

In-situ modification of PVC UF membrane by SiO₂ sol in the coagulation bath during NIPS process

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Abstract. Polyvinyl chloride (PVC) ultrafiltration (UF) membrane was modified by silica sol in the coagulation bath during non-solvent induced phase separation (NIPS) process. The effects of silica sol concentrations on the morphology, surface property, mechanical strength and separation property of PVC UF membranes were systematically investigated. PVC membranes were characterized by Fourier transform infrared spectroscopy (FTIR), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), contact angle goniometry and tensile strength measurement. The results showed that silica had been successfully assembled on the surface of PVC UF membrane. With the increase of silica sol concentration in the coagulation bath, the morphologies of PVC UF membranes changed from cavity structure to finger-like pore structure and asymmetric cross-section structure. The hydrophilicity and permeability of PVC UF membranes were further evaluated. When silica sol concentration was 20 wt.%, the modified PVC membrane exhibited the highest hydrophilicity with a static contact angle of 36.5° and permeability of 91.8 (L·m⁻²·h⁻¹). The structure of self-assemble silica had significant impact on the surface property, morphology, mechanical strength and resultant separation performance of the PVC membranes.

Keywords: polyvinyl chloride; surface modification; silica sol; ultrafiltration membrane

1. Introduction

Currently, polymer is still the most widely used material for membrane technology due to the excellent membrane forming ability, flexibility and low cost. Considering the physicochemical stability, polyvinylidene fluoride (PVDF) (Chen *et al.* 2016, Zhang *et al.* 2017) and polysulfone (PSF) (Chen *et al.* 2015) are favorable raw materials. However, their high production cost and strict membrane preparation conditions limit their applications. Therefore, it is of great significance to prepare low price ultrafiltration (UF) membrane with common polymer.

Polyvinyl chloride (PVC) is one of the most extensively applied membrane materials in industry for its robust mechanical strength, low cost and excellent chemical properties (e.g., acid, alkali and solvent resistance) (Fang *et al.* 2017, Xu and Xu 2002, Bilad *et al.* 2015, Chi *et al.* 2016, Endo *et al.* 2002). The development of sanitary products greatly expands the application field of PVC. Meanwhile, the price of PVC raw material is much less than that of PSF or PVDF. At the same time, the strong polarity of PVC polymer molecules, as well as good processing performance, endows it with congenial conditions for preparation of high strength membrane. Therefore, the study of PVC membrane has attracted a lot of attentions in recent years (Xu *et al.* 2015, Behboudi *et al.* 2016, Kong *et al.* 2016, Cui *et al.* 2015, Rabiee *et al.* 2015, Fan *et al.*

2014). However, its hydrophobic nature which often results in severe membrane fouling and decline in permeability, has affected its application in water treatment (Bilad *et al.* 2015, Marbelia *et al.* 2016). Many studies have attempted various techniques to improve the hydrophilicity of PVC membranes, such as physical blending (Fang *et al.* 2017, An *et al.* 2003), chemical grafting (Bierbrauer *et al.* 2010), nano-composite technology (Mei *et al.* 2011) and surface modification (Hosseini *et al.* 2013). For example, Zhu *et al.* (2008) blended PVC with nanosilica and found that inorganic silica can improve the tensile strength, mechanical properties and heat resistance of the PVC composites. However, the compatibility of the composite system should be further reinforced. Among these methods, nano-composite technology and surface modification (Kim *et al.* 2002, Karan and Livingston 2015) are worthy of study due to their convenient operation and mild condition (Ulutan 1996). The sol-gel technique has provided new opportunities for the preparation of organic-inorganic materials (Velev *et al.* 1997). Furthermore, the remaining hydrogen bond clusters at the surfaces of the materials after the sol-gel reaction improve the membrane hydrophilicity and enhance the stability of composite materials (Xu *et al.* 2015). Yu *et al.* (2009) reported organic-inorganic PVDF-SiO₂ composite hollow fiber UF membranes prepared using the sol-gel and wet-spinning process. The microstructure, mechanical property, hydrophilicity, permeation and antifouling performance of composite membranes were improved apparently by the addition of tetraethoxysilane (TEOS).

Generally, in the process of immersion precipitation phase transformation, the compositions of casting solution

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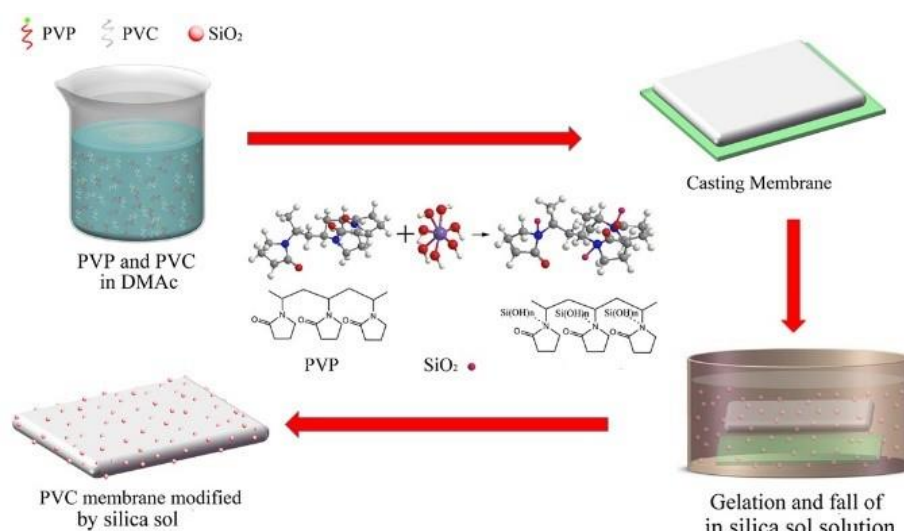


Fig. 1 Preparation process of PVC UF membrane modified by silica sol

and coagulation bath are the two important factors which affect the membrane structure and properties. In recent years, some people conducted work on improving the membrane performance by changing the composition of coagulation bath. Zhang *et al.* (2017) synthesized CNS sol solution and added them into the coagulation bath, for enhancing anti-fouling ability of PVDF membrane. The in-situ modified membrane had enhanced surface physicochemical properties. Meng *et al.* (2015) investigate the effect of graphene oxide (GO) nanosheets in coagulation bath on the morphology, surface property, mechanical strength and separation property of the PSF membranes. The hydrophilicity of the PSF/GO membranes increased with the increase of GO concentration. In fact, when the compositions of coagulation bath changed, the exchange rate of solvent and coagulation bath will be inevitably changed. Fixing the other parameters, Xu *et al.* (2002) used DMAc solution instead of pure water as bore liquid, the pure water flux and the rejection rate were both improved. Yang and Liu (2003) investigated the effect of sodium chloride coagulant on PAN membrane. SEM pictures indicated that the macrovoids were lessened drastically. With some novel physical and chemical properties, nanoparticles can greatly improve the membrane performance when added into the casting solution. Compared with GO and CNS sol solution, the preparation of silica sol is much more convenient and low-cost. However, few people investigate the effect of silica sol in coagulation bath on the membrane structure and properties.

In some studies, polyvinyl pyrrolidone (PVP) was used as surfactants with nanoparticles to reduce its aggregation effect and improved the disperse ability in different solvents (Vatanpour *et al.* 2011). However, in other research, both PVP and nanoparticles were used together to form nanocomposites (NCs) so as to improve the dispersibility of nanoparticles and reduce PVP elution from the polymer matrix (Irfan *et al.* 2014). They were complexed due to the Van der Waals force and hydrogen bonding. The prepared NCs could modify the membrane surface and enhanced the membrane performance. The blending method could be

conducted easily while the functionality of nanoparticles can not be fully utilized because the majority of nanoparticles were entrapped within the membrane matrix rather than on the membrane surface.

In this work, a certain concentrations of silica sol are dispersed in a coagulation bath to prepare PVC membranes. During the membrane precipitation process, PVP molecules in the casting solution will immigrate to the membrane surface and silica nanoparticles in the coagulation bath will also be transferred to the membrane surface. They are collided and complex at the interface due to the Van der Waals force and hydrogen bonding. Therefore, the membrane surface is embedded in nanoparticles. It is aimed to systematically reveal the change in morphology, surface hydrophilicity, as well as permeability and mechanical properties for the membranes. This work will pave the way for the preparation of high-performance membranes.

2. Experimental

2.1 Materials

PVC resins (1300, $M_w = 62,500$) were purchased from Shanghai General Plant of Chloric Alkali, China. PVP ($M_w = 30,000$), dibutyltin dilaurate (DBD, stabilizer), N,N-dimethylacetamide (DMAc), tetraethoxysilane (TEOS) and glycerol were purchased from Shanghai Chemical Reagents Co., Ltd, China. All chemicals were analytical grade and were used without further purification.

2.2 Preparation of PVC membrane

The casting solutions containing 15 wt.% PVC were prepared by blending of PVC resin, PVP, DBD and DMAc at a mass ratio of 15.0: 4.0: 0.5: 80.5 under constant stirring for 4 h at 60°C. The preparation method of silica sol has been described by Harmer *et al.* (2000 and 1996). The solutions were casted over a glass plate with the help of a special blade. The cast membranes were evaporated for

Table 1 Compositions of casting solutions and membrane fabrication conditions

Membrane No.	Casting solution		Coagulant bath	
	Temperature/ °C	Composition/ wt.%	Temperature/ °C	Composition wt.% silica sol /H ₂ O
FM1	60	PVC/PVP/DB D/DMAc=15/4 /0.5/80.5	25	0/100
FM2	60	PVC/PVP/DB D/DMAc=15/4 /0.5/80.5	25	5/95
FM3	60	PVC/PVP/DB D/DMAc=15/4 /0.5/80.5	25	10/90
FM4	60	PVC/PVP/DB D/DMAc=15/4 /0.5/80.5	25	20/80
FM5	60	PVC/PVP/DB D/DMAc=15/4 /0.5/80.5	25	40/60

30s, followed by immersion in a coagulation bath containing water and silica sol with different concentrations at 25°C. The detailed preparation parameters are listed in Table 1.

After the formation of membranes, the membranes were stored in the water bath for at least 1 day to remove the solvents and then immersed in a tank containing 60% glycerol solution for at least 1 day to prevent the collapse of porous structures. And the membranes were dried in air at room temperature for measurement. The thickness of prepared membranes was measured in different places of membrane, the average membrane thickness was 0.10 ± 0.02 mm. The schematic diagram of the membrane preparation is illustrated in Fig. 1.

2.3 Membrane characterization

2.3.1 Precipitation kinetics

Light transmission experiments were used to simulate the precipitation kinetics of casting solutions in silica sol coagulants. These experiments were carried out using a lab-made device as described by Guo *et al.* (2014). A collimated laser was directed toward the glass plate immersed in the coagulants. The light intensity was captured by the detector and the data were recorded on a computer. The precipitation rate of the PVC casting solution in the coagulants could be characterized by curves of light transmittance versus immersion time.

2.3.2 Characterizations of silica on membrane surface

To verify the silica on membrane surface, the FTIR spectra of the membranes were measured using a FTIR-ATR spectrometer (Thermo Electron Corp, Nicolet 5700, U.S.A.) operating in the wavenumber range of 4000-500 cm⁻¹. Energy dispersive spectroscopy (EDS) was used to detect the silicon element of membrane surface. The membrane was immersed in pure water, with 60% glycerol and 0.1% aqueous solution of formaldehyde. After that it will be removed and rinsed with pure water.

2.3.3 Morphology observation

The morphology of membranes was examined by a scanning electron microscopy (SEM) (JEOL Model JSM-6360 LV, Japan). The membranes were firstly immersed into liquid nitrogen for a few minutes, then broken and deposited on a copper holder. All samples were coated with gold under vacuum before test. The top surfaces of membranes FM1 and FM2, in terms of the mean surface roughness (Ra), were measured by an atomic-force microscopy (BioScopeTM, U.S.A.) using the tapping mode. The prepared membranes were placed on a glass substrate and the surface was scanned in a size of $5 \mu\text{m} \times 5 \mu\text{m}$ with a scanning speed of 2 Hz.

2.3.4 Hydrophilicity measurements

The contact angle between water and the external surface of membrane was measured to evaluate the membrane hydrophilicity using a JC2000A Contact Angle Meter produced by Shanghai Zhongchen Digital Equipment Co., Ltd. (China). To minimize experimental error, the contact angles were measured 5 times for each sample and then averaged.

2.3.5 Mechanical properties

Mechanical properties of membranes were measured by a material test machine (Z010, Germany) at a loading velocity of 50 mm/min. The report values were measured 3 times for each sample and then averaged.

2.3.6 Thermal stability analysis

Differential scanning calorimetry (DSC) was used to investigate the glass transition temperature (T_g) of membranes and their thermal property. In DSC measurement (PerkinElmer Pyris Diamond), the sample was first heated to 300°C at a speed of 10°C/min and kept for 5 min under nitrogen atmosphere to eliminate the effect of the thermal history, then the sample was cooled down to 50°C and the second scan started from 50°C to 300°C. The onset of the transition in the heat capacity was defined as glass transition temperature (T_g).

2.3.7 Permeation property measurements

The permeation flux was measured by UF experimental equipment, as described by Chen *et al.* (2015). All experiments were conducted at 25°C and under the feed pressure of 0.1 MPa. The flux and rejection rate were measured three times and then averaged. The newly prepared membranes were pre-pressured at 0.1 MPa using the pure water for 30 minutes before measurement, then the pure water permeation (J_w) was measured. The permeation flux (J_w) was defined as follows:

$$J_w = \frac{Q}{A \times T} \quad (1)$$

where J_w was the permeation flux of membrane for pure water (L·m⁻²·h⁻¹), Q was the volume of the permeate pure water (L), A was the effective area of the membrane (m²) and T was the permeation time (h). The pure water flux was recorded every 5 minutes at transmembrane pressure of 0.1MPa. Then the pure water was replaced with 500ppm

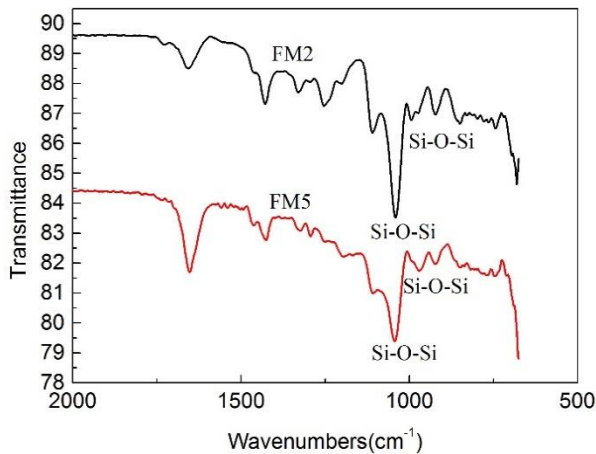


Fig. 2 FTIR spectra of PVC-SiO₂ composite membranes (FM2 and FM5)

BSA for the rejection rate test. The rejection rate (R) was calculated as follows (Zhang *et al.* 2013):

$$R(\%) = (1 - C_p / C_b) \times 100\% \quad (2)$$

where C_p and C_b were protein concentrations in permeate and feed (mg/ml), respectively.

3. Results and Discussion

3.1 FTIR analysis

The FTIR curves of PVC membranes are shown in Fig. 2. The peaks appeared at 1080 cm⁻¹ and 980 cm⁻¹ are both stretching vibration of asymmetrical Si-O-Si groups and stretching vibration of symmetrical Si-O-Si groups appeared at 796 cm⁻¹, respectively. These results confirm that silica has been successfully immobilized on the surface of membranes. The FTIR data clearly showed that the membrane surface contains silicon.

3.2 DSC analysis

As it known to us, PVC is a kind of amorphous polymer with a glass transition temperature (T_g) of 70-80°C (Endo 2002). In Fig. 3, with the addition of silica sol in the coagulation bath, the membrane glass transition temperature increased from 98°C (FM1) to 117°C (FM2). It means that FM2 has a better thermal stability than FM1. In general, inorganic nanoparticles can improve the thermal stability of the blend membrane (Mei *et al.* 2011). The nano silica has a physical cross-linking effect due to the strong interaction between nano silica and PVC molecular chain, which reduce the movement of the polymer chain. In our research system, PVC is a kind of amorphous polymer with low crystallinity. Thus the physical crosslinking effect of nano silica is much more obviously. Therefore, the introduction of nano silica reduces the mobility of polymer chains and increases the T_g of the membrane. The higher the content of nano silica in the membrane, the more obvious the physical cross-linking effect is and the higher the T_g of the PVC membrane is. Actually, the thermodynamic compatibility of

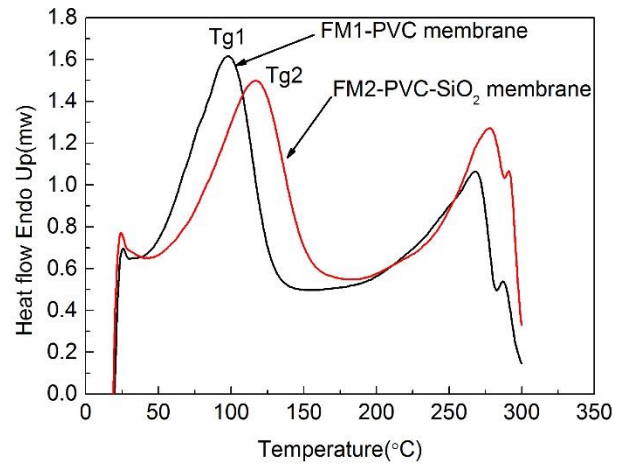


Fig. 3 DSC analysis of PVC membrane (FM1) and PVC-SiO₂ composite membrane (FM2)

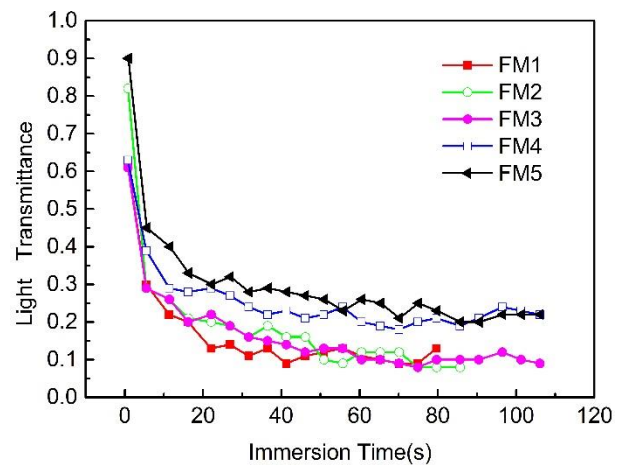


Fig. 4 Precipitation rates with different silica sol contents in the coagulation bath

PVC and silica nanoparticles is related to the Flory-Huggins interaction parameter. Rana *et al.* (1993, 1996a, 1996b) carried out a series of fruitful work in polymer thermal compatibility, which has great significance to our work. Li *et al.* (2009) prepared PES-TiO₂ composite membranes via phase inversion by dispersing TiO₂ nanoparticles in PES casting solutions. DSC results showed that the interaction existed between TiO₂ nanoparticles and PES and the thermal stability of the composite membrane had been improved by the addition of TiO₂ nanoparticles. The shifting of T_g is caused by the interactions between silica nanoparticles and polymers. The surface hydroxyl group can also form a hydrogen bond with the PVC molecules or other group of PVP.

3.3 Precipitation kinetics

As shown in Fig. 4, the order of gelation rate is: FM2>FM1>FM3>FM4>FM5 at 50 seconds. The slowest precipitation rate is observed when the silica sol content is 40 wt.%. The addition of silica sol in the coagulation bath accelerates the precipitation rate when the content of silica sol ranges from 0 wt.% to 5 wt.%. However, with the continues increase in silica sol content, the precipitation rates slow down.

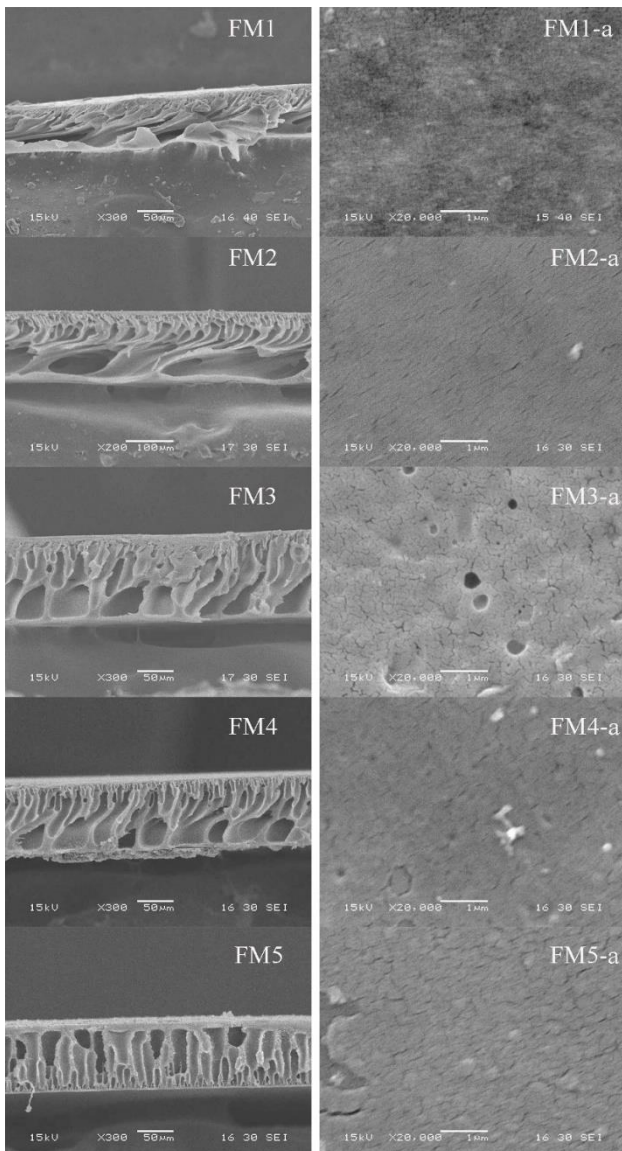


Fig. 5 SEM photographs of the of PVC membranes (Left: original magnification cross section $\times 300$; Right: external surface $\times 20000$)

The effects of silica sol on the precipitation rate lie in two aspects. On one hand, when the content is relatively low, the thermodynamic stability of the coagulation bath will decrease, which lead to a rapid phase separation. On the other hand, when the silica sol content is higher, the diffusion rate between casting solution and coagulation bath will reduce, which lead to a lower precipitation rate. This is similar to the addition of solvent in the coagulation bath. Jian Xu and Z.L. Xu (2002) added DMAc into the coagulation bath to reduce the exchange rate of solvent and non-solvent, delayed phase separation occurs on the inner surface of the membrane. Therefore, the prepared PVC membrane has a dense inner surface and porous structure, high water flux and rejection rate.

3.4 Morphologies of PVC membranes

The top surface morphologies of PVC composite membranes are shown in Fig. 5. It is noted that when the

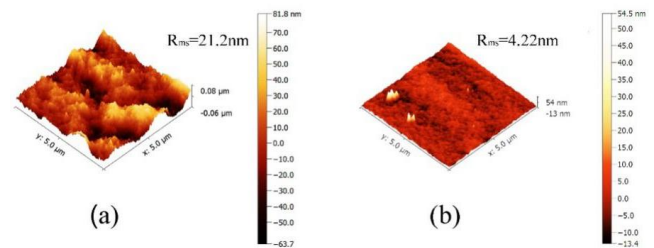


Fig. 6 AFM images of surface morphologies of (a) FM1 (b) FM2

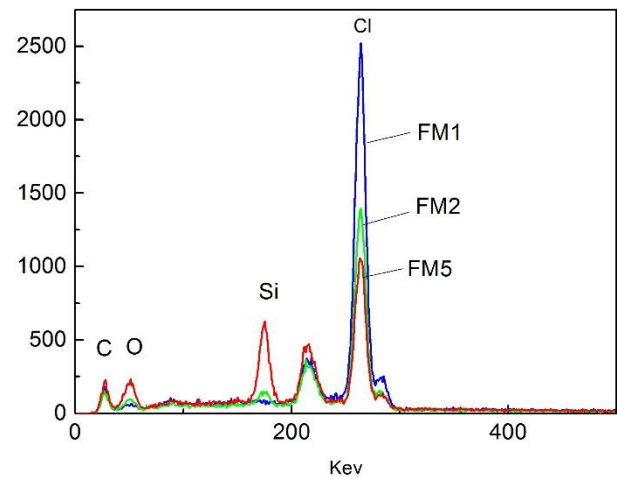


Fig.7 EDS analysis of PVC membranes

silica sol concentration increased, the surface of membranes was gradually covered by a layer of nanoparticles, especially for FM4 and FM5. The EDS data in Fig. 7 also confirmed this situation. It can be seen that the dispersion of nanoparticles is uniform, which will greatly improve the hydrophilicity of the membrane surface. Moreover, when the silica sol concentration continues increases, it will result in a lower precipitation rate and finally lead to a denser surface.

The top surface of PVC membranes were also detected by the AFM technique using the tapping mode. The 3D images of FM1 and FM2 are illustrated in Fig. 6. The membranes prepared with silica sol coagulation bath show lower surface roughness than that of the pristine PVC membrane (FM1), which lead to a relatively smooth structure. As we all know, the lower roughness commonly leads to an increase in anti-fouling performance (Endo 2002, Yu *et al.* 2009). The reduction of “valleys” quantity on the membrane surface will decrease the foulants accumulation, which results in improvement of membrane anti-fouling performance.

The cross-section morphologies of PVC membranes are shown in Fig. 5. The results showed that the cavities are formed in the absence of silica sol due to the instantaneous demixing of casting solution. With the increase of silica sol concentration (< 20 wt.%), a typical transition from cavity structure to finger-like pore structure and asymmetric cross-section structure could be observed in membranes. The reason might be the hydrophilic groups combined with the silica particles lead to an acceleration of solvent and non-solvent exchange and facilitation to form a porous structure

Table 2 EDS data of elements distribution on the membrane surface

Element	FM1(wt.%)	FM2(wt.%)	FM5(wt.%)
C K	34.89	37.38	39.14
N K	0.06	7.52	6.93
O K	2.87	7.94	11.98
Si K	not detected	2.55	10.27
Cl K	62.18	44.60	31.69

Table 3 Mechanical properties of PVC membranes with different silica sol concentrations

Membrane No.	Elongation strength (MPa)	Elastic modulus(MPa)	Yield strength(MPa)
FM1	1.62 ± 0.02	43.28 ± 1.84	0.89 ± 0.07
FM2	1.68 ± 0.09	65.29 ± 0.63	1.17 ± 0.02
FM3	1.68 ± 0.09	63.40 ± 1.62	1.27 ± 0.09
FM4	1.99 ± 0.26	71.17 ± 0.82	1.34 ± 0.05
FM5	3.43 ± 0.46	150.8 ± 0.53	2.97 ± 0.06

(Yu *et al.* 2009). At this point, the composition of the coagulation bath is the main influencing factor that caused the change in membrane structure.

When the silica sol concentration is higher than 20 wt.%, the time of phase separation became much longer and the precipitation velocity is quite lower. The macro-pores are gradually disappeared, the pore-diameter tend to be uniform and the cross-section is symmetrical.

The formation of homogeneous structure is probably caused by the increase of silica sol concentration and is responsible for lower precipitation rate and slower separation between solvent and non-solvent. In this situation, the increasing concentration of silica sol in the coagulation bath is the main factor that prolong the phase separation time. Because the stress of the membrane curing cannot be completely disappeared, the dense surface of the membrane will be formed in the stress concentration.

3.5 EDS analysis

To characterize the silica on the membrane surface, energy dispersive spectroscopy (EDS) was used to detect the silicon element of membrane surface. Fig. 7 and Table 2 reveals that the Si element is successfully inserted on the surface of the membrane. With the silica sol concentration changing from 0 wt.% to 40 wt.%, the energy related to Si element become more intensive, which means more Si element is inserted on the surface.

3.6 Mechanical properties of PVC membranes

The mechanical properties of PVC membranes are shown in Table 3. The results display that the elongation strength, elastic modulus and yield strength of membranes increase with the larger of silica sol concentration and reach to the maximum at concentration of 40 wt.%. The elongation strength of FM5 is more than double that of FM1. The reasons may be the addition of silica sol not only

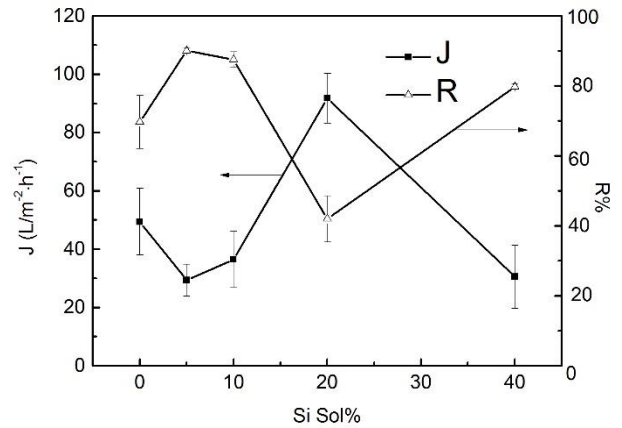


Fig. 9 Permeability of PVC membranes

intensify the interaction force among PVC macromolecules, but also form a crosslinking structure between polymeric chains and silica particles (Yu *et al.* 2009). These factors are enhanced with the increase of silica sol concentration and lead to the increase of mechanical properties. In fact, the blending method will have a great effect on the polymer thermal stability and mechanical properties. A few years ago, Rana *et al.* (1998, 2000a, 1999, 2000b) conducted some research work in this area and achieved good results. In our research system, PVC is a kind of amorphous polymer with low crystallinity. Thus the physical crosslinking effect of nano silica is much more obviously. Therefore, the introduction of nano silica reduces the mobility of polymer chains and increases the mechanical properties of the membrane. The higher the content of nano silica in the membrane, the more obvious the physical cross-linking effect is and the higher the mechanical properties of the PVC membrane.

3.7 Hydrophilicity of PVC membranes

As it known to us, the hydrophilicity is estimated by the water contact angle and the smaller of contact angle, the higher of hydrophilicity. Fig. 8 shows the contact angles obtained from the modified PVC membranes. It is observed that the addition of silica sol in the coagulation bath decrease the contact angle obviously compare to the pristine PVC membrane. For FM5, the contact angle reduces approximately 60%, suggesting that hydroxyl groups of nano silica embedded on the surface can improve the hydrophilicity of the composite membrane. Meanwhile, the higher hydrophilic property is beneficial to the anti-fouling performance.

3.8 Permeability of PVC membranes

The permeability of PVC membranes with different silica sol concentration in the coagulation bath are shown in Fig. 9. It is clearly that the permeation flux enhances with the increase of silica sol content after a small drop, especially for FM4 and then declines with further increase of silica sol concentration. When the silica sol is added into the coagulation bath, the precipitation rate is a little slower and the membrane surface is covered with a layer of silicon.

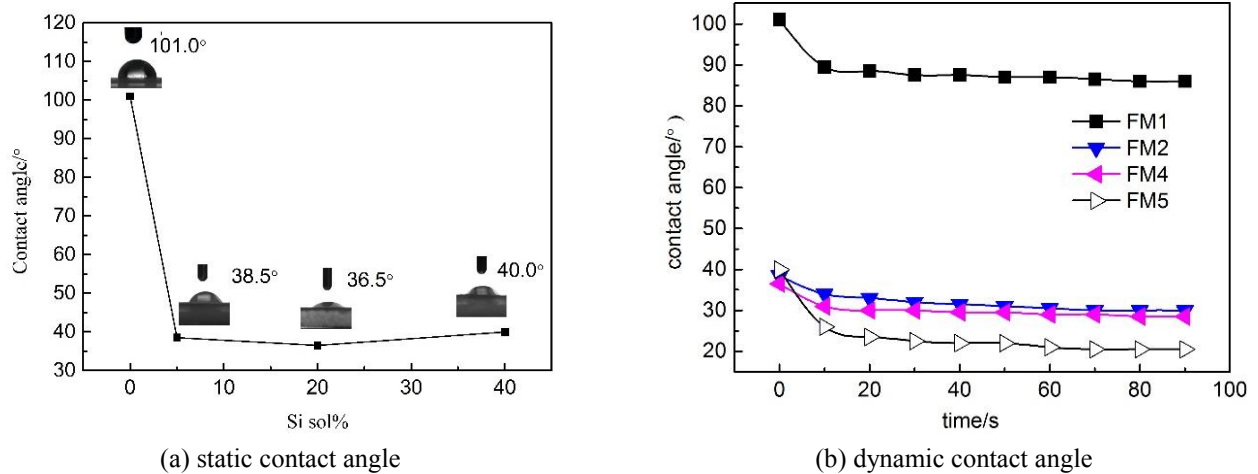


Fig. 8 Contact angle of PVC membranes

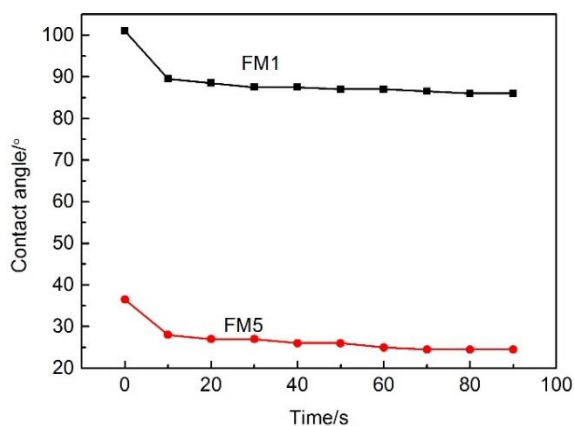


Fig. 10 Contact angles of PVC membranes rinsed after 5 hours under 0.1 Mpa

Therefore, the permeation flux decreases slightly. After that, as it is shown in Figure 5, with the continue increase of silica sol concentration, the surface boundary layer becomes thinner, the membrane flux increases. At the same time, the increase of the membrane hydrophilicity caused by large amount of highly dispersed hydroxyl groups is in favor of attracting water molecules to pass through the membrane matrix. A large amount of finger-like pores generate by instantaneous demixing make the water molecules easier to go through the membrane. The reason of the last reduction is due to the membrane surface covered with a thicker layer of silicon, which reduce the membrane flux. However, silica nanoparticles aggregate and block the pores of PVC membrane surface when the concentration is higher than 20 wt.%, resulting in the hydroxyl exposed on the surface and pore size of the membranes decreased.

3.9 Hydrophilic stability

After 5 hours running under 0.1 Mpa, the membranes were rinsed and the contact angle was tested again, in order to investigate the hydrophilic stability of membrane surface. In Fig. 10, the contact angle of modified membrane FM5 is consistent with that in Fig. 8, much lower than that of FM1, indicating that the hydrophilicity of membrane is very stable.

4. Conclusion

PVC UF membranes were in-situ modified by silica sol in the coagulation bath. The surface hydrophilicity of the PVC membranes increased with the addition of silica sol in the coagulation bath. The FTIR and EDS showed that silica had been successfully immobilized on the surface of membranes and hydroxyl groups on the nano silica particles were generated. The silica sol concentration had effects on the membrane structure and hydrophilicity of PVC membranes. Particularly, the modified membrane with the highest hydrophilicity and permeability was obtained when silica sol concentration was 20 wt.%. The addition of silica sol not only intensified the interaction force among PVC macromolecules, but also formed a crosslinking structure between polymeric chains and nano silica particles, which finally increased the mechanical properties. The self-assembly PVC membranes can not only be applied to the field of water treatment, but also had potential applications in the field of supported catalysts, sensors and so on.

Acknowledgments

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References

- An, Q.F., Qian, J.W., Sun, H.B., Wang, L.N., Zhang, L. and Chen, H.L. (2003), "Compatibility of PVC/EVA blends and the pervaporation of their blend membranes for benzene/cyclohexane mixtures", *J. Membr. Sci.*, **222**(1-2), 113-122.
- Behboudi, A., Jafarzadeh, Y. and Yegani, R. (2016), "Preparation and characterization of TiO₂ embedded PVC ultrafiltration membranes", *Chem. Eng. Res. Des.*, **114**, 96-107.
- Bierbrauer, K., López-González, M., Riande, E. and Mijangos, C. (2010), "Gas transport in fluorothiophenyl modified PVC

- membranes”, *J. Membr. Sci.*, **362**(1-2), 164-171.
- Bilad, M.R., Marbelia, L., Laine, C. and Vankelecom, I.F. (2015), “A PVC-silica mixed-matrix membrane (MMM) as novel type of membrane bioreactor (MBR) membrane”, *J. Membr. Sci.*, **493**(1), 19-27.
- Chen, G.E., Liu, Y.J., Xu, Z.L., Tang, Y.J., Huang, H.H. and Sun, L. (2015), “Fabrication and characterization of a novel nanofiltration membrane by the interfacial polymerization of 1,4-diaminocyclohexane (DCH) and trimesoyl chloride (TMC)”, *RSC Adv.*, **5**(51), 40742-40752.
- Chen, G.E., Zhu, W.W., Xu, S.J., Xu, Z.L., Shen, Q., Sun, W.G., Wu, Q. and Zheng, X.P. (2016), “A PVDF/PVB composite UF membrane improved by F-127-wrapped fullerene for protein waste-water separation”, *RSC Adv.*, **6**(87), 83510-83519.
- Chi, L.N., Wang, J., Chu, T.S., Qian, Y.J., Yu, Z.J., Wu, D.Y., Zhang, Z.J., Jiang, Z. and Leckie, J.O. (2016), “Modeling and optimizing the performance of PVC/PVB ultrafiltration membranes using supervised learning approaches”, *RSC Adv.*, **6**(33), 28038-28046.
- Cui, Y., Yao, Z.K., Zheng, K., Du, S.Y., Zhu, B.K., Zhu, L.P. and Du, C.H. (2015), “Positively-charged nanofiltration membrane formed by quaternization and cross-linking of blend PVC/P(DMA-co-MMA) precursors”, *J. Membr. Sci.*, **492**, 187-196.
- Endo, K. (2002), “Synthesis and structure of poly(vinyl chloride)”, *Prog. Polym. Sci.*, **27**(10), 2021-2054.
- Fan, X.C., Su, Y.L., Zhao, X.T., Li, Y.F., Zhang, R.N., Zhao, J. J., Jiang, Z.Y., Zhu, J.A., Ma, Y.Y. and Liu, Y. (2014), “Fabrication of polyvinyl chloride ultrafiltration membranes with stable antifouling property by exploring the pore formation and surface modification capabilities of polyvinyl formal”, *J. Membr. Sci.*, **464**(6), 100-109.
- Fang, L.F., Zhu, B.K., Zhu, L.P., Matsuyama, H. and Zhao, S.F. (2017), “Structures and antifouling properties of polyvinyl chloride/poly(methyl methacrylate)-graft-poly(ethylene glycol) blend membranes formed in different coagulation media”, *J. Membr. Sci.*, **524**, 235-244.
- Guo, J.L., Li, Y., Xu, Z.L., Zhang, P.Y. and Yang, H. (2014), “Investigation of polyvinylidene fluoride membranes prepared by using surfactant OP-10 alone or with a second component, as additives, via the non-solvent-induced phase separation (NIPS) process”, *J. Macromol. Sci., Phys.*, **53**(8), 1319-1334.
- Harmer, M.A., Farneth, W. E. and Sun, Q. (1996), “High surface area nafion resin/silica nanocomposites: A new class of solid acid catalyst”, *J. Am. Chem. Soc.*, **118**(33), 7708-7715.
- Harmer, M.A., Sun, Q., Vega, A.J., Farneth, W.E., Heidekum, A. and Hoelderichb, W.F. (2000), “Nafion resin-silica nanocomposite solid acid catalysts. Microstructure-processing-property correlations”, *Green Chem.*, **2**(1), 7-14.
- Hosseini, S.M., Madaeni, S.S., Zendeenam, A., Moghadassi, A.R., Khodabakhshi, A.R. and Sanaeepur, H. (2013), “Preparation and characterization of PVC based heterogeneous ion exchange membrane coated with Ag nanoparticles by (thermal-plasma) treatment assisted surface modification”, *J. Ind. Eng. Chem.*, **19**(3), 854-862.
- Irfan, M., Idris, A., Yusof, N.M., Khairuddin, N.F.M. and Akhmal, H. (2014), “Surface modification and performance enhancement of nano-hybrid f-MWCNT/PVP90/PES hemodialysis membranes”, *J. Membr. Sci.*, **467**(19), 73-84.
- Karan, S., Jiang, Z.W. and Livingston, A.G. (2015), “Sub-10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation”, *Science*, **348**(6241), 1347-1351.
- Kim, D.S., Kang, J.S., Kim, K.Y. and Lee, Y.M. (2002), “Surface modification of a poly(vinyl chloride) membrane by UV irradiation for reduction in sludge adsorption”, *Desalination*, **146**(1-3), 301-305.
- Kong, X., Zhou, M.Y., Lin, C.E., Wang, J., Zhao, B., Wei, X.Z. and Zhu, B.K. (2016), “Polyamide/PVC based composite hollow fiber nanofiltration membranes: Effect of substrate on properties and performance”, *J. Membr. Sci.*, **505**(2016), 231-240.
- Li, J.F., Xu, Z.L., Yang, H., Yu, L.Y. and Liu, M. (2009), “Effect of TiO₂ nanoparticles on the surface morphology and performance of microporous PES membrane”, *Appl. Surf. Sci.*, **255**(9), 4725-4732.
- Marbelia, L., Bilad, M.R., Bertels, N., Laine, C. and Vankelecom, I.F. (2016), “Ribbed PVC-silica mixed matrix membranes for membrane bioreactors”, *J. Membr. Sci.*, **498**, 315-323.
- Mei, S., Xiao, C.F., Hu, X.Y. and Shu, W. (2011), “Hydrolysis modification of PVC/PAN/SiO₂ composite hollow fiber membrane”, *Desalination*, **280**(1-3), 378-383.
- Meng, N., Wang, Z.Y., Low, Z.X., Zhang, Y.Q., Wang, H.T. and Zhang, X.W. (2015), “Impact of trace graphene oxide in coagulation bath on morphology and performance of polysulfone ultrafiltration membrane”, *Sep. Purif. Technol.*, **147**, 364-371.
- Rabiee, H., Vatanpour, V., Farahani, M.H.D.A. and Zarrabi, H. (2015), “Improvement in flux and antifouling properties of PVC ultrafiltration membranes by incorporation of zinc oxide (ZnO) nanoparticles”, *Sep. Purif. Technol.*, **156**, 299-310.
- Rana, D., Cho, K., Woo, T., Lee, B.H. and Choe, S. (1999), “Blends of ethylene 1-octene copolymer synthesized by Ziegler-Natta and metallocene catalysts. I. Thermal and mechanical properties”, *J. Appl. Polym. Sci.*, **74**(5), 1169-1177.
- Rana, D., Kim, H.L., Kwag, H. and Choe, S. (2000a), “Hybrid blends of similar ethylene 1-octene copolymers”, *Polymer*, **41**(19), 7067-7082.
- Rana, D., Kim, H.L., Kwag, H., Rhee, J., Cho, K., Woo, T., Lee, B. H. and Choe, S. (2000b), “Blends of ethylene 1-octene copolymer synthesized by Ziegler-Natta and metallocene catalysts. II. Rheology and morphological behaviors”, *J. Appl. Polym. Sci.*, **76**(13), 1950-1964.
- Rana, D., Lee, C.H., Cho, K., Lee, B.H. and Choe, S. (1998), “Thermal and mechanical properties for binary blends of metallocene polyethylene with conventional polyolefin”, *J. Appl. Polym. Sci.*, **69**(12), 2441-2450.
- Rana, D., Mandal, B.M. and Bhattacharyya S.N. (1996b), “Analogue calorimetric studies of blends of poly(vinyl ester) and polyacrylate”, *Macromolecules*, **29**(5), 1579-1583.
- Rana, D., Mandal, B.M. and Bhattacharyya, S.N. (1993), “Miscibility and phase diagrams of poly (phenyl acrylate) and poly (styrene-co-acrylonitrile) blends”, *Polymer*, **34**(7), 1454-1459.
- Rana, D., Mandal, B.M. and Bhattacharyya, S.N. (1996a), “Analogue calorimetry of polymer blends: Poly(styrene-co-acrylonitrile) and poly(phenyl acrylate) or poly(vinyl benzoate)”, *Polymer*, **37**(12), 2439-2443.
- Ulatan, S. and Balköse, D. (1996), “Diffusivity, solubility and permeability of water vapor in flexible PVC/silica composite membranes”, *J. Membr. Sci.*, **115**(2), 217-224.
- Vatanpour, V., Madaeni, S.S., Moradian, R., Zinadini, S. and Astinchap, B. (2011), “Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite”, *J. Membr. Sci.*, **375**(1-2), 284-294.
- Velev, O.D., Jede, T.A., Lobo, R.F. and Lenhoff, A.M. (1997), “Porous silica via colloidal crystallization”, *Nature*, **389**(6650), 447-448.
- Xu, H.P., Yu, Y.H., Lang, W.Z., Yan, X. and Guo, Y.J. (2015), “Hydrophilic modification of polyvinyl chloride hollow fiber membranes by silica with a weak in situ sol-gel method”, *RSC Adv.*, **5**(18), 13733-13742.
- Xu, J. and Xu, Z.L. (2002), “Poly(vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from

- PVC/additives/solvent”, *J. Membr. Sci.*, **208**(1), 203-212.
- Yang, S. and Liu, Z.Z. (2003), “Preparation and characterization of polyacrylonitrile ultrafiltration membranes”, *J. Membr. Sci.*, **222**(1), 87-98.
- Yu, L.Y., Xu, Z.L., Shen, H.M. and Yang, H. (2009), “Preparation and characterization of PVDF-SiO₂ composite hollow fiber UF membrane by sol-gel method”, *J. Membr. Sci.*, **337**(1-2), 257-265.
- Zhang, J., Wang, Z.W., Liu, M.X., Zhao, F.L. and Wu, Z.C. (2017), “In-situ modification of PVDF membrane during phase-inversion process using carbon nanosphere sol as coagulation bath for enhancing anti-fouling ability”, *J. Membr. Sci.*, **526**, 272-280.
- Zhang, P.Y., Yang, H., Xu, Z.L., Wei, Y.M., Guo, J.L. and Chen, D.G. (2013), “Characterization and preparation of poly(vinylidene fluoride) (PVDF) microporous membranes with interconnected bicontinuous structures via non-solvent induced phase separation (NIPS)”, *J. Polym. Res.*, **20**(2), 66-78.
- Zhu, A.P., Cai, A.Y., Zhou, W.D. and Shi, Z.H. (2008), “Effect of flexibility of grafted polymer on the morphology and property of nanosilica/PVC composites”, *Appl. Surf. Sci.*, **254**(13), 3745-3752.

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