

Article

Crosslinked P84 copolyimide/MXene mixed matrix membrane with excellent solvent resistance and permselectivity☆

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ABSTRACT

MXene is a novel 2D lamellar material with excellent hydrophilicity and permselectivity. MXene was introduced in the P84 polymer matrix and the matrix was crosslinked with triethylenetetramine (TETA) to improve the permselectivity and solvent resistance of the polyimide membrane. The membrane was characterized with SEM, AFM and ATR-FTIR, and effects of MXene content on the membrane morphology and separation performance are investigated. The membrane prepared with 18% P84 and 1% MXene shows high rejection (100%) to gentian violet (408) and high flux ($268 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) at 0.1 MPa and ambient temperature. MXene endows the membrane with much water channel and denser functional layer which improves the membrane performance obviously. The membrane shows excellent solvent resistance to dimethylformamide (DMF), acetone and methanol after crosslinking with TETA during the 18 days of immersion.

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1. Introduction

Nanofiltration (NF) membranes with nominal molecular weight cut-off from 200 to 1000 are extensively used in (waste) water treatment thanks to their excellent performance, low cost and relative energy efficiency [1]. The most prevalent nanofiltration membranes are thin film composite (TFC) membranes with a thin dense top layer and a porous support on non-woven substructure for mechanical strength [2]. The dense top layer is typically made of polyamide (PA) via interfacial polymerization [3]. However, this PA layer is highly reactive towards oxidizing agents such as chlorine and its derivatives which are often used as water disinfectants and bactericides [4]. The classical uncrosslinked nanofiltration (NF) membranes prepared through non-solvent induced phase inversion are unstable in organic solvents, again demonstrating their poor chemical resistance. In contrast, polyimide (PI) exhibits high thermal and chemical stability, and good mechanical properties. PI membranes with elevated chlorine resistance are prepared by interfacial polymerization of m-phenylene diamine (MPD) and 1,2,4,5-benzene tetracarbonyl chloride (BTC) with subsequent thermal imidization [5]. PI is also widely used for membranes in the field of solvent resistant nanofiltration (SRNF), since it can easily be crosslinked with polyamines and polyalcohols [6–11]. These crosslinking agents can react on both ends with polyimide chains, resulting in breakage of imide bonds and formation of intermolecular amide bonds [12,13].

Recently, a new 2D materials named ‘MXene’ has attracted significant research interest because it exhibits hydrophilic surfaces, good structural and chemical stability [14–16]. MXene is a type of layered 2D material, which is produced by Al etched from MAX phase material (where M represents an early transition metal, A corresponds to III A or IV A group elements, and X is C or N) powders in HF solutions. MXene is studied in preparation of composite membrane for its excellent hydrophilicity, permselectivity and 2D layer structure which is a potential membrane material [17–19].

The combined mixed matrix membrane (MMM) with comprehensive performance is attractive and easy to scale up [20,21]. Polyimide (PI) (P84) is often used to prepare organic solvent nanofiltration (OSN) membranes with crosslinking agent and well-studied in the literature because of its membrane forming ability and permselectivity [20,22]. In this work, triethylenetetramine (TETA) is used to improve the solvent resistance of P84 membrane after the nascent membrane is formed, while MXene is used to prepare P84/MXene MMM with comprehensive performance. Effects of MXene content on membrane performance are investigated in detail and membranes are characterized with SEM, AFM, FTIR and solvent resistance measurements.

2. Experimental

2.1. Materials and instruments

The average particle size of the Ti_3AlC_2 used in the experiment was about $3 \mu\text{m}$ (98%, Beijing Fusiman). It was etched with HF (49 wt%, Aladdin) to get layer MXene. First, 1g Ti_3AlC_2 is dispersed in 10 ml HF with strong stirring for 10 h then filtrated with de-ionized water. The

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MXene is dried at 60 °C for 24 h before utilization. The P84/MXene mixed matrix membranes were prepared with phase inversion method. P84 (HP Polymer Inc., Mw: 25000) was used to prepare the casting solution with MXene as the inorganic additive. TETA was introduced to crosslink the nanofiltration membrane to get solvent resistant nanofiltration membrane. *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), acetone, methanol and other chemicals used in the experiments were all of analytical purity grade, and were used without further purification. A flat sheet dead-end filtration set-up was used to evaluate the performance of the nanofiltration membrane with a magnetic stirrer below the membrane to alleviate the concentration polarization as shown in Fig. 1. The dye concentration was analyzed with UV–Vis Spectrometer (721, Shanghai Youke).

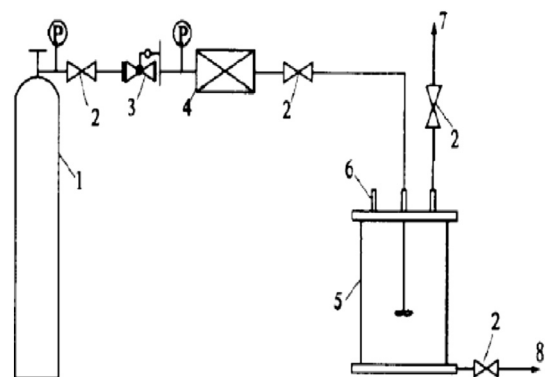


Fig. 1. Flow process chart of test (1. Nitrogen gas cylinder; 2. stop valve; 3. reducing valve; 4. pressure maintaining valve; 5. membrane evaluation apparatus; 6. feed inlet; 7. emptying hole; 8. discharge hole).

2.2. Membrane preparation

Eighteen percent (w/w) P84 solutions in solvent DMAc were used as the membrane solution. In order to prepare P84/MXene mixed matrix membrane, inorganic additive MXene with different contents is added in the casting solution with strong stirring. The membranes with the inorganic additive were prepared by the same method except a certain amount of MXene added in the casting solution. The casting solution is stirred and degassed before use. The membranes were prepared on a glass plate with phase inversion method and the evaporation time of 5 s in the air. The coagulation bath was filled with water at the temperature of about 20 °C. The thickness of prepared membrane is about 150–200 μm. The generated membranes were dipped in the crosslinking reagent solution with 1 wt% TETA at 80 °C for 10 min. Then the excessive solution in the membrane was washed by de-ionized water and stored in de-ionized water before use.

2.3. Membrane characterization

SEM (FEI Nova NanoSEM 450) is used to characterize the morphology of the mixed matrix membrane with the gold sputtering. The membrane was also tested with AFM (Dimension ICON, Bruker) in the 2 μm × 2 μm area. FTIR-ATR spectrum obtained by Nicolet-20DXB was used to characterize the membrane with or without MXene additive. The performance of the membranes is mainly described by product flux (F) and dye rejection (R). The separation performance is characterized with the dead-end membrane set-up with a stirring apparatus. The membranes were pressed under 0.2 MPa for 30 min in order to obtain stabilized membrane performance. The concentrations of Gentian Violet solution were fixed 0.1 g·L⁻¹. The membrane performances including dye solution flux and rejection t were

measured under the pressure of 0.1 MPa at 20 °C. The permeation flux (F) was calculated as follows:

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

where V is the total volume of the solution permeated during filtration process; A is the valid membrane area and the effective membrane area is 41cm²; and t is the operation time. Rejection, R , is calculated using the following equation:

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

where C_p and C_f are the concentration of the permeate solution and the feed solution, respectively. All the experiments on flux and rejection are repeated for three times.

Membranes prepared with different ingredients are listed in Table 1.

Table 1
Substance constitution of the nanofiltration membrane

Membrane	M0	M1	M2	M3	M4
MXene content /%	0	0.5	1	1.5	2
P84 content /%	18	18	18	18	18

3. Results and Discussion

3.1. Morphology of P84/MXene membranes with different MXene contents

The layered MXene material used in this work is characterized with SEM (Fig. 2). The MXene etched with HF has obvious layered structure which is potential channel of mass transfer and the channel size is about 200 nm as shown in the inset of Fig. 2. After the P84 is well-dissolved in DMAc, a certain amount of MXene powders is added into casting solution followed by 30-min sonication and strong stirring to obtain uniform dispersion.

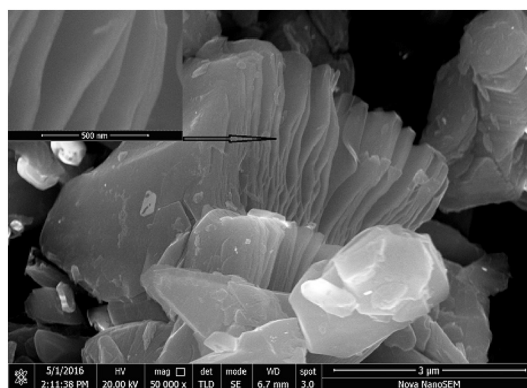


Fig. 2. The layered MXene (the magnification of inset is 200000×).

To investigate the efficacy of various contents of MXene in the P84 membrane, SEM analysis is utilized as shown in Fig. 3. It is evident that the addition of MXene to the matrix of P84 membrane changes the smooth surface to rough surface in the low magnification (×1000) SEM images because of high viscosity of casting solution and phase interface between the additive and polymer matrix at high MXene content. With the increase of MXene, no defect or obvious agglomeration is

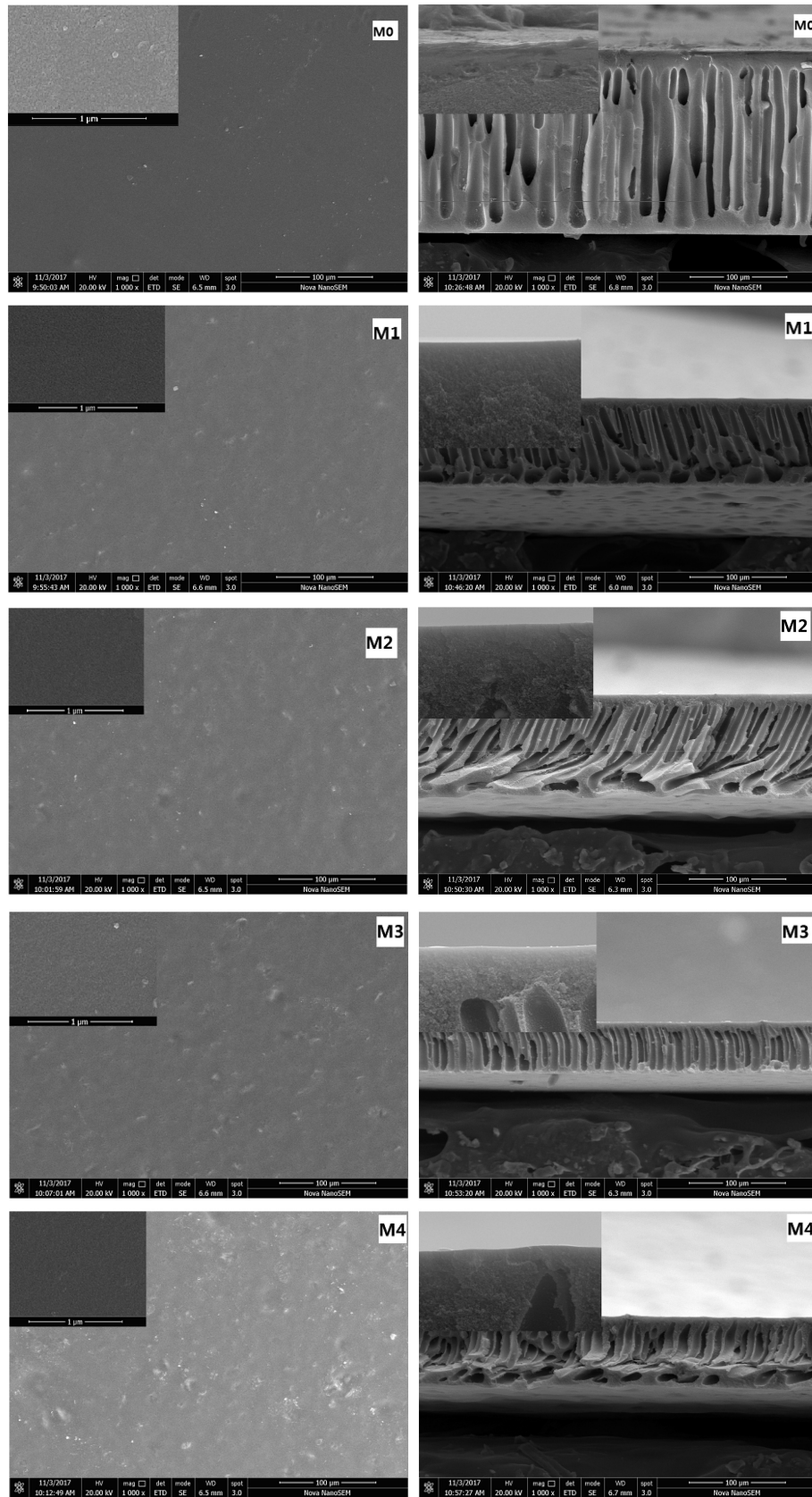


Fig. 3. Effect of MXene content on the morphology of membranes (left: the top surface morphology and the magnification times of inset is 10000 $\times$. Right: the cross-section morphology and the magnification times of inset is 10000 $\times$).

observed at high magnification images in the inset of Fig. 3. The membrane surfaces are all very smooth which demonstrates the good compatibility of these two materials. The asymmetric structure containing finger-like porous sub-layer is shown on the right-hand side of Fig. 3. As can be seen, the top layers of the fabricated membranes are all dense with increase of MXene content. With the increase of MXene content, the membrane thickness is also decreased. However, the membrane flux is dominated by the dense layer of the membrane. So it is found that the membrane flux decreases at last even if the membrane thickness decline. When the MXene content increase further, the casting solution is very viscous which is similar as the characteristic of high polymer concentration. High viscosity and solid content of the casting solution will endow the membrane with denser functional layer and lower flux. Furthermore, a more thin membrane and a vast macro-pores are observed at the bottom of the prepared membranes. The change of membrane cross-section morphology may be induced by the faster exchange of water and the solvent in the phase

inversion method because hydrophilic MXene has good affinity with water [23].

3.2. AFM images of the membrane with different MXene content

Fig. 4 shows AFM images of membranes prepared with different MXene content with a scanning area of $2\ \mu\text{m} \times 2\ \mu\text{m}$. In the small scanning area, pure P84 membrane has a relatively rough surface with some peaks in the surface. With the increase of MXene content, the membrane surface show more small protuberances as shown in the Fig. 4. This trend means that the MXene has good compatibility with the polymer matrix. As shown in the inset of Fig. 3, the membrane surface all dense and smooth at higher magnification ($\times 100000$) for the low aggregation of MXene sheets. But at low magnification ($\times 1000$), the membrane surface changes rougher because of high viscosity of the casting solution and rigid MXene blocks in the polymer matrix at high MXene content.

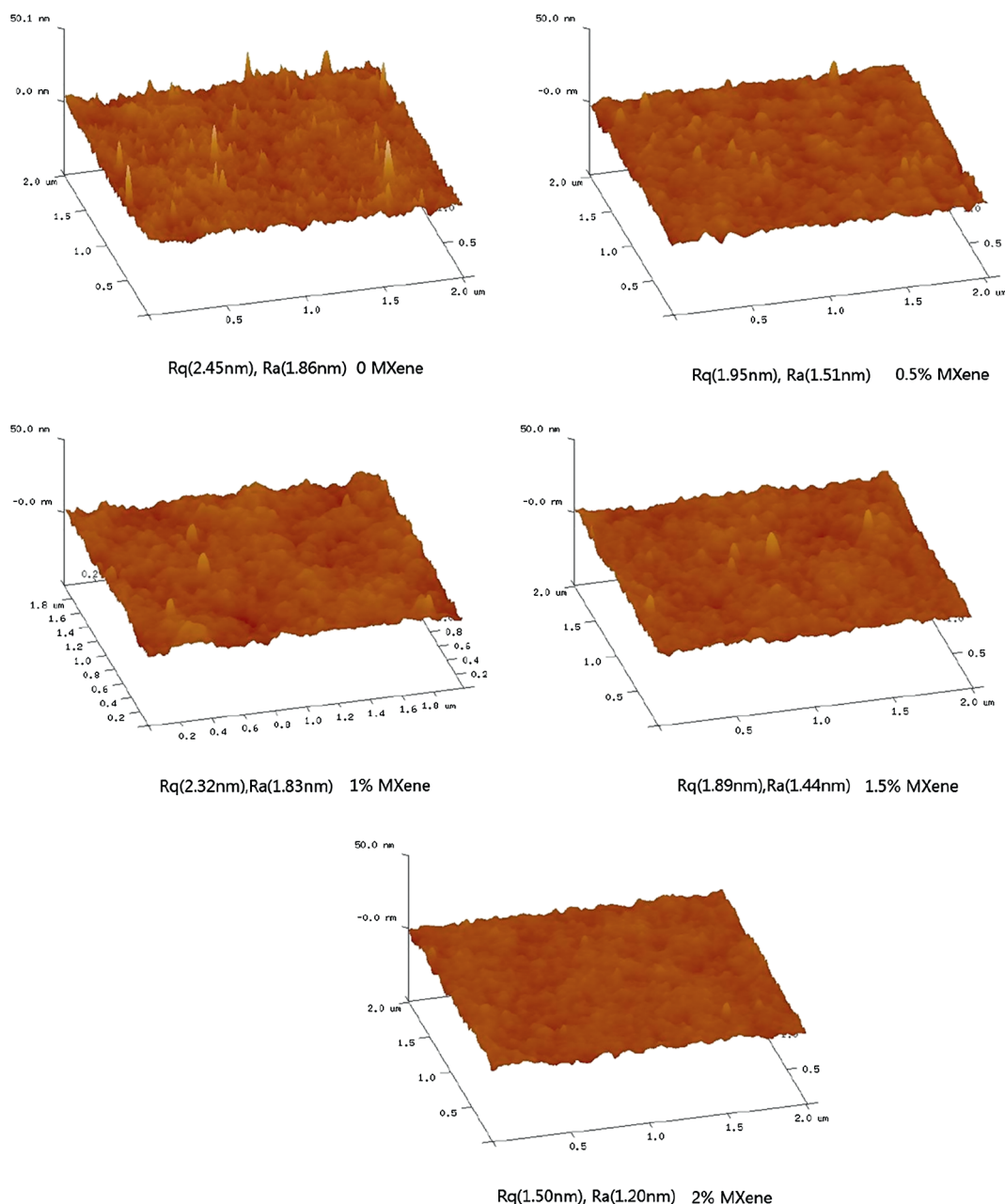


Fig. 4. AFM images of membranes prepared with different MXene contents.

3.3. ATR-FTIR of the membranes prepared with different MXene contents

The ATR-FTIR spectra of P84/MXene mixed matrix membranes prepared with different MXene contents were characterized ranging from 400–4000 cm^{-1} . The chemical components of membranes prepared with different MXene content are illustrated in Fig. 5. All the membranes were crosslinked with TETA and absorption bands include C=O stretching (at 1717, 1779 cm^{-1}), and C–N stretching (at 1362 cm^{-1}) are observed in all spectrums. With the increase of MXene content, the characteristic peaks changes little, because the inorganic MXene does not have obvious absorption bands.

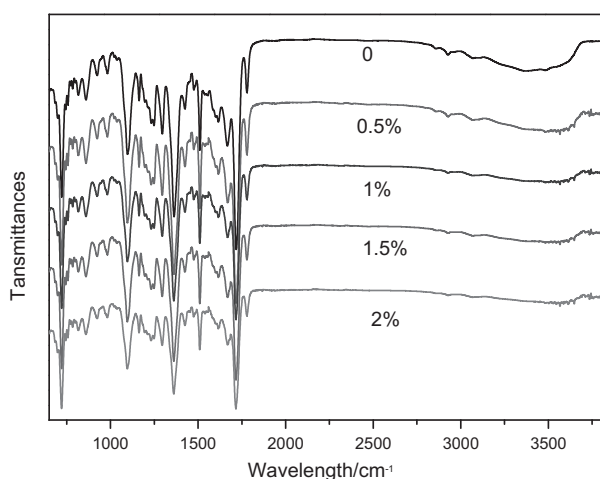


Fig. 5. The ATR-FTIR spectra of the P84/MXene membrane (from top to the bottom are: membranes with 0, 0.5%, 1%, 1.5%, 2% MXene).

3.4. Effect of MXene content on the performance of P84/MXene membrane

P84/MXene mixed matrix membranes with different MXene content were prepared with phase inversion method and cross-linked with TETA to improve the comprehensive performance of the membrane. It can be found from Fig. 6 that the rejections to gentian violet dye of membranes are all 100% demonstrating the dense functional layer and good compatibility of the membrane materials. With the increase of MXene content, the membrane flux increases obviously first, then declines. The mixed matrix membrane shows great flux elevation because the layer MXene has excellent hydrophilicity and abundant water channel. It is demonstrated that regularly channeled lamellar MXene will greatly increase the membrane flux because layered MXenes are used as rigid building blocks and provide multiple water channel for the excellent permeation [24].

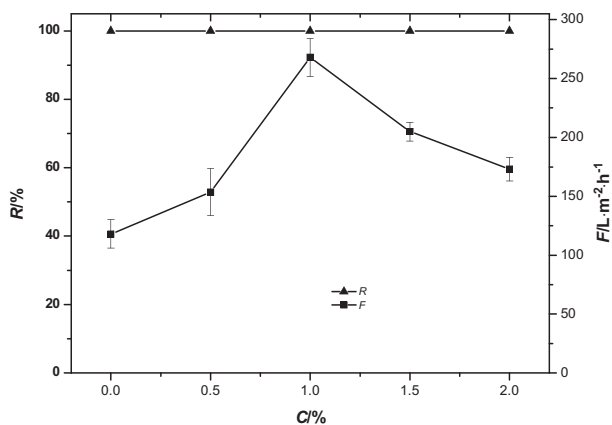


Fig. 6. Effect of MXene content on the performance of P84/MXene membrane (0.1 MPa, 0.1 $\text{g} \cdot \text{L}^{-1}$ gentian violet).

The membranes are also tested with Contact Angle Meter (WCA, SL200KB), and the data are the mean value of ten data shown in Table 2. With the increase of MXene content, the contact angle decreases which demonstrates improved hydrophilicity of the membrane surface with MXene incorporated in it, but with the further increase of MXene content, the membrane flux declines. The incorporation of inorganic additive will produce a lot of water channels because of phase interface between additive and polymer matrix. The interlayer in the MXene particles also provides a great channel for water molecule which increases the membrane flux obviously. Although MXene particles are very hydrophilic, they are encapsulated in the polymer matrix which will not obviously affect the hydrophilicity of the membrane surface. However, with the further increase of MXene content, viscous casting solution is formed and the denser functional layer is formed which will decrease the membrane flux. This is caused by the high viscosity of the casting solution which in turn delays the phase separation and improves the compactness of the functional layer [23].

Table 2
Contact angle of the MMMs

MXene content /%	0	0.5	1	1.5	2
Contact angle /($^{\circ}$)	77	77	75	73	72

In order to investigate the solvent resistance of the MMMs, the membranes were immersed in the static acetone, DMF and methanol separately because these solvents with good solubilizing properties are often used in chemical industry. The membrane was soaked in solvent then tested in dye/water solution and then soaked back again in solvent and tested every three days. It is found that the pure PI membrane without crosslinking is very unstable in polar organic solvent. It will dissolve in the DMF and seriously swell in acetone and methanol in 10 min. So it is difficult to test the permselectivity of the membrane after immersion in solvent. The control experiments showed that P84/MXene membranes without crosslinking are also ruptured and difficult to test after immersed in solvents like acetone, DMF and methanol for 1 day. As shown in Fig. 7, the rejection to gentian violet did not change during 18 days of immersion in acetone. At the same time, rejections of the membranes immersed in DMF and methanol also did not decline with time as shown in Figs. 8 and 9. So TETA is an effective crosslinking agent that makes the P84/MXene MMMs thoroughly resistant to these common solvents. All of the membranes show obvious flux decline which may be ascribed to the fouling of membrane surface when dealing with dye solution. The membrane immersed in DMF compared with membrane immersed in acetone and methanol shows greater flux decline, apparently because DMF is a good solvent of P84 and induces

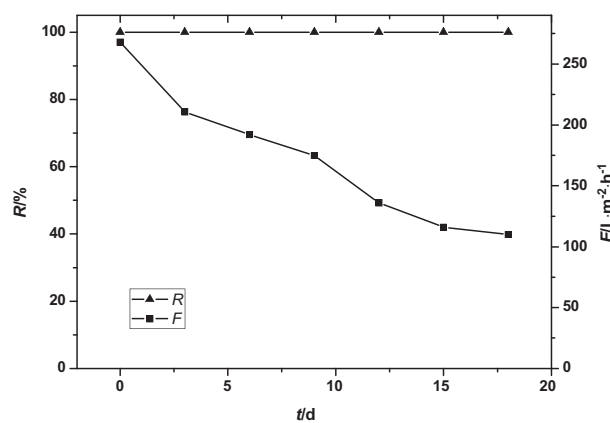


Fig. 7. Solvent resistance of the MMM with 1% MXene (0.1 $\text{g} \cdot \text{L}^{-1}$ gentian violet, 0.1 MPa, acetone).

more serious swelling of the polymer matrix, therefore small dye molecules will penetrate in the membrane pores and induce irreversible fouling.

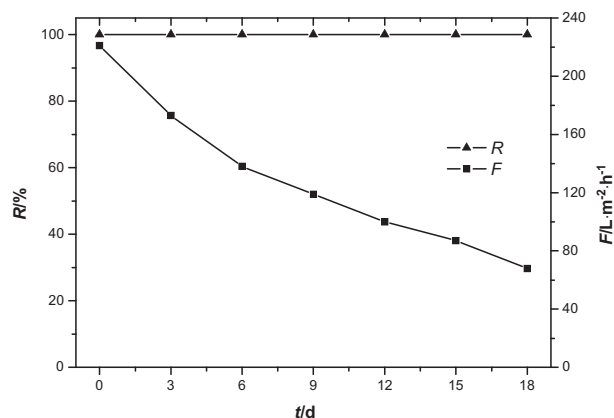


Fig. 8. Solvent resistance of the MMM with 1% MXene (0.1 g·L⁻¹ gentian violet, 0.1 MPa, methanol).

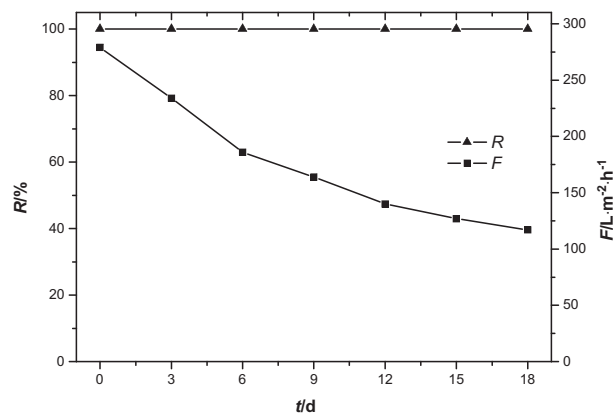


Fig. 9. Solvent resistance of the MMM with 1% MXene (0.1 g·L⁻¹ gentian violet, 0.1 MPa, methanol).

In order to evaluate the performance of the MMM with 1% MXene, different solutes are utilized in filtration solutions, respectively. From Table 3, the membrane shows highest rejection to gentian violet with molecular weight of 408 Da but lower rejections to congo red (697) and methyl orange (327). It may be caused by that the congo red and methyl orange are all linear molecules which can easily pass through the membrane pores. The polyimide membranes crosslinked with amines are often positively charged because the remaining amine groups on the membrane surface shows positively charged character [13]. So the P84/MXene membrane in this work should have the similar

character and higher rejection to cations. The congo red and methyl orange are both negatively charged molecule which is another reason for the relative lower rejection. In Economy's work [13], the P84 membrane has a flux of 67 L·m⁻²·h⁻¹ at 1.38 MPa and high rejection to CaCl₂ (about 62%) and NaCl (about 30%) after crosslinking with polyethylenimine. In this work, our membrane flux is about 4 times higher at 0.1 MPa and the membrane has a rejection of 100% to gentian violet (408). The membrane with loose structure has little rejection to salts, and high flux has a potential use in waste water treatment with lower osmotic pressure and operation cost.

4. Conclusions

It was found that the P84/MXene MMM has excellent performance with facile phase inversion method. The MXene with good hydrophilicity and water channel plays positive role on the membrane performance. At 0.1 MPa and ambient temperature, its rejection to gentian violet is 100% with high flux about 268 L·m⁻²·h⁻¹. The incorporation of inorganic additive will produce a lot of water channels because of the phase interface between additive and polymer matrix. The inter-layer in the MXene particles also provides a great channel for water molecule which increases the membrane flux obviously. The denser functional layer with high rejection is formed because of high viscosity and solid content of the casting solution. After crosslinking with TETA at 80 °C for 10 min, the membrane shows excellent solvent resistance. During static immersion in pure solvents such as DMF, acetone and methanol, the rejection to gentian violet does not decline, while the flux decreases with operation time. The membrane shows high rejection to some dyes but little rejections to salts which can be used in waste water treatment with high salinity.

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Table 3

Separation performance of the MMM with 1% MXene (0.1 MPa, dyes are tested with 0.1 g·L⁻¹ solution while salts are tested with 1 g·L⁻¹ solution)

Feed	Gentian Violet	Congo Red	Methyl Orange	Na ₂ SO ₄	MgCl ₂
Molecular weight	408	697	327	142	95
Structure					
Rejection/%	100	78.5	4	0	0
Flux/L·m ⁻² ·h ⁻¹	268	380	408	423	418

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