Fabrication of thin film composite nanofiltration membranes by coating water soluble disulfonated poly (arylene ether sulfone) and in situ crosslinking

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Abstract

Thin film composite nanofiltration membranes were fabricated by coating a water-soluble disulfonated poly (arylene ether sulfone) which contained pendant amine groups (SPES-NH₂) onto a polysulfone support in conjunction with covalent crosslinking. Two different crosslinkers, glutaric dialdehyde (GA) and poly (ethylene glycol) diglycidyl ether (PEGDGE), were utilized with various concentrations and curing temperatures to optimize the performance of the resulting membranes. Both GA and PEGDGE crosslinked membranes exhibited optimal performance with a 1 wt% polymer concentration and 90 °C curing temperature. In particular, the optimized PEGDGE crosslinked membranes exhibited a higher permeation flux of 25.5±3.0 L m⁻² h⁻¹ while that of the GA crosslinked membranes was 8.9±3.2 L m⁻² h⁻¹; each membrane exhibited similar levels of Na₂SO₄ rejection at 96.1±1.1% and 96.6±2.1%, respectively, at 4 bar. The higher flux for the PEGDGE crosslinked membranes was attributed to higher hydrophilicity. Furthermore, the rejection of methyl orange and methyl violet was above 99.9% for both the GA and PEGDGE crosslinked

membranes. A fouling study of the PEGDGE crosslinked membrane was carried out using humic acid as a model foulant, and the membranes exhibited excellent antifouling ability, attributed to their high hydrophilicities and strongly anionic characteristics.

Keywords: Sulfonated poly (arylene ether sulfone); Nanofiltration membrane; Crosslinking; Water treatment; Thin film composite

1. Introduction

Reverse osmosis and ultrafiltration have wide-ranging applications, however the dearth of available membranes with molecular weight cut-offs between 200 and 2,000 g/mol represents an area of significant need [1, 2]. Thus, there has been a substantially increased interest in nanofiltration (NF) membranes in the last decade [3, 4]. These NF membranes are designed to reject small organic molecules and/or multivalent ions with a relatively high flux at low operating pressure, making them particularly attractive for large scale utilization in industrial fields such as waste water treatment, dye reclamation, water softening, and membrane bioreactors [5, 6].

Currently, most commercial NF membranes are prepared by an interfacial polymerization process [7, 8]. More recently, however, new coating materials have shown the potential to form an ultrathin selective layer via dip-coating techniques [9-11]. In developing new methods, two main aspects must be considered: the coating material and an appropriate solvent that can completely solvate the coating material. Materials for NF membranes must be of a charged character with excellent hydrophilicity to produce membranes with both high solute rejection and high water permeability [1, 11]. Coating materials that have been used for NF include sulfonated poly (arylene ether sulfone) (SPES) [12], sulfonated poly(ether ether ketone) (SPEEK) [13], quaternary ammonium poly(ether ether ketone) (QPEEK) [14, 15], polyethylene glycol (PEG) [16], and polyethyleneimine (PEI) [11]. Among which, SPES has garnered particular attention since its introduction by McGrath and co-workers several

years ago due to its excellent chloride resistance [17]. Solvent also plays an important role in the coating process. A multitude of solvents, such as formic acid [14, 15, 17], di (ethylene glycol) [18], ethylene glycol monomethyl ether (EGME)-acetone [1], methanol [13, 19], and chloroform [9], have been used to dissolve the coating materials. However, many of these solvents are toxic to the human body, corrosive to metal equipment, and even have adverse effects on the porous support layer structure. Thus, the development of environmentally friendly processing conditions for composite membranes using these novel materials is also of considerable interest in recent years [18, 20]. Water is naturally the most environmentally friendly solvent and many studies have reported using it as the solvent for the dissolution and reaction steps [10, 11].

To stabilize water-soluble materials and form an insoluble membrane, crosslinking is often employed. Additionally, crosslinked networks can limit the swelling of polymer membranes associated with increased levels of sulfonation. Covalent crosslinking is particularly stable and relatively insensitive to its environment. Recently, polymers containing pendant tertiary amines, sulfonic acid, and hydroxyl groups have been reacted with p-xylylene dichloride (XDC) [21], poly (vinylalcohol) (PVA) [22, 23], and dialdehyde [24] respectively, to form crosslinked architectures. Most of approaches involved a small loss in functionality and charge density.

In the present work, we report the preparation of a novel disulfonated poly (arylene ether sulfone) copolymer with pendant amine groups (SPES-NH₂) and tunable aqueous solubility; the solubility of SPES-NH₂ could be controlled by modifying the degree of sulfonation. Copolymers with a high degree of sulfonation of (70%: SPES-NH₂-70) could be fully dissolved in water. Furthermore, SPES-NH₂-70 could react with glutaric dialdehyde (GA) and polyethylene glycol diglycidyl ether (PEGDGE) to produce crosslinked networks. Multiple thin film composite membranes were fabricated using the SPES-NH₂-70 as the active layer material in

conjunction with an in-situ crosslinking process. The properties of the crosslinked membranes have been optimized by two variables: curing temperature and polymer concentration. The effects of crosslinking on membranes properties such as water permeability, salt rejection, and antifouling ability were systematically analyzed.

2. Experimental

2.1. Materials and reagents

3,3'-Disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) was prepared according to a literature method [25]. The amino group modified phenolphthalein (PPH-NH₂) monomer was synthesized according to our reported methods [12]. 4,4'-Dichlorodiphenylsulfone (DCDPS) was purchased from Acros Organics and dried at 100 °C for 24 h in a vacuum oven before used. Dimethyl sulfoxide (DMSO), anhydrous potassium carbonate (K₂CO₃), glutaric dialdehyde (GA) (50%) and poly (ethylene glycol) diglycidyl ether (PEGDGE) (MW: 500) were purchased from Sigma-Aldrich Co. and used without further purification. Microporous polysulfone (PSf) membranes with a molecular cut off (MWCO) of 100,000, prepared according to our previous report was used as substrate for the thin film composite membrane fabrication[26].

2.2. Synthesis of polymer (SPES-NH₂-70)

Water soluble disulfonated poly (arylene ether sulfone) copolymer bearing pendant amine groups with a sulfonation degree of 70% (SPES-NH₂-70) was synthesized following the procedure published elsewhere via nucleophilic polycondensation reaction of PPH-NH₂, SDCDPS, and DCDPS in DMSO/toluene mixture solvent system with K₂CO₃ as catalyst [12]. The chemical structure of SPES-NH₂-70 is shown in Fig. 1. The obtained SPES-NH₂-70 exhibited a high

molecular weight with the Ubbelohde viscosity of 0.76 dL g^{-1} measured at a concentration of 0.5 dL g^{-1} in DMAc at 30°C .

Fig. 1. Chemical structure of the polymer SPES-NH₂-70

2.3. Fabrication of thin-film composite membrane

Thin film composite membranes were prepared by coating SPES-NH₂-70 aqueous solutions on PSf supports. At first, PSf substrates were immersed into 0, 10, 20 and 40 wt% glycerol aqueous solution for 5 min to find the optimized pretreatment condition for the porous PSf support. The PSf substrate was wiped with tissue paper before coating treatment [14]. Coating solutions containing SPES-NH₂-70 and a crosslinker (GA or PEDGDE) were then poured onto the PSf substrates. Four concentrations (0.5, 0.8, 1.0, and 1.5 wt%) of SPES-NH₂-70 were used, and the molar ratio of crosslinker to amine group in SPES-NH₂-70 in the coating solution was set at 2 to 1. After a 5 minute immersion period, the excess casting solution was drained off by holding the substrates vertically. At last, the membranes were heated in an oven to induce the crosslinking reaction for 10 min.

2.4 Characterization

2.4.1 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS, ESCALAB 280 system) was used to analyze the surface elemental compositions of the prepared membranes. Al/Kα ($h\nu=1486.6 \text{ eV}$) was used as the X-ray source. The full range data was collected by survey scan (0–1000 eV, step size: 1). Narrow scan (step size: 0.1) was conducted in the range of each atoms including carbon (C, 279.5–294.5 eV), oxygen (O,

527.9–542.9 eV), sulphur (S, 177.3-157.3 eV) and nitrogen (N, 392.2-412.2eV).

2.4.2 Scanning electron microscopy (SEM)

The surface and cross-section morphologies of the studied membranes were observed using scanning electron microscopy (SEM, XL 30 ESEM FEG, FEI Company). The cross-section was obtained by fracturing the membranes in liquid nitrogen. All samples were sputtered with gold prior to SEM analysis.

2.4.3 FT-IR measurements

Fourier transform infrared (FT-IR) spectroscopy (Bio-Rad Digilab Division FST-80) was employed to investigate the chemical structure changes of the SPES-NH₂-70 active layer before and after crosslinking. The samples for FT-IR measurements were prepared by coating the polymer solutions, containing crosslinking agents, onto a glass plate. After curing under the same conditions as those used for the fabrication of the thin film composites, the transparent films were peeled off of the glass plate. The individual films subsequently were compressed into a KBr pellet for FT-IR spectroscopy measurements.

2.4.4 Surface zeta potential measurement

The surface streaming potential of the membranes were measured using an electrokinetic analyser (SurPASS, Anton Paar GmbH, Austria) according to a method reported in the literature [27]. A pair of prepared membranes, having an area of 25-55mm², was placed in the measuring cell. The membranes were separated by a spacer that forms a streaming channel. The streaming potential was detected by the Ag/AgCl electrodes. 10 mM KCl solution served as background electrolyte and the pH was adjusted with 0.1M HCl and 0.1M NaOH. The zeta potential (ξ) of the membranes was obtained from the streaming potential using Eq.(1).

$$\xi = \frac{\Delta E}{\Delta P} \frac{\eta \kappa}{\varepsilon \varepsilon_0} \quad (1)$$

where ΔE is the streaming potential, ΔP is the pressure drop across the streaming channel, ε_0 is the vacuum permittivity, ε is the dielectric constant of the solution, η is

the solution viscosity, and κ is the electrical conductivity of the bulk solution.

2.4.5 Water contact angle measurements

The static contact angles were recorded by the sessile drop method, using a Drop Shape Analysis DSA10 (Krüss GmbH, Germany) at ambient temperature. Water droplets (4 μ L) were dropped onto membrane surfaces with a micro-syringe. When the drop ages were 10 s, photos were taken and the contact angles were determined using imaging software. The resulting values were averages from measurements on at least 10 different positions for each sample.

2.4.6 Water uptake measurement

The water uptake of separate active layer was determined by measuring the difference in weight between dry and hydrated membranes. The water uptake was calculated according to the Eq. (2):

$$\text{Water uptake (\%)} = \frac{W_1 - W_2}{W_2} \times 100 \quad (2)$$

where W_1 and W_2 are the weights of water-swollen and corresponding dry membranes, respectively.

2.5 Nanofiltration test

Permeation tests were carried out in cross-flow cells with an effective area of 23.75 cm^2 for each membrane at 4 bar pressure. The membrane samples were initially compacted under this pressure for 4 h with deionized water. Then the membranes were subjected to salt or dye solutions, and the corresponding flux (F) was calculated from Eq. (3):

$$F = \frac{V}{At} \quad (3)$$

where F is the permeate water flux ($\text{L m}^{-2} \text{h}^{-1}$), V is the volume of permeate (L) collected over a period of time t (h), and A is the effective area of the membrane (m^2).

The rejection ratio (R) by the membranes is expressed as Eq. (4):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where C_p and C_f ($\text{mg}\cdot\text{L}^{-1}$) are the concentrations of the permeation and the feed, respectively. In this study, electrolytes of NaCl, MgCl_2 , MgSO_4 , and Na_2SO_4 , each with concentration of $500 \text{ mg}\cdot\text{L}^{-1}$, and dyes methyl orange and methyl violet, each with each concentration of $100 \text{ mg}\cdot\text{L}^{-1}$, were used for NF tests, respectively. The characteristics of the dyes used are listed in Table 1. The salt concentrations of electrolytes in the feed and permeate were measured using a conductance meter (Elmeiron conductivity meter CC-501, Poland), and that of the dyes by UV Spectrophotometer-1800 (SHIMADZU).

Table 1 The characteristics of dyes used

Dye	Structure	Molecular weight(g/mol)	Charge	Wavelength (nm)
Methyl violet (MV)		394.0	+1	580.5
Methylorange (MO)		327.0	-1	465.0

The molecular weight cut offs (MWCO) of the membranes were determined by filtration of polyethylene glycol (PEG) with different molecular weight ranging from 200 to 1000 Da at an aqueous solution concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ and an operating

pressure of 4 bar. The MWCO value is defined as the molecular weight of PEG that was 90% rejected. The concentrations of PEG in both the feed and permeate were measured using a total organic carbon analyzer (TOC-VCPH SHIMADZU). All the measurements were based on at least three samples, and the average values were adopted.

2.6 Antifouling experiments

Humic acid (HA) was used as a model foulant for natural organic matter to evaluate the antifouling ability of the studied membranes. Three HA aqueous solution concentrations, 5, 200, and 600 mg. L⁻¹, were tested. In a typical test procedure, the membrane was firstly stabilized by filtering pure water for 4 h at 4 bar, and the initial pure water flux (F_{w1}) was measured. Then the filtration of HA solution was carried out with each concentration for 30 min, respectively. At last, the membrane was washed thoroughly with deionized water for another 1 h, (this time was not counted in the filtration plots (Fig. 10)), and the final pure water flux (F_{w2}) was measured. The flux recovery ratio (FRR) was calculated by the following equation:

$$FRR(\%) = \frac{F_{w2}}{F_{w1}} \times 100 \quad (5)$$

3. Results and discussion

3.1 Effects of crosslinking conditions on the performance of membranes

The SPES-NH₂-70 membranes were crosslinked by two types of crosslinking reagents, GA and PEGDGE, with different hydrophilic/hydrophobic characteristics, and their proposed reaction mechanisms are shown in Scheme 1. The aldehyde or epoxy groups of the crosslinking agents reacted with the amino groups of the polymer side chains, resulting in the formation of $-C=N-C$ or $-C-O-N-C-$ linkages, respectively.

Scheme 1 In situ crosslinking process of SPES-NH₂-70

3.1.1 Optimization of the support membranes pretreatment conditions

In the preparation of thin film composite (TFC) membranes, porous supports are often saturated by hydrophilic molecules (such as glycerol and poly (ethylene oxide)) to protect the pore structure during curing process [28, 29]. In this work, aqueous solutions of glycerol with concentrations of 0, 10, 20, and 40 wt% were investigated to obtain the optimized pretreatment conditions for the PSf supports. The membrane preparation conditions were set at 1 wt% coating polymer concentration, with PEGDGE serving as the crosslinking agent, and a 90 °C curing temperature. As seen from Table 2, the initial flux of PSf support was 272.4 L m⁻²h⁻¹ at 1 bar pressure. After 10 min thermal treatment, the PSf support treated without glycerol solution had no flux at 1 bar pressure, suggesting the porous structure collapsed. Furthermore, by increasing the glycerol concentration to 10, 20, or 40 wt%, the flux of the support increased initially and remained stable at 40 wt% glycerol concentration. In order to find the proof of glycerol preserving the support membrane pore structure, we carried out SEM measurements of the support membranes under different treatment steps. As

seen from the Fig. 2, the max pore size range of the support membranes after thermal treatment with glycerol treatment reduced from 76-83 nm (Fig. 2 (c)) to 60-82 nm (Fig. 2 (b)). However, the max pore size range of its counterpart heated without glycerol treatment reduced to 44-63 nm (Fig. 2 (a)). McGrath et al. also obtained similar results. After thermal treatment, Udel polysulfone support membrane had 58% pore size reduction and no water flux due to the collapse of porous structure [18]. E. Sivaniah and co-workers stated that glycerol can protect the membrane pore from collapsing and characterized membrane surface pore with SEM [30]. Thus, glycerol was vital to protect pore structure of support membrane against thermal damage. Also, we observed that the support membrane surface morphology changed after glycerol and thermal treatment. This may concern with the membrane hydrophilicity. After the SPES-NH₂-70 active layer was coated onto the 10 wt% glycerol pretreated supports, the TFC membrane exhibited optimal performance with 6.33 L m⁻² h⁻¹ bar⁻¹ water flux and 96.1% Na₂SO₄ rejection. When the concentration of glycerol was higher (exceed 20%), the TFC membranes exhibited higher water flux but lower Na₂SO₄ rejection. It is believed that it was difficult to completely coat the polymer solutions onto the PSf support surfaces which were saturated with high concentrations of glycerol solution, resulting in defects in the membranes. Thus, the 10 wt% glycerol solution was selected as the pretreatment solution for the support membranes.

Table 2 The performance of support and PEGDGE crosslinked TFC membranes by the pretreatment with different concentration of glycerol solution

Glycerol concentration	Support Flux (L m ⁻² h ⁻¹ bar ⁻¹)	TFC membranes performance	
		Flux (L m ⁻² h ⁻¹ bar ⁻¹)	Na ₂ SO ₄ rejection (%)
0 %	0	—	—
10 %	173.4 ± 10.2	6.33 ± 3.0	96.1 ± 1.1
20%	221.8 ± 8.7	10.1 ± 3.8	82.4 ± 2.6
40%	243.1 ± 6.5	23.5 ± 8.9	65.7 ± 7.8

Fig. 2 Surface SEM images of polysulfone supports treated under different condition, (a) heated without glycerol treatment, (b) heated with glycerol treatment, (c) neither heated nor glycerol treatment.

3.1.2 Effects of coating solution concentration

Fig. 3 shows the membranes permeate flux and rejection of Na_2SO_4 with respect to different concentrations of the membrane coating solutions. For GA or PEGDGE crosslinkers, the dependence of permeate flux on concentration was the same. The permeate flux decreased and rejection of Na_2SO_4 rose with the increasing concentration of coating solutions from 0.5 to 1.5 wt% because of the increase in coating layer thickness. SEM images were used to characterize the thickness of coating layer in the membrane cross-section (Fig. 4). As seen from the SEM images, the thickness of coating layers for GA crosslinked membranes increased from 0.36 μm to 0.955 μm with increasing concentration of GA. PEGDGE crosslinked

membranes of the same coating solution concentrations were slightly thicker, with the thickness of coating layer from 0.46 to 1.74 μm . At lower coating solution concentrations, SPES-NH₂-70 may penetrate into the support membrane pores and form thinner and incontinuous coating layers. These led to very high flux and low rejection as shown in Fig. 3. With rising concentration, the amount of polymer which penetrated the support declined and the coating layer became thicker and denser. Thus, the performance of membranes revealed a trade-off relationship; the flux decreased and rejection increased with increasing crosslinker concentration of the coating solution. According to this analysis of the performance, a coating solution of 1.0 wt% was used for further investigations.

As seen from the Fig. 3, an interesting phenomenon emerged: the PEGDGE crosslinked membranes have higher flux and lower rejection than the GA crosslinked ones. Furthermore, with higher concentration coating solutions, the Na₂SO₄ rejection of PEGDGE crosslinked membranes reached that of GA crosslinked membranes. This phenomenon is discussed below.

Fig. 3 Effect of coating solution concentration on permeate flux and Na₂SO₄ rejection of GA and PEGDGE crosslinked membranes

Fig. 4 Cross-sectional morphology of the thin film composition membranes with various coating solution concentration of 0.5, 0.8, 1.0, and 1.5 wt%, and different

crosslinked agents types, GA (A-D) and PEGDGE (E-H).

3.1.3 Effects of curing temperature

The effects of curing temperature during membrane fabrication on the permeation and rejection properties of the resulting membranes are illustrated in Fig. 5. Because the polymer and crosslinking reagents were soluble in water and easily washed away, the data for membranes without thermal curing are omitted from the figure. With the curing temperatures from 70 to 110 °C, the flux of GA crosslinked membranes sharply declined from 32.1 to 5.6 L m⁻² h⁻¹ and the Na₂SO₄ rejection increased from 65.7 to 96.6 %. The similar trends for PEGDGE crosslinked membranes showed that post-treatment via thermal curing resulted in a decrease of permeated flux and increase of rejection, however the flux of the PEGDGE crosslinked membranes remained significantly higher than that of GA crosslinked membranes.

Fig. 5 Effect of curing temperature on the membranes performance in terms of permeate flux and Na₂SO₄ rejection.

3.1.4 Effects of operation pressure

In order to test the effect of operation pressures on the performance of the membranes, the flux and rejection of the membranes were tested with 500 mg.L⁻¹ Na₂SO₄ solutions under pressures ranging from 4 to 10 bar. It can be seen from Fig. 6 that water flux increases almost linearly with the rise of operating pressure, and there is a slight influence on salt rejection for the two types of crosslinked membranes. These phenomena can be explained by the solution–diffusion model, in which permeants dissolve in membrane body and then diffuse across the membrane with a concentration gradient [31]. The solution-diffusion model assumes that the flux of permeants increases with the increase of the driven pressure when the concentration of the feed solution is low. These results also are in good agreement with the literature’s experimental data [11]. Additionally, these experiments demonstrated that the performances of the two types of crosslinked membranes were stable under the range of operating pressures.

Fig. 6 Effects of operation pressure on the permeate flux and Na₂SO₄ rejection for GA

and PEGDGE crosslinked membranes

3.2 Membranes characterization

3.2.1 Crosslinking reaction and thin film surface elemental composition analysis

The crosslinking reactions of the active layer were confirmed by FT-IR spectroscopy (Fig. 7). Compared with the uncrosslinked membrane, a new weak peak at 1637 cm^{-1} , ascribed to C=N stretching vibrations [32], was found for the crosslinked SPES-NH₂-70-GA membrane, revealing the formation of Schiff base linkages between the aldehyde groups of GA and amino groups of SPES-NH₂. The new peak may be partially covered by the strong amide -C=O peak at 1670 cm^{-1} . For the PEGDGE crosslinked membranes, strong new adsorption bands at $1094\text{-}1127\text{ cm}^{-1}$ corresponding to C-O-C stretching vibration [33] were observed, indicating the occurrence of a crosslinking reaction between PEGDGE and SPES-NH₂-70.

Table 3 presents the surface elemental composition of crosslinked (SPES-NH₂-70-PEGDGE, SPES-NH₂-70-GA) and uncrosslinked (SPES-NH₂-70) membranes from XPS analysis. The XPS data show an increased O:C ratio in the PEGDGE crosslinked membranes compared to the uncrosslinked films, as PEGDGE is an oxygen-rich molecule. The aldehyde group of GA reacted with the primary amine of SPES-NH₂, producing C=N- groups. The carbon content increased, oxygen content declined, and correspondingly the O:C ratio decreased with GA crosslinking in the skin layer. These XPS results are consistent with the FT-IR results.

Fig. 7 FT-IR spectra of crosslinked (SPES-NH₂-70-PEGDGE, SPES-NH₂-70-GA) and uncrosslinked (SPES-NH₂-70) membranes

Table 3 Surface elemental composition of crosslinked (SPES-NH₂-70-PEGDGE, SPES-NH₂-70-GA) and uncrosslinked (SPES-NH₂-70) membranes

Membrane	C1s	N1s	O1s	S2p	O/C
SPES-NH ₂ -70	70.72	1.86	24.02	3.40	0.340
SPES-NH ₂ -70-PEGDGE	69.40	1.63	26.17	2.80	0.383
SPES-NH ₂ -70-GA	74.65	1.08	22.35	1.92	0.313

3.2.2 Zeta potential, hydrophilicity and water uptake

Fig. 8 presents the surface zeta potentials of GA and PEGDGE crosslinked membranes measured at different pH values. The obtained values were compared with that of a reported commercial NTR 7450 NF membrane comprised of a sulfonated poly (arylene ether sulfone) (SPES) active layer and porous PSf support. For the GA and PEGDGE crosslinked membranes, the zeta potential values were similar between

-20 and -45 mV at pH 2-10. Zeta potential values of the SPES membranes have previously been reported between -1 and -60 mV at pH 2-10 [19]. Thus, the zeta potential values of the GA and PEGDGE crosslinked membranes are in good agreement with the literature reported results. The zeta potential value of commercial NTR 7450 was between 1 and -23 mV at pH 3-12 [34] and more positive than the studied GA and PEGDGE crosslinked membranes. Such a discrepancy between the zeta potential of lab-made and commercial membranes may arise from two reasons: (1) the coating polymer used may have a different degree of sulfonation; (2) different crosslinking methods may have been used.

The contact angles for the polysulfone (PSf) support membrane, coated GA and PEGDGE crosslinked SPES-NH₂-70 films and commercial NTR 7450 NF membranes are presented in Table 3. The decreased contact angles for the coated membranes indicated that the sulfonated polymer on the surface of PSf support increased the hydrophilicity of the membranes. In addition, the contact angle value of the PEGDGE crosslinked membrane was lower than that of the GA crosslinked one and the NTR 7450 membrane suggested higher hydrophilicity for the PEGDGE crosslinked membrane. M. Stamm et al. have also reported the crosslinked sulfonated polyethersulfone-based filtration membranes exhibited a reduced contact angle after polyethylene glycol crosslinking [23]. These contact angle measurement results are in good agreement with the higher observed flux for PEGDGE crosslinked NF membranes relative to those crosslinked by GA.

Charged functional groups, which attract water molecules and repel ions with the same charge, play an important role in the construction of a hydrophilic layer that transports water molecules. Through the side chain crosslinking methods, no ionic groups were sacrificed during crosslinking. However, the membranes may have swelled during the nanofiltration process due to their high hydrophilicity. Thus, the water uptake of the crosslinked active layer was measured, via calculating the difference in weight between dry and hydrated coating polymer, to be a function of

the crosslinking degree. The water uptake values of the studied active layer are listed in Table 4. It can be seen that the water uptake of the membranes were significantly suppressed after crosslinking. For instance, the uncrosslinked SPES-NH₂-70 membrane could be dissolved in water at room temperature. However, both the GA and PEGDGE crosslinked membranes exhibited relatively good stability in hydrated condition, with water uptakes of about 21.0 and 26.0 %, respectively. The water uptake values of crosslinked sulfonated poly (arylene ether sulfone)s membranes reported in the literature are between 15% and 40 % [35], similar to our results. As observed previously, PEGDGE is more hydrophilic than GA, which may lead to higher water uptakes value for membranes containing PEGDGE.

Table 4 Contact angle and water uptake of lab-made crosslinked SPES-NH₂-70-GA and SPES-NH₂-70-PEGDGE membranes and commercial NTR 7450

	PSf	SPES-NH ₂ -70- GA	SPES-NH ₂ -70- PEGDGE	NTR 7450
Contact angle (°)	89.2±3.0	70.0±1.5	66.0±2.2	70 [34]
Water uptake (%)	—	21.0±1.9	26.0±2.1	—

Fig. 8 Zeta potentials of SPES-NH₂-70-GA, SPES-NH₂-70-PEGDGE crosslinked membranes and commercial NTR 7450 [34] at different pH values

3.2.3 Molecular weight cut-off

The molecular weight cut-offs (MWCO) and surface pore sizes of the studied membranes were evaluated by a solute transport method using poly (ethylene glycol) (PEG) with molecular weight from 200 to 1000 Da. The rejection curves of the membranes are shown in Fig. 9. And the MWCOs of PEGDGE and GA crosslinked membranes were estimated to be about 860 and 900 Da, respectively. According to the relationship between the MWCOs of PEG and their Stokes radii [36], the pore size of PEGDGE and GA crosslinked membranes were 0.72 and 0.74 nm, respectively, in good agreement with 0.5–2.0 nm target pore size range for NF membranes. The higher MWCO observed for the PEGDGE crosslinked membranes agrees with the other results obtained; higher water uptake and flux suggest larger pore sizes.

Fig. 9 MWCO curves of the membranes SPES-NH₂-70-GA and SPES-NH₂-70-PEGDGE

3.3 Separation of different ions and dyes

Four inorganic salts (Na₂SO₄, MgSO₄, NaCl, and MgCl₂) and two dyes (acid dye methyl orange (MO) and basic dye methyl violet (MV)) were selected for NF tests (Fig. 10). As the GA and PEGDGE NF membranes have similar MWCO and zeta potential, they exhibited similar rejection rates of salts and dyes. The rejection rates of inorganic salts for GA and PEGDGE NF membranes both followed the order of Na₂SO₄ > MgSO₄ > NaCl > MgCl₂, which is a typical characteristic for a negatively charged NF membrane. Donnan exclusion and sieving mechanisms influenced the rejection behavior of solutes with NF membranes, as characterized by the high rejection of divalent ions and low rejection of monovalent ions [24, 37]. As verified from zeta-potential measurements, the GA and PEGDGE NF membranes were negatively charged at neutral pH, thus they had higher rejection rate for the divalent anions than divalent cations due to strong electrostatic repulsive interactions. The

existence of size exclusion effect for the studied membranes was confirmed by the high rejection of MO and MV, which was above 99.9% and could be maintained for 6 h.

Table 5 presents a survey of the separation properties of literature reported NF membranes fabricated by coating methods. The PEGDGE crosslinked membranes reported here exhibited the highest Na_2SO_4 rejection without significantly sacrificing permeate flux. This may be attributed to both the strongly anionic characteristics and higher hydrophilicity of the PEGDGE crosslinked SPES-NH₂-70 membrane.

Fig. 10 Separation property of different inorganic salts and dyes for the GA and PEGDGE crosslinked membrane

Table 5 Comparisons of the separation properties of PEGDGE crosslinked membrane with that of literature reported NF membranes fabricated by coating methods

Membrane	PWF ($\text{Lm}^{-2}\text{h}^{-1}$ bar^{-1})	Salt rejection (%)				Operating pressure (bar)	Salt concentration (mg L^{-1})	Ref.
		Na_2SO_4	MgSO_4	NaCl	MgCl_2			
PEGDGE crosslinked membrane	6.33	96.2	80.4	61.7	42.1	4	500	This work
SPEEK/PEI-PI NF	2.94	86	90	60	90	13.8	500	[38]
Membrane 140-1.0-2	5-8	78	—	22	2	2	500	[13]
SPPBES	7.3	84	—	—	—	10.0	1000	[1]
NTR7450	10.9	92	48	53	16	10.0	1000	[32]

3.4 Fouling study

Humic acid is abundant in natural water sources and can cause fouling of separation membranes during the filtration process. There are a number of studies on humic acid fouling of ultrafiltration (UF), NF, and reverse osmosis (RO) membranes [39-41]. In this study, PEGDGE crosslinked SPES-NH₂-70 NF membranes were used for antifouling characterization. Three concentrations of humic acid were tested in the feed aqueous solution. The flux recovery curve was used to evaluate the hydraulic cleaning efficiency and fouling resistance. The flux recovery ratio (FRR) and time-dependence curve for PEGDGE crosslinked SPES-NH₂-70 membranes are shown in Fig. 11. The initial pure water flux for the membrane was $25.5 \pm 3.0 \text{ L m}^{-2} \text{ h}^{-1}$ at 4 bar. It could be seen that the flux decreased slightly when the humic acid feed solution was added, because of the adsorption of humic acid on the membrane surface. The concentration of humic acid had no obvious adverse impact on the antifouling properties of the membrane surface. When the humic acid solution was changed to de-ionized water, the flux recovered to the initial value. Therefore, we concluded that, with increased cleaning time, the FRR increased because of the hydrophilicity of the membrane surface and the electrostatic repulsion. These results illustrated the PEGDGE crosslinked SPES-NH₂-70 membranes could resist fouling caused by humic acid.

Fig. 11 Flux recovery ratio as a function of time during the filtration of humic acid (4 bar, 25 °C, pH 7.4)

4. Conclusions

Novel nanofiltration membranes were developed by coating a water-soluble disulfonated poly (arylene ether sulfone) copolymer with pendant amine groups (SPES-NH₂-70) on porous supports in conjunction with glutaric dialdehyde (GA) or poly (ethylene glycol) diglycidyl ether (PEGDGE) crosslinking. Crosslinked NF membranes with different rejection and flux combinations were obtained by changing polymer concentration and curing conditions. Favorable nanofiltration performance was obtained with the optimized condition of 1 wt% polymer concentration and 90 °C curing temperature. The separation performance, contact angle, water uptake, molecular weight cut-off, surface charge properties and stability of the membranes were extensively investigated. A permeation flux of 25.5±3.0 Lm⁻²h⁻¹ for the PEGDGE crosslinked membranes was much higher than that of the GA crosslinked

membranes ($8.9 \pm 3.2 \text{ Lm}^{-2}\text{h}^{-1}$) and did not sacrifice rejection at 4 bar. The result was ascribed to the higher hydrophilicity and water uptake of the PEGDGE crosslinked active layer. In an antifouling study, the PEGDGE crosslinked membranes exhibited good fouling resistance for humic acid due to their high hydrophilicity and strong anionic characteristics. Thus, the PEGDGE-crosslinked SPES-NH₂-70 is a promising coating material for high-performance NF membranes.

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