

Preparation and Characterization of Sulfonated Polyetherimide/Polyetherimide Blend Membranes

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ABSTRACT: Polyetherimide (PEI) was sulfonated by chlorosulfonic acid (CSA) in 1,2-dichloroethane for the first time. With the increase of the CSA/PEI repeat unit ratio and/or reaction time, the ion-exchange capacity (IEC) of the sulfonated polyetherimide (SPEI) increased accordingly. Water-uptake testing and contact-angle measurement showed that the hydrophilicity of the SPEI increases with the increase of the IEC. Membranes were fabricated from SPEI/PEI blends with different ratios. The morphologies of the blend membranes were examined by scanning electron microscopy, which showed that the membrane pore size is

larger when SPEI with higher IEC was used. With the increase of SPEI ratio in the blend membranes, the membrane pore size also increased. The contact-angle data of the membranes showed that the hydrophilicity of the blend membrane was elevated because of the sulfonate group on the SPEI molecular backbone. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1709–1715, 2004

Key words: polyetherimide; sulfonated polyetherimide; hydrophilic polymers; blends; membranes

INTRODUCTION

Membrane fouling is a main drawback in the practical application of ultrafiltration membranes. It is generally agreed that increasing the hydrophilicity can improve the antifouling property of the membranes. Thus, much research work on hydrophilization of hydrophobic ultrafiltration membrane materials has been carried out.^{1–7} Usually, a hydrophilic polymer is blended with the membrane-forming polymer to obtain hydrophilic membranes.^{1,2} In another way, a number of investigations on the hydrophilization of the hydrophobic membrane materials by chemical modification or graft polymerization have been carried out.^{3–7} It was reported that the polyethylene microfiltration hollow-fiber membranes were grafted with hydrophilic monomers by electron-beam irradiation to reduce the adsorption of protein.³ Hydrophilic monomers were also grafted onto polyethersulfone ultrafiltration membranes by use of the photochemical method.⁴ Sulfonation of the hydrophobic polymer was also used to render the polymer hydrophilic. For example, Kim et al.⁶ sulfonated polyether-

sulfone to obtain a hydrophilic polymer for membrane preparation.

Polyetherimide (PEI) is a versatile high-performance polymer. It has good thermal and chemical stability. Moreover, it has an advantageous gas separation property for some gas pairs; for example, the selectivities of PEI dense membrane for He/N₂, CO₂/N₂, and O₂/N₂ gas pairs are 264, 37.4, and 7.6 at 35°C, respectively.⁸ It was also reported that PEI could be used in the vapor permeation of water/1-propanol and the ultrafiltration field.^{1,2,9,10} However, because of its hydrophobic nature, it is desirable to make the PEI membrane hydrophilic when PEI is used in ultrafiltration applications.

In this study, we sulfonated PEI with chlorosulfonic acid and the sulfonation condition was examined. The sulfonated PEI (SPEI) was blended with PEI to fabricate hydrophilic PEI membranes.

EXPERIMENTAL

Materials

PEI (Ultem 1000) was purchased from General Electronic Co. It was dried at 150°C for 4 h before being used. *N,N*-Dimethyl acetamide (DMAc), chlorosulfonic acid (CSA), and isopropanol were all purchased from Acros Organics (Beijing, China) and used without further purification. 1,2-Dichloroethane (DCE) was purchased from Alfa Aesar (Beijing, China) and refluxed with phosphorous pentoxide for 1 h and distilled before being used.

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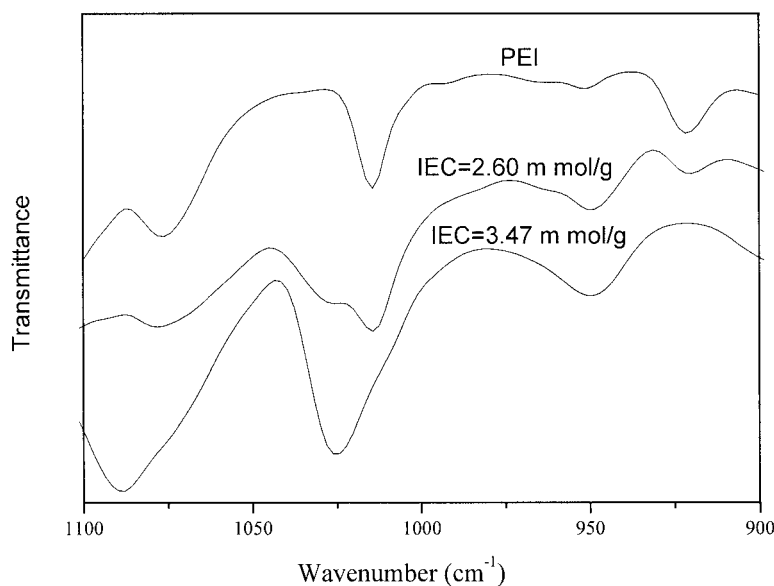


Figure 1 FTIR spectra of PEI and the SPEIs.

Sulfonation of PEI

PEI (20 g) was dissolved in 100 mL of DCE at 60°C and subsequently the PEI solution was kept at 30°C. CSA mixed with 75 mL of DCE was added to the PEI solution within 1 h with vigorous stirring. After being reacted for a definite period, the reaction product, which precipitated in the reaction medium, was dissolved in DMAc at 50°C, coagulated with excess isopropanol, filtered, washed with isopropanol, and dried at 40°C in a vacuum oven. The sodium salt form of the product was obtained by soaking it in excess 0.1 mol/L NaOH aqueous solution for 2 days.

Preparation of SPEI/PEI blend membranes

PEI and SPEI blends with different ratios were dissolved in DMAc at 60°C and a 17 wt % solution was obtained. The solution was cast onto a glass plate with a casting knife at 20°C. After standing in air for 5 min, the nascent membrane was immersed in deionized water at 20°C to coagulate and the membrane was formed. Subsequently, all the membranes were stored in water until later use.

Characterization of the SPEIs

The ion-exchange capacity (IEC) of the SPEI was determined by the method of Fisher and Kunin.¹¹ About 1 g SPEI was soaked in 50 mL of 0.1 mol/L NaOH solution for 1 day, after which the SPEI was filtered off and 25 mL of the filtrate was titrated with 0.1 mol/L HCl solution.

FTIR spectrum of the polymer was recorded with a Bruker Vector 22 FTIR spectroscope (Bruker Instruments, Darmstadt, Germany). The ¹H-NMR spectrum of the polymer was recorded on a Bruker Avance DMX500 spectroscope. The PEI was dissolved in CDCl₃ and the SPEI was dissolved in deuterated dimethyl sulfoxide.

The glass-transition temperature (T_g) of the polymer was examined with a Perkin-Elmer Pyris 1 DSC (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10°C/min.

Weight-average molecular weight (M_w) of the polymer was measured through a laser light-scattering photometer (DAWN DSP, Wyatt Technology Corp., USA) operated at batch mode. DMAc was used to dissolve the PEI and SPEIs. M_w of the polymer was obtained by the construction of the Zimm plot from data collected in the batch mode.

Scanning electron microscopy (SEM) examination

The membrane was immersed in ethanol for 1 day, and then in hexane for 1 day before being dried in air. The dried membrane was then fractured in liquid nitrogen for SEM examination with a Hitachi S-570 SEM apparatus (Hitachi, Osaka, Japan). The surface of the sample was coated with gold to prevent charging before the SEM micrographs were taken.

Water-uptake measurement

Either SPEI or PEI was dissolved in DMAc and cast onto a glass plate to form transparent films after being dried at 40°C in a vacuum oven. The weighed films

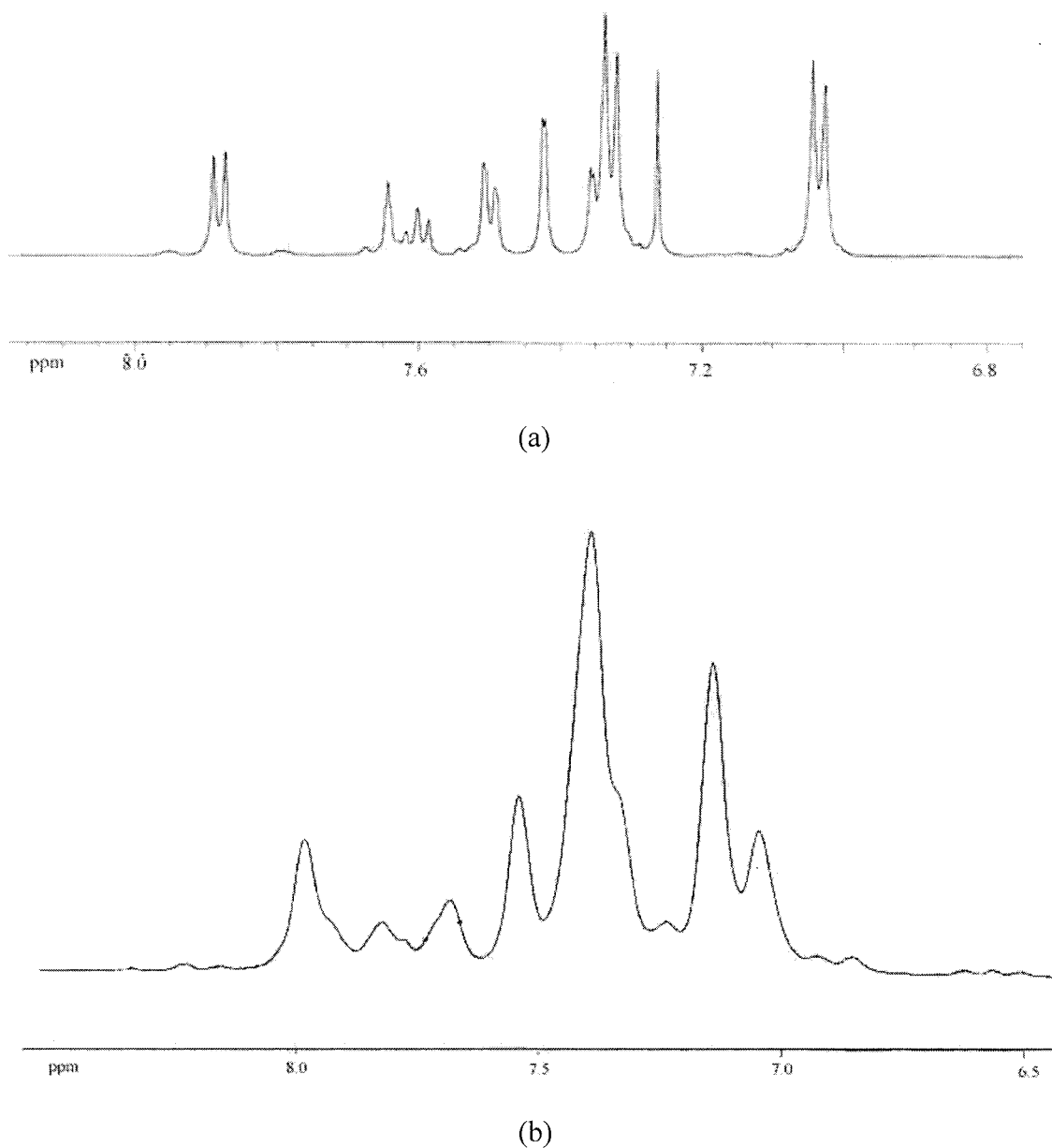


Figure 2 $^1\text{H-NMR}$ spectra of (a) PEI and (b) SPEI.

were immersed in deionized water for 3 days at room temperature to reach equilibrium. Then the swollen films were weighed after quickly wiping the films with filter paper. The water uptake was expressed as the ratio of swollen weight to dry weight.

Contact-angle measurement

Water contact-angle measurement of the films or membranes was carried out with a Krüss DSA 10 MK2 goniometer (Krüss, Hamburg, Germany) by the sessile drop method. Ten angles were measured and averaged for every sample.

RESULTS AND DISCUSSION

Introduction of sulfonic acid group onto PEI

Figure 1 shows the FTIR spectra of PEI and the SPEIs. Two new absorption peaks were observed in the SPEI spectra: one is the peak at around 1028 cm^{-1} , attributed to the symmetric $\text{O}=\text{S}=\text{O}$ stretching of the sulfonate group; the other is the peak at around 950 cm^{-1} , also attributed to the introduction of sulfonic acid group.^{6,12} It was also determined that the absorption intensity of the peaks at around 1028 and 950 increased with the increase of the IECs of the SPEIs.

Figure 2 shows the $^1\text{H-NMR}$ spectra of PEI and the

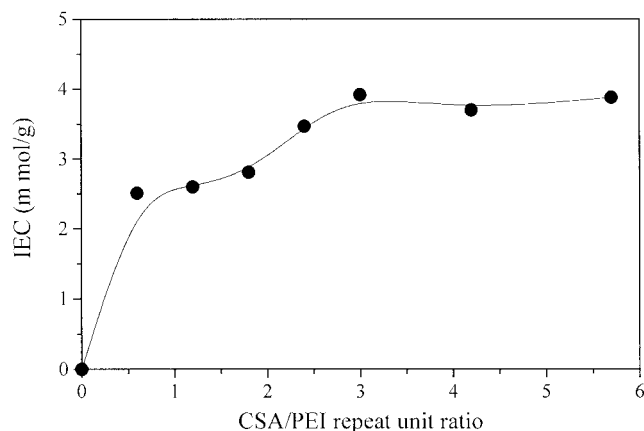


Figure 3 Effect of CSA/PEI repeat unit ratio on the IEC of SPEI.

SPEI. The peaks between 6.5 and 8.5 ppm are assigned to the protons of aromatic rings of the polymer backbone. The integral value of these peaks indicates that there are about 16.9 protons in the aromatic rings of the SPEI repeat unit, whereas there are 18 protons in the aromatic rings of the PEI repeat unit. It is obvious that the sulfonic acid group was incorporated into the aromatic rings of the PEI molecule.

Through the above investigation, we can conclude that the PEI can be sulfonated by the method described in this work.

The effect of CSA/PEI repeat unit ratio on the IEC of SPEI is displayed in Figure 3, where it may be seen that the IEC of the SPEI increases with the increase of CSA/PEI repeat unit ratio. In the initial stage, the IEC of the SPEI increases rapidly, although when the CSA/PEI repeat unit ratio is above about 2.4, the IEC of the SPEI evidently does not increase. In the meantime, the SPEI became yellow and brittle because of partial degradation of the polymer.

Properties of the SPEIs

The effect of reaction time on the sulfonation degree of SPEI was investigated. With the increase of reaction time, the sulfonation degree of the product increases, as shown by the IECs of samples 2 and 3 and samples 4 and 5 in Table I. Because the SPEI does not dissolve in DCE, the product precipitates from the solution and the whole reaction system forms a heterogeneous system after about 1 h from the beginning of reaction. Thus, in the following reaction period, the diffusion of CSA to the reaction site of the polymer backbone is more difficult, the speed of reaction is slowed, and more time is needed to complete the reaction.

Table I also shows the M_w values of the SPEI samples, where it may be observed that the higher the IEC of the SPEI, the higher the reduction of the polymer

TABLE I
Sulfonation of PEI by Chlorosulfonic Acid

Sample	Reactant mole ratio CSA/PEI repeat unit	Reaction time (h)	IEC (mmol/g)	M_w
1	0	0	0	40,000
2	0.6	2	2.51	25,000
3	0.6	4	2.69	19,000
4	1.2	2	2.60	15,000
5	1.2	4	2.88	8,700
6	1.8	2	2.81	7,900

M_w . Therefore, it can be concluded that there is some kind of degradation of the polymer molecule. However, we can see that a lower CSA/PEI ratio with longer reaction time is preferable to a higher CSA/PEI ratio with shorter reaction time, if the same hydrophilicity is expected, because the molecular degradation of the latter is more significant, as indicated by samples 3 and 4 and samples 5 and 6 in Table I.

The SPEIs can be in either the free acid form or the salt form. In this study, it was neutralized with 0.1 mol/L NaOH and cast into film for water-uptake testing. The results in Table II show that the SPEIs absorb more water with the increase of the IEC of the SPEI. Eventually, the SPEIs become soluble in water, as shown by samples 5 and 6 in Table II. However, when the acid form of the SPEI was tested for water uptake, it showed very low, nearly zero, water absorbency. This result illustrates that the hydrophilicity of the SPEI is mainly attributed to the ionic nature of the Na salt form of SPEI. A similar phenomenon was also reported in the study by Noshay et al.¹³

Contact angles for the films fabricated from the sodium salt form SPEIs were measured, the results of which are shown in Table II. In this measurement, only the SPEIs, whose sodium salt form does not dissolve in water, were cast into films. Compared against the original PEI film, it can be seen that the SPEI films show a reduction in contact angle of about 10°.

T_g values of the SPEIs of the sodium salt form are displayed in Table II. The T_g values of the SPEIs are

TABLE II
Properties of the SPEIs

Sample	IEC (mmol/g)	Water uptake	Contact angle (°)	T_g (°C)
1	0	7%	90	217
2	2.51	37%	—	243
3	2.60	42%	83	232
4	2.69	39%	82	—
5	2.81	Soluble	—	262
6	2.88	Soluble	—	—

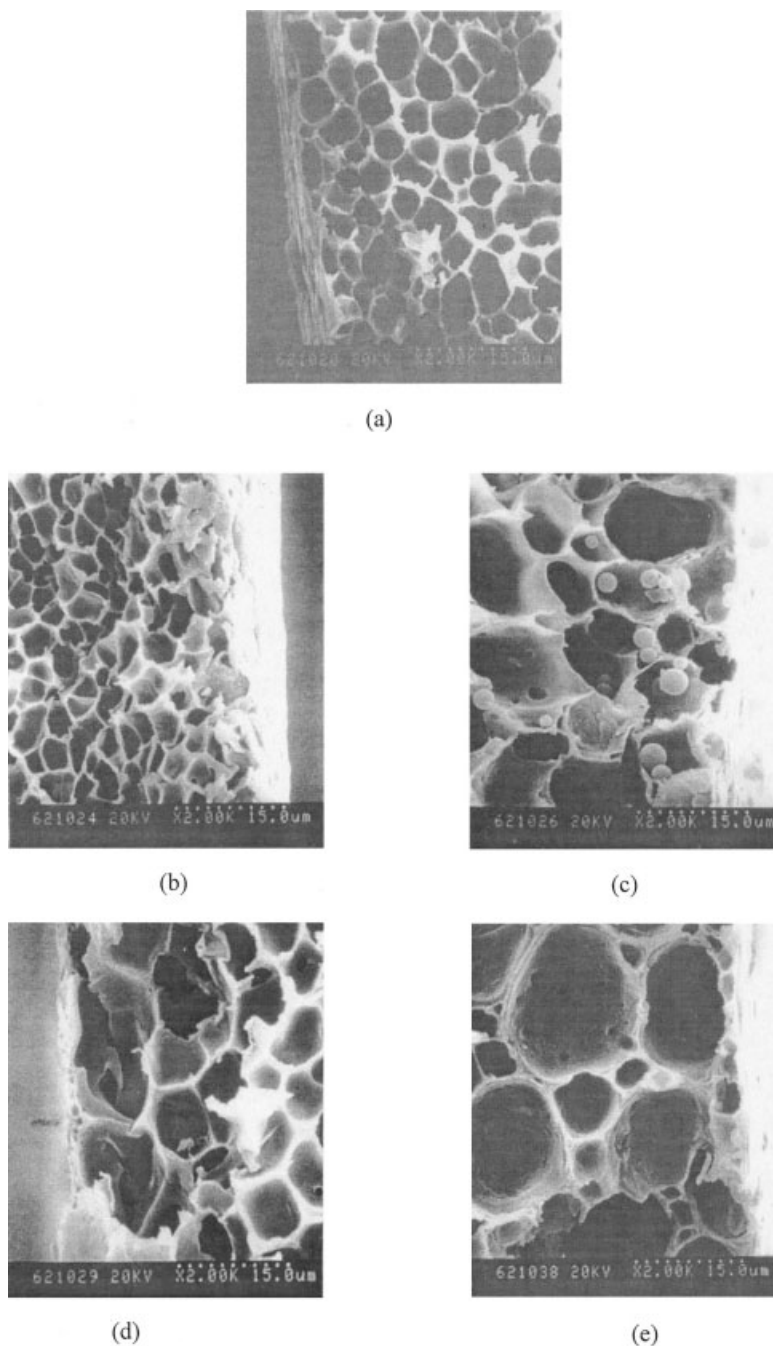


Figure 4 SEM micrographs of the cross-sectional morphologies of the PEI/SPEI blend membranes: (a) PEI; (b) PEI/SPEI = 95/5, IEC = 2.51 mmol/g; (c) PEI/SPEI = 80/20, IEC = 2.51 mmol/g; (d) PEI/SPEI = 95/5, IEC = 2.60 mmol/g; (e) PEI/SPEI = 80/20, IEC = 2.60 mmol/g.

higher than that of PEI, attributed to the ionic interaction of the molecular backbone of the SPEI, which restricts the mobility of the molecule.

Characterization of the SPEI/PEI blend membranes

SPEIs of different degrees of sulfonation were blended with PEI to form blend membranes. The sodium salt form of the SPEI was used in this study because of its

hydrophilicity compared with that of the acid form of the SPEI.

SEM micrographs in Figure 4 show the cross-sectional morphologies of the blend membranes, from which it may be observed that the membrane pores are of cell size. As we know, there are two types of phase-separation process in the formation of membranes by the phase-inversion method¹⁴: one is a delayed demixing process; the other is an instantaneous

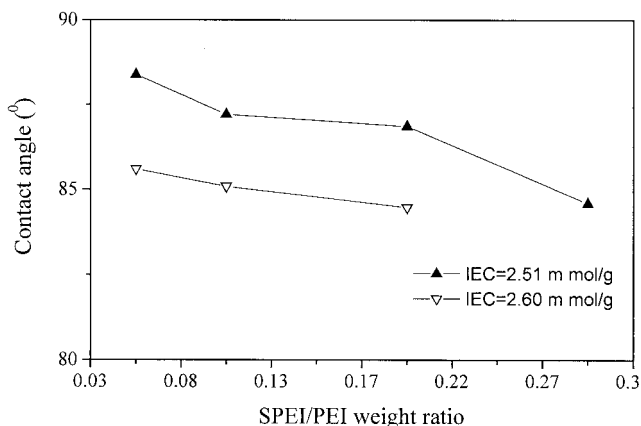


Figure 5 Effect of SPEI content on the contact angle of the SPEI/PEI blend membrane.

demixing process. In the delayed demixing process, a spongelike pore morphology tends to form, whereas in the instantaneous demixing process, a fingerlike morphology is more likely to form. In this study, after being cast onto a glass plate, the nascent membranes were allowed to stand in air for some time. Because air with a certain humidity could be considered as a weak nonsolvent for the polymer solution, the phase-separation process of the membrane tended to be the delayed demixing process and to form a spongelike membrane morphology, that is, the cell-size pores were formed in the membranes, as shown in Figure 4.

It may also be observed that the pore size of the membrane increases with the increase of the IEC of the SPEI. The pore size is in the following sequence: 0 mmol/g < 2.51 mmol/g < 2.60 mmol/g. This may be the result of the immiscibility of the SPEI and PEI, which can be ascribed to the difference in the hydrophilicity between the two polymers. With higher IEC and higher water uptake, the difference in hydrophilicity of the SPEI and PEI was more evident, and thus the membrane pore size became larger.

The sodium salt form SPEIs were blended with PEI at different ratios. Figure 4(b)–(e) show the effect of the amount of SPEI on the morphologies of membranes. It shows that the membrane pore size become larger with the increase of SPEI/PEI ratio. This is useful information for the fabrication of SPEI/PEI blend membranes.

Contact angles of the SPEI/PEI blend membranes were measured, as shown in Figure 5. It was found that the blend membranes show a moderate, but only slight, reduction of contact angle. Also, with the increase of SPEI/PEI ratio, the contact-angle reduction increases.

Hydrophilicity of the blend membranes with SPEI neutralized after membrane formation

The free acid form SPEIs with IEC values of 2.81 and 2.88 mmol/g were blended with the PEI to form membranes because of the solubility of the sodium salt form of these two SPEIs in water. After the blend membranes were formed, they were soaked in 0.1 mol/L NaOH solution to convert the SPEIs into the sodium salt form. The results of contact-angle measurement for these membranes are shown in Figure 6.

As may be seen in Figure 6, the contact-angle reduction of the blend membranes is larger than that of SPEIs with IEC of 2.51 and 2.60 mmol/g shown in Figure 5. Finally, a contact angle of 73° was reached with SPEI/PEI ratio of 2/8 for the SPEI of 2.88 mmol/g, whereas the contact angle of the PEI film was 90°.

In the meantime, the sodium salt of SPEI is negatively charged. Therefore, it may have an interesting property with respect to the antifouling property of the membrane when blended with PEI for membrane formation. The work was carried out in our lab.

CONCLUSIONS

The SPEI was obtained by sulfonation by chlorosulfonic acid in DCE, although there was partial degradation of the polymer during the sulfonation process. By increasing the CSA/PEI repeat unit ratio or increasing the reaction time, the sulfonation degree of the SPEI was elevated and eventually the sodium salt form of the SPEI became soluble in water with the increase in degree of sulfonation.

The SPEIs were blended with PEI at different ratios for membrane preparation. The pore size of the membrane cross section was found to increase with the increase of sulfonation degree of the SPEI; and the

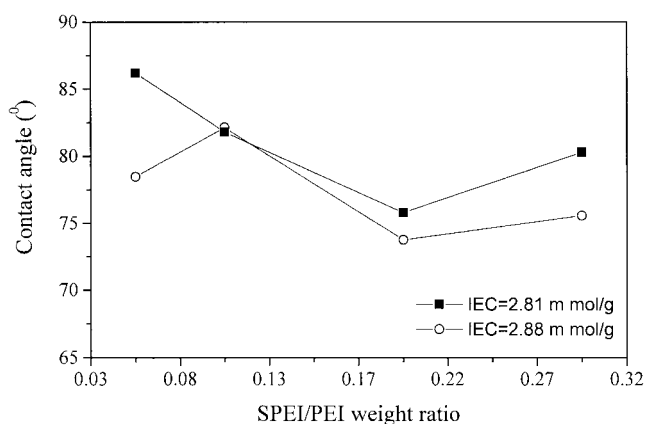


Figure 6 Effect of SPEI content on the contact angle of the SPEI/PEI blend membrane with SPEI neutralized after membrane formation.

higher the SPEI/PEI blend ratio, the larger the membrane pore size.

The hydrophilicity of the blend membrane increased because of the hydrophilic nature of the SPEIs. Finally, a blend membrane with water contact angle of 73° was obtained.

Results of this study should prove to be useful in the fabrication of SPEI/PEI blend membranes for antifouling usage in future investigations.

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