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Synthesis and characterization of low content of different SiO₂ materials composite poly (vinylidene fluoride) ultrafiltration membranes

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ABSTRACT

A comparison of the morphology and performance of virgin poly (vinylidene fluoride) (PVDF) ultrafiltration (UF) membrane, and PVDF-composite membranes with low content of two different SiO₂ (N-SiO₂ and M-SiO₂ particles) was carried out. Cross-sectional area and surface morphology of the membranes were observed by scanning electron microscopy and atomic force microscopy. Surface hydrophilicity of the porous membranes was determined through the measurement of a contact angle. Performance tests were conducted on the composite membranes through water flux and bovine serum albumin (BSA) retention. Average pore size and surface porosity were calculated based on the permeate flux. Thermal stability and mechanical stability were determined by thermogravimetric analysis and tensile stress tests. The results indicate that N-SiO₂/PVDF (P-N) membranes possessed larger average pore size and porosity, which led to higher water flux and slight decline in BSA retention. On the other hand, M-SiO₂/PVDF (P-M) membranes had better mechanical stability and astiface roughness. Both of the P-N and P-M membranes exhibited typical asymmetric morphology and improved thermal stability.

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1. Introduction

Poly (vinylidene fluoride) (PVDF) is a commonly used ultrafiltration (UF) membrane material because of its excellent chemical resistance and thermal stability [1,2]. However, these membranes are susceptible to fouling by proteins and oils because of the high hydrophobicity of PVDF materials, which leads to a sharp drop in pure water flux of membrane and limits their application in filtrating aqueous mixtures, such as wastewater treatment and biomedical technology. Numerous attempts to modify membrane materials that are less susceptible to fouling have been reported in literature. Recent studies of PVDF modifications have focused on blending the polymer with inorganic materials. The addition of inorganic fillers has led to increased membrane permeability and improved control of membrane surface properties [3–11].

Inorganic materials that have been blended with PVDF include Al₂O₃ [3], Fe₃O₄ [4], ZrO₂ [5], TiO₂ [6], silica [7–10], and some small-molecule inorganic salts, such as lithium salts [11]. Among these materials, silica is the most convenient and widely used because of its mild reactivity and well-known chemical properties. Bottino et al. [7] prepared novel organic–inorganic membranes formed by uniform dispersion of fine silica particles in the porous matrix of PVDF, and observed that as the concentration of SiO₂ in PVDF increased,

the permeate flux increased with the lowered protein retention. Liu et al. [8] presented a new method to prepare organic-inorganic hybrid PVDF/Si membranes by adding tetraethyl orthosilicate (TEOS) into the PVDF casting solution. Tensile stress and elastic modulus of the hybrid membrane were almost doubled when TEOS content was approximately 12 wt.%. Arhtanareeswaran et al. [9] reported that increasing appropriate concentration of SiO₂ in CA polymer increased the molecular weight cutoff (MWCO), pore radius, surface porosity, pore density, and obtained outstanding flux recovery property of the blend membranes. A common feature of these modifications was the addition of a high proportion of inorganic materials. The morphology and the properties of PVDF membranes were affected by the quantity of inorganic materials added. A high concentration of inorganic particles could improve membrane surface hydrophilicity, water flux, thermal stability, anti-fouling performance clearly, but give negative effect on membrane mechanical stability and molecular weight cut-off with inorganic particle aggregation. These big aggregation particles might cause macroscopic voids and cracks by polymer shrink for inorganic–organic interfacial tension. Accordingly, M-SiO₂/ PVDF UF membranes were prepared and reported by our group, and the result indicated that adding a small amount of M-SiO₂ could improve membrane performance effectively without changing the morphology of hybrid membranes [10].

In the present study, membrane structure and performance of N-SiO₂/PVDF were compared with the M-SiO₂/PVDF membranes we have reported [10]. The surface and inner structures of the sample membranes were studied using several methods. The contact angle,

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thermal stability, mechanical stability, water flux, and BSA retention efficiency of the membranes were also measured. The main purpose of the present study was to keep original membrane pore structure by adding low contents of silica particles and improve the performance of PVDF membrane effectively. Meanwhile, utilizing various methods to investigate and compare the effects of N-SiO₂ and M-SiO₂ materials on the performance and structure of the PVDF UF membrane at the same condition.

2. Experimental

2.1. Materials

PVDF used was obtained from Shanghai New Materials Co., Ltd. (FR-904, intrinsic viscosity = 1.4-1.9 dL/g). N-SiO₂ (nano-SiO₂) was obtained from Wuhan University Silicone New Material Co., Ltd. in Hubei. M-SiO₂ (mesoporous SiO₂, SBA-15) was provided by our lab. Polyvinylpyrrolidone (PVP, K30, MW = 25,000-40,000) and dimethylacetamide (DMAC) were procured from Sinopharm Chemical Reagent Co., Ltd. Bovine serum albumin (BSA, MW = 67,000) was provided from Shuangxuan Microorganism Substrate Plant in Beijing.

2.2. Membrane preparation

N-SiO₂/PVDF and M-SiO₂/PVDF composite membranes were prepared by the phase-inversion method. Casting dopes were prepared by adding SiO₂ particles into the solvent including PVDF, PVP, and DMAC, and then stirring them at 60 °C to obtain optimal particle dispersion. The polymer solutions were then kept in a vacuum oven at 60 °C to remove air bubbles. The composition of the casting solution was illustrated in Table 1. The membranes were labeled as P-N and P-M, where N-SiO₂/PVDF was represented by P-N and M-SiO₂/PVDF was represented by P-M.

The solutions were cast uniformly onto a glass substrate by means of a hand-casting knife and then immersed in a bath filled with deionized water. The formed membranes were peeled off and subsequently washed thoroughly with deionized water to remove residual solvent until they were used as samples for testing. The wet thickness of the sample membranes was maintained at 250 µm.

2.3. Membrane characterization

2.3.1. Morphology observation

N-SiO₂ and M-SiO₂ particles were observed in a 2010FEF (JOEL, Japan) TEM, its surface area was obtained by the Brunauer-Emmett-Teller (BET) method on a Micromeritics Tristar 3000 system (USA) at 77 K before degassed in a vacuum at 180 °C. All specimens of P-N and P-M were coated with a conductive layer of sputtered gold. The cross-section morphologies of the composite membranes were observed using scanning electron microscopy (SEM) (FEI Quanta 200, Holland). A contact mode atomic force microscopy (AFM)

Table	1
Table	

omposition (of	casting	solutions.
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Composition of casting solutions.						
Membranes	PVDF	DMAC	N-SiO ₂	M-SiO ₂	PVP	
	(wt.%)					
P-0	20	76	0	-	4	
P-N-1	19.96	76	0.04	-	4	
P-N-2	19.93	76	0.07	-	4	
P-N-3	19.89	76	0.11	-	4	
P-N-4	19.86	76	0.14	-	4	
P-M-1	19.96	76	-	0.04	4	
P-M-2	19.93	76	-	0.07	4	
P-M-3	19.89	76	-	0.11	4	
P-M-4	19.86	76	-	0.14	4	

(SPM-9500J3, SHIMADZU) in air was used to investigate the membrane surface roughness parameters.

2.3.2. Contact angle and thermal gravimetric analysis (TGA)

Contact angle θ was measured with a DSA100 instrument (Germany, Kruss Company). Each concentration of inorganic particles membrane was measured 5 times at five different points. Each value was obtained 3 min after dropping water on the membrane surface. And the average value was recorded.

Thermal stability of the hybrid PVDF samples was analyzed with Setaram SETSYS Evolution 16 thermogravimetric analyzer by heating from room temperature to 800 °C at a rate of 10 °C/min under nitrogen gas.

2.3.3. Mechanical stability

Tensile stress and strain at break of the wet porous membranes were measured using an AGS-J (SHIMADZU) universal tensile testing machine under ambient conditions. The samples were tested at least three times, and the average value was recorded. Measurements were carried out at room temperature with the rate of pull at 2 mm/min.

2.3.4. UF performance

The flux of hybrid PVDF membranes was carried out using a 300 ml stirred (500 rpm) dead-ended filtration cell with approximately 32.2 cm² membrane area. The membrane was previously filtered with pure water for 40 min (0.1 MPa) to obtain a steady flux, and then the retention was characterized with a BSA aqueous solution (200 mg/L, pH 8.5). Protein concentration in the permeation and the solution was determined by an UV-1700 spectrophotometer (SHIMADZU, Japan) at λ_{max} of 280 nm. The ratio of permeate flux decline was ascertained with the reduction percentage of the initial permeate flux and the stable permeate flux (obtained after filtrated BSA aqueous solution for 120 min at 0.1 MPa) of the BSA aqueous solution. Water flux (J_w) was determined using the following equation

$$J_W = \frac{Q}{A \times \Delta T} \tag{1}$$

where Q was the quantity of pure water permeated (L), A was the membrane area (m²), and ΔT was the sampling time (h).

The BSA retention was calculated by Eq. (2).

$$R\% = \frac{C_f - C_p}{C_f} \times 100\% \tag{2}$$

where C_p and C_f were the concentrations of BSA in permeate and in feed, respectively.

The ratio of permeate flux decline was calculated as Eq. (3).

$$m\% = \frac{J_0 - J_1}{J_0} \times 100\% \tag{3}$$

where J_0 and J_1 were the initial permeate flux and the stable permeate flux of the BSA aqueous solution, respectively.

2.3.5. Pore analysis

Membrane porosity was measured in the method of dry-wet weight which was determined according to a procedure reported by Chen et al. [12]. Porosity ε (%) of the membranes was determined according to Eq. (4) [13].

$$\epsilon = \frac{(W_1 - W_2)/\rho_{water}}{(W_1 - W_2)/\rho_{water} + W_2/\rho_{PVDF}} \times 100\%$$
(4)

where, W_1 was the wet sample weight, W_2 was the dry sample weight, ρ_{water} was the density of pure water at 25 °C (kg/m³) and ρ_{PVDF} was the density of dry state membrane (kg/m³).

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Table

Average pore size r_m (m) was determined by the filtration velocity method. According to the Guerout–Elford–Ferry equation, r_m can be calculated as follows [14,15]:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta IQ_t}{\varepsilon \times A \times \Delta P}}$$
(5)

where, η was the water viscosity at 25 °C, *l* was the membrane thickness (m), Q_t was the volume of the permeate water per unit time (m³/h), *A* was the effective area of the membrane (m²), and ΔP was the operational pressure (0.1 MPa).

3. Results and discussion

3.1. Membrane morphology

To investigate the effects of the presence of N-SiO₂ and M-SiO₂ particles, the composite membranes of P-N and P-M were observed using SEM and AFM apparatus. The cross-section SEM images of P-N-2, P-M-2, and virgin membrane are shown in Fig. 1. The same inner finger-like porous-surface structures and the sponge wall porous structures with a relatively thick skin layer were distributed on their cross-sections. Moreover, all of the membranes exhibited typical asymmetric morphology with finger-like pores linked by sponge walls and contained large numbers of micropores for the finger-like pores communicating with each other [10]. The cross-section structures clearly had no apparent differences between the original and the modified PVDF membranes. These results demonstrated that the addition of low contents of SiO₂ particles with different morphologies did not have an apparent effect on the structures of the cross-section.

The surface roughness parameters of the membranes from the images over areas of 4.0 μ m × 4.0 μ m are given in Table 2. Fig. 2 shows the three-dimensional AFM surface images of P-0, P-N-4, and P-M-4. R_a is the arithmetic mean roughness, R_{ms} is the square average roughness, and R_p is the average depth within the given surface area. All roughness parameters of neat PVDF membrane were larger. All values of the P-M-4 were lesser. The M-SiO₂/PVDF membrane had denser skins and smoother surface.

Table 3 shows the porosity and average pore size data of P-N and P-M composite membranes. The porosity and average pore size of composite membranes, which had inconspicuous change from P-M, also clearly had a slight increase with the addition of N-SiO₂. For the high surface energy, nanometer materials which aggregated easily were difficult to disperse uniformly. Adding a certain amount of N-SiO₂ particles enhanced the formation of larger pores in the vicinity of N-SiO₂ aggregates as well as the defects in the membrane, thereby increasing porosity. Furthermore, there were interfacial stresses between the polymer and N-SiO₂ particles, causing the formation of interfacial pores due to the shrinkage of the organic phase during the demixing process, which in turn caused an increase in average pore size with the addition of the lower amount of N-SiO₂ [16]. Therefore, a low content of smaller SiO₂ particles had no effect on the macrostructure but led to a slight change in the inner pore of the membrane.

2		
an managementance of M C:O	M CO	and the DVDE membrane

Surface	parameters	01 14-21	O_2 , ivi-Si	O_2 , and	une .	PVDF	memorane.

Membranes BET Surface Area of SiO ₂ (m ² g ⁻¹)	Surface Roughness (4 μ m $ imes$ 4 μ m)			
	R_a (nm)	R_{ms} (nm)	R_p (nm)	
P-0	0	34.191	42.508	156.510
P-N-4	447.8809 (N-SiO ₂)	32.372	40.799	135.660
P-M-4	579.0868 (M-SiO ₂)	27.246	34.767	124.550

3.2. Hydrophilicity of membrane

Hydrophilicity is one of the important properties of membranes that could affect the water flux and anti-fouling ability of PVDF membrane. In the present study, membrane hydrophilicity was evaluated through contact angle with pure water, and membrane surface hydrophilicity was higher when its contact angle was smaller. The contact angle data of P-N and P-M are shown in Fig. 3. Compared with that of virgin PVDF membrane, the contact angle data of both modified membranes with different SiO₂ concentrations decreased dramatically. This result indicates that the hydrophilicity of the composite membranes was improved with the addition of SiO₂ particles because the hydrophilic SiO₂ particles, which contained hydroxyl groups adsorbed on the membrane surface, were responsible for the increased hydrophilicity. The hydrophilicity of each concentration of P-M membrane was better than that of the P-N membrane. This observation could be associated with the different morphologies between N-SiO₂ and M-SiO₂. From Fig. 4 and Table 2, the BET surface area of N-SiO₂ and M-SiO₂ was 448 and 579 cm²g⁻¹, respectively. Moreover, a highly ordered two-dimensional hexagonal mesostructure and thick uniform silica walls were observed on M-SiO₂. Compared with N-SiO₂ particles, M-SiO₂ had a large surface area, high porosity, controllable and narrowly distributed pore sizes, and high density of silanol groups (SiOH) distributed over the silica surfaces. However, the contact angle increased when the M-SiO₂ concentration was more than 0.07 wt.%. The same trend of P-N membrane was obtained in Fig. 3. This result could be attributed to the partial particle aggregation, resulting in a decrease in the effective hydrophilic area and hydroxyl group number [10]. N-SiO₂ aggregation was more pronounced than that of M-SiO₂ because of the distinctive nature of the nanometer materials. The results demonstrate that adding low content of M-SiO₂ into the PVDF membrane could improve its hydrophilicity, the effect of which was more obvious than adding N-SiO₂.

3.3. Thermal stability

The thermal stabilities of the membranes were investigated by TGA, and the results of neat PVDF, P-N-4, and P-M-4 are shown in Fig. 5 and Table 4. The thermal decomposition temperature (T_d , defined as the temperature at 3% weight loss) [15] of the composite membranes increased when compared with P-0. The silica particles may hinder the volatility of the decomposed products obtained from pyrolysis and limit the continuous decomposition of PVDF content because of the dispersion and good thermal transmission



Fig. 1. SEM images of the cross-section structures of original PVDF (P-0), N-SiO₂/PVDF (P-N-2), and M-SiO₂/PVDF (P-M-2) membranes.

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Fig. 2. Three-dimensional AFM surface images of the membranes: (a) original PVDF (P-0); (b) N-SiO₂/PVDF (P-N-4); (c) M-SiO₂/PVDF (P-M-4).

properties; this effect could result in the enhancement of the thermal decomposition temperature [16,17]. For all the membranes, two main weight loss regions were observed. A slight weight loss before 320 °C was observed for all samples. This weight loss was considered to correspond to the absorbed water in the membranes. At the region of 320–440 °C, P-N-4 had lesser weight loss at 13.94% and higher T_d at

Table 3

The ratio of porosity and average pore size of N-SiO₂/PVDF (P-N) and M-SiO₂/PVDF (P-M) UF membranes.

Membrane	Porosity (%)		Average pore (10 ⁻⁸ m)	es size
	P-N	P-M	P-N	P-M
0	67.7 ± 0.2	67.7 ± 0.2	7.5 ± 0.3	7.5 ± 0.3
1	70.9 ± 0.1	67.7 ± 0.3	7.4 ± 0.2	7.7 ± 0.2
2	74.7 ± 0.1	65.1 ± 0.4	8.0 ± 0.2	8.1 ± 0.3
3	75.3 ± 0.2	67.3 ± 0.3	7.8 ± 0.1	7.5 ± 0.2
4	75.4 ± 0.3	70.8 ± 0.2	8.5 ± 0.3	7.5 ± 0.2



Fig. 3. Contact angle of N-SiO₂/PVDF (P-N) and M-SiO₂/PVDF (P-M) composite membranes.

385 °C. These results were probably due to the larger number of interactions between PVDF chains and N-SiO₂ surface groups [15]. The second weight loss region appeared at 440–530 °C, which was due to the degradation of random scission of PVDF units [18]. In the range of overall weight loss, the weight loss percentage of P-N-4 and P-M-4 were observed to be both lower than that of P-0. These results demonstrated that the thermal stabilities of both hybrid membranes increased with the addition of low inorganic silica content, and that the different morphologies of silica had a certain influence on the pyrolysis process of hybrid membranes but had inconspicuous effect on weight residue. The results also demonstrated that two kinds of SiO₂ particles were inserted in the PVDF membranes successfully. The presence of SiO₂ (with hydroxyl) in the membrane-forming materials strengthened the inorganic silica network of the hybrid PVDF membranes, which led to a corresponding enhancement in their thermal stabilities [19].

3.4. Mechanical stability

In industrial applications of membranes, mechanical properties are very important for consistent stable performance. Therefore, data on tensile stress and strain at break of flat membranes were determined. Fig. 6 shows the mechanical properties of PVDF, N-SiO₂/PVDF, and M-SiO₂/PVDF composite membranes. The mechanical stability of the membranes was clearly enhanced with the addition of silica. This trend was interpreted by the interactions between silica and PVDF. According to the reported paper, silica particles could act as a cross-linking point in the composite membranes to link the polymeric chains and increase the rigidity of polymeric chains, indicating that more energy was needed to break down the bond between silica and PVDF [15]. However, both tensile stress and strain at break value of the N-SiO₂ composite membranes were less than that of the M-SiO₂ composite membranes. The high surface energy of nano



Fig. 4. TEM images of N-SiO₂ and M-SiO₂.

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Fig. 5. TGA curves of original PVDF (P-0), N-SiO₂/PVDF (P-N), and M-SiO₂/PVDF (P-M) hybrid membranes.

materials caused N-SiO₂ particles to aggregate and disperse nonuniformly in the polymer matrix, thereby forming a number of stress convergence points in the membrane system under the action of external force, which eventually led to the weakening of the mechanical stability of the membrane. These results were consistent with the data of membrane pore and contact angle. Therefore, blending PVDF with M-SiO₂ improved the membrane mechanical stability more effectively than blending with N-SiO₂.

3.5. Effect of the addition of different silica on membrane water flux and BSA retention

The water flux and BSA retention of P-N membranes were compared with those of P-M membranes. After completion of compaction, the water flux and BSA retention of the blended membranes were studied at 0.1 MPa pressure, the results of which are shown in Fig. 7. The water flux increased with the addition of silica, whereas the addition of N-SiO₂ improved water flux more effectively than the addition of M-SiO₂. These results could be associated with the cooperation of membrane hydrophilicity and inner pore morphology. However, the BSA retention of P-N membranes was decreased by the blending of silica materials distinctly. This result was caused by the increase in membrane porosity and average pore size (Table 3). Moreover, the P-N composite membranes had lower BSA retention compared with the P-M membrane. As mentioned in Sections 3.2 and 3.4, further aggregation and non-uniform dispersion of N-SiO₂ in the polymer matrix not only led to the weakening of the mechanical stability but also caused larger inner pore. The results observed in Table 3 confirmed the trends of water flux and BSA retention shown in Fig. 6.

3.6. Anti-fouling performance

The anti-fouling performance of the UF membranes could be evaluated through the ratio of permeate flux decline (m). A lower m is equal to better anti-fouling performance of the composite membrane. Fig. 8 shows the permeate fluxes (initial and stable permeate fluxes)

Table 4

Weight loss percentages of the membranes.

Temperature (°C)	Weight loss percentage (%)		
	P-0	P-N-4	P-M-4
30-800	84.44	73.39	72.10
320-440	24.06	13.94	21.73
440-530	50.12	50.61	42.36



Fig. 6. Tensile stress and strain at break of N-SiO₂/PVDF and M-SiO₂/PVDF composite membranes with various SiO₂ contents.

and the ratio of permeate flux decline of P-N and P-M membranes in the filtration test of BSA aqueous solution. As the silica concentration increased, the permeate flux of both P-N and P-M also increased effectively. After comparing the initial permeate flux with the stable one, m was calculated and is given in Fig. 8. Each concentration of P-M membrane clearly had a lower *m* than that of the P-N membrane. As observed in Figs. 3 and 8, the lower contact angle value corresponded to the smaller ratio of the permeate flux decline value, suggesting that the anti-fouling performance of the composite membranes was better than that of P-0, and each P-M membrane had superior anti-fouling performance over the P-N membranes. This observation could be explained by the hydrophilicity and membrane surface roughness of the membranes if the operating conditions are not taken into account. Membrane hydrophilicity and surface roughness are known to be the two main effective factors that affect the surface-adsorption properties of the membrane [3,6]. From the results of the contact angle test and AFM analysis, the M-SiO₂/PVDF membrane had lower contact angle and denser skins as well as smoother surface than that of the N-SiO₂/PVDF membrane. The membrane with hydrophilic and smoother surface is known to have greater anti-fouling capability because the coarser membrane is liable to absorb protein in water to reduce surface energy [6]. Accordingly, the P-M membrane with less surface roughness had low m. Consequently, with the interaction of surface roughness and hydrophilicity, M-SiO₂ improved membrane anti-fouling performance more effectively than P-N.



Fig. 7. Water flux (0.1 MPa) and BSA retention of PVDF membranes made with different concentrations of N-SiO₂ and M-SiO₂.

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Fig. 8. The ratio of permeate flux decline and permeate flux (BSA aqueous solution) of N-SiO_2/PVDF (P-N) and M-SiO_2/PVDF (P-M) membranes.

4. Conclusion

PVDF composite membranes blended with different morphology silica were fabricated using a phase inversion method. A comparison of the morphology, hydrophilicity, thermal stability, mechanical stability and permeation performance of composite membranes between N-SiO₂/PVDF and N-SiO₂/PVDF membranes was carried out. The results of various measurements demonstrated that silica morphology had an obvious effect on the performance of the PVDF membranes. Low M-SiO₂ content had an inconspicuous effect on

membrane morphology, but P-N had a slight increase in membrane porosity and average pore size. The P-M membrane had better hydrophilicity and less surface roughness than the P-N membrane. The thermal stability and water flux of both composite membranes were enhanced. Higher tensile stress and stain at break were obtained on P-M. The UF experiments also suggest that M-SiO₂ had more effective influence on membrane anti-fouling performance.

References

- [1] M. Khayet, C.Y. Feng, K.C. Khulbe, T. Matsuura, Polymer 43 (2002) 3879–3890.
- [2] P. Wang, K.L. Tan, E.T. Kang, J. Membr. Sci. 195 (2002) 103-114
- [3] L. Yan, Y.S. Li, C.B. Xiang, J. Membr. Sci. 276 (2006) 162-167.
- [4] Z.Q. Huang, K. Chen, S.N. Li, X.T. Yin, Z. Zhang, H.T. Xu, J. Membr. Sci. 315 (2008) 164–171.
- [5] A. Bottino, G. Capannelli, A. Comite, Desalination 146 (2002) 35-40.
- [6] X.C. Cao, J. Ma, X.H. Shi, Appl. Surf. Sci. 253 (2006) 2003–2010.
- [7] A. Bottino, G. Capannelli, V. D'Asti, P. Piaggio, Sep. Purif. Technol. 22 (2001) 269–275.
- [8] X.J. Liu, Y.L. Peng, S.L. Ji, Desalination 221 (2008) 376-382.
- [9] G. Arthanareeswaran, T.K. Sriyamuna Devi, M. Raajenthiren, Sep. Purif. Technol. 64 (2008) 38–47.
- [10] C.J. Liao, J.Q. Zhao, P. Yu, H. Tong, Y.B. Luo, Desalination 260 (2010) 147-152.
- [11] A. Mansourizadeh, A.F. Ismail, Chem. Eng. J. 165 (2010) 980-988.
- [12] Z.A. Chen, M.C. Deng, J. Membr. Sci. 235 (2004) 73-86.
- [13] K.S. McGuire, K.W. Lawson, D.R. Lloyd, J. Membr. Sci. 99 (1995) 127-137.
- [14] L. Ye, Z. Fan, J. Zhou, Membr. Sci. Technol. 2 (1981) 24 (in Chinese).
- [15] L.Y. Yu, Z.L. Xu, H.M. Shen, H. Yang, J. Membr. Sci. 337 (2009) 257-265.
- [16] L.Y. Yu, H.M. Shen, Z.L. Xu, J. Appl. Polym. Sci. 113 (2009) 1763-1772.
- [17] R. Song, D.B. Yang, L.H. He, J. Mater. Sci. 42 (2007) 8408-8417.
- [18] G.G. Kumar, P. Kim, A.R. Kim, K.S. Nahm, R.N. Elizabeth, Mater. Chem. Phys. 115 (2009) 40-46.
- [19] S.L. Yu, X.T. Zuo, R.L. Bao, X. Xu, J. Wang, J. Xu, Polymer 50 (2009) 553-559.