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Thin film composite (TFC) membranes with improved thermal stability from sulfonated poly(phthalazinone ether sulfone ketone) (SPPEsk)

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Abstract

Sulfonated poly(phthalazinone ether sulfone ketone)s (SPPEsk) were used to prepare thin film composite (TFC) membranes having increased thermal stability, hydrophilicity and potentially improved fouling-resistance. TFCs were prepared from SPPEsk having a degree of sulfonation (DS) 1.5 as the top selective layer coated onto polysulfone (PSF) or poly(phthalazinone ether sulfone ketone)s (PPEsk) asymmetric support membranes. At room temperature and 0.25 MPa pressure SPPEsk/PSF composite membrane rejections for 1000 ppm Na₂SO₄ and NaCl were 91 and 41%, respectively and solution fluxes were 30 and 35 kg m⁻² h⁻¹. A SPPEsk/PPEsk, TFC membrane had rejections for Na₂SO₄ and NaCl of 67 and 30%, respectively with similar solution fluxes. Another SPPEsk/PPEsk membrane had a rejection 63% for 100 ppm Clayton Yellow dye (CY, MW = 695) while the solution flux was 62 kg m⁻² h⁻¹. When the feed solution temperature increased from 20 to 120 °C, solution flux was increased four-fold and the rejection decreased by 14%. The properties of the membrane were almost unchanged from the original values after the membrane was heated at 130 °C for 1 h and then decreased to 20 °C. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Composite membrane; Nanofiltration; Ultrafiltration; Thermostability

1. Introduction

Nanofiltration (NF) is useful in many industrial sector applications, both for the removal of organic and inorganic components. NF membranes are often negatively charged, displaying separation characteristics in the intermediate range between reverse osmosis (RO) and ultrafiltration (UF). NF membranes have a looser skin layer structure enabling higher fluxes and lower operating pressures than RO membranes and are

able to reject small organic molecules having molecular weights as low as 200–500 Da. In salt separation, a Donnan effect [1] stemming from the membrane charge leads to a difference in rejection according to ion charge. Rejection is lower for monovalent ions and higher for divalent ions.

Thin film composite membranes have higher performance than asymmetric membranes due to a thin selective layer on a porous support. The TFC approach has key advantages compared with asymmetric membranes because the selective layer can be optimized for the desired combination of solvent flux and solute rejection, while the porous support layer can

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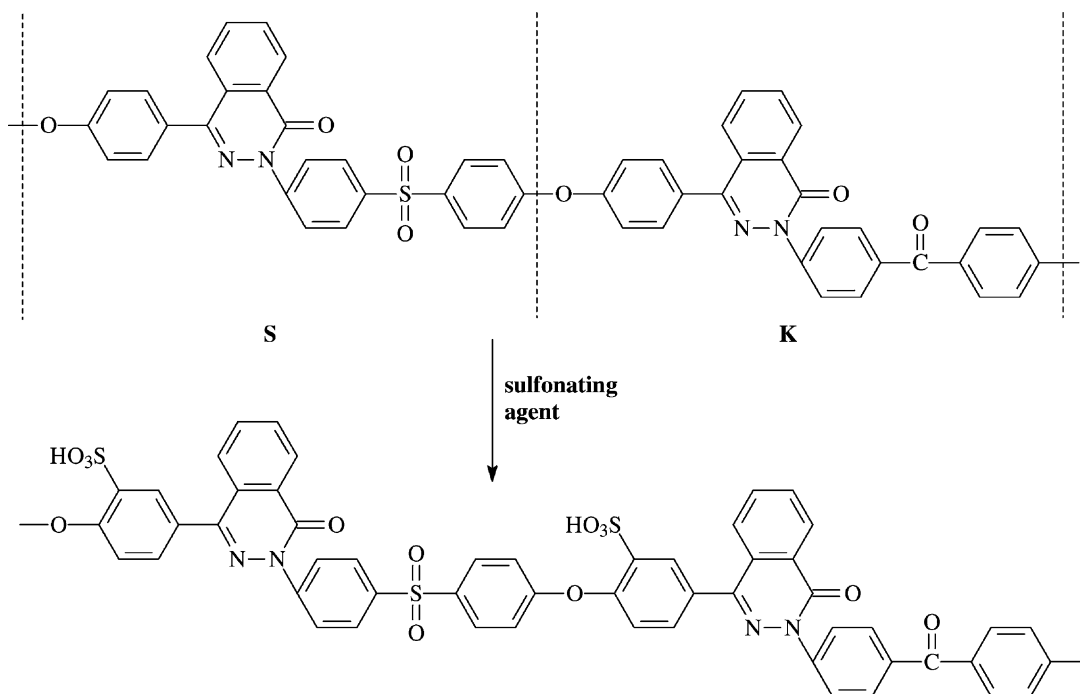
be optimized for maximum strength and compression resistance combined with minimum resistance to permeate flow [1].

The application of high-temperature membranes is increasingly gaining attention in industry. This interest is reinforced by advances in the need for the thermal and mechanical stability of new materials as well as more demanding separation processes.

A series of novel poly(phthalazinone ether sulfone ketone) (PPESK) copolymers containing different ratios of diphenylsulfone and diphenylketone units were previously synthesized [2–4] from 1,2-dihydro-4-(4-hydroxy-phenyl)phthalazin-1-one [5,6]. There are plans to commercialize these condensation polymers, derived from this phthalazinone monomer that is readily prepared from the commodity chemicals 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 both gas and liquid separations [4,7].

Sulfonation is commonly applied to modify polymers in order to increase hydrophilicity. Many homopolymers as well as random and block copolymers containing aromatic rings or double bonds can be sulfonated [8]. Sulfonation of membrane materials such as polysulfone (PSF) and polyetheretherketone (PEEK) has been reported [9–15]. Sulfonated PSF has been used for making hydrophilic membranes [16–18]. Sulfonated poly(phthalazinone ether sulfone ketone)s (SPPEESKs) were prepared from previously synthesized polymers to improve the polymers' hydrophilicity and thereby utilize this type of polymer for membrane applications in water treatment [19,20]. Scheme 1 shows the sulfonation reaction (degree of sulfonation, DS 200%) of PPESK composed of randomly connected units **S** and **K** in the ratio of 1:1.

In this work, we describe the preparation and characterization of two kinds of composite nanofiltration membranes. Composite NF membranes were prepared with SPPEESKs as the top selective layer and asymmetric membranes of either PSF or the more thermally stable PPESK as the support substrate. The



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

thermostability of SPPEsk/PPEsk membranes was tested by increasing the operating temperature from 20 to 130 °C.

2. Experimental

2.1. Materials and instruments

The synthetic procedure for preparing PPEsk and SPPEsk was reported previously [4,19]. The PPEsk random copolymer used in this study had a sulfone:ketone ratio of 1:1 and the DS of SPPEsk was 1.5. All chemicals used in the experiments were analytical grade. Clayton Yellow (CY, a sulfonated dye having a MW 695 also known as Thiazol Yellow G), Na₂SO₄, NaCl, MgSO₄ and MgCl₂ were used as solutes for the membrane characterization.

Contact angles of membranes were determined on a level surface with water for 1 min in air using a JY-82 Contact Angles Equipment (Chengde Experimental Equipment, China). PEG and CY dye solute concentrations for permeation tests were 100 ppm and were measured using a UV Spectrophotometer-751 (Shanghai Angles Instrument, China). Salt concentrations for permeation tests were 1000 ppm and were determined by Electrical Conductivity DDS-11A (Shanghai Leichi Instrument, China). The membrane feed solution side was stirred. Membrane permeation tests at ambient temperatures 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. Permeation tests at higher temperatures were performed using a metal test cell module (Dalian Institute of Chemistry and Physics of the Chinese Academy of Science) having an effective membrane area of 28 cm² and a feed volume of 51.

2.2. Membrane preparation

Composite nanofiltration membranes were prepared using asymmetric support PSF and PPEsk membranes. Commercial PSF asymmetric membranes with >90% rejections for PEG 10000 (PSF10000) and PEG 30000 (PSF30000) were purchased from Ecological Environment Center of the Chinese Academy of Science. PPEsk asymmetric membranes having

92% rejection for PEG12000 and pure water flux of ~500 kg m⁻² h⁻¹ were prepared in our laboratory [7]. The solution for the selective skin layer was prepared by dissolving SPPEsk (DS 1.5) in a mixture of ethanol–water–ethyleneglycoldimethylether (ratio 70:17:13, 0.5–1.5% concentrations by weight). To this solution was added by weight 25% glycerol and 5% *N,N*-dimethylformamide (DMF). Before applying the coating layer of the composite membrane, PSF and PPEsk support membranes were rinsed with water and not dried completely. TFC membranes were prepared by two methods: (a) by soaking PSF and PPEsk support membranes in the SPPEsk coating solution or (b) by casting SPPEsk solution onto the surface of the support membranes then drying at room temperature. The resulting TFCs were heat-treated at 100 °C for 1 h. The composite membrane fabrication conditions for CM1 to CM11 are summarized in Table 1.

2.3. Membrane characterization

Salts and CY were employed to characterize the membrane properties. The salts chosen contained mono- and divalent anions and cations that are routinely used for NF membrane experiments. CY is a low MW dye easily detectable by UV spectrometry. Before testing, the membranes were immersed in water for 36 h and pre-pressurized at 0.3 MPa for 0.5 h. The solution fluxes and rejection of CY (100 ppm), PEG (100 ppm) and salts (1000 ppm) were measured initially under a pressure difference of 0.25 MPa and at ambient temperature. The permeation flux, F , is calculated as Eq. (1):

$$F = \frac{W}{At} \quad (1)$$

where W is the total weight of the water or solution permeated during the experiment, A the membrane area, and t is the operation time. Rejection, R , is calculated using the Eq. (2):

$$R = \frac{1 - C_p}{C_f} \quad (2)$$

where C_p and C_f are the concentration of the permeate and the feed, respectively. A minimum of three membrane disks were cut from sheets and used for each test. The water fluxes and solution rejections given are average values of these data.

Table 1
Conditions for composite membrane fabrication

Membrane number	Conditions of membrane making
CM1	PSF30000 ^a soaked in 1% SPPEsk ^b , treating at 100 °C
CM2	PSF10000 ^a soaked in 1% SPPEsk, treating at 100 °C
CM3	PSF10000 soaked in 0.6% SPPEsk, 100 °C curing treatment
CM4	1.5% SPPEsk casting on PSF10000, 60 °C curing treatment
CM5	1.5% SPPEsk casting on PSF10000, 100 °C curing treatment
CM6	1.2% SPPEsk casting on PSF10000, 100 °C curing treatment
CM7	1.5% SPPEsk casting on PPESK ^a , 100 °C curing treatment
CM8	1.0% SPPEsk casting on PPESK, 100 °C curing treatment
CM9	0.6% SPPEsk casting on PPESK, 100 °C curing treatment
CM10	0.6% SPPEsk casting on PPESK, 60 °C curing treatment
CM11	PPESK soaked in 0.6% SPPEsk, 60 °C curing treatment

^a Asymmetric support membrane.

^b Sulfonated polymer solution for skin layer.

3. Results and discussions

3.1. SPPEsk/PSF composite membrane

3.1.1. Coating solution preparation

A solvent mixture of ethanol–water was selected as the solvent for the SPPEsk skin layer. Ethyleneglycoldimethylether was used as an additive that had a tendency to result in increased flux and rejection when incorporated in these membrane formulations. Glycerol was used as a cross-linking agent for the selective skin layer.

A small amount of aprotic solvent DMF was added which is a solvent for the support. Addition of DMF solvent decreases the interfacial tension and increases the swelling of the support, thereby making it more compatible with the surface coating solution. Hence, the coating solution is better distributed on the support, while the pore size of the support is decreased through swelling.

3.1.2. Properties of composite membranes prepared by soaking onto different supports

Three composite membranes SPPEsk (1.0%)/PSF-30000 (CM1), SPPEsk (1.0%)/PSF10000 (CM2), SPPEsk (0.6%)/PSF10000 (CM3) were prepared by soaking PSF support membranes in different concentrations of SPPEsk solutions (0.6 and 1.0%) for 8 min then drying and heat-curing. The contact angles of the commercial PSF asymmetric support membranes and SPPEsk/PSF composite membranes are listed in Table 2. The contact angles of composite membranes are lower than those of the PSF support membranes indicating an increase in surface hydrophilicity due to the introduction of $-SO_3H$ groups to the membrane skin layer.

The initial factor that was determined in this study was the choice of the PSF membrane support in terms of molecular weight cut-off. The separation performances of each composite membrane are compared in Table 2. SPPEsk/PSF10000 CM2

Table 2
Properties of composite membrane on different PSF supports

Membrane	Contact angle	Na ₂ SO ₄		NaCl	
		R (%)	F (kg m ⁻² h ⁻¹)	R (%)	F (kg m ⁻² h ⁻¹)
Support membrane PSF 30000	72	–	–	–	–
SPPEsk (1%)/PSF 30000, CM1	58	61	24	23	26
Support membrane PSF 10000	72	–	–	–	–
SPPEsk (1%)/PSF 10000, CM2	54	88	9.3	39	13
SPPEsk (0.6%)/PSF 10000, CM3	–	83	32	36	38

membrane had higher rejection for both Na_2SO_4 and NaCl than SPPEK/PSF30000 CM1 membrane and gave rejection values in the nanofiltration range. The PSF10000 support membrane was selected for subsequent work due to its more favorable characteristics.

Table 2 also shows the effect of SPPEK solution concentration on composite membrane performance. A comparison of CM2 and CM3 in Table 2 shows that a higher solution concentration of SPPEK resulted in slightly higher salt rejections but the solution fluxes were reduced by a factor of about three. As the solution concentration of coating polymer increases, the thickness of the selective layer also increases, leading to lower flux and higher rejection. Using the coating procedure, a SPPEK solution concentration of 0.6% gave much more favorable membrane performance. The soaking and coating methods were compared and evaluated to determine the method giving the best performance data. After the initial experiments, it became clear that the coating method was preferable.

3.1.3. Effect of curing treatment temperature on the properties of SPPEK/PSF membranes prepared by casting

Two kinds of SPPEK/PSF10000 composite membranes CM4 and CM5 were prepared using the casting method described in Section 2.2, where the SPPEK concentration was 1.5%. Membranes CM4 and CM5 were cured at 60 and 100 °C, respectively for 1 h, then measured for Na_2SO_4 rejection and solution flux at room temperature. A comparison of CM4 and CM5 in Table 3 shows that the CM5 membrane had a similar rejection to that of CM4 but with reduced solution flux at the higher curing treatment temperature. There are two possible reasons for this result. One is that the higher temperature reduced the size and number

Table 3
Effect of curing treatment temperature on the properties of SPPEK/PSF membranes

Membrane number	Treatment temperature (°C)	Na_2SO_4	
		R (%)	F ($\text{kg m}^{-2} \text{h}^{-1}$)
CM4	60	89	72
CM5	100	91	30

Table 4

Performance of SPPEK/PSF composite membrane for different salt feed solutions

Salt	CM5		CM6	
	R (%)	F ($\text{kg m}^{-2} \text{h}^{-1}$)	R (%)	F ($\text{kg m}^{-2} \text{h}^{-1}$)
Na_2SO_4	91	30	84	32
NaCl	41	35	36	38
MgSO_4	32	35	22	38
MgCl_2	21	36	14	39

of open pores on the supporting layer so that the flux resistance was increased. Another reason is that the higher temperature resulted in a higher cross-linking density of the skin layer.

3.1.4. Salts rejection for SPPEK/PSF composite membranes

A SPPEK/PSF10000 composite membrane (CM6) was prepared by the casting method using a 1.2% SPPEK concentration. The rejection for different salts and their solution flux was compared for CM5 and CM6 as shown in Table 4. The salts rejections order of both membranes is $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{MgSO}_4 > \text{MgCl}_2$. This sequence shows the predictable Donnan characteristic [1] of salt rejection for a negatively charged nanofiltration membrane. The membranes have higher rejections for high-valence anions and low-valence cations than low-valence anions and high-valence cations. Membrane CM5 had higher rejection rates and slightly lower fluxes than CM6. This is probably due to a denser selective layer prepared from the more concentrated SPPEK coating solution.

3.1.5. Influence of Na_2SO_4 concentration on R and F

The influence of Na_2SO_4 salt concentration on rejection rate and solution flux for composite membrane CM6 is shown in Fig. 1. Na_2SO_4 concentration exerts a very marked effect on its rejection. Both R and F decrease with an increase in Na_2SO_4 concentration. Donnan equilibrium theory [1] explains this decrease in rejection rate with increasing salt concentration, whereby the higher the feed ionic concentration, the weaker the influence of the polymeric electrolytic membrane on ions permeated. As the ionic concentration increases, the repulsion effect of the electrolytic membrane on the ions decreases, while the osmotic

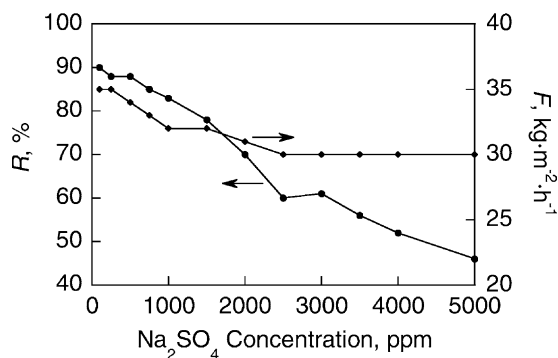


Fig. 1. Influence of Na₂SO₄ concentration on R and F for SPPEsk/PSF composite membrane.

pressure increases and partially counteracts the exerted driving force. As a result, the net driving force ($\Delta p - \Delta \pi$) of the system is reduced, resulting in a decrease in water flux.

3.1.6. Influence of operating pressure on R and F

Nanofiltration membranes operate in the range between ultrafiltration and reverse osmosis, with the implication that transport occurs through a skin layer having characteristics intermediate between a finely porous structure and a non-porous dense structure. Fig. 2 shows that when the salt Na₂SO₄ concentration 1000 ppm is fixed, water flux increases somewhat linearly with increasing pressure for composite CM6. This can be partly explained by the solution-diffusion model:

$$\text{water flux : } F = A(\Delta p - \beta \Delta \pi) \quad (3)$$

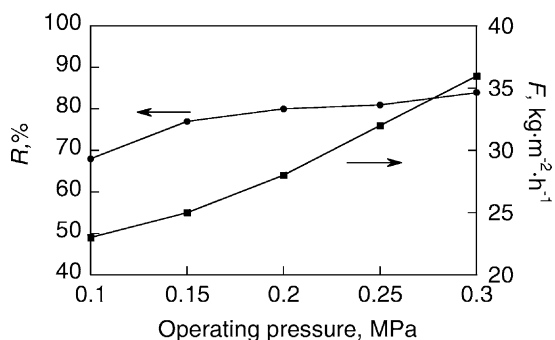


Fig. 2. Influence of operating pressure on R and F for SPPEsk/PSF composite membrane.

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

$$\text{salt flux : } F_s = B(\beta C_1 - C_2) \quad (4)$$

where B is the salt permeation coefficient, C_1 and C_2 the salt concentrations on the upstream and downstream sides of the membrane, respectively, $\beta = C_b/C_m$, where C_b is the salt concentration on the membrane surface, and C_m is the salt concentration of the feed.

Eq. (3) shows that F increases linearly with increasing Δp and Eq. (4) shows that salt permeation is a function of salt concentration on both sides of the membrane. Therefore, as water flux increases, Δp increases, but salt flux remains constant thereby resulting in an increase in salt rejection. At the same time, C_2 is reduced and the concentration difference on the two sides of the membrane increases, which results in a salt flux increase that is unfavorable to salt rejection. These opposing effects combine to result in a gradual increase in salt rejection to a definite value. Moreover, salt rejection is related to the interface properties (adsorption) of the surface material, and the exerted pressure drives water molecules to permeate through the membrane. Levenstein et al. [21] used different models showing the same result of both the influence of operating pressure and salt concentration.

3.1.7. Influence of operation temperature on R and F

Higher T_g of SPPEsk (DS = 1.5, 321 °C) [19] compared with sulfonated polysulfone allows the polymer to maintain mechanical properties better with less plasticization when subjected to heat. The influence of operating temperature on Na₂SO₄ and CY rejection and solution flux was determined using composite membrane CM4. Table 5 shows a trend

Table 5
Influence of operating temperature on R and F for SPPEsk/PSF composite membrane

T (°C)	CM4, Na ₂ SO ₄		CM4, CY	
	R (%)	F (kg m ⁻² h ⁻¹)	R (%)	F (kg m ⁻² h ⁻¹)
20	89	72	98	40
40	85	104	–	–
60	77	141	–	–
80	72	182	98	110

Table 6
Performance of SPPEsk/PPESK composite membrane for different salts feed solutions

Salt	CM7		CM8		CM9	
	R (%)	F (kg m ⁻² h ⁻¹)	R (%)	F (kg m ⁻² h ⁻¹)	R (%)	F (kg m ⁻² h ⁻¹)
Na ₂ SO ₄	67	32	33	75	21	100
NaCl	30	37	16	86	–	–
MgSO ₄	22	26	10	63	–	–
MgCl ₂	9	26	6	68	–	–

that rejection for Na₂SO₄ decreased from 89 to 72% but the solution fluxes increased more than two-fold within the operation temperature range increase. Composite CM4 maintained 98% CY rejection even though the solution flux increased nearly three-fold. When the temperature was cycled back to 20 °C, results similar to the original values were obtained. When the temperature increase cycle was repeated, similar values were again obtained. This indicates that the composite SPPEsk/PSF membrane is thermostable at or below 80 °C and undergoes reversible changes, giving reproducible flux and rejection characteristics when cycled back to the higher temperatures.

3.2. SPPEsk/PPESK composite membrane

In order to obtain more thermostable composite membranes, the support membranes were prepared from PPESK instead of PSF. PPESK has a substantially higher T_g (278 °C) [19] than PSF (186 °C) [18]. Composite nanofiltration membranes were prepared using PPESK asymmetric support membranes [7] having 92% rejection for PEG12000 and pure water fluxes of ~500 kg m⁻² h⁻¹.

A dilute solution of SPPEsk was cast onto the support membrane and allowed to evaporate at ambient temperature. The membranes were then cured by heating at 100 °C for 1 h to cross-link the skin layer.

3.2.1. Performance of composite membranes prepared from different casting solution concentrations

Three kinds of SPPEsk/PPESK composite membranes were prepared using the casting method described in Section 2.2. SPPEsk concentrations were 1.5% (CM7), 1.0% (CM8) and 0.6% (CM9).

The contact angles of PPESK support and SPPEsk/PPESK composite membrane (CM7) were measured first. The contact angle of CM7 was decreased to 52 compared with 68 for the PPESK support. This indicated that the hydrophilicity of the composite membrane surface is higher than the PPESK asymmetric membrane substrate due to the introduction of –SO₃H group to the membrane surface.

The rejections for different salts and solution fluxes of the membranes measured at ambient temperature are listed in Table 6. Following the same sequence observed before, the order of salts rejections of all the membranes was Na₂SO₄ > NaCl > MgSO₄ > MgCl₂. Composite CM7 prepared from the highest casting concentration showed better membrane performance than CM8 and CM9 with a Na₂SO₄ rejection rate of more than double.

3.2.2. The effect of curing temperature on SPPEsk/PPESK composites

Another SPPEsk/PPESK composite membrane (CM10) was prepared using the same method and formulation as CM9, but with a 60 °C curing treatment instead of 100 °C. The CY and Na₂SO₄ rejections and their solution fluxes of CM9 and CM10 were measured at ambient temperature and compared in Table 7. The higher curing temperature resulted in

Table 7
Effect of curing treatment temperature on the properties of SPPEsk/PPESK membranes

Solute	CM9 (curing temperature 100 °C)		CM10 (curing temperature 60 °C)	
	R (%)	F (kg m ⁻² h ⁻¹)	R (%)	F (kg m ⁻² h ⁻¹)
CY	76	72	59	149
Na ₂ SO ₄	21	100	14	192

Table 8
Effect of process operating temperature on the SPPEsk/PPESK membrane properties

T ($^{\circ}\text{C}$)	R (%)	F for CY solution ($\text{kg m}^{-2} \text{h}^{-1}$)
20	63	62
80	62	127
100	60	167
120	54	228
130	31	250
20	61	57

a denser, more cross-linked skin layer and gave a membrane with higher rejection and lower solution flux.

3.2.3. The effect of operating temperature on membrane properties

Composite membrane CM11 was prepared by soaking PPESK support in 0.6% concentration SPPEsk solution for 5 min followed by a 60°C curing treatment. The CY rejection and the solution flux for CM11 membranes were measured at higher operating temperatures to determine their short-term thermal stability. The apparatus for higher operating temperatures consisted of a metal pressure test cell immersed in an oil bath at the required temperature. The results are listed in Table 8. A temperature increase from 20 to 100°C resulted in negligible changes in rejection, but solution flux was increased 2.7-fold. Above 100°C , significant reductions in rejection and increase in flux were obtained. A temperature increase from 100 to 120°C resulted in a 14% reduction in rejection and a 3.7-fold increase in solution flux compared with the original 20°C value. When the oil bath temperature was increased to 130°C , the rejection was reduced by 50% and the solution flux was increased four-fold. The process operating temperature was maintained at 130°C for 1 h and then decreased to 20°C . The flux and rejection measurements were repeated and found to be almost unchanged from the original values. Although the properties changed with an increase in temperature, they are reversible. 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, further testing will be required to evaluate longer-term thermostability.

4. Conclusion

Thin film composite membranes were prepared using SPPEsk (DS 1.5) as the selective skin layer. Composites with separations in the nanofiltration range were prepared either by soaking the support in SPPEsk multi-component solutions or by coating the selective layer onto the support. After an initial comparison of the two procedures, the coating method was adopted predominately. The coating solution concentration range was 0.6–1.5%. The higher concentrations and higher curing temperatures (100°C versus 60°C) resulted in membranes with greater salts rejection, most likely due to the higher cross-link density of the skin layer. Two different asymmetric membrane polymeric support materials were used. PSF support membranes having the narrower pore size (PEG10000 rejection) were found to have better characteristics for coating nanofiltration range skin layers than the more open membranes having PEG30000 rejection. In order to improve the thermostability of the composites further, a PPESK support membrane (PEG12000) was also used for composites.

The charged composite membranes exhibited predictable Donnan characteristics for salt rejection of mono- and divalent anions and cations. Rejection rates for the best SPPEsk/PSF membranes were 91 and 41% for Na_2SO_4 and NaCl, and solution fluxes were 30 and $35 \text{ kg m}^{-2} \text{ h}^{-1}$, respectively at room temperature. When subjected to temperature cycles up to 80°C , the composite membranes showed a more than two-fold reversible increase in solution flux, indicating that significant membrane swelling occurred. Sodium sulfate rejection was reduced steadily as the temperature increased, but the values were recovered on cooling. However, rejection of the larger charged dye molecule was maintained over the temperature range even though flux also increased to the same extent.

A SPPEsk/PPESK membrane having higher thermostability was prepared by a similar casting method and had 67 and 30% for the same salts, with solution fluxes of 32 and $37 \text{ kg m}^{-2} \text{ h}^{-1}$, respectively. Another SPPEsk/PPESK membrane prepared by the soaking method had a 63% rejection for Clayton Yellow (MW = 695) while the solution flux was $62 \text{ kg m}^{-2} \text{ h}^{-1}$. This membrane was used to determine the thermal stability characteristics under different

feed solution temperature cycles up to 130 °C. Up to 100 °C, a nearly three-fold increase in solution flux was observed with minimal reduction in rejection. This suggests that up to 100 °C, the increase in swelling was insufficient to accommodate passage of the charged dye. However, at 120–130 °C, sharp decreases in rejection and four-fold increases in flux indicated that swelling was much greater at the higher temperatures. When the membranes were cycled back to ambient temperature, flux and rejection values recovered to approximately initial values, showing that the membranes could be subjected to temperatures above 100 °C with reversible swelling. This suggests that the composite membranes have good thermostability, at least for the short-term.

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