

Preparation and application of P84 copolyimide/GO mixed matrix membrane with improved permselectivity and solvent resistance

Runlin Han^{a,b,*}, Yuhang Zhang^b, Xufeng Ma^b, Da Teng^b, Yongli Xie^b, Qibin Luan^b

^aSchool of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an 343009, China, Tel. +86-13842712519; Fax: +86-4272631518; email: hanrunlin@163.com

^bSchool of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin 124221, China, emails: zhangyuhang666@mail.dlut.edu.cn (Y. Zhang), maxufeng19940320@mail.dlut.edu.cn (X. Ma), tengdabetty@163.com (D. Teng), lililu@mail.dlut.edu.cn (Y. Xie), qbluan@126.com (Q. Luan)

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ABSTRACT

Multilayer graphene oxide (GO) is introduced to prepare P84/GO hybrid membrane to enhance the permselectivity of polyimide membrane while triethylenetetramine is used to improve the solvent resistance of the membrane. Effect of GO content on performance and morphology of P84/GO mixed matrix membrane is researched in detail. The membrane shows high rejection (100%) to gentian violet (408 Da) and high flux ($118 \text{ L m}^{-2} \text{ h}^{-1}$) at 0.1 MPa and ambient temperature when the casting solution contains 18% P84 and 2% GO. The membrane shows excellent solvent resistance in dimethylformamide, acetone and methanol when it is immersed in the pure solvent for 18 d.

Keywords: Solvent resistance; Polyimide membrane; Mixed matrix membrane; Thermal resistance; Graphene oxide (GO)

1. Introduction

Nanofiltration (NF) membrane is introduced in the early 1980s with nominal molecular weight cut-off (MWCO) ranging from 200 to 1,000 Da. Because of low operating pressure and reduced costs, it is widely used in water desalination, wastewater treatment, pharmaceutical and food industry [1]. Organic solvents which are greatly used in chemical engineering are often difficult to recycle during the process of chemical synthesis or dissolution. Development of a green method to reuse organic solvents is demanding. Due to the low resistance of polymer material in strongly polar aprotic solvent, NF is limited in the chemical and petrochemical process [2]. Solvent resistant nanofiltration (SRNF) which is an effective technology in solvent treatment has been paid more and more attention in these decades. However, the solvent resistance of the polymer membrane is still the main problem in the development of SRNF

technology because most of the polymer materials will swell or dissolve in some strong organic solvents such as acetone and *N,N*-dimethylformamide (DMF) during separation process [3]. Different polymer materials which are solvent resistant after cross-linking are used to prepare SRNF membrane including polyacrylonitrile [4,5], polyimide (PI) [6] and polydimethylsiloxane [7]. Ethylene-chlorotrifluoroethylene, low melting point HALAR® ECTFE (LMP ECTFE), is also used as a polymer for the preparation of solvent-resistant membranes with excellent solvent resistance [8].

PIs are widely studied for the preparation of membranes used in SRNF process because of their comprehensive performance including solvent resistance, thermal resistance and chemical stability [9–12]. Diols including ethylene glycol, 1,4-butylene glycol and diamines such as aliphatic, aromatic and polymeric diamines have been selected as cross-link reagents of PI SRNF membranes. These active molecules will react with PI chains and form new amide bond between polymer chains [13,14]. PI membrane after

* Corresponding author.

cross-linking often shows improved solvent resistance with MWCO ranging from 200 to 400 Da. Polyethylenimine is also used to prepare SRNF membrane and it is positively charged and shows excellent solvent resistance [15].

Graphene oxide (GO) is one of the most studied nano-sized materials for membrane preparation because of its polar structure with epoxide, hydroxyl and carboxy groups which is favorable for the good compatibility with the polymer matrix [16]. It is also demonstrated a good membrane material for its stratified structure which provides suitable ion channels and improves the selectivity during the membrane separation process [17–19]. At the same time, it has good solvent resistance and is stable in the polymer matrix [20].

Mixed matrix membrane often has improved fouling resistance and good permselectivity because of the hydrophilic inorganic additive and interaction with polymer matrix [21]. P84/MXene membrane with high permselectivity and solvent resistance has been prepared in our group which shows meaningful application in dye separation [22]. It is found that the 2D material MXene has positive effect on the membrane performance. However, the preparation process of MXene is a little complicated and dangerous for using concentrated HF [23]. GO, which possesses the similar performance as MXene, is easy to obtain. In this work, GO is incorporated in the P84 matrix to improve the permselectivity of the mixed matrix membranes while triethylenetetramine (TETA) is utilized to improve the solvent resistance of the membrane. Scanning electron microscope (SEM), atomic force microscope (AFM), fourier transform infrared spectroscopy (FTIR) and solvent stability measurements were used to test the influence of GO on membrane morphology and performance.

2. Experimental

2.1. Materials and instruments

P84 (HP Polymer Inc., Mw: 25,000) is used to prepare the casting solution with GO (Tanfeng Tech Inc., China) as the inorganic additive. The P84/GO mixed matrix NF membranes are fabricated with non-solvent immersion phase conversion method. TETA is introduced to crosslink the nascent NF membrane. *N,N*-Dimethylacetamide (DMAc), DMF, acetone, methanol and other chemicals utilized in this work are all analytical purity grade and used as received. A dead-end filtration apparatus with membrane area of 41 cm² is used to analyze the permselectivity of the NF membrane. Continuous stirring of the filtration solution with a magnetic stirrer is to decrease the effect of concentration polarization during the dead-end filtration. UV–Vis Spectrometer (721, Shanghai Youke, Shanghai, China) is used to test the dye concentration. The water contact angle of the membrane top surface is tested with contact angle meter (WCA, SL200KB).

2.2. Membrane preparation

18% (w/w) P84 is dissolved in solvent DMAc to prepare casting solution. In order to prepare P84/GO mixed matrix membrane, inorganic additive GO with different contents is added in the casting solution with strong stirring. The

membranes are cast with a scraper on a clean glass plate and then immersed in the coagulation bath at about 20°C. The nascent membranes are immersed in the coagulation bath at least 12 h for solvent exchange, then immersed in the cross-link reagent with 1 wt.% TETA at 80°C for 10 min. Then the excessive reagent in the membrane matrix is cleaned with de-ionized water. The membranes are named as M0 (no GO), M1 (0.5% GO), M2 (1% GO), M3 (1.5% GO) and M4 (2% GO) according to the additive content of GO.

2.3. Membrane characterization

Membranes with different GO content are prepared with phase inversion method and cross-linked with TETA to improve the comprehensive performance of the membrane. The membranes are tested with contact angle meter. SEM (FEI Nova NanoSEM 450) is used to characterize the morphology of the mixed matrix membrane with the gold sputtering. Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) (Nicolet-20DXB) is utilized to characterize the composition of the membrane surface with different content of GO. Flux (F) and rejections (R) to different dyes are introduced to characterize the permselectivity of the mixed matrix membrane. The membranes are tested at 0.1 MPa and 20°C and pre-pressed under 0.2 MPa for 30 min. The concentrations of Gentian Violet and Congo Red solution are all fixed 0.1 g L⁻¹. F , the permeation flux, can be calculated as follows:

$$F = \frac{V}{At} \quad (1)$$

where V means the permeated solution volume; A represents the area of filtration solution passing through; while t means the process time. Following equation is used to calculate the rejection (R):

$$R = \left(1 - \frac{C_p}{C_f} \right) \% \quad (2)$$

C_p means the concentration of permeated solution while C_f is the concentration of the filtration solution. All the data are based on the three repeated experiments.

3. Results and discussion

3.1. Morphology of NF membranes with different GO content

Heterogeneous mixed matrix membrane which embeds inorganic additive in the polymer matrix combines the advantages of inorganic material and polymer material. It often shows improved permselectivity and mechanical stability. Fig. 1 displays the SEM images of top surface and cross-section morphology of the mixed matrix membranes. With the increase of GO content, the membrane surface becomes more and more rough and more protuberances shown in the membrane surface. As shown in the inset of top surface morphology with magnification of 100,000, there is no defect even the membrane is prepared with 2% GO, which demonstrates that all the membrane surfaces are very dense.

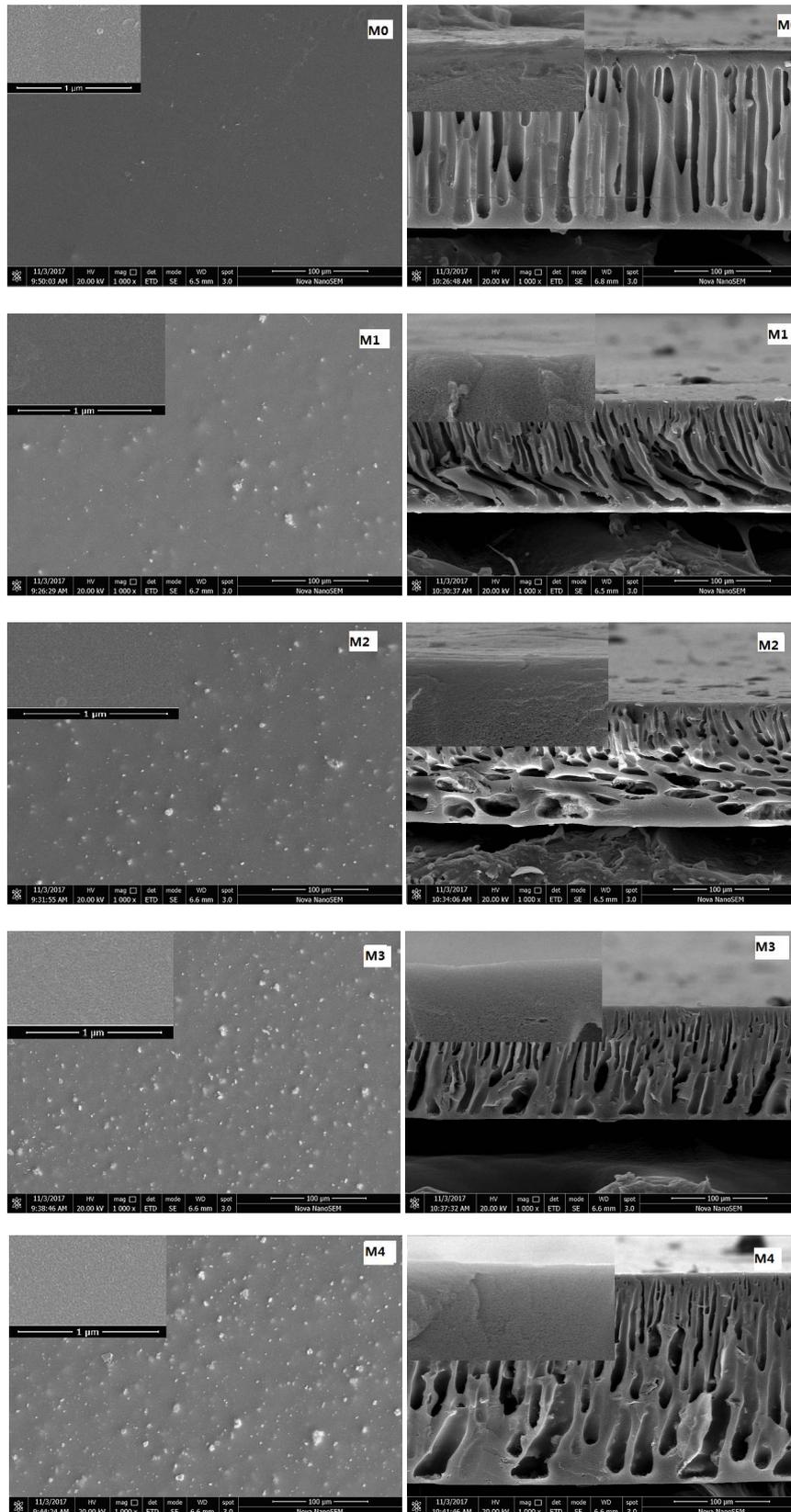


Fig. 1. Effect of GO content on the morphology of nanofiltration membranes (a): the top surface morphology with magnification times of 1,000 and the inset is top surface morphology with higher magnification times of 100,000. (b): the cross-section morphology with magnification times of 1,000 and the inset is cross-section morphology with higher magnification times of 10,000.

Neat finger-like pores in the cross-section morphology changes to irregular pores obviously and the dense skin layer becomes thinner. As shown in the inset of cross-section morphology, the membranes with different contents of GO all have very dense skin layer.

3.2. AFM images of the membrane with different GO concentrations

As shown in Fig. 2, AFM images of membranes prepared with different GO content change obviously. The pure P84 membrane shows little peaks in the top surface while P84/GO membranes show more peaks or protuberances in the top surface. The root mean square data also demonstrate

that rougher membrane surface will be formed at high content of GO. This phenomenon is consistent with the images observed by SEM, which is caused by the particle aggregation of GO in P84 matrix.

3.3. ATR-FTIR of the mixed matrix membranes prepared with different GO contents

The characteristic peaks of membranes prepared with different GO content are displayed in Fig. 3. The peaks at 1,717 and 1,779 cm^{-1} represent the absorption bands of C=O symmetric stretch vibration and C=O asymmetric stretch vibration of the imide group while peak at 1,362 cm^{-1} is the C–N stretching. Because the mixed matrix membranes are

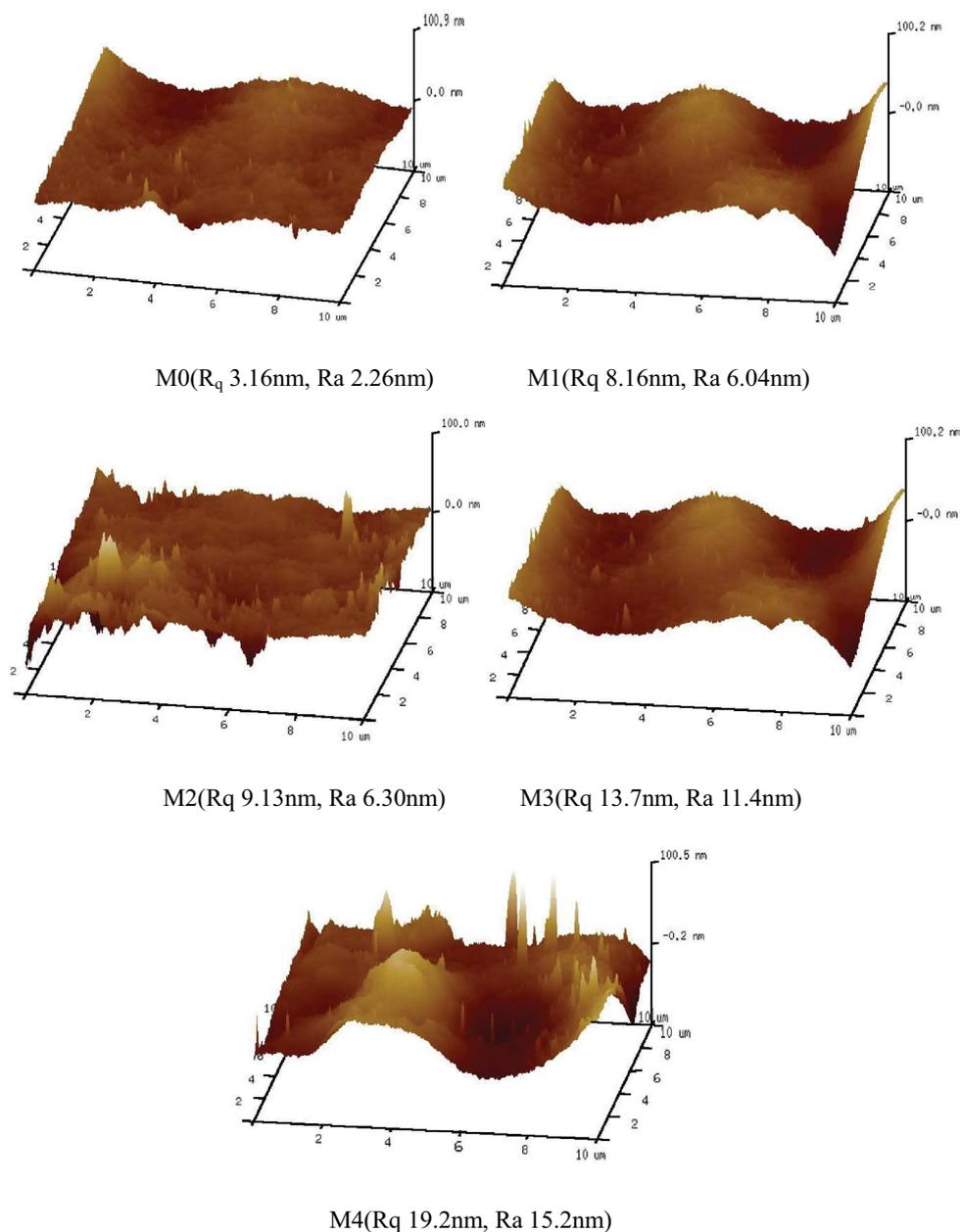


Fig. 2. AFM images of membranes prepared with different GO contents.

prepared at room temperature, GO with polar functional groups will not react with P84 polymer matrix and little change of characteristic peak is observed in the spectrum.

3.4. Effect of GO content on the performance of P84/GO mixed matrix membrane

It is found that the contact angle of the membrane does not change obviously as shown in Table 1. The GO is uniformly encapsulated in the polymer matrix which changes

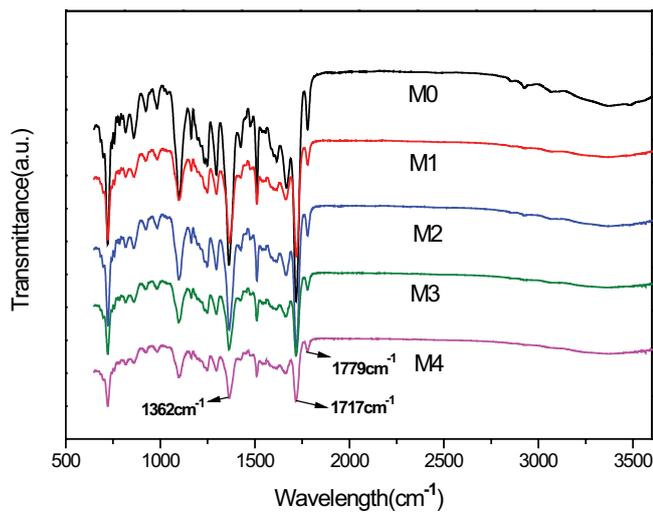


Fig. 3. FTIR-ATR spectrum of the top surface of membranes with different GO content (From top to the bottom are: M0, M1, M2, M3 and M4.).

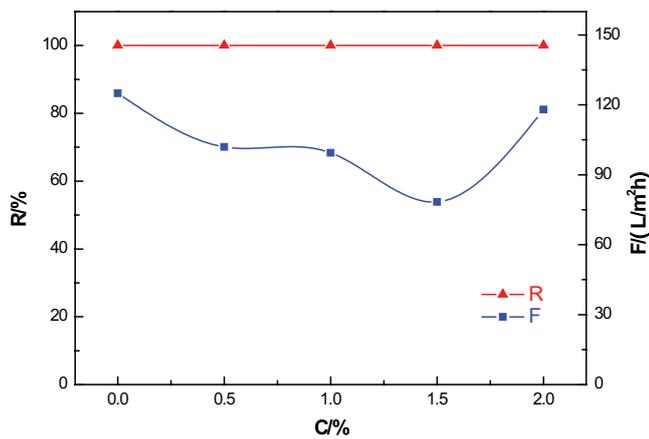


Fig. 4. Effect of GO content on the performance of P84/GO membrane (0.1 MPa, 100 mg L⁻¹ Gentian Violet).

Table 1
Contact angle of the mixed matrix membranes

Membrane	M0	M1	M2	M3	M4
GO content %	0	0.5	1	1.5	2
Contact angle°	74	74	74	73	72

the membrane surface characteristic little. It can be found from Fig. 4 that all the membrane’s rejections to Gentian Violet dye are 100%. It demonstrates that the functional layer is very dense. According to the inset of cross-section morphology, the membrane functional layer becomes denser with the increase of GO content which will decrease the membrane flux. However, More GO also induces thinner skin layer as shown in the cross-section morphology. So the membrane flux decreases first then increases because of the synergetic effect.

In order to study the solvent resistance of the mixed matrix membrane, the membrane (M4) with relatively high flux is immersed in different polar solvents including acetone, DMF and methanol statically and characterized every 3 d. As shown in Figs. 5–7, the membranes show excellent solvent resistance because none of the membranes falls apart and the rejections to different dyes are all kept 100%. Clearly, TETA is an effective cross-link reagent that endows the P84/GO membrane with excellent solvent resistance. During the stability test, the membrane surface is dyed. Adsorption of dye molecules in the membrane surface may be the main reason for the continuous decline of membrane

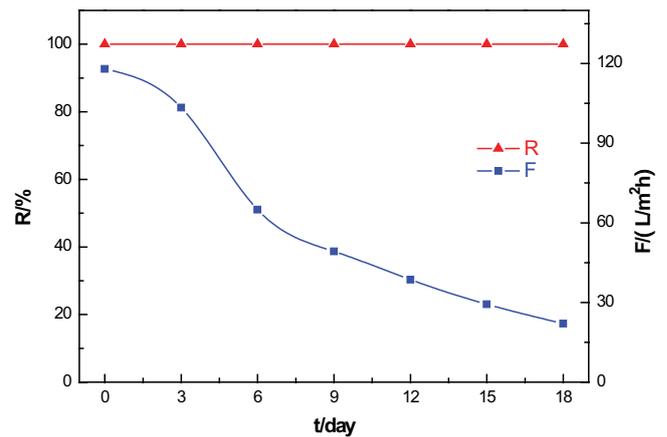


Fig. 5. Solvent resistance of the mixed matrix membrane (0.1 MPa, 100 mg L⁻¹ Gentian Violet, acetone).

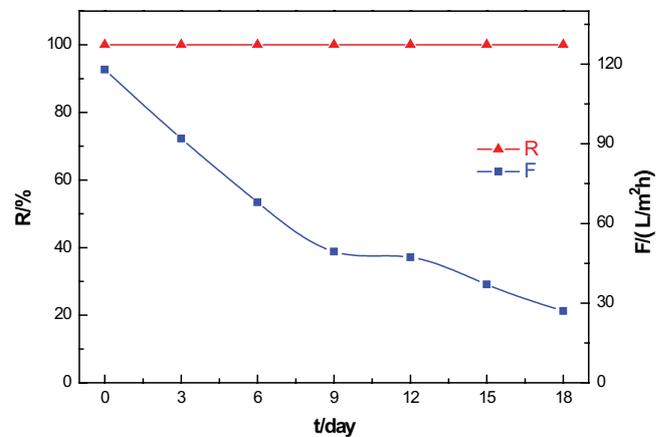


Fig. 6. Solvent resistance of the mixed matrix membrane (0.1 MPa, 100 mg L⁻¹ Gentian Violet, DMF).

flux. Moreover, the P84 membrane is often prepared with DMF used as solvent because DMF is a good solvent of P84. So the mixed matrix membrane cross-linked with TETA shows excellent solvent resistance and is a potential treatment technology candidate of organic solvent wastewater.

Congo Red (697 Da) dye is also applied to investigate the separation performance and solvent resistance of mixed matrix membrane and the results are shown in Fig. 8. It is found that, under the pressure of 0.1 MPa, the rejection

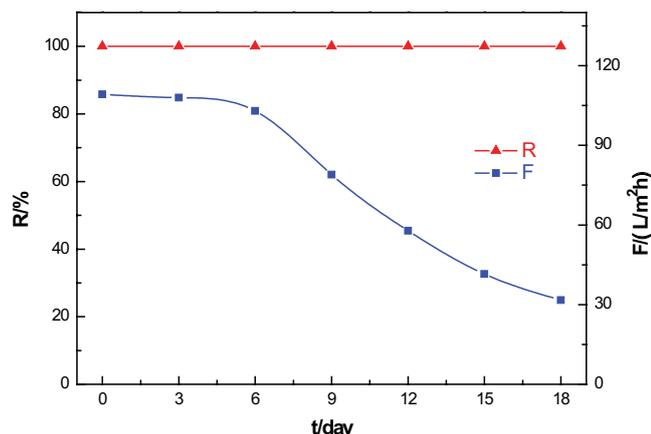


Fig. 7. Solvent resistance of the mixed matrix membrane (0.1 MPa, 100 mg L⁻¹ Gentian Violet, methanol).

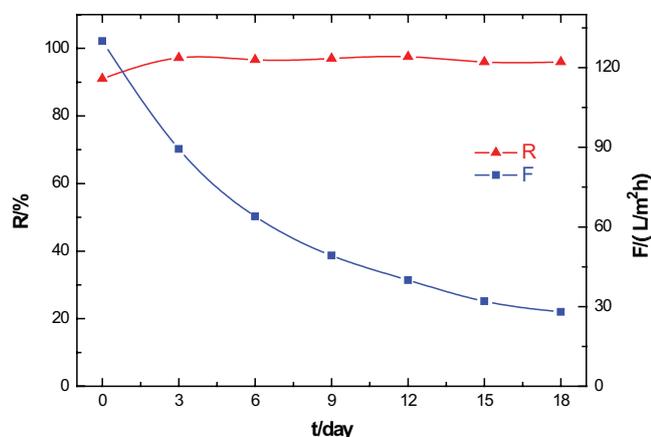


Fig. 8. Solvent resistance of the mixed matrix membrane (0.1 MPa, 100 mg L⁻¹ Congo Red, DMF).

to Congo Red dye remains stable while membrane flux decreases during 18 d. The flux decreases persistently which may be caused by dye adsorption in the membrane pores, but it is still 27 L m⁻² h⁻¹ at 0.1 MPa at last.

PI membrane often has excellent thermal resistance because of its heterocyclic structure. In order to test the thermostability of the mixed matrix membrane, the operation temperature is elevated to 80°C operated with cross-flow apparatus with flow velocity of 5 L h⁻¹. The membrane rejection to Gentian Violet is still 100% while the membrane flux is elevated. It is found from Fig. 9 that the membrane flux increases about four times compared with the flux at 20°C. The permselectivity of the P84/GO membrane is also compared with other SRNF membranes although the solutes used are different. As shown in Table 2, the P84/GO membrane shows excellent performance especially high flux.

4. Conclusions

It is found that the P84/GO mixed matrix membranes have excellent performance with facile preparation method. At 0.1 MPa and ambient temperature, the membrane's rejections to Gentian Violet and Congo Red are all 100% with high flux about 118 L m⁻² h⁻¹. As the improvement of GO content, the membrane shows denser and rougher functional layer. After crosslinking with TETA at 80°C for 10 min,

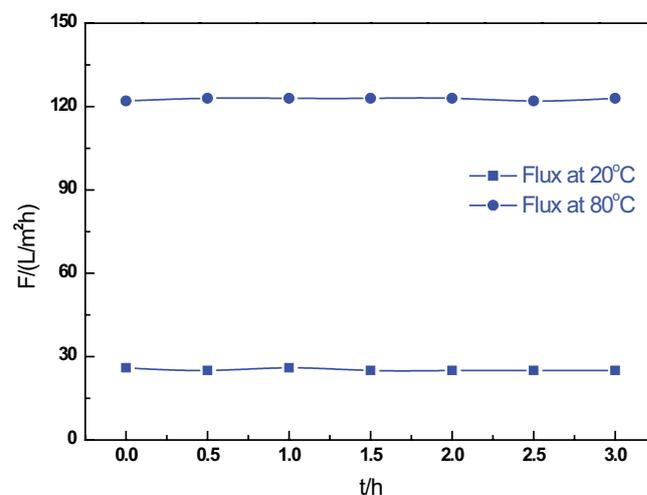


Fig. 9. Thermal resistance of the mixed matrix membrane (100 mg L⁻¹ Gentian Violet, flow velocity 5 L h⁻¹).

Table 2
Comparison of the membrane performance with literatures

Membrane materials	Testing solution (MW)	Concentration/(mg L ⁻¹)	F/(L m ⁻² h ⁻¹ bar ⁻¹)	R/%	References
Polyimide-P84	Gentian violet (408)	100	118	100	This work
PAN	Methyl orange (327)	/	1	20	[4]
Polyimide-P84	Methyl orange (327)	100	~6	92	[14]
Polyimide-Matrimid®	Methyl orange (327)	11.5	5.4	95	[24]
Polyimide-P84	Eosin Y (648)	50	16.4	98	[25]

MW – molecular weight (g mol⁻¹).

the membrane shows excellent solvent resistance. During static immersion in pure solvents such as DMF, acetone and methanol, the rejections to Gentian Violet and Congo Red do not decline while the flux decrease with operation time. The membrane filtration experiment is also run at elevated temperature in the cross-flow filtration. When the operation temperature is elevated from 20°C to 80°C, the membrane rejection does not decline while the membrane flux increases about four times which is meaningful for the high temperature fluid operation.

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