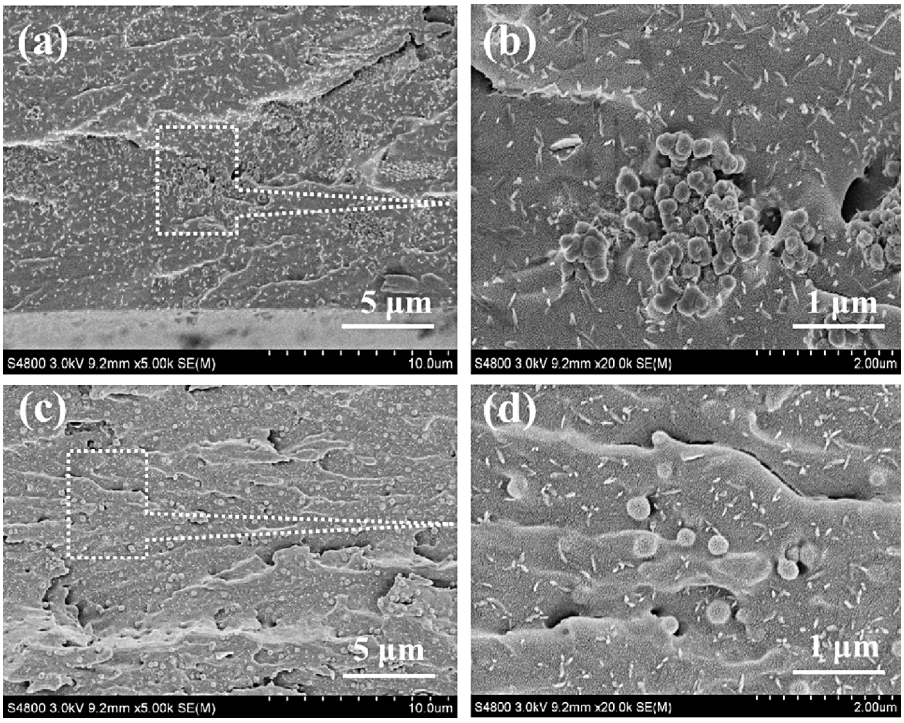

Fig. 6. Fractured morphology images of PECNMs containing (a and b) 5 wt.% unmodified SiO_2 and (c and d) 5 wt.% SiO_2-PAMPS nanoparticles at low and high magnifications.

of SiO_2-PAMPS nanoparticles reduces the surface energy and enables them to disperse uniformly in the PEC matrix (Wu et al., 2002). Meanwhile, PECNMs containing SiO_2-PAMPS nanoparticles demonstrated an obvious enhancement of the mechanical property due to their electrostatic interaction between charged nanoparticles and the polyelectrolytes of the PEC matrix.

The maximum tensile strength and elongation at break of the membrane in our previous work reached up to 37.6 MPa and 2.4%, which were 1.5 and 1.4 times as high as those of the pristine PEC membrane, respectively (Zhao, Qian, Zhu, An, et al., 2009). With respect to the enhancement efficiency, the membrane containing the SiO_2-PAMPS nanoparticles in this work displayed much greater values (Section 3.2, paragraph 1), despite the difference in absolute values. In conclusion, great progress has been made related to the modification of nanoparticles compared with previously published work.

Meanwhile, the fracture morphology of the PECNMs was investigated by SEM. It was observed that the fracture morphology of PECNMs containing SiO_2-PAMPS and unmodified SiO_2 nanoparticles displayed rough surfaces as shown in Fig. 6. Noticeably, the unmodified SiO_2 nanoparticles were likely to aggregate, while the SiO_2-PAMPS nanoparticles were dispersed uniformly in the PECNM. Moreover, the enhancement of the PECNM containing SiO_2-PAMPS is ascribed to a successful debonding of the SiO_2-PAMPS nanoparticles from the matrix due to the robust interfacial adhesion via electrostatic interaction as shown in Fig. 1. Therefore, it was observed that many SiO_2-PAMPS nanoparticles were anchored onto the fracture surface of the PECNM.

3.3. Pervaporation performance of PECNMs

Pervaporation has gained wide application in chemical separation for product purification due to its energy-saving feature, compared with traditional distillation (An et al., 2011; Kalyani, Smitha, Sridhar, & Krishnaiah, 2006; Krishna Rao et al., 2006; Smitha, Dhanuja, & Sridhar, 2006). Pervaporation dehydration with 10 wt.% water/isopropanol was performed on the as-made PECNMs. It was observed that the permeation flux increased linearly, while the water content in the permeate remained constant as the operation temperature increased, as shown in Fig. 7. This phenomenon is usually regarded as an anti-trade-off behavior. The permeation flux increased with increasing feed temperature, which is due to the enlarged diffusion rate of the solvent. Additionally, polyelectrolyte complex aggregates, the basic building blocks of PECs, have high hydrophilicity due to the external carboxylate groups (—COONa) (Zhao et al., 2010). Hence, the interaction between the water and membranes increases correspondingly. The selectivity of the PECNMs was maintained due to the stabilized ionic crosslinked structure in the PECs (Zhao et al., 2011). Different from the acid blend method for PEC membranes, the degree of ionic complexation for the PEC membrane is high and controllable from the solution process method, which leads to a heat-resisting chemical structure.

PSI is the most commonly accepted parameter for evaluating the pervaporation separation performance, which is obtained from the product of the membrane flux and the separation factor (Rachipudi, Kariduraganavar, Kittur, & Sajjan, 2011). The values of the PSI for PECNM-0 and PECNM-5 were 3.6×10^6 and 1.0×10^7, respectively, which indicates that the incorporated modified SiO_2-PAMPS nanoparticles improved the pervaporation performance of the PECNMs. This is caused by the enhancement of the selectivity demonstrated by the PECNMs, as is shown in Fig. 7. It was revealed that the desired separation performance was obtained with the incorporation of SiO_2-PAMPS nanoparticles.

Moreover, Fig. 8 shows the performance stability of PECNM-5 for dehydrating 10 wt.% water/isopropanol mixtures at 70 °C. The flux and water in the permeate of PECNM-5 held good stability over 20 h operations. Inorganic nanoparticles are materials with high mechanical strength, thermal and chemical stability (Tai, Fu, & Don, 2012; Zhu et al., 2012). These results suggest that the SiO_2-PAMPS nanoparticles would not only enhance the mechanical property of the nanocomposite, but also endow their membranes with excellent stability for long-term operation. This demonstrates the potential superiority of inorganic–organic hybrid membranes

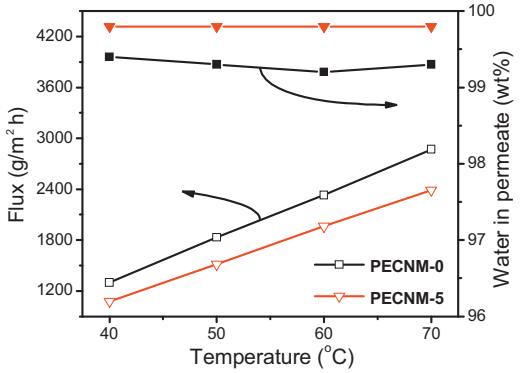

Fig. 7. Effect of operation temperature on the pervaporation performance of PECNMs for dehydrating 10 wt.% water/isopropanol mixtures.

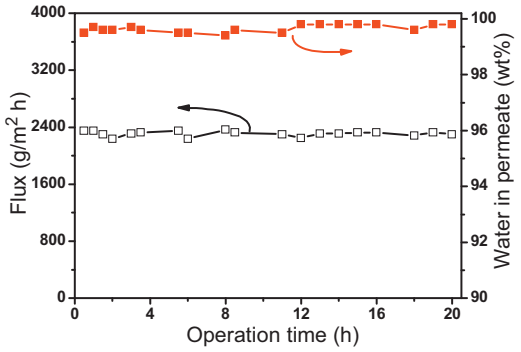

Fig. 8. Performance stability of PECNM-5 for dehydrating 10 wt.% water/isopropanol mixtures at 70 °C.

enhanced with the merits of the matrix and the nanofiller (Liu, Hsu, Su, & Lai, 2005).

4. Conclusion

Novel PECNMs based on CMC with SiO_2-PAMPS contents from 1 to 7 wt.% were successfully made. FT-IR spectra revealed that the SiO_2-PAMPS nanoparticles were incorporated into the PEC matrix. PECNM-5 gave a maximum tensile strength and elongation at break of 68 MPa and 7.1%, which were 1.9 and 2.6 times as high as those of the pristine PEC membrane, respectively. Due to the homogenous dispersion of SiO_2-PAMPS nanoparticles in the PEC matrix as well as the strong interfacial adhesion caused by the ionic complexation, the mechanical property was significantly improved. Moreover, PECNMs were subjected to pervaporation dehydration of 10 wt.% water/isopropanol. PECNMs displayed an improved separation performance in terms of PSI and long-term stability. This work provides a facile method to fabricate a polysaccharide-based hybrid membrane with high performance.

Acknowledgements

This research was financially supported by the NNSFC (51173160), the National High Technology Research and Development Program of China (No. 2012AA03A602), the Fundamental Research Funds for the Central Universities (No. 2013QNA4049), the National Basic Research Program of China (No. 2009CB623402).

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