RSC Advances

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Advances*, 2013, **3**, 1855

UV-crosslinked chitosan/polyvinylpyrrolidone blended membranes for pervaporation†

Qiu Gen Zhang,* Wen Wei Hu, Ai Mei Zhu and Qing Lin Liu*

Received 16th August 2012,
Accepted 27th November 2012

DOI: 10.1039/c2ra21827e

www.rsc.org/advances

Chitosan is an important biomacromolecule and polyvinylpyrrolidone (PVP) is a biocompatible synthetic polymer. The crosslinked chitosan/PVP blended membranes were prepared *via* UV irradiation. The as-prepared membranes have a highly crosslinked chitosan/PVP network structure originated from self-crosslinking of PVP and branching of chitosan onto PVP chains during UV irradiation. UV-Crosslinking significantly enhanced the mechanical strength and thermal stability of the blended membranes. Their highest tensile strength is twice as much as that of the pristine chitosan membrane. Maintaining the same swelling degree of the pristine chitosan membrane, the blended membranes have high sorption selectivity towards methanol and water. The as-prepared membranes exhibit an excellent performance in pervaporation separation of methanol/ethylene glycol and water/ethanol and show great potential as new biomedical materials and in the removal of alcohol and water from organics.

Introduction

Chitosan, an excellent biomacromolecule produced from the deacetylation of chitin, has been widely used in biomedical engineering, drug delivery systems, solid polyelectrolytes, ultrafiltration, reverse osmosis, and pervaporation.[1–6] Of those, chitosan-based membranes are widely applied in dehydration of organics and removal of alcohol from organics for its high hydrophilicity and good film-forming ability.[7–10] For example, dehydration of ethanol, 1,4-dioxane and caprolactam aqueous solutions can be realized using a chitosan–silica complex, chitosan/polyvinylalcohol blending and chitosan/konjac glucomannan blended membranes respectively.[7,11,12] Methanol/dimethyl carbonate mixtures are separated through chitosan hollow fiber membranes.[13] Methanol is removed from methyl *tert*-butyl ether using chitosan and poly(*N*-vinyl-2-pyrrolidone) (PVP) blended membranes.[14] These chitosan-based membranes have high permselectivity for water and methanol. However, they lose both the permselectivity and mechanical strength for the high swelling in water and alcohol solutions.

To improve the mechanical strength and separation properties of chitosan-based membranes, various methods have been attempted. Blending with other polymers and filling with inorganic chemicals are easy methods to adjust the structure and properties of chitosan membranes.[10,11,14–18] A high hydrophilic polymer is usually used to prepare chitosan-based blended membranes, such as polyvinylalcohol, PVP and gelatin.[11,14,16,17] The resulting blended membranes have higher permselectivity and permeation flux than the pristine chitosan membranes, while suffering more swelling for pervaporation dehydration of organics. A convenient and effective approach to improve their mechanical strength is to form a crosslinked network in the membrane. The hydroxyl and amino groups on chitosan chains can easily react with organic reagents (glutaraldehyde, toluylene diisocyanate, maleic anhydride, *etc.*) and silica precursors (tetraethoxysilane and γ-glycidoxypropyltrimethoxysilane).[9,19–23] Nevertheless, this approach usually consumes vast amounts of hydrophilic groups and significantly depresses the permeation flux. Thus, how to enhance the mechanical stability and simultaneously enlarge permeation flux and selectivity of chitosan-based membranes is crucial for modification of chitosan membranes.

Herein we report new UV-crosslinked chitosan/PVP blended membrane prepared *via* UV radiation. They were applied for pervaporation separation of methanol/ethylene glycol (EG) and dehydration of ethanol. EG is an important organic used to produce polyester monomer and antifreeze in automobiles, and forms an azeotrope with methanol by-products in the direct synthesis from syngas.[24] Meanwhile, pervaporation dehydration of ethanol is the most successful in the chemical industry. Recently, chitosan was blended with PVP to prepare novel pervaporation membranes.[14,21,25] As a non-ionic water soluble polymer with excellent adsorption, adhesion capacity, biocompatibility and good thermal stability, PVP exhibits good

Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, P. R. China. E-mail: qgzhang@xmu.edu.cn; qlliu@xmu.edu.cn; Fax: 86-592-2184822; Tel: 86-592-2188072

† Electronic supplementary information (ESI) available: Composition and irradiation time of the membranes, exaction experiments of the membranes in ethanol aqueous solution, Characterization of the membranes, pervaporation performance of the membranes. See DOI: 10.1039/c2ra21827e

miscibility with other polymers. The resulting chitosan/PVP blended membranes have high permeation flux. However, introduction of PVP reduced mechanical stability of the chitosan membrane and aggravated their swelling in methanol/EG mixture and ethanol aqueous solution therefore, transparent blends of chitosan and PVP were prepared at the molecular level in this work, and then crosslinked using a UV lamp. Self-crosslinking of PVP and branching of chitosan onto PVP chains can generate a highly crosslinked chitosan/PVP network during UV irradiation (Fig. 1). Compared to the pristine chitosan membrane, the as-prepared membranes demonstrate strong mechanical strength and an excellent performance in pervaporation separation of methanol/EG and dehydration of ethanol.

Experimental

Membrane preparation and characterization

Chitosan with an average molecular weight of 200 kDa and deacetylation degree of 95% (*Golden Shell Marine Biological Chemical Co. Ltd.* China) and PVP with an average molecular weight of 70 kDa (*Xi Long Chemical Co. Ltd.* China) were dissolved in 1 wt% acetic acid solution under magnetic stirring at 60 °C for 2 h to yield a solution containing 1.5 wt% chitosan/PVP. Weight percentage of PVP in the chitosan/PVP blend is 0, 4.76, 6.25, 9.09 and 16.70 wt% (Table S1, see ESI†). Then, the solution was spread on a glass plate to form a 150 μm thick liquid film, subsequently put under a high pressure UVA Hg lamp with a radiant flux of 1000 W cm^{-2} (*Bluesky Special Lamps Development Co*, *Ltd*, China) in a dark chamber for UV irradiation. The lamp emission presents a main peak at 360 nm, a strong peak at 254 nm, and a set of secondary peaks in the range of 250–550 nm. Distance between the samples and the lamp is 15 cm. Irradiation time was varied for 0, 2, 4, 6 and 8 min (Table S1, see ESI†). After that, the resulting liquid film was slowly dried in an oven at 35 °C for 24 h, and then peeled off and dried completely in a vacuum oven at 100 °C for another 4 h to get the UV-crosslinked chitosan/PVP blended membranes.

The as-prepared membranes were characterized using field emission scanning electron microscopy (SEM) (LEO 1530, *LEO*, Germany) to observe their morphology. Before SEM observation, a 5 nm thick Pt layer was deposited on the samples to prevent electric charging. The samples for cross-sectional observation were prepared by freeze fracturing in liquid nitrogen. The mechanical property was measured by a WDS-5 testing machine (*Tianshui Hongshan Testing Machine Co. Ltd.*, China). Their tensile strength of the membranes was estimated by stretching the samples. And the thermal stabilities were analyzed using a STA 409EP analyzer (Netzsch, Germany) with a heating rate of 10 °C min^{-1} in the temperature range 25–900 °C under nitrogen atmosphere.

Swelling and pervaporation measurements

The swelling and pervaporation experiments were performed by the method described in the previous work.[26] The UV-crosslinked chitosan/PVP blended membranes were dried at 80 °C for 8 h in the vacuum oven to evacuate their moisture. They were immersed in the methanol/EG azeotrope (6 wt% methanol) or 85 wt% ethanol aqueous solution at 25 °C until swelling equilibrium was achieved. After weighing, the swollen membrane was placed into a dry flask. The sorbate in the swollen membrane was completely desorbed at 90 °C under vacuum and collected in a liquid nitrogen cold trap. The weight percentage of components in the sorbate was measured by gas chromatography (GC-950, *Shanghai Haixin Chromatographic Instruments Co. Ltd.* China).

The degree of swelling (*DS*, %) and sorption selectivity (α_{sor}) of the membranes are calculated by

$$DS(\%) = \left(\frac{W_s - W_d}{W_d}\right) \times 100 \quad (1)$$

$$\alpha_{sor} = \frac{C_i^a/(1 - C_i^a)}{C_i^l/(1 - C_i^l)} \quad (2)$$

where W_s and W_d are the weight of the swollen and the dried membranes, C_i^a and C_i^l are the concentration of species i in the sorbate and the feed respectively.

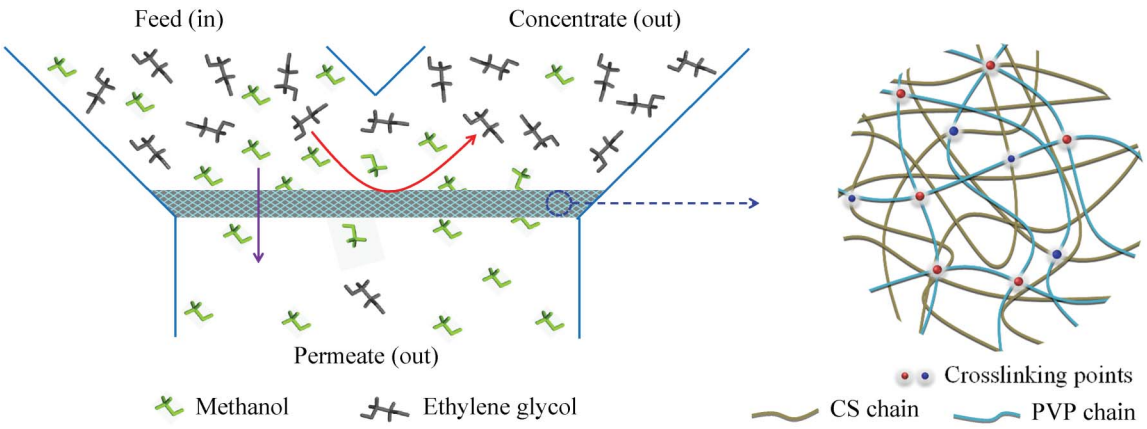


Fig. 1 The schematic pervaporation separation of methanol/EG and crosslinked network of the UV-crosslinked chitosan/PVP blended membranes on the left.

Pervaporation experiments were carried out on a laboratory scale apparatus (*Sulzer Chemtech.*, Germany) with an effective membrane area of 71 cm^2. The pressure on the permeate side was kept at 10 mbar and the feed flow rate was 40 L h^{-1}. Both the methanol/EG azeotrope and 85 wt% ethanol aqueous solution were used as feed. The membrane was immersed in a liquid mixture with the temperature and composition the same as the feed for 48 h before pervaporation. PVP suffered slight extraction in the feed, and did not extract after being immersed into the feed for 24 h (Fig. S1, see ESI†). After that, they were assembled to perform pervaporation. The permeate was collected for 5 h in liquid nitrogen cold traps and measured by gas chromatography (GC-950). The total permeation flux (J, kg m^{-2} h^{-1}) and the separation factor (α) are calculated by

$$J = \Delta M/(A\cdot\Delta t) \quad (3)$$

$$\alpha = \frac{y_i/(1-y_i)}{x_i/(1-x_i)} \quad (4)$$

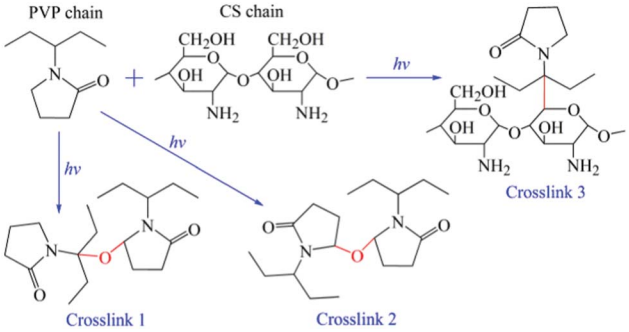
where ΔM is the weight of the permeate (kg); A is the effective area of the membrane (m^2); Δt is the permeation time (h). y_i and x_i are the concentration of species i in the permeate and the feed respectively.

Results and Discussion

Formation and characterization of the UV-crosslinked chitosan/PVP blended membranes

UV radiation has been successfully used to produce PVP hydrogels recently.[27–29] PVP interchain crosslinking can be easily realized in aqueous solution by a UV light to form a highly crosslinked polymer network. This facile preparation procedure shows a great potential in incorporating guest molecules into the crosslinked network by dispersing them into the PVP solution. Thus, we blended chitosan with PVP to form a homogeneous solution at the molecular level, and subsequently irradiated the solution using the UV light. During UV irradiation, the pyrrolidone substituents and cyclic amides on the PVP chains in the aqueous medium generated PVP macroradicals whose recombination could eventually lead to intermolecular crosslinking of PVP.[29] Consequently, the crosslinked PVP network was formed in the chitosan/PVP blended membranes *via* interchain recombination of the macroradicals (Scheme 1). Besides, chitosan macroradicals are also produced during UV treatment, and branched with the PVP macroradicals to form crosslinking points (crosslink 3 in Scheme 1) between chitosan and PVP chains.[30] In this case, PVP can be regarded as a long chain crosslinker with abundant active sites. The highly crosslinked network of the resulting membranes is shown in Fig. 1. Chitosan chains are intertwined and connected with the PVP chains at the molecular level in the membranes.

Fig. 2 shows photos of the pristine chitosan, PVP and their blended membranes. The UV-irradiated PVP membrane is still transparent. The pristine transparent chitosan membrane became light yellow after irradiation for 8 min, while the blended membrane containing 9.09 wt% PVP is a transparent



Scheme 1 Crosslinking between chitosan chains and PVP chains (crosslink 3) and intermolecular crosslinking of PVP (crosslinks 1 and 2) in the UV-crosslinked chitosan/PVP blended membranes.

deep yellow after irradiation for 8 min. This is because chitosan macroradicals are formed and conjugated double bonds are produced by slight photodegradation of chitosan during UV exposure.[30] The introduction of PVP possibly promoted chitosan photodegradation due to the branching reaction between chitosan and PVP. Irradiation time intensively influenced the reaction in the blends. The longer the irradiation time, the higher the reaction degree is. As the most direct evidence, the colour of the as-prepared membranes was deepened with extended irradiation time (Fig. S2, see ESI†).

Membrane morphology and cross-sectional structure was observed by SEM. Since chitosan/PVP blends are miscible in the solid state and interact at the molecular level,[30] the resulting UV-crosslinked chitosan/PVP blended membranes have a smooth surface at the microscale (Fig. S3, see ESI†). These blended membranes are also uniform in their internal matrix from cross-sectional observation (Fig. 3). However, their

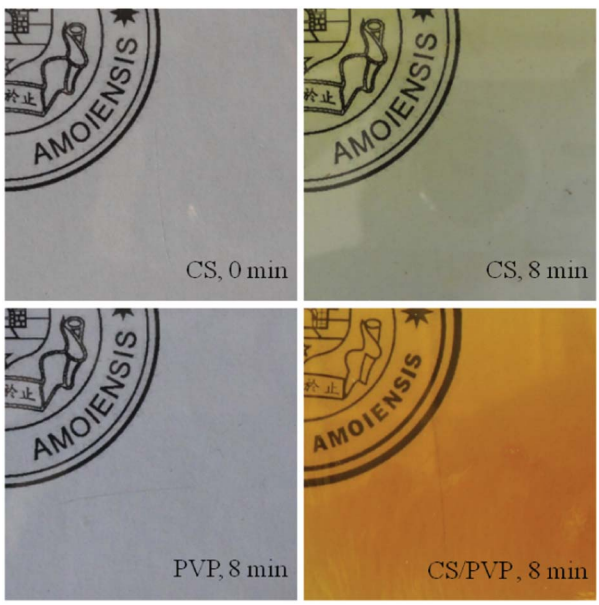


Fig. 2 Photos of the pristine chitosan, the UV-crosslinked chitosan, PVP and chitosan/PVP blended membranes (9.09 wt% PVP) *via* irradiation for 8 min.

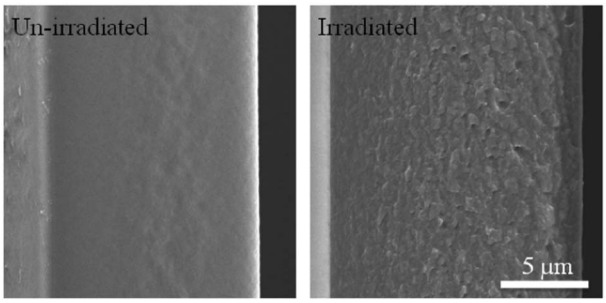


Fig. 3 Cross-sectional SEM images of the chitosan/PVP blended membrane (9.09 wt% PVP) and its UV-crosslinked (UV irradiation for 4 min) counterpart.

uniform internal structure became rough and compact after UV irradiation due to the formation of a crosslinked network, as shown in Fig. 3. This is also confirmed by measuring the density of membranes. Density of the UV-crosslinked chitosan/PVP blended membranes almost linearly decreased with increasing PVP content, whereas the density increased rapidly and then slightly with extending irradiation time (Fig. S4, see ESI†). Thus, UV irradiation made the chitosan/PVP blended membranes more compact.

Fig. 4 shows the tensile strength of the UV-crosslinked chitosan/PVP blended membranes. Introduction of PVP significantly enhanced the tensile strength of the blended membranes after UV irradiation. The tensile strength rapidly increased and then slightly depressed with increasing PVP content after irradiation of 4 min, while it continually increased with increasing irradiation time. For the membranes considered, the membrane containing 9.09 wt% PVP with 8 min irradiation has a high tensile strength of 80.6 MPa that is twice the pristine chitosan membranes (40.5 MPa). The thermal stability of the membranes is illustrated by DTG curves measured under a nitrogen atmosphere, as shown in Fig. 5. The introduction of PVP disordered the packing of chitosan chains, and thus slightly depressed the decomposition temperature of the blended membranes. However, their thermal stability was enhanced after UV irradiation owing to the formation of a highly crosslinked polymer network.

Pervaporation separation of the methanol/ethylene glycol azeotrope

As discussed above, ethylene glycol (EG) is an important organic used in polyester and antifreeze production, and can form the azeotrope with methanol by-products in the direct synthesis from syngas. Thus, the performance of the as-prepared membranes was evaluated in pervaporation separation of the methanol/EG azeotrope in this work. Fig. 1 shows the schematic pervaporation separation of the methanol/EG azeotrope. Methanol molecules preferentially permeate through the UV-crosslinked chitosan/PVP blended membranes in the pervaporation process, and are removed from the feed and enriched in the permeate.

Performance of the membranes can be generally evaluated by swelling testing and pervaporation measurements. Fig. 6 shows swelling behaviour of the as-prepared membranes in the methanol/EG azeotrope. UV irradiation greatly depressed

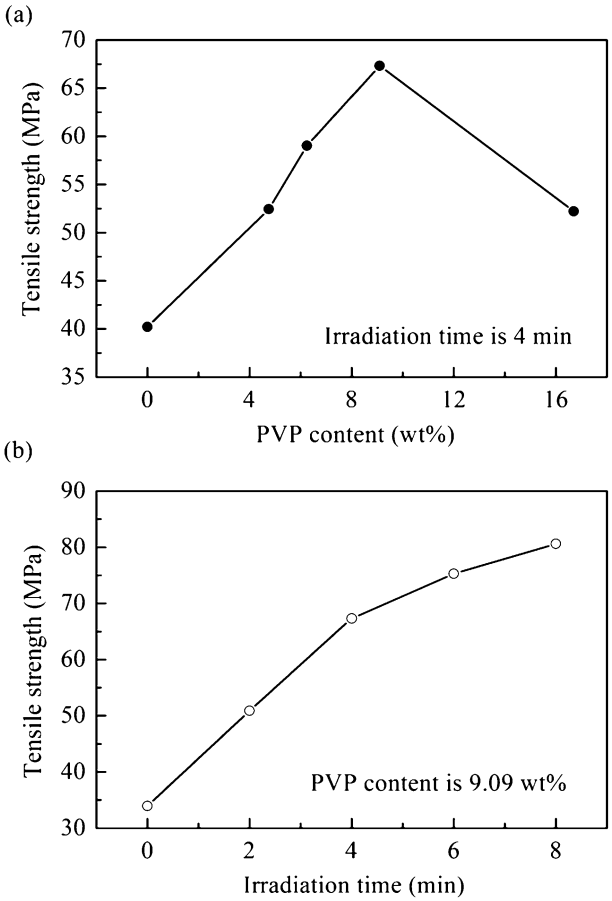


Fig. 4 The tensile strength of the UV-crosslinked chitosan/PVP blended membranes at 25 °C: (a) effect of PVP content, (b) effect of irradiation time.

their swelling that decreased with extending irradiation time progressively. The UV-crosslinked blended membrane (9.09 wt% PVP, irradiation for 8 min) only swelled half of the

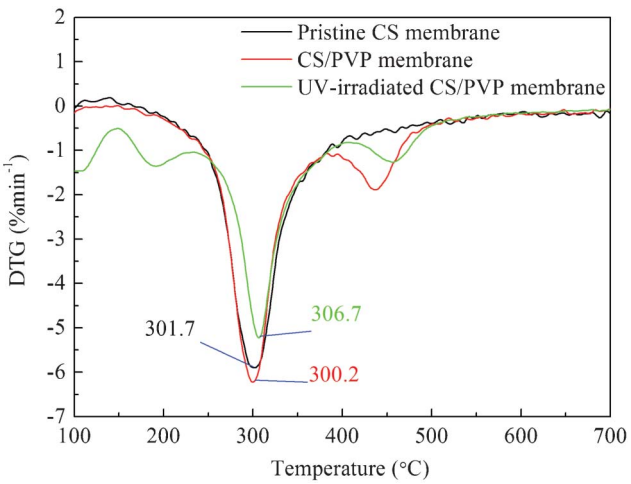


Fig. 5 DTG curves of the pristine chitosan membrane, the blended membrane containing 9.09 wt% PVP and its UV-crosslinked counterpart with 8 min irradiation.

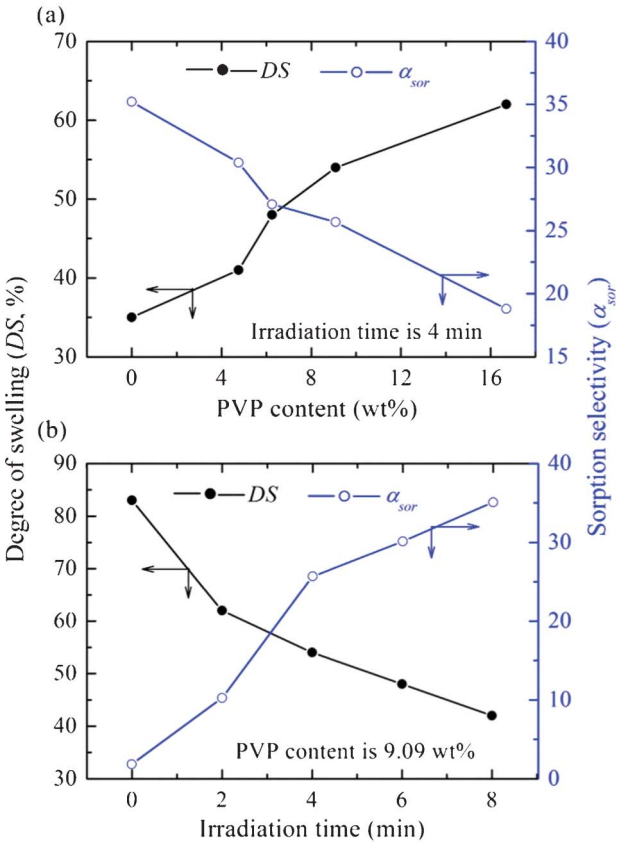


Fig. 6 Swelling properties of the UV-crosslinked chitosan/PVP blended membranes in the methanol/EG azeotrope at 25 °C: (a) effect of PVP content, (b) effect of irradiation time.

swelling degree of its un-crosslinked counterpart (Fig. 6b). This is because UV-crosslinking can shorten the interchain spacing and make the membranes more compact. And the higher the degree of crosslinking, the less the degree of swelling is. Besides, their degree of swelling enlarged with increasing PVP content due to the high hydrophilic PVP and readjustment of membrane structure. Sorption selectivity (α_{sor}) calculated from swelling testing is also an important factor in describing the solubility properties of a membrane in feed solution. UV irradiation leads to a crosslinked network in the membrane and makes the membranes more compact. This results in difficult adsorption of large molecules onto the membrane surface and then difficult diffusion into the inner membrane (Fig. 1). Therefore, methanol sorption selectivity of the membranes is greatly enhanced with extended irradiation time, and decreased with increasing PVP content (Fig. 6).

Fig. 7 shows pervaporation performance of the UV-crosslinked chitosan/PVP membranes in separation of the methanol/EG azeotrope. Compared to the pristine chitosan membrane, most of the as-prepared membranes have both higher permeation flux and permselectivity. Introduction of PVP disordered the packing of chitosan chains, resulting in an increase of the diffusion tunnels in the membrane matrix. Besides, the interpenetrating chitosan/PVP crosslinked net-

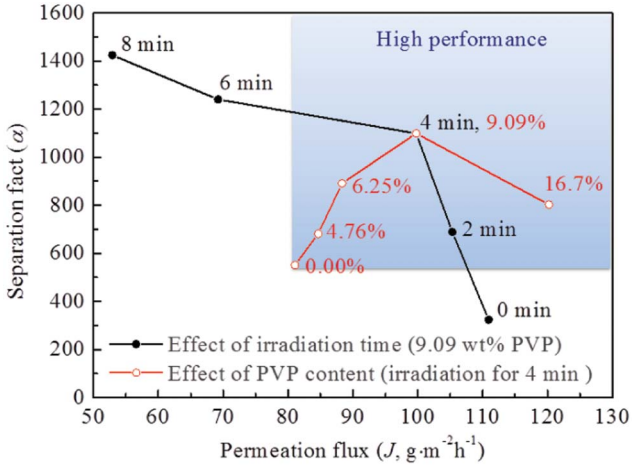


Fig. 7 Pervaporation performance of the UV-crosslinked chitosan/PVP blended membranes for separating the methanol /EG azeotrope at 60 °C.

works can shrink available channels that solvent molecules can diffuse through the membranes.

Consequently, the separation factor of the UV-crosslinked blended membranes is largely enhanced, methanol flux through the membranes increases with increasing PVP content, whereas EG flux first decreased and then increased (Fig. S5, see ESI†). Besides, UV irradiation time plays an important role in pervaporation performance. Separation factor of the membranes rapidly increased with extended irradiation time (equivalent to increasing the degree of crosslinking), and the flux decreased progressively. Individual flux of methanol and EG decreased simultaneously with extended irradiation time. However, the latter has a greater decrease than the former since the EG molecules are bigger than methanol. Therefore, the UV-crosslinked chitosan/PVP blended membranes should have a great potential in pervaporation separation of methanol/EG azeotrope and removal of alcohol from organics.

Pervaporation dehydration of ethanol aqueous solution

Hydrophilic polymer membranes are widely used to remove water from organics (alcohols, acids, ethers, ketones, *etc.*) by pervaporation.[31] Chitosan is one of the most important hydrophilic membrane materials for pervaporation. We evaluated pervaporation performance of the UV-crosslinked chitosan/PVP blended membranes for dehydration of an ethanol aqueous solution. Fig. S6† shows swelling properties of the as-prepared membranes in 85 wt% ethanol aqueous solution (see ESI†). Similar to their swelling in the methanol/EG azeotrope, the degree of swelling enlarged with increasing PVP content and decreased with extended irradiation time. Instead, water sorption selectivity reduced with increasing PVP content and increased with extended irradiation time. Solubility of the chitosan membrane in ethanol aqueous solution was enhanced by PVP blending and UV-crosslinking. Compared to the pristine chitosan membrane, the membrane containing 9.09 wt% PVP with 8 min UV irradiation has a

similar degree of swelling and higher water sorption selectivity (Fig. S6, see ESI†).

Fig. 8 shows pervaporation performance of the as-prepared membranes for dehydration of 85 wt% ethanol aqueous solution. Permeation flux through the membranes increased with PVP content whereas decreased with extending irradiation time. Separation factor of water/ethanol, as another important parameter, decreased with increasing PVP content and increased with extending irradiation time. This results from the combined effects of PVP blending and UV-crosslinking. From pervaporation separation index (*PSI*), the as-prepared UV-crosslinked chitosan/PVP blended membranes have high pervaporation performance in separating a water/ethanol solution. The membrane containing 9.09 wt% PVP with 8 min irradiation has the highest *PSI* of 167.1 that is double that of the pristine CS membrane (Fig. 8c).

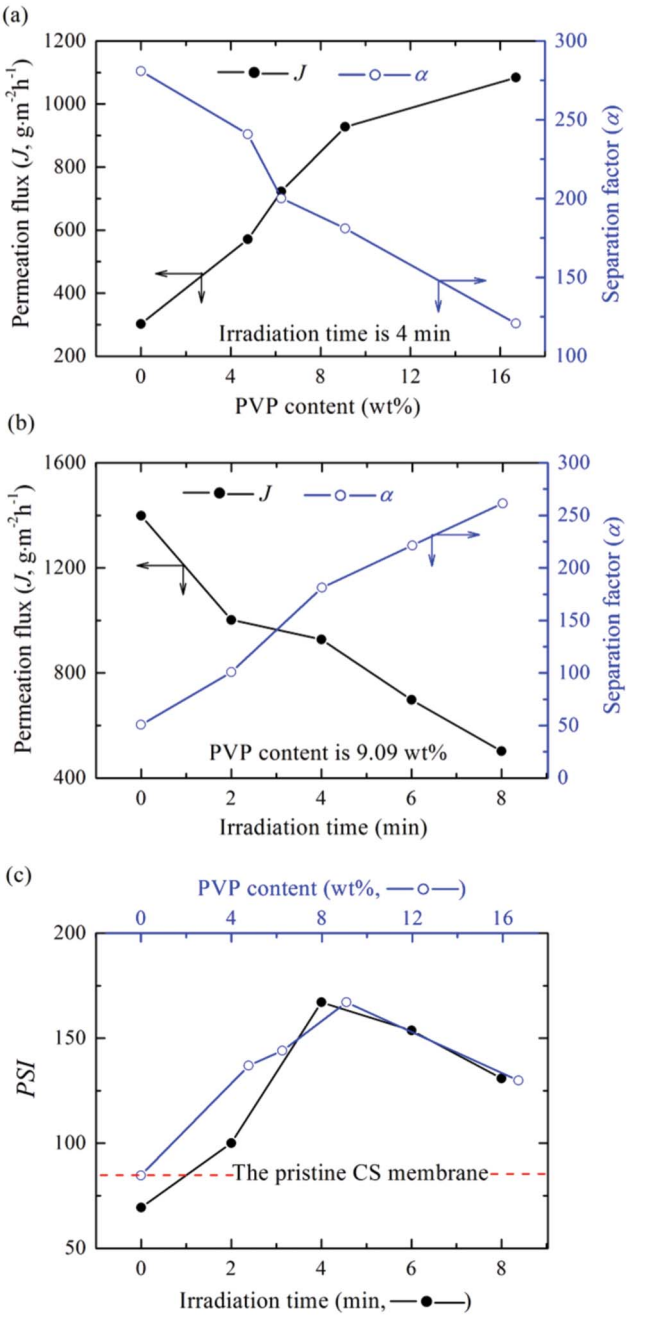


Fig. 8 Pervaporation performance of the UV-crosslinked chitosan/PVP blended membranes for dehydration of 85 wt% ethanol aqueous solution at 50 °C: (a) effect of PVP content, (b) effect of irradiation time, (c) pervaporation separation index (*PSI*).

Conclusions

Novel crosslinked chitosan/PVP blended membranes were prepared by exposing an aqueous solution of them to UV light. The as-prepared membranes have a highly crosslinked chitosan/PVP network resulting from self-crosslinking of PVP and branching of chitosan onto PVP chains during UV irradiation. They have a smooth surface and rough inner structure and good stability. UV-Crosslinking significantly enhanced the mechanical strength and thermal stability of the blended membranes. Their highest tensile strength is twice that of the pristine chitosan membrane.

The crosslinked chitosan/PVP blended membranes have excellent performances for pervaporation separation of methanol/EG and water/ethanol. Their degree of swelling increased with PVP content and decreased with extended irradiation time. Most of the membranes have both higher permeation flux and permselectivity than the pristine chitosan membrane in the separation of the methanol/EG azeotrope. They have also high pervaporation performance in separating water/ethanol. The membrane containing 9.09 wt% PVP with 8 min irradiation has the highest PSI of 167.1 that is double of the pristine CS membrane. The membranes we newly developed have a great potential in pervaporation and biomedical engineering for their excellent biocompatibility.

Acknowledgements

This work was supported by the National Nature Science Foundation of China Grant Nos. 20976145 and 21076170, the Nature Science Foundation of Fujian Province of China Grant No.2009J01040, the research fund for the Doctoral Program of Higher Education (No. 20090121110031) and the Fundamental Research Funds for the Central Universities (No. 2012121029).

References

1 R. A. A. Muzzarelli, F. Greco, A. Busilacchi, V. Sollazzo and A. Gigante, *Carbohydr. Polym.*, 2012, **89**, 723.
2 S. A. Agnihotri, N. N. Mallikarjuna and T. M. Aminabhavi, *J. Controlled Release*, 2004, **100**, 5.
3 A. Gandini, S. Hariri and J.-F. Le Nest, *Polymer*, 2003, **44**, 7565.
4 Y. Matsuoka, N. Kanda, Y. M. Lee and A. Higuchi, *J. Membr. Sci.*, 2006, **280**, 116.
5 T. Yang and R. R. Zall, *J. Food Sci.*, 1984, **49**, 91.

6 M. G. M. Nawawi and R. Y. M. Huang, *J. Membr. Sci.*, 1997, **124**, 53.
7 Y.-L. Liu, C.-Y. Hsu, Y.-H. Su and J.-Y. Lai, *Biomacromolecules*, 2005, **6**, 368.
8 S. Biduru, S. Sridhar, G. S. Murthy and S. Mayor, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 1416.
9 R. Y. M. Huang, R. Pal and G. Y. Moon, *J. Membr. Sci.*, 1999, **160**, 17.
10 M. B. Patil and T. M. Aminabhavi, *Sep. Purif. Technol.*, 2008, **62**, 128.
11 S. Reddy, S. Kalyani, N. S. Kumar, V. M. Boddu and A. Krishnaiah, *Polym. Bull.*, 2008, **61**, 779.
12 W. Lin, Q. Li and T. Zhu, *J. Ind. Eng. Chem.*, 2012, **18**, 934.
13 T. Xiao, X. Xu, Y. Cao, M. Deng, S. Chen and X. Jie, *J. Appl. Polym. Sci.*, 2010, **115**, 2875.
14 S. Cao, Y. Shi and G. Chen, *J. Appl. Polym. Sci.*, 1999, **74**, 1452.
15 D. Xu, L. S. Loo and K. Wang, *J. Polym. Sci., Part B: Polym. Phys.*, 2010, **48**, 2185.
16 S. Teli, G. S. Gokavi, T. M. Tak and T. M. Aminabhavi, *Sep. Purif. Technol.*, 2009, **44**, 3202.
17 K. S. V. Krishna Rao, M. C. S. Subha, M. Sairam, N. N. Mallikarjuna and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, 2007, **103**, 1918.
18 R. S. Veerapur, K. B. Gudasi and T. M. Aminabhavi, *J. Membr. Sci.*, 2007, **304**, 102.
19 D. A. Devi, B. Smitha, S. Sridhar and T. M. Aminabhavi, *J. Membr. Sci.*, 2005, **262**, 91.
20 A. S. Reddy, S. Kalyani, N. S. Kumar, V. M. Boddu and A. Krishnaiah, *Polym. Bull.*, 2008, **61**, 779.
21 D. A. Devi, B. Smitha, S. Sridhar and T. M. Aminabhavi, *J. Membr. Sci.*, 2006, **280**, 45.
22 T. Uragami, T. Katayama, T. Miyata, H. Tamura, T. Shiraiwa and A. Higuchi, *Biomacromolecules*, 2004, **5**, 1567.
23 Y. L. Liu, Y. H. Su and J. Y. Lai, *Polymer*, 2004, **45**, 6831.
24 J. F. Knifton, *J. Am. Chem. Soc.*, 1981, **103**, 3959.
25 X. H. Zhang, Q. L. Liu, Y. Xiong, A. M. Zhu, Y. Chen and Q. G. Zhang, *J. Membr. Sci.*, 2009, **327**, 274.
26 Q. G. Zhang, Q. L. Liu, Z. Y. Jiang and Y. Chen, *J. Membr. Sci.*, 2007, **287**, 237.
27 G. D'Errico, M. D. Lellis, G. Mangiapia, A. Tedeschi, O. Ortona, S. Fusco, A. Borzacchiello and L. Ambrosio, *Biomacromolecules*, 2008, **9**, 231.
28 X. Zhu, P. Lu, W. Chen and J. Dong, *Polymer*, 2010, **51**, 3054.
29 G. J. M. Fechine, J. A. G. Barros, M. R. Alcântara and L. H. Catalani, *Polymer*, 2006, **47**, 2629.
30 A. Sionkowska, M. Wisniewski, J. Skopinska, S. Vicini and E. Marsano, *Polym. Degrad. Stab.*, 2005, **88**, 261.
31 P. D. Chapman, T. Oliveira, A. G. Livingston and K. Li, *J. Membr. Sci.*, 2008, **318**, 5.