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Gao, Haifu, She, Jingguo, Liu, Sihua, Shi, Le, Lu, Xiaolong, Zhang, Jianhua and Wu, Chunrui (2023) 'Green' fabrication of PVC UF membranes with robust hydrophilicity and improved pore uniformity. Desalination, 568. ISSN 0011-9164

Contents lists available at ScienceDirect

Desalination
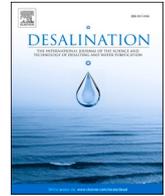
'Green' fabrication of PVC UF membranes with robust hydrophilicity and improved pore uniformity

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HIGHLIGHTS

- 'Green' reaction assisted phase inversion for PVC membranes modification was adopted.
- Hydrophilicity, pore size uniformity and porosity were simultaneously improved.
- 10-fold flux, 27 % BSA rejection, and 55 % anti-fouling ability increase were obtained.

GRAPHICAL ABSTRACT
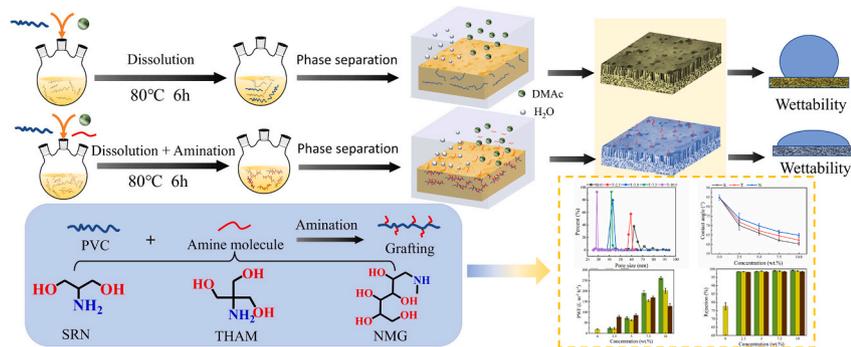
ABSTRACT

Hydrophilicity and pore uniformity are the key parameters for ultrafiltration (UF) membranes to avoid fouling and ensure separation effectiveness. In this paper, a simple 'green' in-situ chemical reaction assisted phase separation method was studied, in which amine molecules bearing hydrophilic hydroxyl groups were grafted onto polyvinyl chloride (PVC) chains in dissolution process without initiator. The influence of modifier concentration on the structure, separation and anti-fouling performance of the PVC membranes was studied. The results indicated that the robust hydrophilicity, and high pore size uniformity and porosity of were achieved by properly anchoring preferable amine molecules. The pure water flux of the modified membrane was 261.5 L·m^{-2}·h^{-1}, BSA rejection was 99.1 % when 10 wt% SRN was added. Approximately 27 % increase of rejection to BSA, and 10-fold pure water flux that of the pristine PVC membrane. Due to the stable existence of modifiers in the membrane, the improved membrane hydrophilicity was maintained through 320 h filtration and acid/alkali soaking tests. This study provides a simple modification approach to enhance PVC UF membrane hydrophilicity and pore uniformity.

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1. Introduction

Ultrafiltration (UF) membranes are membranes with pore size between 2 and 100 nm. It can achieve efficient removal of colloidal nanoparticles, macromolecules, proteins and microorganisms from wastewater, and has been extensively employed in municipal and industrial wastewater treatment, and separation and concentration of products in various industries [1–4]. State-of-the-art commercial UF membrane materials mainly include polyvinylidene fluoride (PVDF), polysulfone (PSF), polyethersulfone (PES) and polyvinyl chloride (PVC). Compared to PVDF, the cost of PVC material is only 1/7 [5,6]. PVC also has excellent chemical stability and good mechanical strength, and is a good candidate for UF membrane fabrication [7–9].

Although there are many advantages of PVC UF membranes compared with other UF membranes, fouling is a significant issue due to inherent hydrophobicity of PVC. PVC membrane can be easily fouled during filtration by the adsorption and deposition of colloidal particles, proteins or other contaminants on membrane surface and inside membrane pores [10,11]. Moreover, the wide distribution of UF membrane pore size would allow large contaminants enter membrane pores, and lead to obstruction of membrane pore channels or passage of contaminants, which will cause irreversible fouling and degradation of separation efficiency [12,13]. Increasing hydrophilicity and narrowing pore size distribution of UF PVC membranes can alleviate these issues [14–16].

Surface grafting and coating [17,18], embedding inorganic nanoparticles [19–21] and polymer blending [22–24] have been applied to mitigate membrane fouling. However, the trade-off between hydrophilicity improvement and pore blockage is a challenge for surface grafting and coating method. Blending method is relatively convenient and efficient for improvement of membrane hydrophilicity and anti-fouling performance. By blending silver/titanium dioxide (Ag/TiO$_2$) nanoparticles into PVC materials during non-solvent induced phase separation (NIPS) process, Haghighat et al. [25] improved the water flux and antifouling performance of the membrane dramatically. Xie et al. [26] introduced amphiphilic sulfonated polysulfone (SPSF) into PVC matrix via NIPS during membrane fabrication, which achieved approximately 96 % flux recovery ratio and tripled pure water flux, compared to the pristine one. Chen et al. [27] enhanced hydrophilicity and antifouling performance of PVC UF membrane by incorporating hydrophilic additives styrene-maleic anhydride (SMA) and polyethylene glycol (PEG). Hence, it is an effective strategy to improve membrane permeability and antifouling performance by introducing hydrophilic substances into PVC substrate. However, the compatibility among materials and leaching of hydrophilic macromolecules or nanoparticles during filtration process will affect the membrane stability [28–31].

An in-situ amination of polymer chains during dissolution was recently applied for membrane modification [32–34]. This approach is an efficient solution to improved membrane performance and stability by a simple one-pot method to graft amine molecules onto PVC chains in polar aprotic solvents. Zhu et al. [35] grafted triethylenetetramine (TETA) on PVC chains during dissolution process and obtained TETA modified PVC UF membranes through non-solvent induced phase separation (NIPS). The permeate flux of the modified membrane was

increased from 137.5 to 171.7 L·m^{-2}·h^{-1} with minor decline of rejection. Qin et al. investigated the influence of the reaction between TETA and PVC during dissolution process on the membrane structure and properties, and from which macropores with open structure were observed [36]. The mean pore size of the modified membranes increased nearly 2 times, which resulted in 2.3 times flux increase and relative rejection decline. These investigations demonstrated that the in-situ amination of PVC chain during dissolution could be an effective way to improve membrane performance. However, the enhancement of the hydrophilicity of polymer chains could facilitate the epitaxial "growth" of the chains towards the coagulation bath during phase separation, which leads to the increase of mean membrane pore size and wide pore size distribution [37,38], and compromise high-precision separation of UF membranes. In addition, conventional aminating agents (such as ethylenediamine, TETA) are strong alkaline, which would damage polymer chains and cause decrease in membrane mechanical properties [39,40]. Due to the above reasons, this method would damage to PVC chains and reduce mechanical strength of the membranes, the obtained membrane usually has a relatively large pore size and a wide distribution. Hence, it is necessary to develop a simple method that could fabricate robust PVC membranes with good hydrophilicity, and narrow pore size distribution.

In this paper, the possibility to anchor amine molecules bearing —OH groups with weak alkalinity onto PVC chains under mild conditions in dissolution process was investigated. Since Serinol (SRN), tris-(hydroxylmethyl)methyl aminomethane (THAM) and *N*-methylglucamine (NMG) are not adverse to human health and the environment according to their Safety Data Sheet [41], they have been selected as modifiers for this article. Compared to conventional aminating agents, the amine molecules with weak alkalinity would have less damage to PVC chains and mechanical strength of the membranes. The —OH groups could provide both high hydrophilicity and polarity of the PVC chains, and increase the intermolecular force. Furthermore, the curing process during phase separation process could also be controlled for the purpose of narrowing the pore size distribution, based on the structure and grafting rate of the modifier molecules. In this study, three amine molecules with different —OH loading were tested to improve persistent hydrophilicity and pore uniformity of the membrane without compromising membrane stability. Effects of molecular structures of different modifiers and the dissolution/reaction conditions on the structure and performance of the PVC membranes were compared.

2. Experimental

2.1. Materials

PVC (S-65, industrial grade, Tianjin Dagu Chemical Co. Ltd., China) was used for membrane fabrication. *N, N*-Dimethylacetamide (DMAc, AR Mitsubishi Chemical Holdings, Japan) was used as solvent. Deionized (DI) water was used as coagulation solution. Serinol (SRN), tris-(hydroxylmethyl)methyl aminomethane (THAM) and *N*-methylglucamine (NMG), (AR, Tianjin Kairuisi Fine Chemical Company, China) were used as amine modifiers. The structures of the amine modifiers were shown in Table 1. Polyethylene glycol (PEG 400) and polyvinyl-pyrrolidone (PVP K30, AR, Tianjin Kermel Chemical Reagent Co., Ltd., China) were utilized as additives for preparation of PVC membranes for comparison purpose. Bovine Serum Albumin (BSA, Beijing Puboxin Biotechnology Co., Ltd., China) was used for challenge of membrane performance.

2.2. Membrane preparation

PVC UF membranes were prepared by NIPS method. The homogeneous casting solution was prepared by mixing PVC powder, amine modifier or additive (PEG/PVP) and solvent DMAc under constant stirring for 6 h at 80 °C, stood at the temperature for 2 h, and then was

Table 1
The structure of amine modifiers.

Abbreviation	Chemical name	Chemical structure
SRN (S)	Serinol	
THAM (T)	Tris(hydroxymethyl)methyl aminomethane	
NMG (N)	*N*-methylglucamine	

Table 2
Composition of the casting solution.

Membrane code	PVC (wt %)	DMAc (wt %)	SRN (wt %)	THAM (wt %)	NMG (wt %)
M-0	15.0	85.0	–	–	–
S-2.5	15.0	82.5	2.5	–	–
S-5.0	15.0	80.0	5.0	–	–
S-7.5	15.0	77.5	7.5	–	–
S-10.0	15.0	75.0	10.0	–	–
T-2.5	15.0	82.5	–	2.5	–
T-5.0	15.0	80.0	–	5.0	–
T-7.5	15.0	77.5	–	7.5	–
T-10.0	15.0	75.0	–	10.0	–
N-2.5	15.0	82.5	–	–	2.5
N-5.0	15.0	80.0	–	–	5.0
N-7.5	15.0	77.5	–	–	7.5
N-10.0	15.0	75.0	–	–	10.0

cast at a thickness of 300 μm evenly on a clean glass board with a casting bar. The film was instantly immersed in DI water at 25 °C. Water-soluble substances were removed from the membranes by repeatedly washing in DI water. Table 2 provides the detailed information of the composition of the casting solutions.

2.3. Characterization of casting solution

Rotational rheometer (NDJ-1F, Shanghai Changji Geological Instrument Co., Ltd., China) was used to determine the viscosity of the casting solution. Titration method was used to determine the cloud points of water/DMAc/PVC/modifier solutions [42]. The phase separation rate is determined by the hardness of the casting solution varying with time [43], which is measured by a digital shore rubber hardness tester (TH220, Libo Instrument Co., Ltd., China). The curing time of the membrane was determined by when the hardness would not vary with time. For each sample, five parallel tests were conducted and the mean value was reported.

2.4. Membrane characterization

Fourier transform infrared spectrometer (FTIR, Nicolet iS50, Thermo-Fisher Scientific, USA) and X-ray photoelectron spectroscopy (XPS, NEXSA, Thermo-Fisher Scientific, USA) were used to determine the chemical composition of membrane surface [44].

The surface and cross-section structure of the PVC membranes was characterized via scanning electron microscope (SEM, Gemini500, ZEISS, Germany). The membrane surface roughness (Ra) was measured through atomic force microscope (AFM, Icon, Bruker, USA). Capillary flow pore size meter (Porolux 1000, Porometer, Belgium) was utilized to determine the membrane pore size distribution [44]. The membrane porosity (ε) was tested through dry-wet weight method using Eq. (1):

$$\varepsilon = \frac{(W_W - W_d)/\rho_W}{(W_W - W_d)/\rho_W + W_d/\rho_\rho} \times 100\% \qquad (1)$$

where W_W, W_d, ρ_W and ρ_ρ are the wet membrane weight (g), dry membrane weight (g), water density (g·cm^{-3}) and polymer density (ρ_ρ = 1.38 g·cm^{-3} for PVC) [45].

Membrane hydrophilicity was evaluated with water contact angle (WCA) of membrane surface measured by a contact angle meter (DSA30S, KRUSS, Germany), in which 5 μL DI water was dropped onto the membrane surface and images for WCA measurement were captured the after the droplet stays on membrane surface for 5 s. The mean value of WCA of ten measurements at random positions was reported.

The membrane mechanical performance was measured by an electronic single yarn strength meter (YG061F, Laizhou Electron Instrument Co., Ltd., China) [5].

2.5. Membrane performance tests

The pure water flux (PWF) was determined through the device depicted in Fig. 1. The membrane with an area of 7.07 cm^2 was pre-compacted at pressure of 0.20 MPa for 30 min and then the filtration was conducted at pressure of 0.10 MPa. The PWF (L·m^{-2}·h^{-1}) was calculated by Eq. (2):

$$PWF = \frac{V}{S \times t} \qquad (2)$$

where V, S and t are volume of permeate liquid (L), effective area of the membrane (m^2) and filtration time (h).

BSA solution (1000 mg·L^{-1}) was used as the feed solution to test the rejection (R, %) of the membranes was calculated by Eq. (3):

$$R = \left(1 - \frac{C_P}{C_F}\right) \times 100\% \qquad (3)$$

where C_P and C_F are the BSA concentration in the permeate and feed solution (mg·L^{-1}).

The robustness of membrane was challenged by long-term filtration (320h) and soaking respectively into HCl solution (2 mol·L^{-1}) and NaOH solution (2 mol·L^{-1}) for 24 h at 25 °C, and validated by PWF, WCA and rejection to BSA solution (1000 mg·L^{-1}).

The membrane anti-fouling ability (F_r) was evaluated by flux decline during filtration of feed containing 1000 mg·L^{-1} BSA for 150 min.

$$F_r = \frac{J_R}{J} \times 100\% \qquad (4)$$

where J_R and J are the membrane flux (BSA solution) post and prior to fouling, respectively.
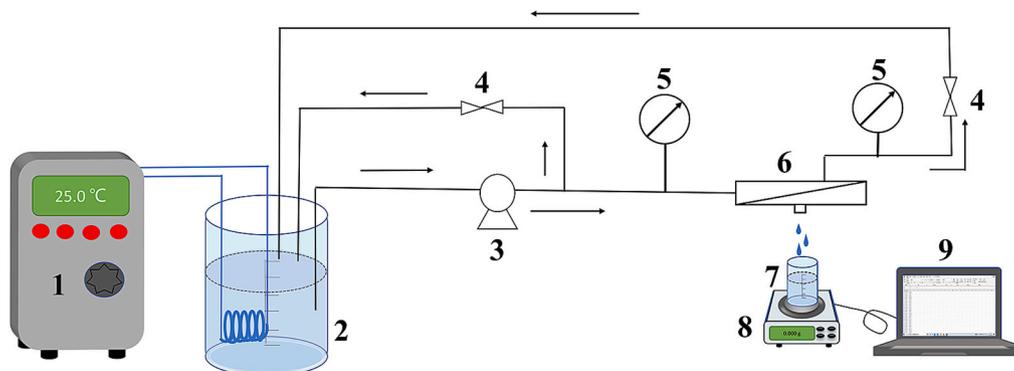
Fig. 1. Schematic of the apparatus for membrane separation performance evaluation. (1. Constant temperature reaction bath, 2. feed tank, 3. pump, 4. valve, 5. pressure gauge, 6. membrane sample, 7. measuring cup, 8. electronic balance, 9. computer).
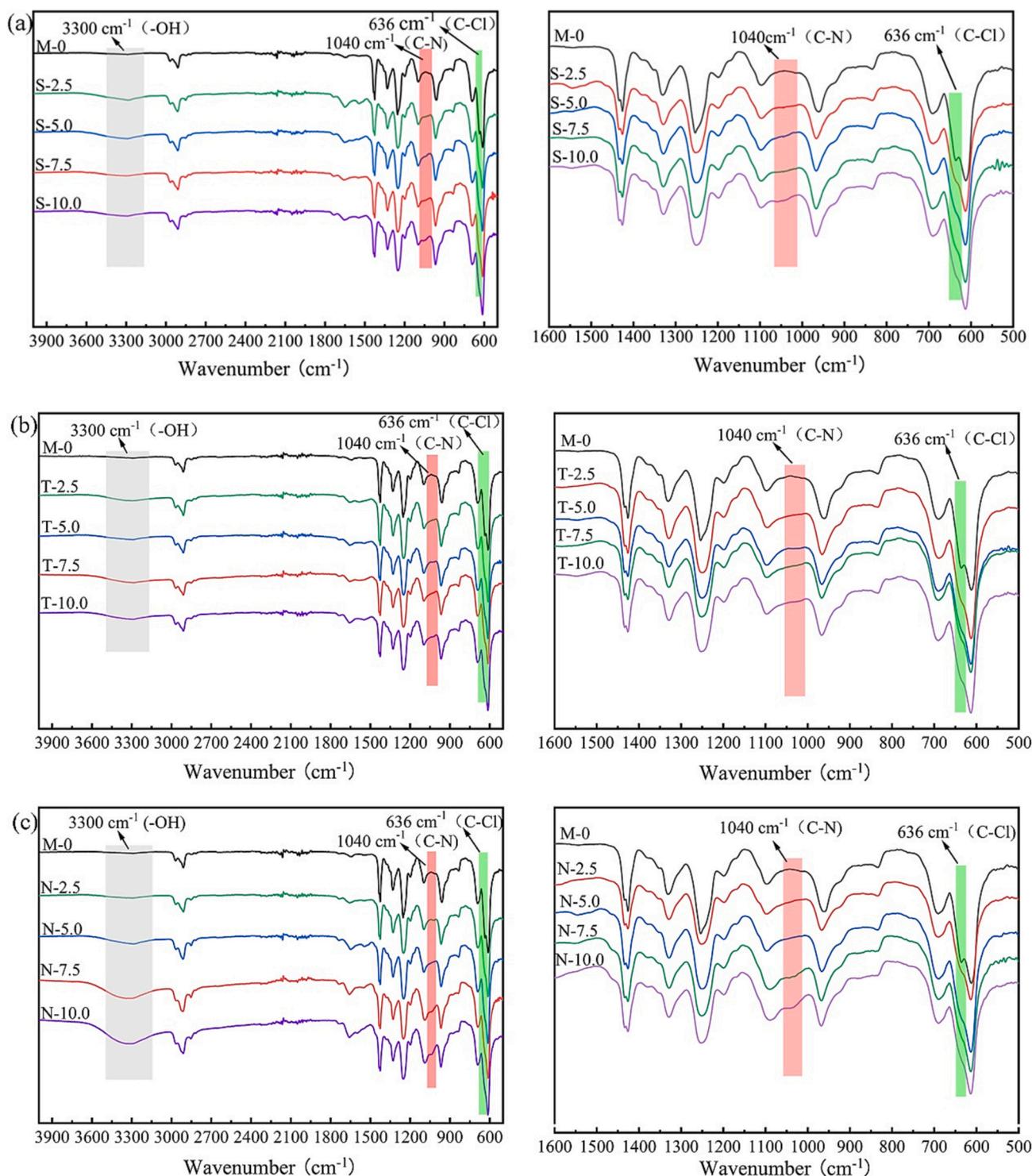
Fig. 2. FTIR spectra of PVC membranes ((a) pristine and SRN modified membranes, (b) pristine and THAM modified membranes, (c) pristine and NMG modified membranes).

3. Results and discussion

3.1. Effect of in-situ amination on the chemical structure of the membranes

The chemical compositions of pristine and modified membranes were characterized by FTIR and XPS displayed respectively in Figs. 2 and 3. From the FTIR spectra (Fig. 2), an absorption peak was observed at 3300 cm^{-1} in modified PVC membranes, which belongs to the —OH

stretching vibration in amine modifiers [40]. Compared to the pristine membrane, C—Cl bond stretching vibration peak at 636 cm^{-1} was not observed, but the C—N bond absorption peak at 1040 cm^{-1} was intensified for the modified membranes. This attributes to the in-situ grafting reaction between amine modifiers and C—Cl sites in PVC molecules, which indicates the successful grafting of amine molecules onto PVC [46].

The XPS spectra were shown in Fig. 3. New peaks belonging to N1s were observed from all modified PVC membranes, as shown in Fig. 3(a),
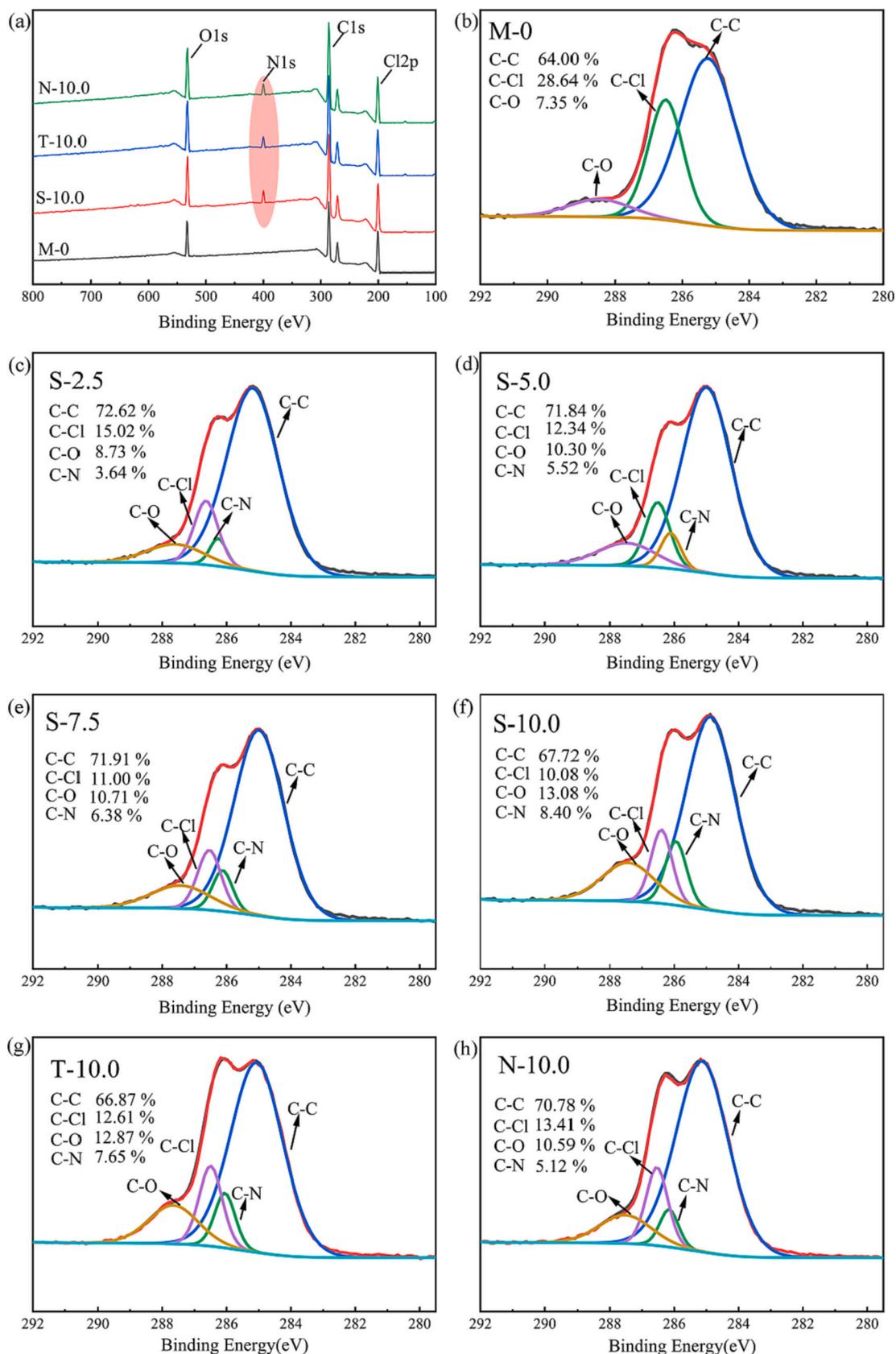
Fig. 3. XPS spectra of pristine and modified PVC membranes.
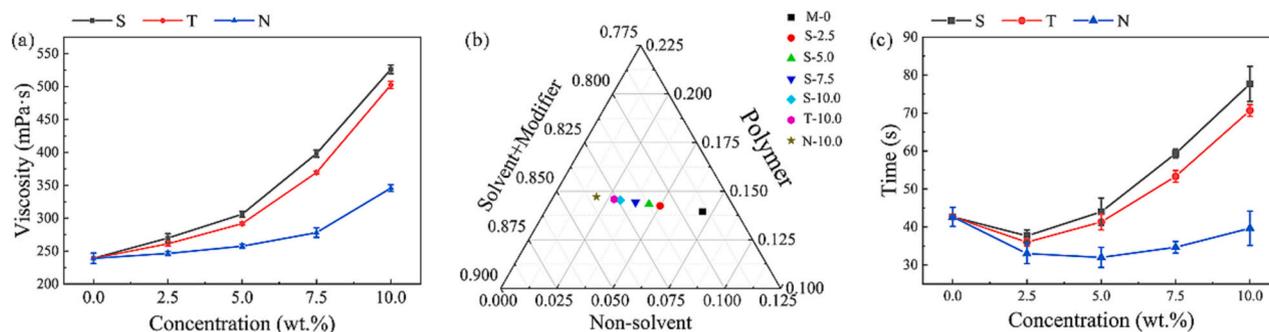
Fig. 4. Effect of amination on the phase separation process. ((a) Effect of t modifier concentrations on viscosities of casting solutions, (b) Cloud points of various water/DMAc/PVC/modifier systems, (c) Influence of modifier concentrations on hardening time of casting solutions).

which could further demonstrate the amination reaction between PVC molecules and modifiers [47]. As shown in Fig. 3b, c, d, e and f, the intensity of C—Cl peak decreased significantly, and the intensity of two new peaks (C—O and C—N) increased with higher SRN concentration. The N/C ratio on the membrane surface also increased with the rise of modifier concentration (Fig. S1). Hence, high modifier concentration facilitates the amination reaction.

From Fig. 2f, g and h, it can be found that with 10 wt% modifiers in the casting solutions, C—N intensities of modified membranes are NMG < THAM < SRN, but C—Cl intensities are NMG > THAM > SRN. Same trend also have be observed based on the C/N ratio, when varying modifier concentrations from 2.5 wt% to 7.5 wt% (Fig. S1). Hence, it can be concluded that the grafting rate between the modifiers and PVC are SRN > THAM > NMG at the same concentration. The chemical reaction formula of active amine molecules and PVC was illustrated in Fig. S2.

3.2. Effect of amination on the NIPS process

To investigate the effect of amination on the phase separation process, the viscosity, cloud points and hardening time of the casting solutions were studied, and the results are shown in Fig. 4.

As shown in Fig. 4(a), the viscosity of the casting solutions became greater with increasing modifier concentration due to the enhanced amination reaction between modifier and PVC chains. The amination reaction between modifier and PVC would have enhanced the interaction between modified PVC polymer chains [48]. The shear stress of the casting solution rose as polymer chain migration was further restricted. Hence, the viscosity of casting solution increased as modifier concentration increased. The increase of the casting solution viscosity would hinder the mass transfer between the phases, thus affecting the property and structure of the membranes. The increase rates of viscosity with concentration are SRN > THAM > NMG, which are corresponding to grafting rates observed via XPS spectra (Figs. 3 and S1). The viscosities of SRN, THAM and NMG are 526.0, 502.3 and 345.7 mPa·s respectively, when the modifier concentrations are 10.0 wt%.

Fig. 4(b) showed the thermodynamic stability of non-solvent (DI water)/DMAc/PVC/modifier systems tested by a titration method for cloud points. It shows that as the modifier concentration increases, to reach the cloud point, the non-solvent concentration will decrease. This is attributed to the increase in hydrophilic —OH group content in the casting solution reduces the miscibility of the casting solution with non-solvent water. Hence, the increase in modifier concentration reduces the thermodynamic stability of casting solution. The thermodynamic instability casting solution systems would shorten the delayed demixing time [49], which is beneficial in obtaining porous membranes via NIPS [50]. Furthermore, with the same modifier concentrations, the non-solvent concentrations required to achieve the cloud point were NMG < THAM < SRN, due to the difference of grafting rates of the modifiers onto PVC and the —OH group content in modifier molecules (Table S1), which changed the interaction among the PVC chains and compatibility

of PVC with solvent system.

In Fig. 4(c), the hardening time varying with the modifier concentrations is shown. It can be found that the hardening times decreases initially as the modifier concentrations increase to 2.5 wt%, but starts to increase as the modifier concentrations become higher. With the modifier concentration of 10 wt%, the hardening times of PVC modified respectively by SRN, THAM and NMG are 77.7, 68.0 and 38.0 s. Due to the presence of hydrophilic OH— groups in the modifiers, the diffusion rate between the coagulation solution and initial casting films can be promoted [36], which accelerated the precipitation process. However, the viscosity increase of the casting solution would hinder the mass diffusion across different phases. Therefore, when the mass diffusion is not dominated by viscosity, the decreasing thermodynamic stability of casting solution systems with higher modifier concentration (<2.5 wt%) could reduce the hardening time. However, with increasing modifier concentration (>2.5 wt%), the hindering of viscosity suppresses the promoting of —OH groups on mass diffusion, which increase the hardening time. From Fig. 4a and b, it can be found that both the thermodynamic stability and viscosity of the NMG modified PVC casting solution was lowest, compared with that of SRN and THAM modified PVC casting solutions. Hence, the shortest hardening time is observed in Fig. 4(c).

3.3. Effect of in-situ amination on membrane characteristics

3.3.1. Morphology of the membranes

In Fig. 5, the SEM images of membrane surfaces and cross sections were shown. It can be seen from Fig. 5a that with the increase of modifier concentration, the surface of the membrane became rougher, which is also proved by the AFM scanning as shown in Fig. 6.

The morphology of channels/voids of the membrane also varied with the modifier concentration as shown in Fig. 5b. As the content of modifiers increased, the size of the channels/voids became greater. However, when the modifier concentration increased to 10 wt%, the visible number of channels/voids reduced dramatically and the transition layers between the smallest and largest sizes of channels/voids become much thinner than that of with lower modifier concentrations.

These phenomena could be attributed to the influence of hydrophilicity and viscosity of the casting solutions on the precipitation rate, and the exchange rate between the coagulation solution and the upper surface. The increase in modifiers concentration reduces the thermodynamic stability of casting solution. Simultaneously, the addition of modifiers would enhance the hydrophilicity of the casting solution, and the exchange rate between the coagulation solution and the upper surface of initial casting films would be accelerated. These two factors facilitate formation of open pores on membrane surface [51,52]. During phase transformation process, the accelerated diffusion rate of solvents and non-solvents would boost formation of "valleys" and "peaks" on the membrane surface, and increase the surface roughness of the modified membranes [52]. Viscosity increase with higher modifier concentration

would reduce the precipitation rate of the polymer and facilitate formation of large channels/voids and the transformation to sponge-like layer as shown in Fig. 5(b) [53]. Since the viscosity increase with NMG concentration was much lower than that of SRN and THAM (Fig. 4 (a)), the formation of sponge-like layer is not obviously at high concentration (>5 wt%).

3.3.2. Pore size distribution and porosity of the membranes

Fig. 7 illustrates the influence of in-situ amination on membrane pore size, pore size distribution and porosity. With increase of the modifier concentration, mean pore sizes of the membranes become smaller and pore size distributions become narrower However, the porosities (Fig. 7 (d)) of membranes increase initially and plateau, when the concentration is >7.5 wt%. When the modifier concentrations are10 wt%, the mean pore sizes of three membranes are 31.6 nm (SRN), 30.4 nm (THAM) and 36.9 nm (NMG), and the porosities are 82.3 % (SRN), 82.1 % (THAM) and 85.1 % (NMG).

As the viscosity of the casting solution increases with greater modifier concentration in casting solution, the phase separation speed will be reduced, which facilitates formation of pores with small even sizes
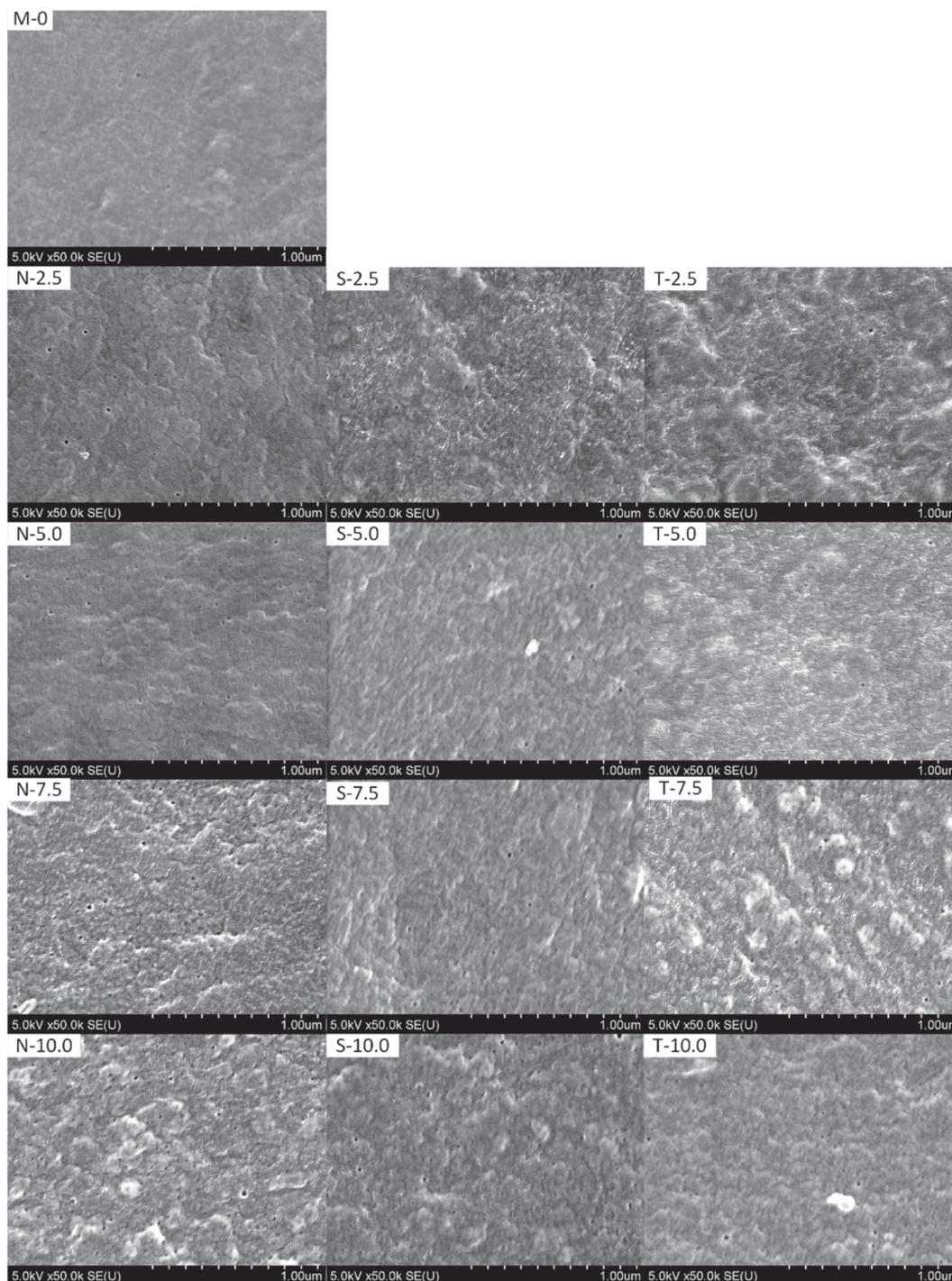
(a) SEM images of the membrane surfaces

Fig. 5. SEM images of the membranes.
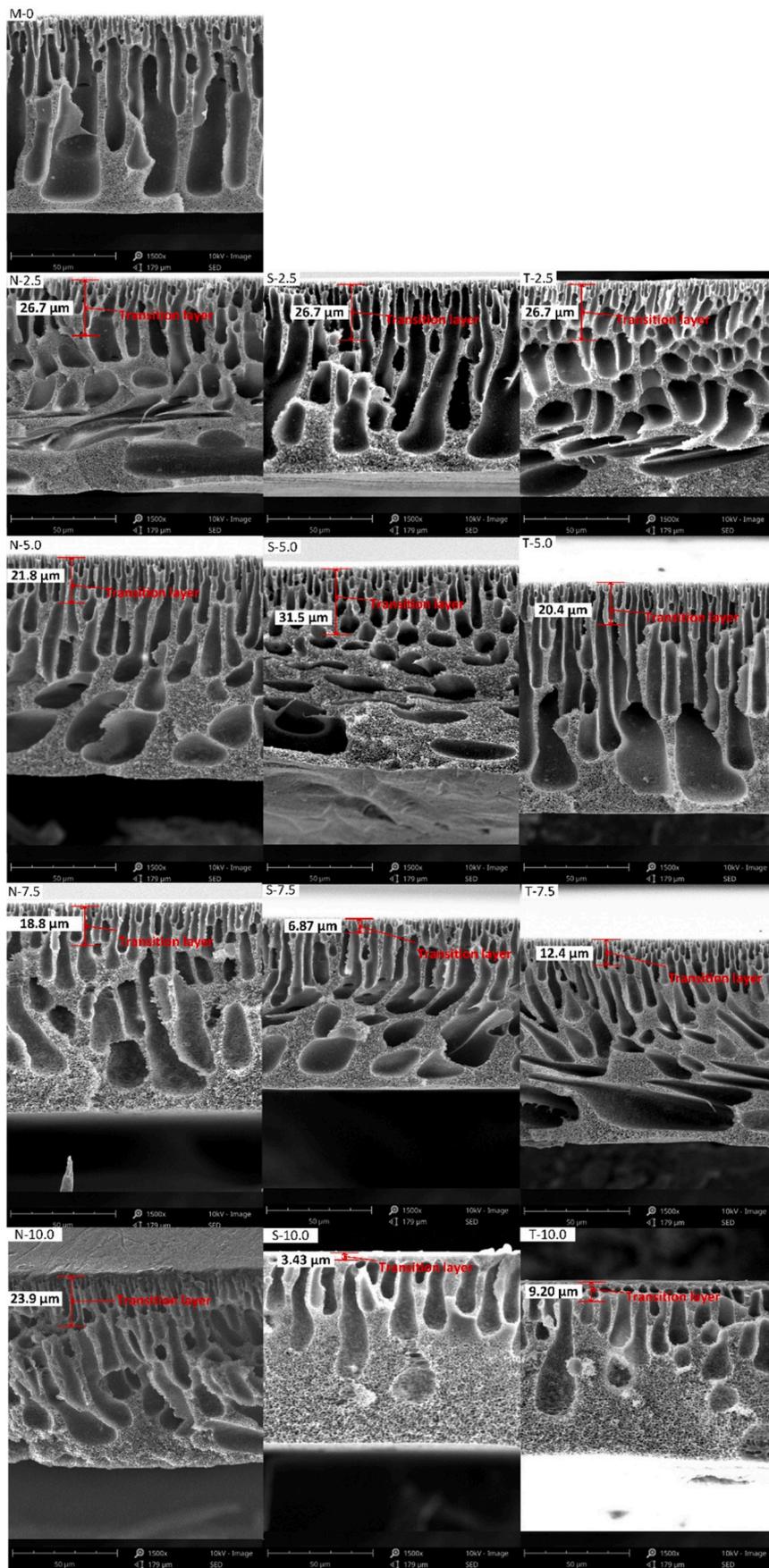
(b) SEM images of membrane cross sections

Fig. 5. (*continued*).
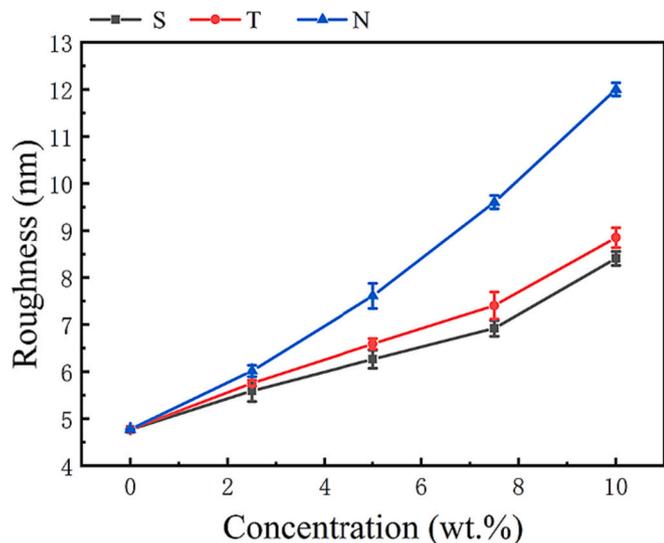
Fig. 6. Roughness of the membranes varied with modifier concentration.

Fig. 8. WCAs of pristine and modified PVC membranes.

[54,55]. Hence, the mean pore size and pore size distribution were reduced. More hydrophilic —OH groups presenting in the casting solutions at higher modifier concentrations could enhance the exchange rate between solvent and non-solvent, which improves the connectivity of the channels/avoids and membrane porosity [56]. Hence, the

membrane porosity increases with the modifier concentration.

3.3.3. Membrane hydrophilicity

Fig. 8 showed the influence on modifier concentration on membrane hydrophilicity. It can be found that the WCAs decrease continuously to 60.3° (SRN), 62.3° (THAM) and 64.8° (NMG) respectively, as the
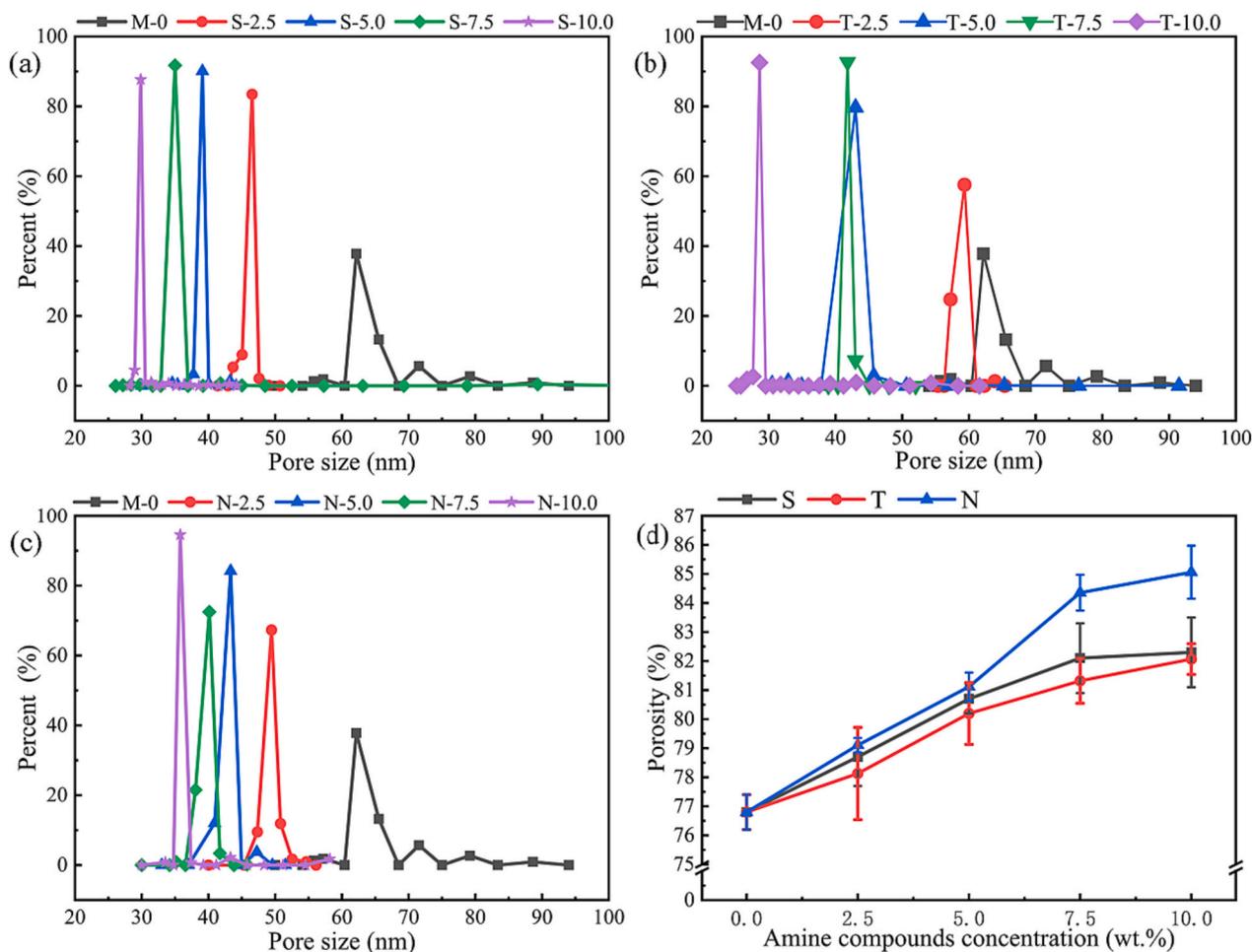
Fig. 7. Pore size distribution and porosity of the membranes ((a) pore size of pristine and SRN modified PVC membranes, (b) pore size of pristine and THAM modified PVC membranes, (c) pore size of pristine and NMG modified PVC membranes, (d) porosity of pristine and modified PVC membranes).
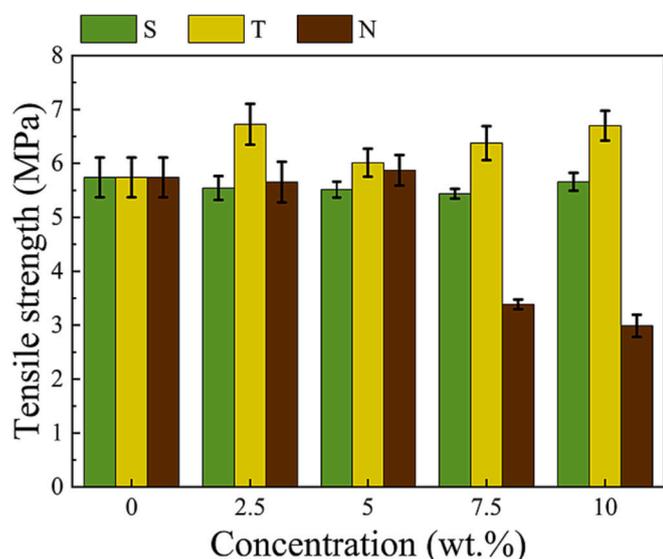
Fig. 9. Tensile performance of pristine and modified PVC membranes.
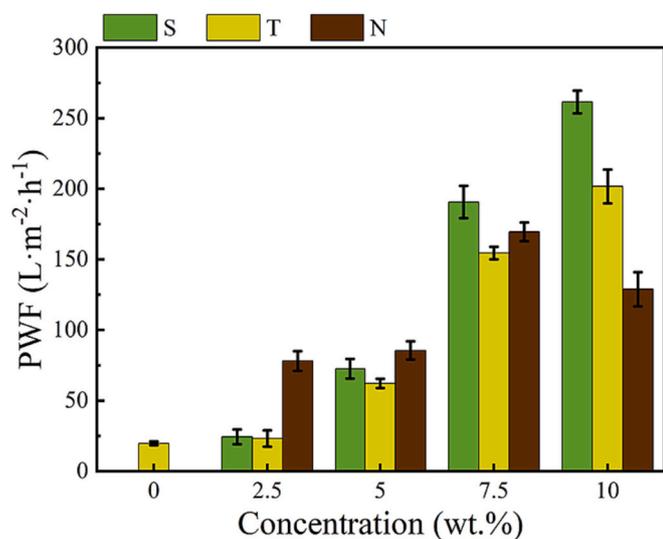
Fig. 10. PWF of pristine and modified PVC membranes.

modifier concentrations increase to 10 wt%. This is attributed to increase of —OH groups in membrane materials due to in-situ amination reaction. Meanwhile, the open pores and roughness on membrane surface
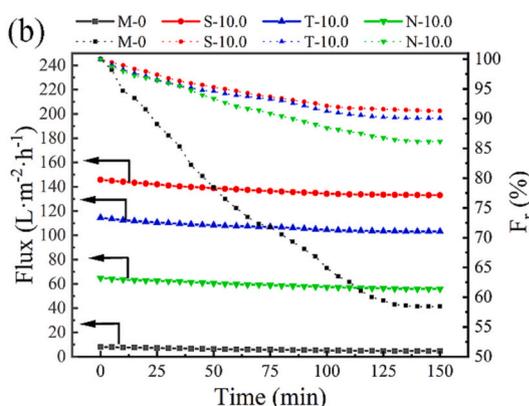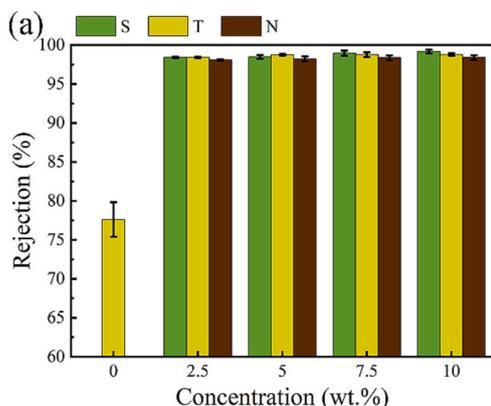
increased obviously as the modifier concentration rose (Figs. 5(a) and 6), which also give help for the membrane hydrophilicity improvement [57,58].

3.3.4. Membrane mechanical properties

Tensile strength varies with the modifier concentration is shown in Fig. 9. It can be found that the tensile strength of M-0, S-10.0, T-10.0 and N-10.0 was 5.7 MPa, 5.7 MPa, 6.7 MPa and 3.0 MPa, respectively. The tensile strengths did not vary significantly with concentration, when SRN and THAM were used as modifier. However, when NMG was used as modifier, the tensile strength of the PVC membrane declined greatly, when the NMG concentration exceeded 5.0 wt%.

For membranes modified by SRN or THAM, the increase of membrane porosity at higher modifier concentration did not compromise the tensile strength of PVC membranes. It could be attributed to the formation of thicker sponge-like layer as shown in Fig. 4(b) at high concentration [51]. Due to lack of sponge-like structure in the NMG modified membrane at high modifier concentration (Fig. 4(b)), the tensile strength of the membrane declined when the modifier concentration was >5 wt% as shown in Fig. 9.

3.4. Membrane separation performance

Fig. 10 showed PWFs of the pristine and modified membranes. It can be found that the PWF was 19.8 $L \cdot m^{-2} \cdot h^{-1}$ for the pristine membrane, and increased continuously as the modifier concentrations became higher, except for NMG. The maximum PWF were 261.5, 201.6 and 169.6 $L \cdot m^{-2} \cdot h^{-1}$, respectively for S-10.0, T-10.0 and NMG-7.5 modified membranes, which are about 10-fold the PWF of the pristine membrane. The boosted fluxes of the modified membranes are due to the increasing hydrophilicity (Fig. 8), total porosity (Fig. 7(d)), surface pore number (Table S2) and surface roughness (Fig. 6), when more modifiers were added into the casting solution [59,60]. Furthermore, the transition layers (Fig. 5b) could also have significant influence on the PWF by changing the mass transfer resistance [61]. It can be found in Fig. (5b) that both the transition layer thicknesses of SRN and THAM modified membranes reduced with the increasing concentrations, but there was no significant change of the transition layer thickness of NMG modified membrane. At low modifier concentration (≤5 wt%) where the thickness of the transition layers are similar for all modified membranes (Fig. 5(b)), the highest flux was achieved by the NMG modified membrane possessing higher porosity in combination with relative larger mean pore size than those of other modified membranes (Fig. 7). However, as the modifier concentration increased further (≥7.5 wt%), SRN modified membrane achieved the highest flux, due to drametical reduction of transition layer thickness.

In Fig. 11, the performance of membranes treating BAS containing feed is shown. It can be found in Fig. 11(a) that compared to rejection of

Fig. 11. Performance of membranes treating BSA containing feed (BSA = 1000 mg/L) ((a) rejection to BSA, (b) flux decline with time).
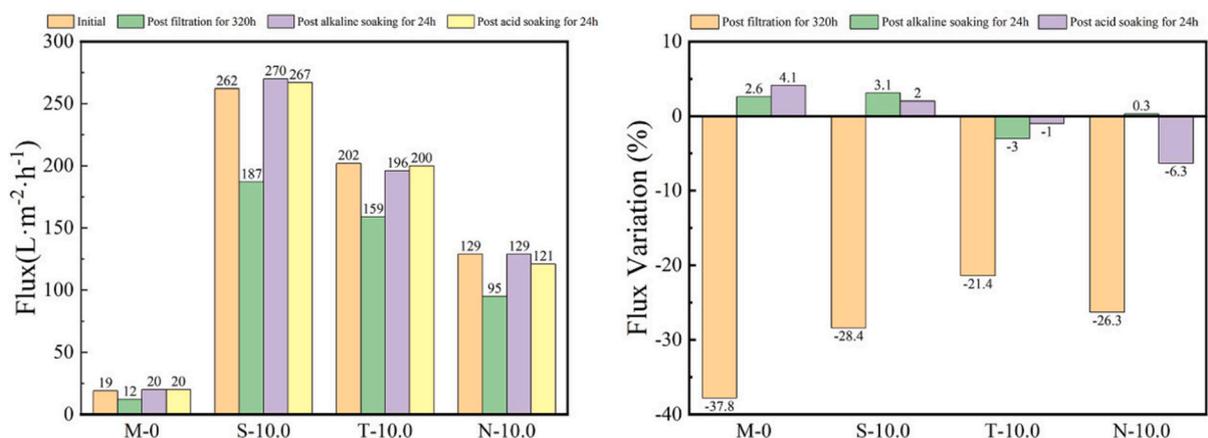
(a) Flux variation post robustness challenges
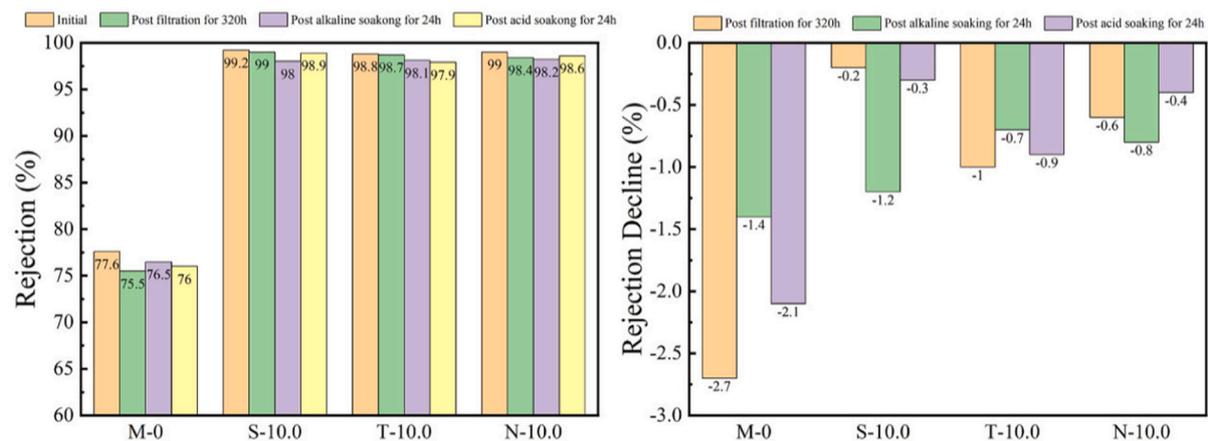
(b) Rejection variation post robustness challenges
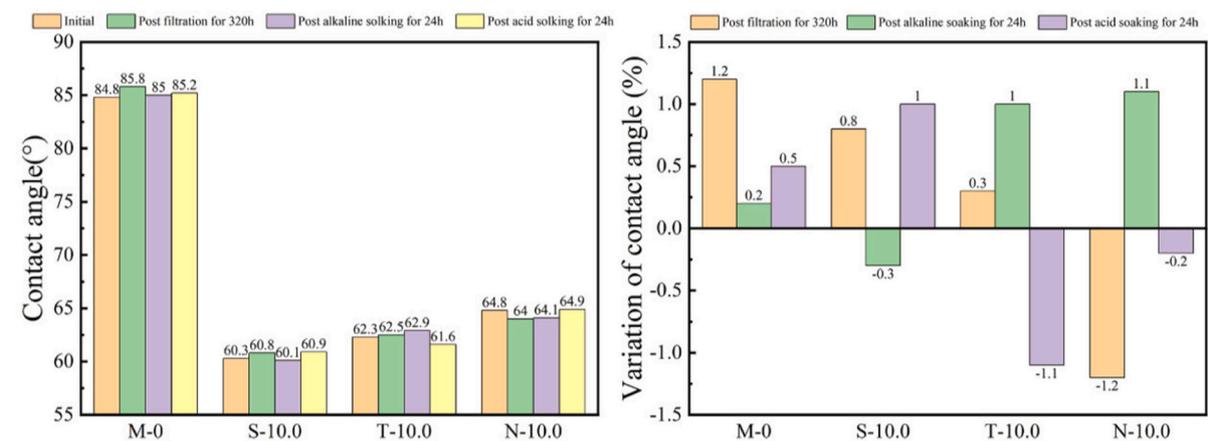
(c) Contact angle variation post robustness challenges

Fig. 12. Challenge tests for membrane robustness (temperature = 25 °C).

77.6 % to BSA by the pristine membrane, rejections of all modified membranes to BSA were >98 % and due to the narrowed pore size distribution and reduced pore size (Fig. 7). When the membrane has wide pore size distribution, the maximum size could be greater than the BSA size (90–185 nm in water solution depending on the pH [62]), which compromises the membrane rejection.

The flux decline with time is shown in Fig. 11(b). Compared to

fouling resistance, Fr = 58.8 % of M-0 (from 8.0 to 4.7 L·m^{-2}·h^{-1}) in a filtration of 150 min, 91.3 %, 90.1 % and 86.1 % of Frs are achieved respectively by S-10.0 (from 133.0 to 130.9 L·m^{-2}·h^{-1}), T-10.0 (from 103.2 to 95.4 L·m^{-2}·h^{-1}) and N-10.0 (from 55.9 to 49.6 L·m^{-2}·h^{-1}). Hence, all the modified membrane showed better resistance to BSA fouling than that of pristine membrane. Since Hashino, et al. had confirmed that physicochemical interactions between polymers and BSA

rather than that between BSA and BSA resulted membrane fouling [63], the characteristics of the membrane surfaces are the kay factors suppressing sorption and accumulation on the membrane surface. The increase of membrane hydrophilicity could have lowered (Fig. 8) the interactions between BSA and membrane surfaces. The membrane with the highest hydrophilicity (S-10.0) also possessed the highest fouling resistance (Fr). The narrow pore size distribution in combination with small pore size could also minimize the risk of pore blockage [64]. Hence, it can be found that S-10.0 and T-10.0 with the narrowest pore distribution and smallest pore size showed the best fouling resistance performance.

The performance of the membranes prior and post the challenges are shown in Fig. 12. It can be found after 320 h filtration that PWFs, rejection and contact angle of the four membranes varied in range of −21.4 % to −37.8 %, −0.1 % to −2.7 % and −1.2 % to 1.2 %. Hence, the long-term filtration has the most influence on the PWFs due to the membrane compaction [65], but has minor influence on both contact angles and rejections related to the surface and pore characteristics. The acid and alkali soaking challenges only show minor influence (≤6.3 %) on all three studied parameters, in which there is no significant difference was observed between the pristine and modified membranes, and more stable than modified membranes via conventional approaches (Fig. S4). Hence, all the modified membrane showed comparable or even better performances to the pristine PVC membrane (M0) post the studied challenges.

4. Conclusion

Modified PVC UF membranes with robust hydrophilicity and narrow pore size distribution were prepared via in-situ hydrophilization assisted phase separation process, in which amine molecules bearing —OH groups were arched on PVC chains through 'green' (without initiator) reaction.

SRN, THAM and NMG were used as amine modifiers in the membrane fabrication. Through the modification, all the membranes achieve improvement hydrophilicity narrowed pore size distribution and increased porosity. Under the optimized conditions, 29 % decrease in WCA, 27 % increase in BSA rejection and 10-fold increase in pure water flux were achieved. The robustness challenges demonstrated that the modified membranes have comparable or better performance than that of the pristine membrane, post the long-term filtration, and acid and alkali soaking.

CRediT authorship contribution statement

Dr. Haifu Gao was involved in the laboratory work and paper drafting.

Dr. Jingguo She was involved in the laboratory work and paper drafting.

Dr. Sihua Liu was involved in supervision and manuscript drafting.

Dr. Le Shi was involved in supervision and manuscript drafting.

Prof. Xiaolong Lu was involved in supervision and manuscript drafting.

Dr. Jianhua Zhang was the key team member, and involved in the paper drafting and supervision.

Prof. Chunrui Wu supervised the laboratory work and drafted the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2023.117022.

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