

UF membrane of PVA modified with TDI

Ying Shang, Yuelian Peng*

*Center of Membrane Technology, College of Environmental and Energy Engineering,
Beijing University of Technology, Beijing 100022, P.R. China
Tel. +0816-67391090; Fax +0816-67391983; email: pyl@bjut.edu.cn*

Received 20 December 2006; accepted 3 January 2007

Abstract

Poly (vinyl alcohol) (PVA) is an excellent membrane material for preparation of hydrophilic ultrafiltration (UF) and nanofiltration membranes. But its chemical constitution and water solubility infer the disadvantage of easier degradation and elimination after use. This study focuses on the modification of interfacial polymerization PVA composite UF membrane with toluene diisocyanate (TDI). The effects of the reaction time and PVA, TDI, sodium dodecyl sulfate and sodium hydroxide with different concentrations were investigated on the performances of composite membranes. Anti-fouling to protein and oil was obtained when it was compared with no modified membrane. Also, the recovery ratio of pure water flux of PVA modified UF membrane is higher than that of support membrane.

Keywords: Modified; PVA; Composite UF membrane

1. Introduction

With high hydrophilicity, good film-forming properties and outstanding physical and chemical stability, poly (vinyl alcohol) (PVA) is an excellent membrane material for preparation of hydrophilic ultrafiltration (UF) and nanofiltration membranes [1]. But its chemical constitution and water solubility infer the disadvantage of easier degradation and elimination after use. Chemical modification is a powerful tool for obtaining

polymers with new properties and therefore for increasing the scope of their applications [2]. PVA has been modified with different compounds, such as aldehydes, carboxylic acid, anhydrides, etc., to increase membrane selectivity and fiber manufacture among other things. This study focuses on the modification of PVA composite UF membrane through interfacial polymerization with toluene diisocyanate (TDI) [3], which has agility properties to be rapid reaction to alcohol, water amine, etc., in the normal temperature. In general, the reaction of PVA and TDI to be used to make agglomerant [4], which has no related

*Corresponding author.

Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

report in the membrane area. In this paper, the effects of the reaction time and PVA, TDI, sodium dodecyl sulfate and sodium hydroxide with different concentrations were investigated on the performances of composite membranes, and anti-fouling and cleaning experiments also were conducted.

2. Experimental

2.1. Materials, reagent and apparatus

Polyethersulfone membrane (MWCO 100,000, Ande membrane), PVA (Beijing organic chemical plant, polymerization degree 1799), TDI (reagent grade, Tianjin Guangfu Fineness Chemical Engineering Institute), SDS (chemically pure, Beijing Xudong Chemical Plant) and sodium hydroxide (chemically pure, Beijing Chemical Plant), cyclohexane (analytical chemical grade, Beijing Chemical Plant), egg albumin (MWCO 43,000, Tianjin Zhongshan Institute). All the materials are commercial products and were used without further purification.

Ultraviolet spectrophotometer (UV-2500, SHIMADZU), Infrared spectrometer (Vert-ex70, BRUKER), TOC determinator (TOC-V CPH, SHIMADZU), flat UF device (Shanghai Yadong Nuclear Grade Resin Co. Ltd).

2.2. Composite UF membrane preparation

In this paper, the thin PVA top-layer of composite UF membrane was prepared by interfacial polymerization. Quantitative PVA was dissolved in the de-ionized water, then SDS and sodium hydroxide were added, and mixed at a certain temperature, and quantitative 2,4-toluene diisocyanate was dissolved in cyclohexane solution, respectively. Then PES support membrane was immersed in the aqueous solution for 5 min, fetched and detached extricate solution and volatilized a part of solvent, then immersed in organic solution for some time, fetched and dried in shade for some time.

2.3. UF performance test

2.3.1. Flux of pure water permeate

The behaviour of an UF membrane is characterized by two experimental parameters namely, flux of pure water permeate ' J ' expressed in $L/(m^2 h)$ and the retention of egg albumin. Flux of pure water permeate is given by

$$J = \frac{Q}{At}$$

where Q represents the mass of water in permeate (L), A is the membrane area ($45 \times 10^{-4} m^2$), and t represents the evaluation time (h). The operating pressure and temperature were 0.1 MPa and 20°C respectively.

2.3.2. Retention

The retention which may be quantified by the dimensionless ratio, R , is defined as follows:

$$R = (C_f - C_p) / C_p \times 100\%$$

where C_f , C_p represents the feed and permeate concentrations of both components (egg albumin or oil). Among other things, egg albumin was determined based on the UV spectrophotometer measured at 280 nm, and oil water was determined based on the TOC determinator.

2.3.3. Anti-fouling and cleaning test

Pure water flux generally represents the highest flux that can be obtained from a membrane, which is also used as an indicator of cleaning efficiency [5]. Pure water flux of each new membrane was determined, J_1 was recorded. Then its water flux was determined under the same operating condition while treating oil water. After cleaning, the pure water flux of the same membrane was determined, J_2 was recorded again, and the recovery ratio of pure water flux (J_2/J_1) was calculated.

3. Results and discussion

Interfacial polymerization reaction is presented in Fig. 1, $-\text{OH}$ in PVA can react with $-\text{NCO}$ in TDI and $-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$ will be created [6].

3.1. Influential factors

3.1.1. Reaction time

The interfacial polymerization can occur at room temperature and quite low concentrations of monomers, but which may slow down the speed of the reaction. To obtain an excellent composite membrane, four assays were designed referring to reaction time (30, 60, 120, and 180 s) with PVA 0.5% (wt.), TDI 0.2% (vol.), sodium hydroxide 0.4% (wt.) and SDS 0.4% (wt.). Pure water flux and retention of composite membranes are listed in Table 1. It was showed that the maximum retention of egg albumin ($R = 100\%$) and lower pure water flux occurred at 30 and 60 s, which further confirmed that the reaction of PVA and TDI could occur quickly. Longer reaction time (120 and 180 s) would lead to higher pure water flux and lower retention. It can be concluded that suitable reaction time was between 30 and 60 s.

3.1.2. Monomers' concentration

The concentration of PVA and TDI greatly affects the performance of top layer of composite membrane. Table 2 shows the pure water flux declined with the increase of TDI concentration, while the retention of egg protein of composite membranes increased during the initial stage and

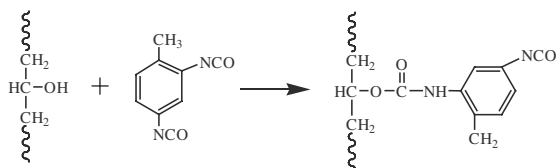


Fig. 1. Interfacial polymerization reaction between PVA and TDI.

Table 1

The effects of the reaction time on the composite membranes' performances

Reaction time, s	30	60	120	180
Pure water flux, L/(m ² h)	204.7	217.4	289.1	298.1
Retention of egg albumin, %	100	100	96	95

then decreased with the increase of TDI as maintaining the content of reaction time 1 min, PVA 0.5% (wt.), sodium hydroxide 0.4% (wt.) and SDS 0.4% (wt.). Considering the two performances, pure water flux and retention, better TDI concentration range should be 0.08–0.5% (wt.).

Table 3 shows the pure water flux increased with the rise of PVA concentration in the first stage and then kept constant, while the retention of egg protein increased during the initial stage and then decreased with the increase of PVA as keep the content of TDI 0.8% (vol.), sodium hydroxide 0.4% (wt.) and SDS 0.4% (wt.) unchanged. Composites with better performances could be obtained at PVA 0.5–2% (wt.).

Tables 2 and 3 tell us that higher PVA and lower TDI concentration could lead to complete interfacial polymerization and largely redundant $-\text{OH}$ on the composite surface, which may be the main reason of hydrophilicity improvement of composite membrane. One more thing is suggested that higher pure water flux of composite is related to higher PVA concentration.

3.1.3. Sodium dodecyl sulfate concentration

Sodium dodecyl sulfate (SDS) could reduce the surface tension of aqueous solution, which would be beneficial to the transport of monomers at the interface between water and organic phase and result in thin and integrated surface layer. The effects of SDS with various concentrations were studied on the performances of composites when reaction time was 1 min, PVA was 0.5% (wt.), TDI was 0.8% (vol.) and sodium

Table 2
The effects of the TDI on the performances of composite membranes

TDI content, %	0.08	0.1	0.2	0.4	0.5	0.8	1.6	3
Pure water flux, L/(m ² h)	248.7	218.7	217.4	190.5	186.6	113.5	129.2	114.0
Retention of egg albumin, %	95	99	100	97	93	99	98	93

Table 3
The effects of the PVA on the performances of composite membranes

PVA content, %	0.1	0.25	0.5	1	2	2.5	5
Pure water flux, L/(m ² h)	32.3	99.6	113.5	145.5	139.55	134.8	137.2
Retention of egg albumin, %	89	100	100	99	96	94	91

hydroxide was 0.4% (wt.), which is shown in Table 4. Pure water flux and retention synchronously increased in the initial stage and then decreased with the increase of SDS concentration. The suitable content of SDS ranges from 0.8% to 1.0%. The performance is better at a higher concentration, especially sodium dodecyl sulfate at 0.8–1% (wt.).

3.1.4. Acid absorbent concentration

Acid absorbent is another factor influencing the characteristics of composite membranes. CO₂ would be produced in the polymerization reaction between PVA and TDI, which could block the reaction if it is not removed from the

products. In this paper, sodium hydroxide (NaOH) was used as the acid absorbent. Table 5 showed the effects of NaOH on the performances of composites (reaction time 1 min, PVA 0.5% (wt.), TDI 0.6% (vol.), SDS 0.8% (wt.)). Pure water flux and retention increased rapidly with the increase of NaOH concentration and then decreased, while the retention of egg albumin changed randomly.

This may be explained as follows. When NaOH concentration was increased, the increase of NaOH is not only neutralize CO₂ on time, but also form sodium alcoholate reaction in polymerization reaction, and make reaction go with aswing. While excessive NaOH would accelerate the hydrolyzation of TDI, which could lead to

Table 4
The effects of SDS on the performances of composite membranes

SDS content, %	0	0.1	0.2	0.4	0.8	1.0	1.5
Pure water flux, L/(m ² h)	46.1	61.4	72.6	71.3	113.5	95.6	94.5
Retention of egg albumin, %	87	85	98	93	100	100	90

Table 5
The effects of sodium carbonate on the performances of composite membranes

NaOH content, %	0	0.1	0.2	0.4	0.8	1.0
Pure water flux, L/(m ² h)	90.3	102.8	152.6	145.3	118.6	98.2
Retention of egg albumin, %	100	93	99	100	94	93

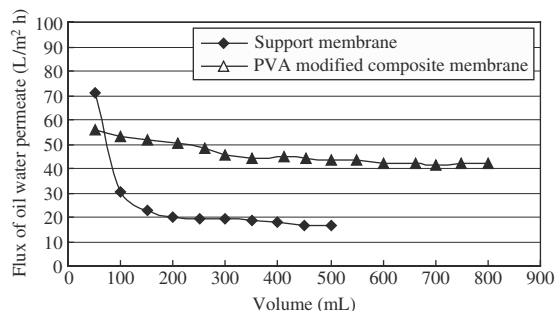


Fig. 2. Oil anti-fouling experiment. (Composite membrane was prepared in the following conditions, PVA 1% (wt.), TDI 0.2% (vol.), sodium hydroxide 0.4% (wt.), SDS 0.8% (wt.), reaction time 1 min).

incomplete interfacial polymerization. The best NaOH concentration was 0.2–0.4% (wt.)

3.2. Anti-fouling and cleaning experiment

3.2.1. Anti-fouling experiment for longer time

The oil removals of both composite and support UF membranes were 92% and 80% respectively when they were used to treat oil waste water under a pressure of 0.1 MPa at room temperature. The water flux were also determined under the same operating conditions and the data are plotted in Fig 2. Although the initial water flux of support was 70 L/(m² h), the final water flux was only 20 L/(m² h) after a long time work, comparing with initial water flux of support was 55 L/(m² h), and the final water flux was 40 L/(m² h) of the composite, which further proved that the composite membrane with thin PVA layer that full of –OH had better anti-fouling

performance than the PES support membrane, because of less adsorption of oil on the surface or in the pores of membranes.

3.2.2. Cleaning experiment

PVA modified composite membrane have very preferable anti-fouling properties, which not only behave in anti-fouling experiment for longer time, but also in cleaning experiment. Both PVA modified composite membrane and support membrane were used to clean with 0.3% NaOH liquor after oil wastewater treatment for a long time, and the regenerated membrane seems to have a comparative performance of anti-fouling (Table 6). Compared with PVA modified composite membrane and support membrane, the recovery ratio of pure water flux of the former is 91% and the latter is only 84%. Pure water flux was still remaining at relatively high level. It is obvious that PVA modified composite membrane has the better oil anti-fouling than support membrane.

3.2.3. PVA identification

The FTIR spectra of three membranes are observed as seen in Fig. 3a–c: Polyethersulfone (PES) support, PVA modified composite membrane, used PVA modified composite membrane after oil water removal test.

There is no absorption maximum at 3400 cm⁻¹ for the support membrane in Fig. 3a, which showed no –OH of PVA exist in the surface. But PVA could exist in the surface after PVA modified Fig. 3b: the strong peaks observed at 3312 cm⁻¹

Table 6

The recovery ratio of pure water flux

Membrane category	Support membrane	PVA modified composite membrane
Pure water flux, L/(m ² h)	361.1	208.4
Pure water flux after cleanout, L/(m ² h)	306.9	189.9
Recovery ratio, L/(m ² h)%	84	91

are the characteristics of the hydroxyl group ($-\text{OH}$) of PVA and the peak at 1650 cm^{-1} is the characteristic peak of the carbonyl group ($\text{C}=\text{O}$) because of production amide, respectively. On the other hand, the group $\text{N}=\text{C}=\text{O}$ peak at 2270 cm^{-1} does not exist, since the group $\text{N}=\text{C}=\text{O}$ in TDI has been depleted when PVA is excessive. The FTIR spectrum in Fig. 3(c) shows the characteristic peak of the carbonyl group ($\text{C}=\text{O}$) at 1645 cm^{-1} as seen in Fig. 3(b) and also related to hydroxyl group ($-\text{OH}$) of PVA near 3400 cm^{-1} is observed.

From the above observation, one can suggest that the existence of PVA molecules on the PVA modified composite membrane, which is the result that the hydroxyl group of PVA modified

is not only physically adsorbed on the membrane but also chemically bound by forming a covalent bond with polymer molecules on the composite layer particles. Therefore, PVA is working as a hydrophilic stabilizer in our present system, and PVA would not efflux from the top layer of the composite membrane with PVA when the membrane was used for performance measurement and long-time poaching.

If PVA modified composite membrane is put into hot water at $90\text{--}100^\circ\text{C}$ for long time, it was tested through pure water flux and retention after that. The result is that the less variety between two tests (pure water flux from 199.2 to $199.1\text{ L}/(\text{m}^2\text{ h})$ and pure water flux from 100% to 100%) These showed that PVA could enter into the top lay of composite UF membrane frame through reaction or adsorption.

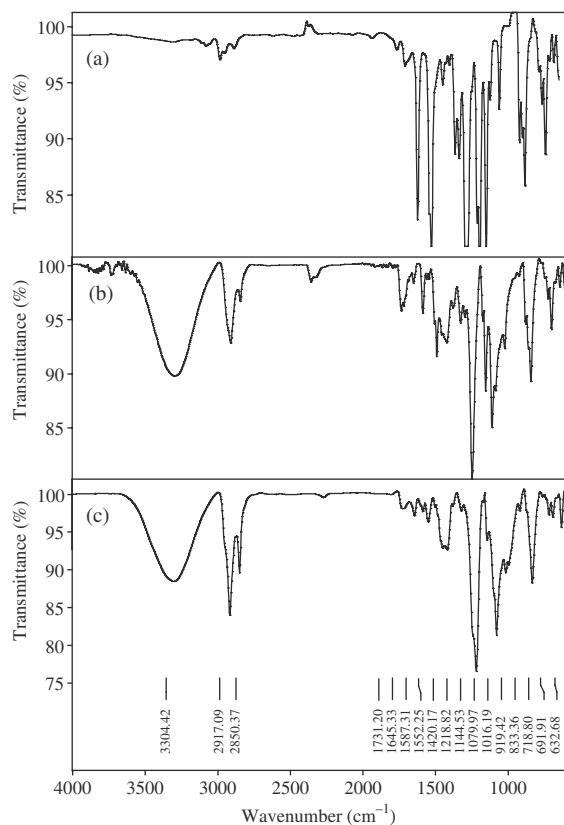


Fig. 3. FTIR spectra of support membrane, PVA modified composite membrane and it after oil water removal test.

4. Conclusions

The modified PVA composite UF membrane with good water flux and anti-fouling performance was prepared by interfacial polymerization in the best condition PVA $0.5\text{--}2\%$ (wt.), TDI $0.08\text{--}0.5\%$ (vol.), sodium hydroxide $0.2\text{--}0.4\%$ (wt.), SDS $0.8\text{--}1\%$ (wt.) and at $30\text{--}60\text{ s}$. The modified PVA composite UF membrane with thin hydrophilic PVA layer had better anti-fouling performance than PES support membrane.

When PES UF membrane was used as the support, the oil removal and water flux could get to 92% and $40\text{ L}/(\text{m}^2\text{ h})$, respectively, for the composite membrane, which were only 80% and $20\text{ L}/(\text{m}^2\text{ h})$ for the support membrane. And PVA could exist in composite membrane through chemical modify, which reserve PVA's hydrophilicity.

Acknowledgements

The authors thank Prof. Liu Zhongzhou (Research Center for Eco-Environmental Science, the Chinese Academy of Sciences for valuable discussions.) for his invaluable and constructive

assessment of the manuscript. The authors also thank the financial support of Beijing Municipal Commission of Education.

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