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Synthesis and Characterization of Sulfonated Poly(phthalazinone ether sulfone ketone) for Ultrafiltration and Nanofiltration Membranes

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ABSTRACT: Modification of poly(phthalazinone ether sulfone ketone) (PPESK) by sulfonation with concentrated or fuming sulfuric acid as sulfonation agents was carried out to prepare membrane materials with increased hydrophilicity and potentially increased fouling resistance. Sulfonated PPESK (SPPEsk) copolymers, with a degree of sulfonation ranging from 10–300%, were prepared and characterized. Factors affecting the sulfonation reaction were studied, and reaction conditions for the preparation of SPPEsk with different degrees of sulfonation were determined. Compared with the properties of PPESK, the hydrophilicity of SPPEsk was increased, as shown by a reduced contact angle with water. The glass transition temperature was increased from 278°C (PPESK) to a maximum of 323°C for the highly sulfonated derivative, due to the strong polarity of $-\text{SO}_3\text{H}$ and hydrogen bonding. Ultrafiltration membranes prepared with PPESK and SPPEsk were compared. For a SPPEsk asymmetric membrane, the PEG12000 rejection was 98% and the water flux was $876 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. SPPEsk/PPESK composite nanofiltration membranes were also prepared and were shown to have short-term operational stability up to 120°C. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1685–1692, 2001

Key words: poly(phthalazinone ether sulfone ketone); sulfonation; polymer modification; degree of sulfonation; ultrafiltration membrane

INTRODUCTION

A series of poly(phthalazinone ether sulfone ketone) (PPESK) copolymers, containing different ratios of diphenylsulfone and diphenylketone units, were previously synthesized.^{1–3} These polymers derived from a phthalazinone monomer that

can be easily prepared from phenol, phthalic anhydride, and hydrazine. The PPESK family of polymers has high glass transition temperatures and excellent physical properties and thermostability. Membranes made from PPESK have shown good separation and permeation properties for gas and liquid separations.^{3,4}

Sulfonation is commonly applied to modify polymers to increase hydrophilicity. Many homopolymers, as well as random and block copolymers containing aromatic rings or double bonds, can be sulfonated.^{5–10} Sulfonation of polysulfone (PSf) and polyetheretherketone (PEEK) has been

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reported.^{11–17} Sulfonated polysulfone membranes have been reported to be useful in desalination applications.^{18–21} Sulfonated PPESKs (SPPEK) have been prepared from previously synthesized polymers to improve the polymers' hydrophilicity and thereby utilize this type of polymer for membranes for applications in water treatment and gas treatment.

In this article, PPESK samples were sulfonated with concentrated or fuming sulfuric under a variety of conditions, and a series of SPPEKs with different sulfonation levels was obtained. Thermal properties, solubility, and some membrane properties of SPPEKs were also determined.

EXPERIMENTAL

Materials

The synthetic procedure for PPESK was reported in a previous publication.³ The PPESK random copolymer used in this study has a sulfone/ketone ratio of 1 : 1. Chloroform, *N*-methyl-2-pyrrolidone (NMP), butan-2-one, ethyleneglycolmethyl-ether, diethyl ether, concentrated (98%) and fuming sulfuric acid (20–25% SO₃), and other chemicals were obtained commercially and used without further purification. All chemicals used in the experiments were analytical grade. Poly(ethylene glycol) (PEG) with an MW of 12,000 was used as a solute for membrane characterization.

Synthesis of SPPEK

PPESK was dried in a vacuum oven at 120°C for 24 h. PPESK and concentrated (98%) or fuming sulfuric acid were placed in a three-neck reaction vessel equipped with a mechanical stirrer. SPPEKs with different degrees of sulfonation (DS) were obtained at certain reaction temperatures and times, as shown in Table I. The poly-

mers were precipitated in ice water and then filtered. Low-sulfonated PPESK (LSPPEK) and medium-sulfonated PPESK (MSPPEK) were purified by redissolving the polymers in chloroform and reprecipitating the solutions in ethanol. The polymers were washed with ethanol/water to remove acid until pH was neutral, then swelled and washed with water. Highly sulfonated PPESK (HSPPEK) and SHSPPEK were purified by swelling and washing with ethanol/water. All the polymers were filtered and then dried in a vacuum oven at 120°C for 24 h.

Analytical Measurements

¹H-NMR spectra were recorded using a Varian Unity Inova 400 MHz spectrometer. IR spectra were recorded on a Bio-Rad FTS7 FTIR spectrometer. The inherent viscosities of SPPEKs were determined using an Ubbelohde viscometer at a polymer concentration of 0.4 g/dL in *N,N*-dimethylacetamide at 25°C. Elemental analysis was determined using a Perkin-Elmer PE-2400-II. Contact angles on dense films were determined by JY-82 Contact Angles Equipment (Chengde Experimental Equipment China) for 1 min. Differential scanning calorimetry (DSC) measurements were conducted on a Perkin-Elmer 7 Thermal Analysis System at a heating rate of 10°C/min in air. The DSC curves obtained during the second heating scan, after an initial heat/quench cycle, were used to determine the T_g values. Polyethyleneglycols (PEG) and Clayton Yellow dye solute concentrations for permeation through membranes were 0.01% and were measured using an UV Spectrophotometer-751 (Shanghai Angles Instrument China). Membrane separation tests at room temperature were performed using a magnetically stirred dead-end cell module (Ecological Environment Center of Chinese Academy of Science) having an effective membrane area of 41 cm² and a feed volume of 550 mL. Membrane

Table I SPPEK Sulfonation Conditions for Different DS Ranges

Codes	Sulfonation Agent	Degree of Sulfonation	Polymer Concentration %	Reaction Temperature °C	Reaction Time (h)	Precipitation Agent
LSPPEK	Sulfuric acid (98%)	0–35	37.5	40	0–4	Ethanol
MSPPEK	Sulfuric acid (98%)	35–150	3	60	0–10	Ethanol
HSPPEK	Oleum (20–25%)	150–200	3	40	1–4	Ice water
SHSPPEK	Oleum (20–25%)	>200	3	40	>4	Ice water

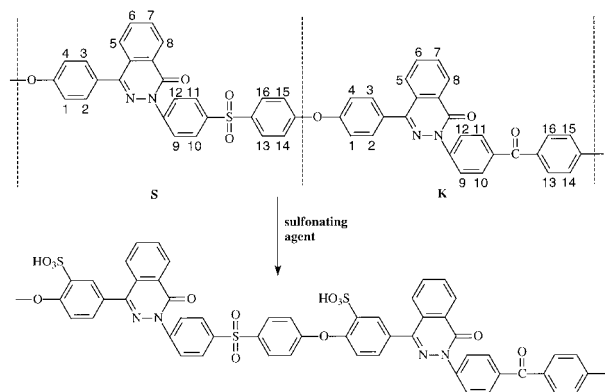
separation tests at temperatures above ambient were performed using a metal cell module (Dalian Institute of Chemistry and Physics of Chinese Academy of Science) having an effective membrane area of 28 cm² and a feed volume of 5000 mL.

The degree of sulfonation was determined by the ion exchange (IE) method²² for samples with a DS \leq 150%. A sample of precisely weighed SPPEK was soaked in excess 0.1 N NaOH containing 5% w/w NaCl, then filtered, and the polymer was titrated to the end point. The reliability of the IE method was tested by comparison with results from elementary analysis, and shown to have a close correlation. For example, the DS of a SPPEK was 84% by the IE method and 87% by elementary analysis (C: 67.58%, S: 5.32%, H: 3.495%, N: 7.09%; carbon/sulfur of SPPEK was 12.920 and carbon/sulfur of PPEK was 13.125). Samples having DS >150 were determined using a DDS-11A Electrical Conductivity Instrument (Shanghai Leichi Instrument China).²³ Precisely measured quantities of HSPPEK and SHSPPEK (0.5 g) were dissolved in water/ethanol and titrated with 0.1 N NaOH to the end point. Electrical conductivity was measured to calculate DS.

RESULTS AND DISCUSSION

Structural Characterization of SPPEK

Sulfonation of aromatic polymers is an electrophilic substitution reaction whereby an aromatic proton on an activated site is replaced by a —SO₃H group. The choice of the sulfonating agent and the site of electrophilic substitution on



Scheme 1 Sulfonation reaction of PPEK (DS 200%).

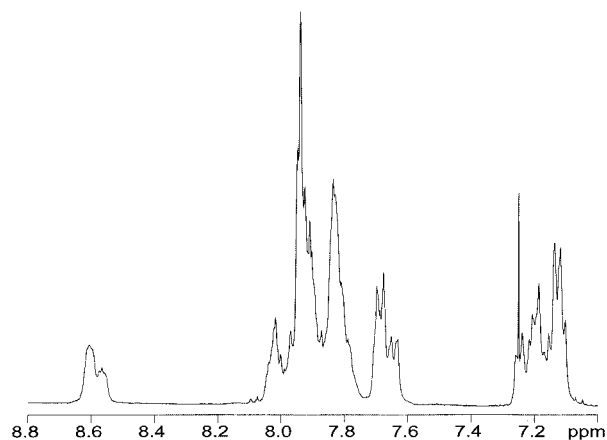


Figure 1 The ¹H-NMR spectrum of PPEK (1 : 1 S : K).

a particular polymer depends on the type of activating substituents linking or attached to the phenyl ring. In the electrophilic aromatic sulfonation reactions of PPEK, electron-donating substituents like oxygen of the phenyl ether are *o,p*-orienting activating groups, whereas electron withdrawing groups such as carbonyl, sulfone, and phthalazinyl are *o,p* deactivating groups (*m*-orienting) on the basis of orientation by electron resonance. When some powerful sulfonating agents such as chlorosulfonic acid are employed, there is a possibility of polymer degradation or crosslinking occurring. It was expected that less aggressive sulfonating agents like concentrated sulfuric acid and fuming sulfuric acid would be less likely to cause undesired side reactions if experimental conditions were carefully chosen.

In this study, PPEK is a random copolymer prepared by condensation polymerization of phthalazinone monomer with a 1 : 1 mixture of 4,4'-dichlorodiphenylsulfone and 4,4'-difluorobenzophenone. Scheme 1 shows a representative repeat unit, which is composed of randomly connected units **S** and **K** in the ratio of 1 : 1.

The IR spectra of SPPEKs with higher DS had larger absorption at 1024 and 1085 cm⁻¹ (sym. O=S=O str.), and 615 cm⁻¹ (C—S bend) than PPEK or SPPEKs with lower DS. The ¹H-NMR spectra of both the starting material PPEK, and a highly sulfonated PPEK (DS = 252%) were complex and difficult to assign due to the random connectivity and nature of the repeat units. The PPEK spectrum (Fig. 1) is broadly divided into four groups of multiplets: δ 8.60–8.56, 8.04–7.79, 7.70–7.63, 7.26–7.10. In the upfield multiplet, there is a doublet centered at δ = 7.13. It is most likely that it corresponds to

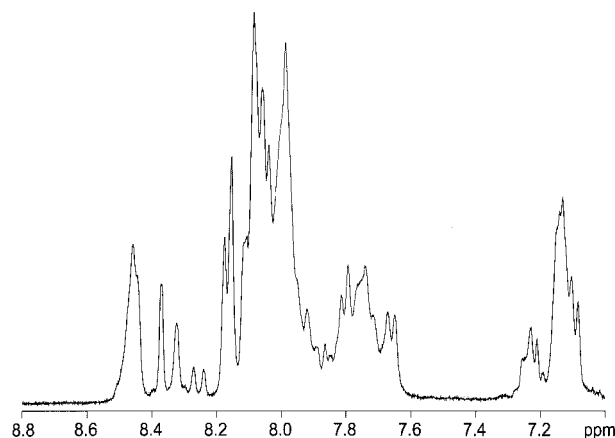


Figure 2 The $^1\text{H-NMR}$ spectrum of SPPEsk (DS 252%).

H1/H4 of **S** or **K** phthalazinone units. This is supported by using $^1\text{H-NMR}$ software (Advanced Chemistry Development Laboratories, ACD Labs, Toronto, Canada), which predicts that H1/H4 (**S** or **K**) have the most upfield chemical shift. A higher chemical shift upfield would indicate that protons on this site would be most susceptible to sulfonation by electrophilic substitution.

The proton spectrum of the sulfonated PPESK in Figure 2 shows a diminished upfield doublet, suggesting that sulfonation occurs at H1/H4. Other characteristics of this complex spectrum are the appearance of a series of downfield signals at δ 8.46, 8.37, 8.32, and two minor ones, as well as the disappearance of the multiplet at δ 8.60–8.56. These obvious changes in chemical shift suggest that the presence of $-\text{SO}_3\text{H}$ groups perturbs the downfield protons in the same aromatic ring. Predictions run on both **S** and **K** type units show that the next upfield proton is H14/H15 of the **K** unit, followed by H6, then H5 of both **S** and **K** units. Therefore, in the absence of definitive assigned $^1\text{H-NMR}$ data, the order of reactivity to sulfonation for the protons of PPESK is as follows: H1/H4 (**S** and **K**) \gg H14/H15 (**K**) $>$ H6 (**S** and **K**) \approx H5 (**S** and **K**). The most downfield protons where sulfonation would be very unlikely to occur are in the order of: H13/H16 (**S**) \approx H10/H11 (**K**) $>$ H9/H12 (**S** and **K**) $>$ H10/H11 (**S**) $>$ H2/H3 (**S** and **K**) \approx H7 and H8 (**S** and **K**).

H1/H4, *meta* to phthalazinone and *ortho* to the phenyl ether group, is the site where sulfonation is likely to occur most readily. When $\text{DS} \leq 200\%$ the product of the sulfonation reaction is expected to occur at H1/H4 on SPPEsk, as shown in Scheme 1. When $\text{DS} > 200\%$, the site of sulfon-

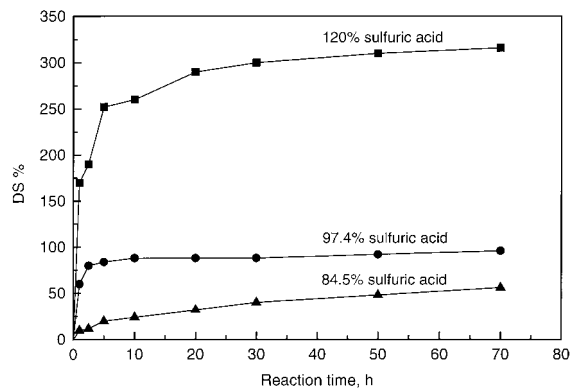


Figure 3 The effect of the concentration of sulfonating agent on DS (40°C, 3% polymer).

ation may occur at H14/H15 (**K** only) or at H6 or H5.

Sulfonation Reaction Conditions for SPPEsk

The DS obtained for sulfonation of PPESK depends on several factors, including the strength of sulfonating agent, reaction time, and reaction temperature, and concentration of polymer. Under the same reaction conditions of fixed temperature (40°C) and fixed polymer concentration (3%), DS increases with the solution concentration of SO_3 , as shown in Figure 3. After 5 h, the DS did not increase significantly with time for 97.4% H_2SO_4 sulfonating agent, whereas the 84.5% and 120% H_2SO_4 (fuming sulfuric acid) sulfonating agents required 20 h to achieve almost constant DS. The 120% H_2SO_4 resulted in a much higher DS (approximately a threefold increase) than 97.4% H_2SO_4 .

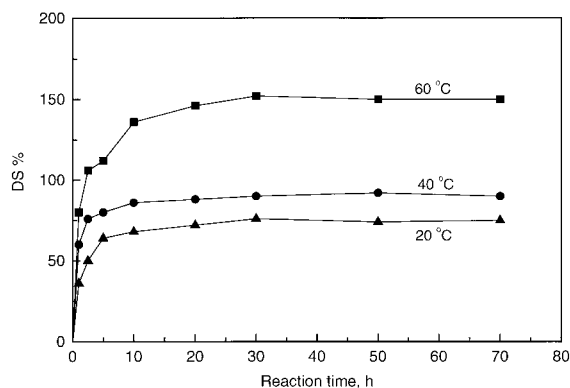


Figure 4 The effect of reaction time and temperature on the DS (98% sulfuric acid, 3% polymer).

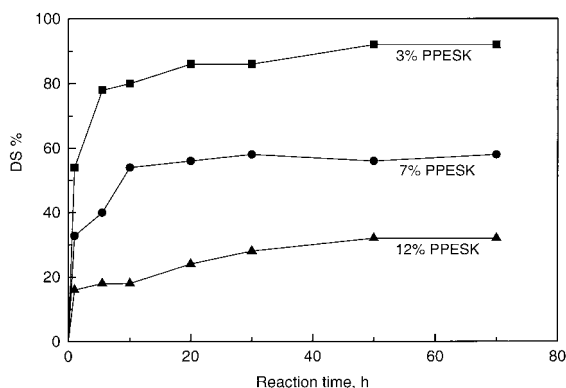


Figure 5 The effect of concentration of PPEsk on the DS (40°C, 98% sulfuric acid).

Under fixed conditions of 3% polymer and 98% H_2SO_4 , increased temperature led to higher DS, as shown in Figure 4. This is due to an equilibrium shift towards higher SO_3 concentration as the temperature increases. Higher temperature is beneficial in facilitating the dissolution of the polymer, but too high a temperature ($>70^\circ\text{C}$) resulted in chain degradation of PPEsk.

Another factor influencing DS is polymer concentration in the reaction mixture. A lower concentration of PPEsk gave SPPEsk with higher DS, as shown in Figure 5. A higher polymer concentration reduces the SO_3 -polymer contact, thereby reducing the reactivity of the sulfonating agent. In addition, less efficient stirring gives reduced distribution and contact area. The DS of the final product was dependent on the concentration of $-\text{SO}_3$.

SPPEsk Characterization

Viscosity of SPPEsk

There is a significant increase in viscosity by the presence of a $-\text{SO}_3\text{H}$ group on the PPEsk polymer chain. This is primarily due to an increase in

Table III Relationship between DS and T_g of SPPEsk

Polymer	DS, %	T_g , °C
PPEsk	0	278
LSPPEsk	23.8	287
MSPPEsk	84.7	292
HSPPEsk	152	321
SHSPPEsk	252	323

intermolecular H-bonding forces of SPPEsk. The inherent viscosity of SPPEsk with respect to DS is shown in Table II. Above 100% DS, there is a large increase in inherent viscosity $[\eta]$.

Thermal Properties of SPPEsk

Glass transition temperature (T_g) results obtained by differential scanning calorimetry (DSC), shown in Table III, indicate that the incorporation of $-\text{SO}_3\text{H}$ groups into PPEsk causes the T_g to rise linearly. The DSC transition also became broader and less defined with increased ionic content. However, when $\text{DS} > 150\%$, T_g did not increase significantly, and the highest T_g obtained was 323°C for $\text{DS} 252\%$, which is only 2°C higher than that for $\text{DS} 152\%$. This may be the result of H-bonding attractive forces offset by ionic repulsive forces of $-\text{SO}_3^-$.

Solubility of SPPEsk

The solubility characteristics of SPPEsk with different DS in selected solvents are listed in Table IV. PPEsk is soluble in selected polar aprotic solvents and in chlorinated solvents such as methylenechloride and chloroform. However, SPPEsk with higher DS can dissolve in the water and methanol, reflecting the more ionic nature of the polymer. Incorporation of $-\text{SO}_3\text{H}$ groups into

Table II Comparison of $[\eta]$ before and after Sulfonation

SPPEsk	DS, %	$[\eta]$ before Sulfonation	$[\eta]$ after Sulfonation	% Increase in $[\eta]$
LSPPEsk	14.2	0.58	0.58	0
	23.8	0.35	0.38	8.57
	57.8	0.58	0.67	15.5
MSPPEsk	79.3	0.58	0.74	27.6
HSPPEsk	152	0.68	1.10	61.7
SHSPPEsk	252	0.68	2.16	217

Table IV Solubility of SPPEsk^a

Solvent	PPESK	LSPPEsk	MSPPEsk	HSPPEsk	SHSPPEsk
Water	–	–	SW	SW	+
Acetic acid (36%)	–	–	SW	SW	+
Methanol	–	–	SW	SW	+
Ethanol	–	–	–	SW	SW
<i>n</i> -Butanol	–	–	SW	SW	SW
Acetone	–	–	–	–	–
Butan-2-one	–	–	–	–	–
<i>N,N</i> -Dimethylformamide	+	+	+	+	+
<i>N,N</i> -Dimethylacetamide	+	+	+	+	+
<i>N</i> -Methyl-2-pyrrolidinone	SW	+	+	+	+
Dimethyl sulfoxide	+	+	+	+	+
Dioxane	–	–	–	–	–
Tetrahydrofuran	–	–	–	–	–
Diethylether	–	–	–	–	–
Ethyleneglycoldimethylether	–	–	SW	+	+
Chloroform	+	+	SW	SW	SW
Dichloromethane	+	+	–	–	–
Hexane	–	–	–	–	–

^a Solubility: (+) soluble at room temperature. (SW) swollen. (–) Insoluble.

PPESK causes an increase of solubility for high polarity solvents and a reduction of solubility for chlorinated solvents. These data were used to select solvents for the membrane casting solution, and for the selective SPPEsk layer in the composite membrane.

Contact Angle Measurements

Dense homogeneous films were prepared for contact angle measurements by preparing 10% filtered polymer solutions in NMP. Solutions were cast on a leveled glass plate in a controlled dust-free environment at a relative humidity of 35–45%. Freshly cast films were initially heated at ~80°C for 24 h, then at ~100°C for 24 h, and finally under vacuum to remove residual NMP. The resulting polymer films were carefully removed from the plate and generally had a thickness of ~20 μm. The contact angles of water on SPPEsk dense film membranes were determined at room temperature, and are shown in Table V.

Table V Relationship between Contact Angles and DS

Degree of Sulfonation, %	0	24	86	150	252
Contact angle with water	78	59	45	39	—

The contact angles decreased with increasing DS, indicating an increase in hydrophilicity of the polymer.

Properties of UF/NF Membranes

The rejection for PEG12000 solute and water flux of membranes were determined, and are listed in Table VI.

As shown in Table VI, the sulfonated asymmetric membrane prepared with butan-2-one additive had a significant increase in rejection of PEG12000 when compared with PPESK, as well as a modest increase in flux. However, the sulfonated asymmetric membrane prepared with ethyleneglycolmethylether additive did not have an increase in solute rejection, but instead showed a fourfold increase in flux.

In addition to asymmetric membranes, composite nanofiltration membranes were prepared using a PPESK asymmetric support membrane having greater than 90% rejection of PEG12000. The selective skin layer for the composite was SPPEsk having a DS of 150%. The solution for the composite skin layer was determined with the help of solubility data. A solution of the selective membrane skin layer was prepared by dissolving SPPEsk (between 0.5 and 1.5%) in a solvent mixture of ethanol–water–ethyleneglycoldimethylether (70 : 17 : 13). To this solution was added by

Table VI Properties of Asymmetric SPPEK UF Membranes (0.1 MPa, 20°C)

Trial	Polymer	Additive	R for PEG12000, %	Flux, $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$
1	PPESK	Butan-2-one	92	496
2	SPPEK	Butan-2-one	97	509
3	PPESK	Ethyleneglycolmethylether	99	219
4	SPPEK	Ethyleneglycolmethylether	98	876

weight 25% glycerol and 5% *N,N*-dimethylformamide. The skin layer solution was cast onto the support membrane, and the solution was allowed to evaporate at ambient temperature. The membrane was heated at 100°C to evaporate residual solvent and crosslink the skin layer. One composite membrane prepared from a 1.0% SPPEK formulation had Na_2SO_4 (0.1%) and NaCl (0.1%) rejection of 67 and 30%, while the solution fluxes were 32 and 37 $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, respectively at 20°C and 0.25 MPa pressure. Another membrane, prepared from 0.8% SPPEK formulation and tested under the same conditions of 20°C and 0.25 MPa, had a rejection of 63% for Clayton Yellow (MW = 695), while the solution flux was 62 $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. The membrane was subjected to higher temperatures to determine its short-term thermal stability. The apparatus consisted of a metal test cell immersed in an oil bath at the required temperature. The feed solute was driven by nitrogen pressure, and the cell pressure was monitored by a gauge. When the temperature was increased from 20 to 120°C, solution flux was increased fourfold, and the rejection was decreased by 30%. When the oil bath temperature was increased to 130°C, maintained for 1 h and then decreased to 20°C, the properties of the membrane were almost unchanged from the original values. This indicates that the composite membranes have excellent thermostability, at least for the short term. Future work on optimizing the substrate and skin layer of the composite should improve the membrane properties. In addition, longer term tests will be required to determine thermostability.

CONCLUSIONS

Modification of poly(phthalazinone ether sulfone ketone) (PPESK) by sulfonation with concen-

trated and fuming sulfuric acid increased hydrophilicity of the polymer. A range of sulfonated PPESKs with DS of 10–300% were prepared and characterized. Reaction condition variables affecting the sulfonation reaction and techniques for preparation of SPPEK with different DS were determined. Compared with PPESK, the hydrophilicity and thermostability of SPPEK were improved, contact angle with water was reduced, and T_g s were increased to a maximum of 322°C from 278°C, due to the strong polarity and H-bonding of $-\text{SO}_3\text{H}$. Asymmetric membranes, having potentially increased fouling resistance, were prepared with SPPEK. The PEG12000 rejection was 98%, and water flux was 876 $\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, considerably higher than PPESK membrane. SPPEK/PPESK composite nanofiltration membranes having good separation properties were also fabricated, and were shown to have short-term operational stability up to 120°C.

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