Hexamethylene Diisocyanate Crosslinking 2-Hydroxypropyltrimethyl Ammonium Chloride Chitosan/Poly(acrylonitrile) Composite Nanofiltration Membrane

Rui-Hua Huang, Guo-Hua Chen, Ming-Kun Sun, Cong-Jie Gao

School of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266003, China

ABSTRACT: The effects of membrane preparation conditions on membrane properties were studied in detail. The results suggested that composite nanofiltration (NF) membrane from 2.0 wt % 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) vaporized for 2.5 h at 50°C, and then crosslinked for 9 h at 50°C with hexamethylene diisocyanate (HDI)/ethanol (0.45/50 wt/wt) were found to have optimal performance. The resultant membrane was called HACC/PAN [poly(acrylonitrile)] NF membrane. The characteristics of this membrane such as pure water permeability, molecular weight cut-off, rejection of salts, and swelling were investigated. And its cut-off molecular weight (MWCO) was ~520 Da. At 25°C and 1.0 MPa, the permeability of water was 17.24 L/h m² MPa. Swelling in water decreased and rejection of salts increased with increasing HDI concentration, indicating pore contraction and increase in hydrophobicity as well as pore tortuosity due to crosslinking. The order of rejection to different salt solutes followed the decreasing of $CaCl_2$, $MgCl_2$, NaCl, KCl, and Na_2SO_4, suggesting that this membrane was positively charged. The rejections to $MgCl_2$ and $CaCl_2$ were more than 0.90; therefore, this membrane can be used for hardness removal in water treatment process. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 673–679, 2007

Key words: 2-hydroxypropyltrimethyl ammonium chloride chitosan; hexamethylenediisocyanate; positively charged; composite NF membrane

INTRODUCTION

Nanofiltration (NF) membranes have been recognized for having properties in between those of ultrafiltration (UF) and reverse osmosis (RO), and have found applications in many areas including drinking water industry[1] and waste water treatment for removal of contaminants such as pesticides,[2] arsenic,[3] soil leachate,[4] dye,[5] etc.

At present, commercially available NF membranes are mainly neural and negatively charged membranes.[6] The preparation and performance of positively charged NF membranes have not been studied extensively yet. In fact, positively charged NF membranes have unique benefits, such as the resistance to compaction, the resistances to acid, alkali, microbe, etc. They are used to adsorb and separate negatively charged bacteria endotoxins, aminophenols, and proteins in all kinds of water supplies. More specifically, they are also adopted to recover cathode electrophoresis lacquer with a wide application prospect.

Chitosan or its derivatives is a kind of good film material with many advantages: nontoxic, antibacterial, and biodegradable. In the light of these advantages, it has been used in the preparation of NF membrane, RO membrane, UF membrane, and pervaporation membrane. Miao et al.[6] has prepared a novel amphoteric composite NF membrane by casting the aqueous solution of sulfated chitosan onto a poly(acrylonitrile) (PAN) UF membrane, and then crosslinked with glutaraldehyde. Musale and Kumar[8] prepared chitosan/PAN composite NF membranes and investigated the effects of surface crosslinking of different glutaraldehyde concentrations and crosslinking times on their surface chemical composition and sieving properties. Besides, the crosslinked membranes were found to be stable over 10-h operation for pure water permeation and the stability increased with increasing glutaraldehyde concentration. But, based on the recent news of our knowledge, there is no report about quaternized chitosan/PAN composite NF membrane so far except our study.

In this study, quaternization is applied to modify chitosan to increase the hydrophilicity and ionic

character, and 2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) was obtained. As a biopolymer, it is used to act as the active layer for composite NF membranes, which was not reported before. Therefore, it is of interest to report the formation of a positively charged composite NF membrane with HACC overcoated on PAN substrate and subsequent crosslinking with HDI. The pure water permeation, molecular weight cut-off (MWCO), rejection behavior, etc., of HACC/PAN composite NF membranes were investigated. The results provide a basis for further study on this kind of membrane material.

EXPERIMENTAL

Materials and apparatus

Chitosan [MW = 5.4×10^5 Da, degree of deacetylation (dd) = 90%] was provided by Haihui Bioengineering (Qingdao, China). HACC (with a degree of quaternization of 89.3%) was synthesized by the modified method according to the literature.[9] H_2SO_4, NaCl, KCl, $MgCl_2$, $CaCl_2$, HDI, anthrone, I_2, $BaCl_2$, Na_2SO_4, glucose, sucrose, and polyethylene glycol (MW 600–1000 Da) were of analytical grade. PAN UF membrane (MWCO = 1.0×10^5 Da) was obtained from the Development Center of Water Treatment Technology, State Oceanic Administration, Hangzhou, China.

Apparatus: salt concentrations were determined by a DDS-11A Electrical Conductivity Instrument (Shanghai Leichi Instrument, China). Membrane evaluation apparatus was provided by the Development Center of Water Treatment technology, State Oceanic Administration, Hangzhou, China. The concentrations of kinds of organic substances were measured using a Spectrophotometer-721 (Shanghai Instrument, China).

Membrane preparation

The casting solution was prepared by dissolving a certain amount of HACC in deionized water. After the solution was filtered with a G3 sand filter, it was overcoated on a surface-dried PAN UF membrane. This membrane, after vaporizing for a period of time at a certain temperature was crosslinked with ethanol solution of HDI in a wind-tight container. Then, the composite membranes crosslinked were heat-treated 30 min at 50°C, washed thoroughly with deionized water, and immersed in deionized water for 24 h.

Permeation experiments

The HACC/PAN NF membrane was characterized by determining the rejection of individual solutes

(NaCl, KCl, $MgCl_2$, etc.) from their aqueous solutions. The concentrations of salts were measured with an electrical conductivity meter. Besides, the pure water permeation was investigated. The area of the membrane used was 19.6 cm^2. All experiments were carried out at 25°C. The recirculation rate of feed was kept at 30 L h^{-1}. Both retentate and permeate were recycled back to the feed tank to keep a constant concentration of salts.

The permeation flux, F, is calculated according to $F = V/At$, where V is the total volume of the water or solution permeated during the experiment; A represents the membrane area; and t denotes the operation time. Rejection, R, is calculated according to $R = 1 - C_p/C_f$, where C_p and C_f are permeate concentration and feed concentration, respectively. The datum presented were the averages of two measurements conducted with standard deviation of 5%.

Swelling experiments

Here, the HACC/PAN NF membranes prepared from different HDI concentration crosslinking were applied to carried on the swelling experiments. They were soaked into water for 48 h at 25°C and then weighing them after gentle blotting with tissue paper. Swelling is a measure for the volume of liquid absorbed by the membrane and is defined as

$$Q = \frac{1}{p_s} \frac{W_{wet} - W_{dry}}{W_{dry}} \tag{1}$$

With Q the degree of swelling, W_{dry} the weight of a dry membrane sample, W_{wet} the weight of a soaked membrane sample, and p_s the density of water.

Molecular weight cut-off

To determine the molecular weight cut-off (MWCO), filtration experiments were carried out at 1.0 MPa and the applied recirculation rate of feed was fixed at 30 L h^{-1}. A set of reference solutes in the molecular weight range of 198–1000 Da is chosen, namely glucose, sucrose, and polyethylene glycols at a concentration of 1000 mg/L. The concentrations of glucose and sucrose in feed and permeate samples were determined by the colorimetry of H_2SO_4-anthrone; and the concentrations of polyethylene glycol were measured with the colorimetry of $BaCl_2$.

RESULTS AND DISCUSSIONS

The effect of preparation conditions on the HACC/PAN NF membrane properties

The experiments for membrane preparation were carried out at 25°C and 0.40 MPa, and the feed

TABLE I
Effect of HDI Concentration on the HACC/PAN NF Membrane Properties

HDI/ethanol (wt/wt)	Flux (L m^{-2} h^{-1})	Rejection
0.25/50	4.07	0.89
0.45/50	3.8	0.92
0.75/50	3.8	0.9

tested was 1000 mg L^{-1} MgCl$_2$ solution without specification. The other operations were conducted according to what mentioned in Permeation Experiments section.

Effect of HDI concentration on HACC/PAN NF membrane properties

HDI is applied to act as the crosslinking reagent because of the reason that HDI can react with —OH and the —NH$_2$ unquaternized in HACC. To investigate this effect, a series of HACC/PAN composite membranes from 2.0 wt % HACC were prepared by being crosslinked with HDI/ethanol in the range of 0.25/50–0.75/50. As shown in Table I, the rejection increases slightly and the flux decreases slightly with the changing HDI/ethanol from 0.25/50 to 0.75/50. Considering the flux and rejection of MgCl$_2$ integrally, HDI/ethanol (0.45/50 wt/wt) is regarded as the proper concentration.

Effect of crosslinking time on HACC/PAN NF membrane properties

For this test, a series of HACC/PAN NF composite membranes were prepared and measured with different crosslinking times in the range of 3–11 h. The results are shown in Figure 1, and it was seen that the flux decreases from 4.4 to 2.4 L m^{-2} h^{-1}, whereas

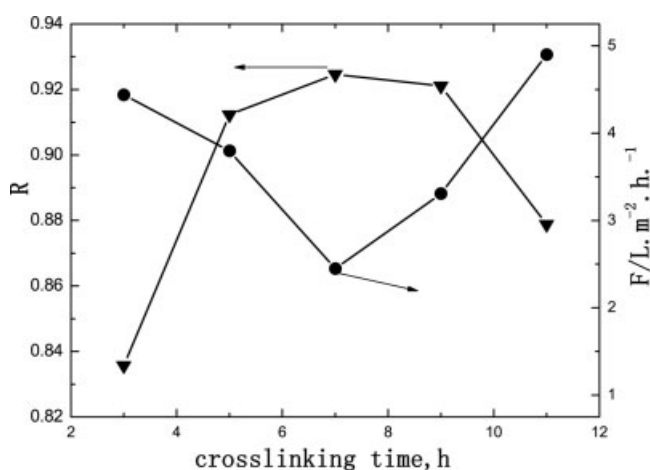the rejection increases from 0.83 to 0.92 with the increasing crosslinking time until it is 7 h. This trend may result from the increase degree of crosslinking because of the pore contraction and the increase in tortuosity. However, when the crosslinking time is longer than 7 h, the rejection begins to decrease, whereas the flux increases markedly, as a result of the decrease in degree of crosslinking due to the decomposition of crosslinking bond. Thus, the crosslinking time of 9 h is adopted here.

Effect of vaporizing methods on HACC/PAN NF membrane properties

As noted earlier, in membrane preparation, the membranes were allowed to stay at a certain temperature for a given time to evaporate the solvent to form a dense skin layer. The longer the evaporation time is, the more the solvent evaporate and the denser the top layer is, which will lead to a lower flux and a higher rejection. Besides, the high vaporizing temperature caused the polymer on the surface to aggregate suddenly. The sudden aggregation came to a result that some of neighboring polymer micelles touched each other, whereas the other polymer micelles became more independent. Thus, the distribution of pore radius of the skin layer formed became wider and the rejection decreased. To check such as expectations and optimize the preparation parameters, membranes from different vaporizing methods were prepared and characterized. The results are listed in Table II. It is obvious that the flux and rejection tendency agree with expectation. These indicate that a quick evaporation at high temperature or a slow evaporation at a low temperature is not beneficial for the membranes preparation with good performances. Furthermore, considering the flux and rejection of MgCl$_2$ integrally, evaporation time of 2.5 h at 50°C is proper.

Effect of HACC concentration on HACC/PAN NF membrane properties

As the composite membranes were prepared by overcoating HACC solution on PAN UF, membrane preparation would fail when the HACC concentration was too low or too high. Thus, the HACC concentrations were selected in the range of 1.5–3.0 wt %.

Figure 1 Effect of crosslinking time on HACC/PAN NF membrane properties.

TABLE II
Effect of Vaporizing Methods on the HACC/PAN NF Membrane Properties

Vaporizing methods	Flux (L m^{-2} h^{-1})	Rejection
Vaporizing at 50°C for 2.5 h	3.06	0.93
Vaporizing at 70°C for 1 h	11.5	0.903
Vaporizing at 25°C for 20 h	1.53	0.963

TABLE III
Effect of HACC Concentration on the HACC/PAN NF Membrane Properties

HACC concentration (wt %)	Rejection	Flux (L m^{-2} h^{-1})
1.5	0.888	8.27
2	0.93	3.07
2.5	0.901	1.96
3	0.905	2.88

As shown in Table III, the rejection increases from 0.888 to 0.93, and the flux has a fourfold decrease from 8.27 to 1.96 L m^{-2} h^{-1} when HACC concentration changes from 1.5 to 2.0 wt %; When HACC concentration is beyond 2.0 wt %, both the rejection and the flux have only a slight change. It could be explained as follows. On one hand, the increase in HACC concentration is favorable for the crosslinking reaction, leading to both the decreasing flux and the increasing rejection due to pore contraction. On the other hand, the increasing HACC concentration results in an increase in membrane thickness, and the permeation resistance increases, thereby the diffusion of HDI toward the base membrane is hindered. As a result, HACC concentration had negligible effect on membrane properties.

Effect of crosslinking temperature on HACC/PAN NF membrane properties

Because of the decomposition of HDI in heat or the division of the crosslinking band between HDI and HACC, the crosslinking temperatures in the range of 30–60°C were investigated. The result is shown in Figure 2, and the rejection increases from 0.862 to 0.93 when the crosslinking temperature changes from 30 to 50°C, afterward it shows the trend to decrease. However, the flux decreases all the time from 4.43 to 2.6 L m^{-2} h^{-1}. These phenomena

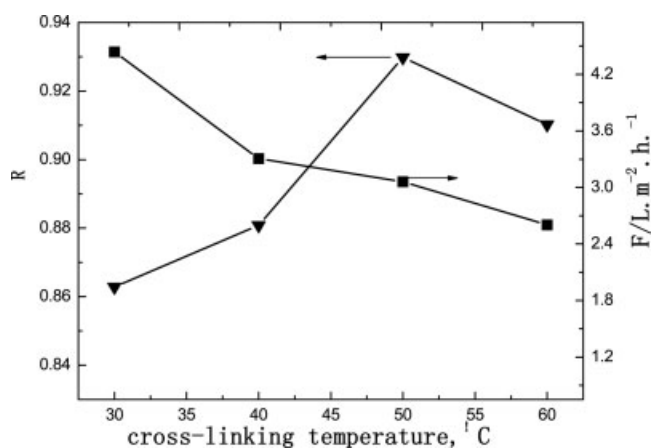indicate that the increasing crosslinking temperature improves the crosslinking degree to some degree because of the approximate complete crosslinking reaction as a result of the increasing rejection and the decreasing flux. However, a high temperature will lead to the decomposition of HDI or the division of the crosslinking band, thereby the rejection decreases. Therefore, it is needful to choose a proper crosslinking temperature. Considering the flux and rejection of MgCl$_2$ integrally, the crosslinking temperature of 50°C is applied.

Coming to a conclusion by the earlier experiments that the HACC/PAN NF membrane from 2.0 wt % HACC vaporized for 2.5 h at 50°C, then crosslinked at 50°C for 9 h with HDI/ethanol, and HDI (0.45/50 wt/wt) is found to have comparatively good performances. This membrane will be adopted for further experiments.

The effect of operation conditions on the HACC/PAN NF membrane properties

Pure water permeability of the HACC/PAN NF membrane

The pure water permeability was measured at different pressures. As shown in Figure 3, the permeation flux of membrane increases linearly with the operating pressure. This linear behavior was described by a slope close to that of pure water permeability according to the Spiegler–Kedem Model.[10] The pure water permeability is obtained at 17.24 L h^{-1} m^{-2} MPa^{-1} through this membrane by the fit of experiment datum.

Effect of feed concentration

The effect of MgCl$_2$ and NaCl at varying concentration on rejection is shown in Figures 4 and 5,
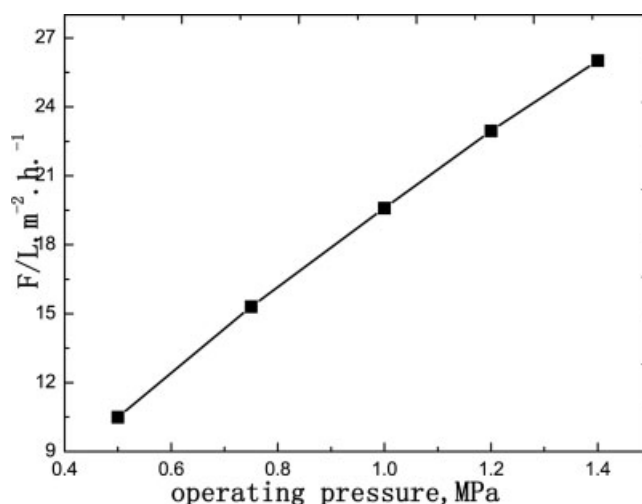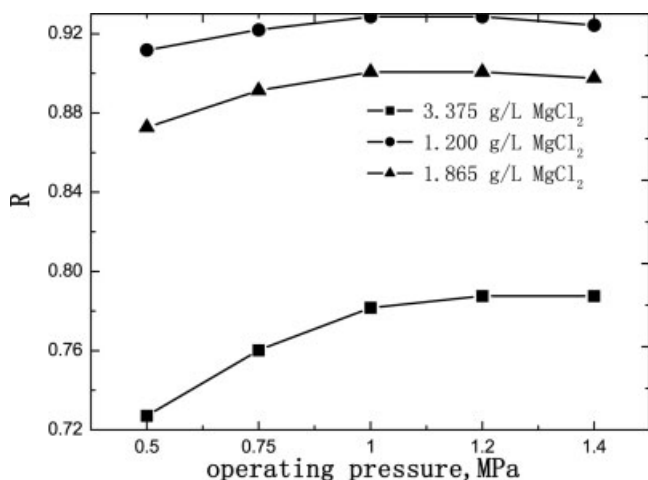

Figure 2 Effect of crosslinking temperature on HACC/PAN NF membrane properties.

Figure 3 Water flux for HACC/PAN NF membrane.

Figure 4 The rejection to MgCl₂ solution at varying concentration against operating pressure.

Figure 6 Effect of operating pressure on membrane properties.

respectively. Obviously, the rejection declines with the increasing concentration. This can be explained by considering the thickness of the double layer formed in the pores of the top layer when the membrane is contacted with the salt solution. The increasing salt concentration (higher ionic strength) produces a decrease in the thickness of the double layer, resulting in a lower retention. Besides, the shielding effect is stronger with an increase in salt concentration, leading to a decrease of the membrane repulsion forces of the cations and thereby the decrease in rejection. The phenomenon was also reported by other authors.[11]

Effect of operating pressure

The feed tested is 1.0 g L^{-1} MgCl₂ solution. The results are shown in Figure 6. It is found that the flux increases almost linearly with the increase of
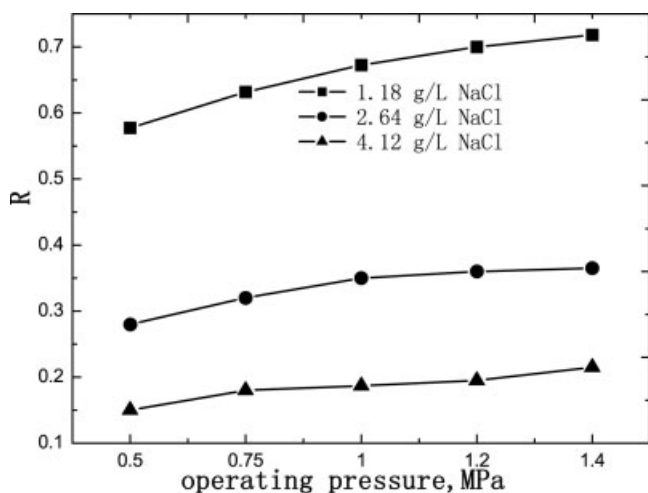

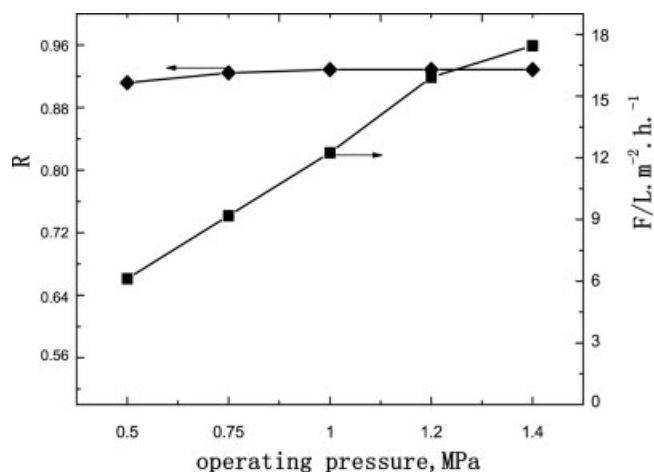**Figure 5** The rejection to NaCl solution at varying concentration against operating pressure.

the operating pressure, and the rejection seems not to be sensitive to the change in operating pressure from 0.5–1.4 MPa. The results can be explained by the solution-diffusion model[12] from which one obtains eqs. (2–4):

$$F_\omega = A(\Delta P - \beta \Delta \pi) \tag{2}$$

where F_ω is the water flux, A is the water permeation coefficient, ΔP is the operating pressure difference, β is the polarization factor of the concentration difference, and $\Delta \pi$ is the osmosis pressure.

$$F_s = B(\beta C_1 - C_2) \tag{3}$$

where F_s is the salt flux, B is the salt permeation coefficient, C_1, and C_2 are the salt concentrations on the upstream and downstream sides of the membrane, respectively,

$$\beta = \frac{C_b}{C_m} \tag{4}$$

where C_b is the salt concentration on the membrane surface, and C_m is the salt concentration of the feed.

It can be seen from eq. (2) that F_ω increases linearly with the increase of ΔP. It can also be concluded from eq. (3) that F_s is a function of salt concentration on both sides of the membrane and has no direct relation to ΔP. Therefore, as ΔP increases, so does the water flux, but the salt flux remains constant, thereby resulting in an increase in salt rejection. At the same time, C_2 is reduced by virtue of the increase of F_ω, which results in the increase of the concentration difference on the two sides of the membrane, leading to an decrease of rejection. These opposing effects combined result in a gradual increase in salt rejection to a definite value.

TABLE IV
Effect of the Type of Electrolytes the HACC/PAN NF Membrane Properties

Type of electrolytes	Rejection	Flux (L m^{-2} h^{-1})
MgCl$_2$	0.929	12.3
CaCl$_2$	0.934	32.8
NaCl	0.673	10.4
KCl	0.503	31.3
Na$_2$SO$_4$	0.196	32.3

Effect of the type of electrolytes

Here, the permeation experiments were performed for the five inorganic salts solutions with a concentration of 1.0 g L^{-1} at the operating pressure of 1.0 MPa. The object was to investigate the effect of the type of salts on membrane properties. The fluxes and rejections are listed in Table IV. For a given operation condition, the rejections follow the order of RMgCl$_2$ ≈ RCaCl$_2$ > RNaCl > RKCl > RNa$_2$SO$_4$, which is typical of a positively charged membrane and may be explained by electrostatic effect and steric effect,[13,14] i.e., the orders of the rejections, RMgCl$_2$ ≈ RCaCl$_2$ > RNaCl, RKCl, corresponding to the increasing order of cation-charge densities, because the active layer HACC of this membrane has the contribution of quaternary ammonium groups and allows stronger repulsion for Mg^{2+}, Ca^{2+} than Na$^+$, K$^+$; the order of the rejections, RNaCl > RNa$_2$SO$_4$, contrary with the increasing order of anion charge densities, because the active layer of the composite membranes contains quaternary ammonium groups as mentioned earlier and has stronger attraction forces for SO$_4^{2-}$ than Cl$^-$; the orders of the rejections, RNaCl > RKCl may owe to the fact the hydrate radius of Na$^+$ is larger than that of K$^+$. Although the difference of electrostatic effect between this membrane and these ions is negligible, the steric effect cannot be neglected in membrane separation. Therefore, it appears that because of the charged nature of this membrane, the separation performance is influenced not only the steric effect but also the electrostatic effect.

MWCO of the HACC/PAN NF membrane

The MWCO was the molecular weight of organic substance with a retention of 90%.[15] The curve showing rejection verses molecular weight is shown in Figure 7. Obviously, the MWCO of this membrane is ~520 Da, which is in NF range.

Swelling characteristic

Swelling was determined as described by Geens et al.[16] As listed in Table V, swelling is higher at pH
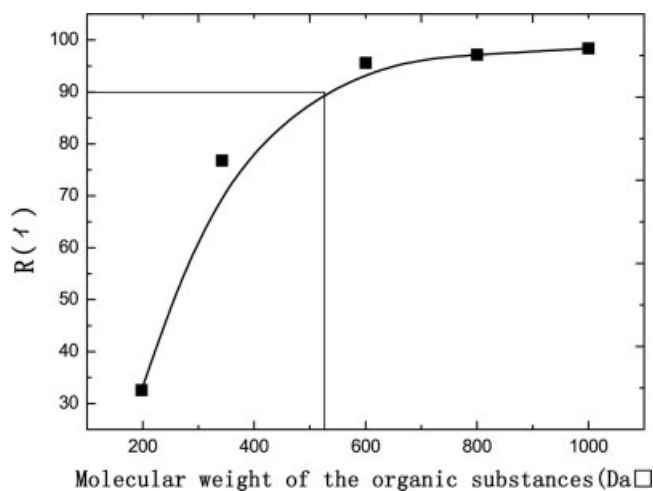
Figure 7 Rejection as a function of molecular weight.

7 than at both pH 4 and 11, about which there is no reasonable explanation. Additionally, the swelling of the membranes crosslinked from the increasing HDI concentration decreases at a smoother step.

Crosslinking of HACC chains may introduce hydrophobic acyl amine groups, which in turn might lead to decrease in both the hydrophilicity and swelling of HACC layer in water and increase in pore tortuosity of membranes. As a result, reduction in swelling as well as increase in hydrophobicity and pore tortuosity leads to a decrease in the flux with the increasing HDI concentration, corresponding with the results obtained in the earlier section. Besides, according to the viewpoint put forward by Ebert,[17] polymeric chains can move further apart during swelling, thus increasing the free volume; the membrane becomes more open, as a result of lower rejections. Thus, it is concluded that a smaller swelling leads to a higher rejection, as expected the results noted in the earlier section.

CONCLUSIONS

The HACC/PAN composite NF membranes may be prepared using HACC and PAN UF membranes as active layer and support layer, respectively. The effect of preparation conditions such as HACC concentration, HDI concentration, crosslinking temperature, etc., on membrane properties was investigated. The results

TABLE V
Swelling for HACC/PAN NF Membranes Cross-Linked with Different HDI Concentration

HDI/ethanol (wt/wt)	Swelling degree (mL g^{-1})		
	pH 4	pH 7	pH 11
0.25/50	0.536	0.602	0.355
0.45/50	0.434	0.506	0.305
0.75/50	0.403	0.459	0.3

suggested that the membrane from 2.0 wt % HACC casting solution, vaporized for 2.5 h at 50°C, and then crosslinked with HDI/ethanol (50/0.45 wt/wt) was found to have excellent performances. The MWCO of the resultant membrane was 520 Da or so. At 25°C, the pure water permeability is obtained at 17.24 L h^{-1} m^{-2} MPa^{-1} through this membrane. When compared with commercially available NF membranes, it had comparatively low permeability, which was relative with both chemical and physical compatibility of selective layer with the substrate.

Some performance tests for this NF membrane were also conducted. It was not difficult to find its performance was influenced by feed concentration, operating pressure, and the type of salt solutes. The rejections to different salt solutes followed the decreasing order of $CaCl_2$, $MgCl_2$, NaCl, KCl, and Na_2SO_4, suggesting that this membrane was positively charged. And the rejections to $MgCl_2$ and $CaCl_2$ were higher than 0.90, therefore this membrane can be expected to have application in the removal of hardness in waste water. Additionally, swelling in water decreased and rejection of salts increased with increasing HDI concentration, indicating pore contraction and increase in hydrophobicity as well as pore tortuosity due to crosslinking.

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