

Poly(ether imide) Membranes Modified with Charged Surface-Modifying Macromolecule—Its Performance Characteristics as Ultrafiltration Membranes

Palsamy Kanagaraj, Sivasubramaniyan Neelakandan, Alagumalai Nagendran

PG & Research Department of Chemistry, Polymeric Materials Research Lab, Alagappa Government Arts College, Karaikudi 630 003, India

Correspondence to: Dr. A. Nagendran (E-mail: nagimmm@yahoo.com)

ABSTRACT: Modification of poly (ether imide) (PEI) ultrafiltration (UF) membranes was attempted by blending charged surface modifying macromolecule (cSMM). Compared to the pure PEI membrane, blending of PEI with cSMM resulted in blend membranes with enhanced UF characteristics such as lower hydraulic resistance (R_m) and higher pure water flux (PWF) coupled with higher water content (WC). Among the various modified membranes, blend membranes with 5 wt % cSMM concentration exhibited higher PWF ($60.38 \text{ L m}^{-2} \text{ h}^{-1}$), WC (73.6%), protein permeate flux ($27.12 \text{ L m}^{-2} \text{ h}^{-1}$) and lower flux decline rate (R_{fd}) (55.1%), R_m ($5.21 \text{ kPa/L m}^{-2} \text{ h}^{-1}$), bovine serum albumin (BSA) rejection (87.1%). Meanwhile, the fouling resistant ability was studied by flux recovery ratio (FRR) after water and alkali cleaning, irreversible and reversible fouling rate. Higher FRR after water cleaning (95.07%), FRR after alkali cleaning (97.1%), reversible fouling rate (50.14%) and lower irreversible fouling rate (5%) exhibited by 5 wt % cSMM membranes showed its better antifouling ability compared to pure PEI and other blend membranes because of its higher hydrophilic nature. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40320.

KEYWORDS: hydrophilic polymers; membranes; blends; PEI; cSMM; BSA; UF; anti-fouling

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INTRODUCTION

Nowadays, membrane technologies are playing an important role in water treatment processes due to reliability of contaminant removal without producing any harmful by-products. However, the most common problem associated with the application of the membrane process in water treatment is surface fouling. The control of surface properties is of scientific and technological importance in many academic and industrial research areas. Currently membrane surface modification is considered as an important to the membrane industry as the bulk membrane material and the membrane preparation process. The key objective is to enhance the flux rate and make the membranes hydrophilic. In the field of ultrafiltration (UF) membranes, polymer blending has been investigated to modify properties such as mechanical strength, hydrophilicity coupled with water permeability, molecular weight cutoff (MWCO), and surface morphology. Blending polymers with hydrophilic functional groups is one of the methods of surface modification.^{1–4}

It is well established that surface-modifying macromolecules (SMMs) play the key role in the surface modification of membranes applied for medical, pharmaceutical, food applications as

well as industrial chemical processes. Membrane surface modification by blending SMMs is clearly targeting the modification of the membrane surface based on the principle of surface migration of SMMs, which renders the membrane surface hydrophilic, hydrophobic or charged. Moreover, SMMs remained at the membrane surface for long period due to the affinity between their central polyurethane segment and the host base polymer. The migration of the hydrophilic or hydrophobic SMM segment is according to the thermodynamic principles of the tendency to minimize the interfacial energy. Due to this fact, when a membrane of blended polymer with SMM is cast, the polymer with the lowest surface energy of hydrophilic or hydrophobic will migrate to the top surface of the membrane.^{5–8} It was proven that SMM blended membranes had a better performance in the separation of volatile organic compounds from aqueous solutions by pervaporation, in the UF of oil–water emulsions, and in the biomedical UF and microfiltration applications.⁹

Polyetherimide (PEI) has been successfully used in preparation of asymmetric membranes for gas separation and oil–water separation. It is an attractive material for preparation of membrane support because of its excellent film formation and mechanical

properties as well as good thermal and moderate chemical resistance. However, the hydrophobic nature of PEI causes heavy fouling on the membrane surface when the substances like proteins, retained colloidal particles, macromolecular materials, natural organic matter, etc. So it is desirable to make the PEI membrane hydrophilic when PEI is used in UF applications.

Many researchers studied that the surface modification using pore forming polymeric additive polyethylene glycol as one of the components in the UF membrane casting solution.¹⁰ Hydrophilic modification of poly(ether sulfone) (PES), membrane is achieved by argon plasma treatment followed by acrylic acid grafting in the vapor phase by Kull et al.¹¹ The modified hydrophilic membrane has higher pure water permeation flux and also less susceptible to protein fouling. Hamza et al. reported that SMMs blended PES membranes were less susceptible to fouling in oil–water separation. They also suggested that SMMs blended membranes might be useful for other water treatment processes as membranes with high fouling resistance.⁹ More recently, Suk et al.¹² demonstrated that both tensile yield strength and percentage of elongation were higher for SMM blended PES membranes compared to the PES membranes without blending. Khayat et al.¹³ reported that flux of SMM blended membranes was higher compared to the pure PEI membranes. The SMM blended PEI membrane was promising for desalination by direct contact membrane distillation. Rana et al.¹⁴ used hydrophilic SMM in producing hydrophilic PES-UF membranes with high fouling resistance. Shao et al.¹⁵ reported that the poly(vinyl chloride)-*g*-poly[poly(ethylene glycol) methyl ether methacrylate]-modified poly(vinylidene fluoride) membrane showed a distinctively enhanced hydrophilicity and antifouling resistance, as suggested by the contact angle (CA) measurement and flux of bovine serum albumin (BSA) solution test, respectively.

In the present study, PEI/charged SMM (cSMM) flat sheet UF blend membranes were prepared in various compositions by phase inversion technique. The prepared membranes were subjected to UF characterizations such as PWF, WC, R_{mp} , protein rejection, protein permeate flux and morphology. Fouling resistant ability of pure PEI and PEI/cSMM blend membranes were studied by R_{fd} , FRR after water cleaning and alkali cleaning, reversible and irreversible fouling rate.

EXPERIMENTAL

Materials

PEI (Ultem® 1000) was supplied by GE Plastics, India as a gift sample. It was dried at 150°C for 4 h before used. N-methyl-2-pyrrolidone (NMP), diethylene glycol (DEG), 4,4'-methylene bis(phenyl isocyanate) (MDI), hydroxyl benzene sulfonate (HBS), N,N-dimethyl acetamide (DMAc), BSA (69 kDa), and sodium lauryl sulfate of analar grades were procured from Sigma Aldrich. Anhydrous sodium monobasic phosphate and sodium dibasic phosphate heptahydrate were also procured from Sigma Aldrich and used for the preparation of phosphate buffer solutions in the protein analysis. All chemicals were used as such without further purification. Deionized and distilled water was used for the UF experiments and for the preparation of the membranes.

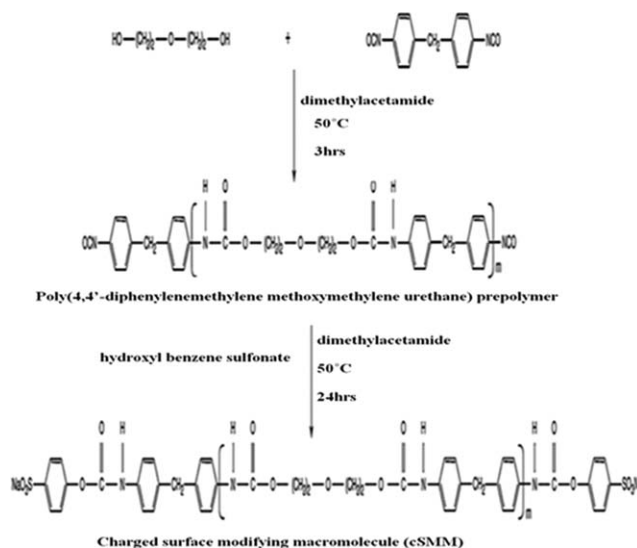


Figure 1. Scheme of the reaction for the synthesis of cSMM.

Synthesis of cSMM

cSMM was synthesized according to the procedure reported by Mohd Norddin et al.^{16,17} The cSMM, endcapped with hydroxyl sulfonate, was synthesized using a two-step solution polymerization method. The first step involved the reaction of MDI with DEG in a common solvent of DMAc. This mixture formed a urethane prepolymer solution. The prepolymer is a segment-blocked urethane oligomer, poly(4,4'-diphenylene methylene methoxymethylene urethane) having both endcapped with isocyanate. The reaction was then terminated by the addition of HBS resulting in a solution of cSMM or sulfonated SMM.

Brief procedure: To a solution of 0.03 mol MDI (7.5 g) in 50 mL of degassed DMAc was loaded in a 1-L pyrex round bottom flask. Then, a solution of the 0.02 mol degassed DEG (2.122 g) in 100 mL of degassed DMAc was added dropwise with stirring to react for 3 h. Then 0.02 mol of HBS (4.644 g) dissolved in 50 mL of degassed DMAc was added dropwise and the solution was left under stirring for 24 h at 48–50°C, resulting in a solution of cSMM. Scheme of the reaction for the synthesis of cSMM is shown in Figure 1. The cSMM solution was added dropwise into a beaker filled with distilled water under vigorous stirring to precipitate the cSMM. Prepared cSMM kept immersed in distilled water for 24 h under stirring to leach out residual solvent. They were then dried in an air circulation oven at 50°C for 5 days and stored in a glass bottle.

Characterization of cSMM by Fourier Transform Infrared Spectroscopy, ¹H-NMR, and ¹³C-NMR. Fourier transform infrared spectroscopy (FT-IR) was used to observe the presence of functional groups in cSMM. The data are collected on a FT-IR spectrometer (TENSOR 27; Bruker Optik GmbH, Germany). The spectra were measured in absorbance mode over a wave number range of 370–4000 cm⁻¹. A concentrated sample for nuclear magnetic resonance (NMR) analysis was prepared by dissolving as much polymer in dimethyl sulfoxide d₆. The NMR data were collected on a NMR spectrometer (Avance 400 MHz; Bruker, Switzerland).

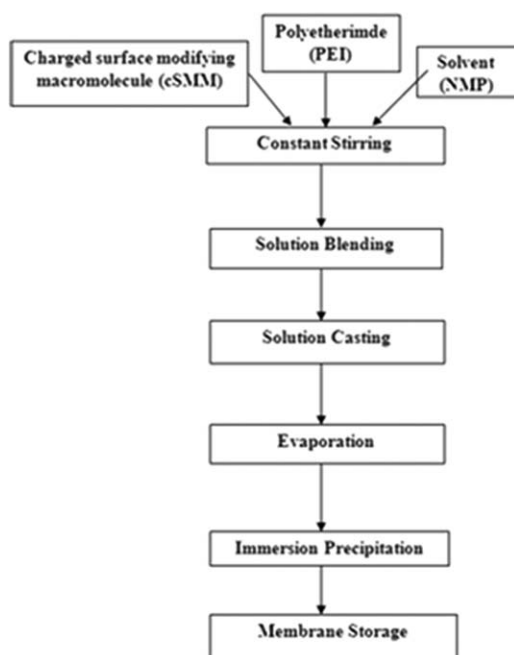


Figure 2. The stepwise preparation of the pure PEI and PEI/cSMM blend membranes.

Membrane Preparation

The phase inversion technique was used to prepare membranes.¹⁸ The casting environment (relative humidity and temperature) was standardized for the preparation of membranes with better physical properties such as the homogeneity, thickness, and smoothness. The membrane-casting chamber was maintained at a temperature of $24 \pm 1^\circ\text{C}$ and a relative humidity of $50 \pm 2\%$. The total polymer concentration was maintained at 17.5 wt % in order to have a balanced casting solution viscosity to yield membranes between a spongy type and a high macrovoidal type. The casting and gelation conditions were maintained constant throughout, because the thermodynamic conditions would largely affect the morphology and performance of the resulting membranes.¹⁹ The stepwise preparation of the pure PEI and PEI/cSMM blend membranes is shown in Figure 2.

Membrane Characterization

The prepared membranes were cut into the required size for use in the UF cell (Amicon 8400-Model; Millipore) fitted with a Teflon-coated magnetic paddle. The effective membrane area available for UF was 38.5 cm^2 . The solution filled in the cell was stirred at 300 rpm using a magnetic stirrer. All the experiments were carried out at $30 \pm 2^\circ\text{C}$ and 345 kPa transmembrane pressure (TMP). The membranes were initially pressurized with distilled water at 414 kPa for 5 h. These pre-pressurized membranes were used in subsequent UF experiments at 345 kPa.

Pure Water Flux. Membranes after compaction were subjected to PWF studies at a TMP of 345 kPa. The flux was measured under steady state flow. The PWF is determined as follows.²⁰

$$J_w = \frac{Q}{A\Delta t}$$

where Q is the quantity of permeate collected (in L), J_w is the water flux ($\text{L m}^{-2} \text{ h}^{-1}$), Δt is the sampling time (in h), and A is the membrane area (in m^2).

Water Content. The WC of the membranes was determined by soaking the membranes in water for 24 h and weighing after mopping with blotting paper. The wet membranes were placed in a vacuum oven at 75°C for 48 h and the dry weights were determined. From these values, the percent WC was derived as follows.²¹

$$\% \text{ WC} = \frac{W_w - W_d}{W_w} \times 100$$

where W_w and W_d are the weight of the wet and the dry membrane, respectively.

Hydraulic Resistance. To determine the R_m of the membrane, the PWF of the membranes were measured at TMP of 69, 138, 207, 276, and 345 kPa after compaction. The R_m of the membrane was evaluated from the slope of PWF versus TMP difference (ΔP) using the following equation²²:

$$J_w = \frac{\Delta P}{R_m}$$

Protein Rejection Studies

Prepared pure PEI and PEI/cSMM blend membranes were subjected to MWCO, BSA rejection and protein permeate flux.

MWCO, BSA Rejection, and Protein Permeate Flux Study.

MWCO is a pore characteristic of membranes and is related to rejection for a given molecular weight of a solute. The MWCO has a linear relationship with the pore size of the membrane.²³ In this study, protein of BSA (69 kDa) was chosen for the estimation of MWCO. The BSA solution was prepared at a concentration of 0.1 wt % in phosphate buffer (pH = 7.2) solution. The permeate protein concentration was estimated using UV-visible double beam spectrophotometer (Systronics, 2201) at a wavelength of 280 nm. The percentage solute rejection (% SR) was calculated from the concentration of the feed and the permeate using the following equation²⁴:

$$\% \text{ SR} = \left[1 - \frac{C_p}{C_f} \right] \times 100$$

where C_p and C_f are the concentrations of permeate and feed solutions, respectively, and also protein permeate flux was determined.

Fouling Activity of Pure PEI and PEI/cSMM Blend Membranes

The prepared pure PEI membrane and surface-modified PEI blend membranes were subjected to fouling studies by means of R_{fd} , FRR and membrane cleaning.

Flux Decline Rate. The 0.1 wt % of BSA solution was prepared in phosphate buffer solution (pH = 7.2) and used as feed solution for the fouling studies. Each membrane was initially compacted for 30 min and the PWF, J_{w1} was measured at a TMP of 345 kPa. After 1 h of water filtration, the BSA solution was added to the UF cell. The initial protein permeates flux, J_{p1} and steady state protein flux, J_p after 30 min of filtration was recorded. The R_{fd} was calculated by the following equation:

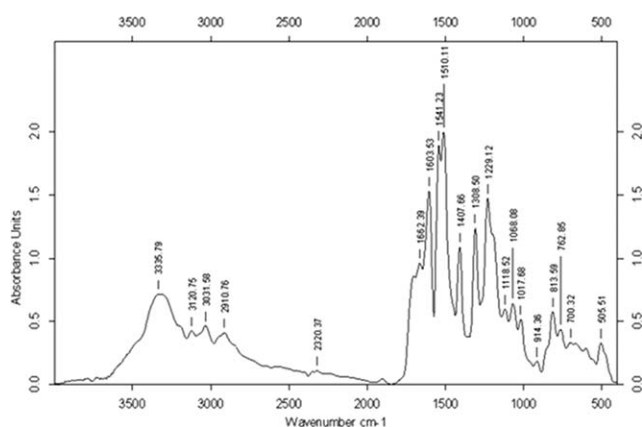


Figure 3. FT-IR spectrum of cSMM.

$$R_{fd} = 1 - \left[\frac{J_p}{J_{w1}} \right] \times 100\%$$

Fouled Membranes Cleaning. The membranes after separation of protein were washed with deionized water and the PWF of the clean membrane was measured (J_{w2}) at 345 kPa. After that the membranes were cleaned with a 0.1 M NaOH solution on a vibrator for 4 h and PWF (J_{w3}) was measured again at 345 kPa. To evaluate the antifouling property of PEI/cSMM blend membranes, the FRR was introduced and calculated after water and alkali cleaning using the following equation²⁵:

$$\text{FRR after water cleaning} = \left[\frac{J_{w2}}{J_{w1}} \right] \times 100\%$$

$$\text{FRR after alkali cleaning} = \left[\frac{J_{w3}}{J_{w1}} \right] \times 100\%$$

where J_{w1} , J_{w2} , and J_{w3} represent the initial water flux, water cleaning flux, and alkali cleaning flux, respectively.

Irreversible and Reversible Fouling. Internal fouling is caused by penetration of solid material into the inner surface of membranes, which results in pore blocking. Internal membrane fouling is generally irreversible. The degree of irreversible flux loss caused by irreversible fouling (R_{ir}) and it cannot be removed by backwashing, which can be calculated using the following expression:

$$R_{ir} = \left[\frac{J_{w1} - J_{w2}}{J_{w1}} \right] \times 100$$

Surface fouling is the deposition of retained colloidal and macromolecular materials on the membrane surface. This fouling can be minimized by regular cleaning and using hydrophilic or charged membranes. Generally surface fouling is reversible. The reversible degree flux loss caused by reversible fouling (R_r) can be removed by backwashing, which can be calculated using the following expression²⁶:

$$R_r = \left[\frac{J_{w2} - J_p}{J_{w1}} \right] \times 100$$

Membrane Surface Analysis

The top surface morphologies of the pure CA and CA/cSMM blend membranes were studied with a scanning electron microscopy (SEM; HRSEM, FEI Quanta 250 Microscope, and

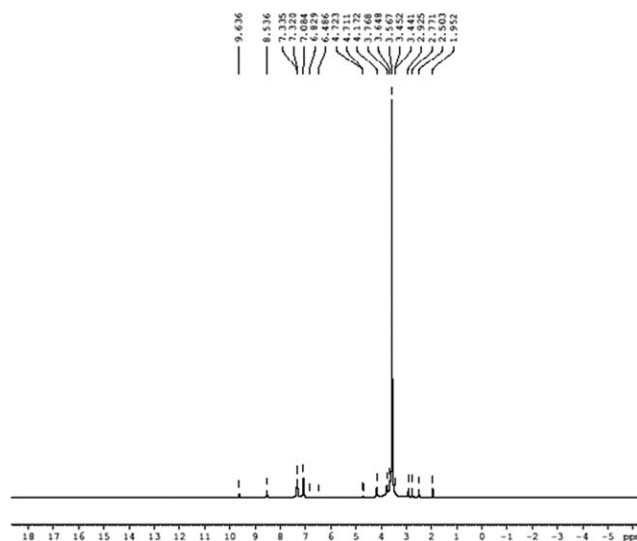


Figure 4. ¹H-NMR spectrum of cSMM.

Netherlands) under vacuum conditions. Sample was gold sputter prior to SEM analysis.

For evaluation of the membrane hydrophilicity the CA between water and the membrane surface was determined and it was measured using a CA (NIMA DST 9005 Dynamic Surface Tensiometer). From values of the CA, the adhesion work (ω_A) necessary to pull water from a square meter of membrane surface can be calculated by the following equation²⁷:

$$\omega_A = \gamma_w (1 + \cos\theta)$$

where γ_w is the surface tension of water ($7.2 \times 10^{-2} \text{ N m}^{-1}$) and θ is the CA.

RESULTS AND DISCUSSION

Characterization of cSMM by FT-IR, ¹H-NMR, and ¹³C-NMR

The structure of the synthesized material is confirmed by FT-IR technique. The FT-IR spectrum of cSMM shows that, the

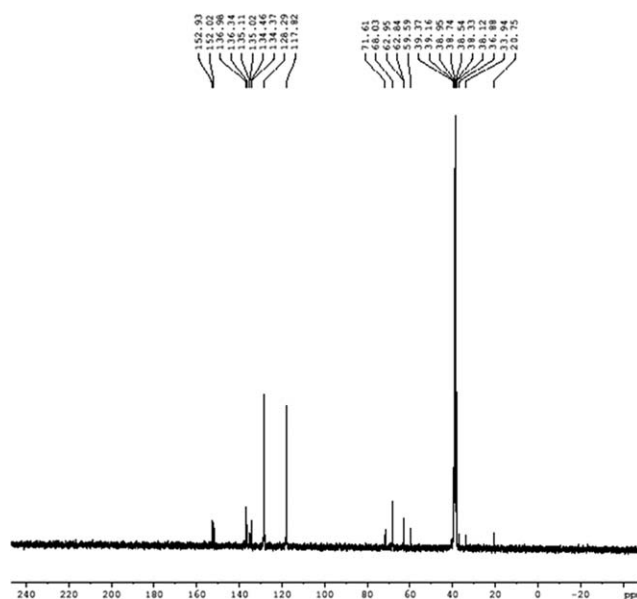


Figure 5. ¹³C-NMR spectrum of cSMM.

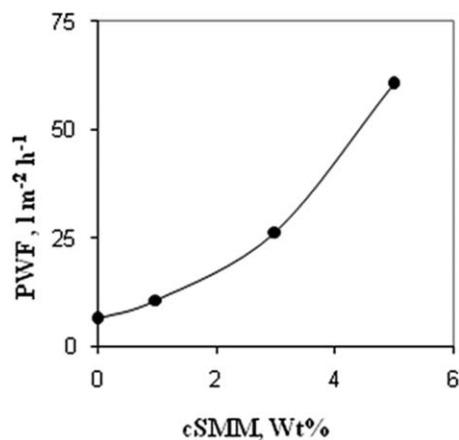


Figure 6. Pure water flux of the membranes.

presence of sulfonic groups in cSMM can be confirmed by the absorption bands at 3336 cm^{-1} (O–H), 1230 cm^{-1} (asymmetric O=S=O), 1068 cm^{-1} (symmetric O=S=O), 1018 cm^{-1} (S=O), and 700 cm^{-1} (S–O) and sulfonic group stretching vibration at 1407 cm^{-1} (Figure 3) and presence of absorption band at 1662 cm^{-1} , which corresponds to amide C=O stretch. The absorption band noted at 1229 cm^{-1} indicates Ph–O–C and the appearance of CH₂ are asymmetric and C–O–C asymmetrical stretching is confirmed by the absorption band noted at 2910 and 1308 cm^{-1} and the aromatic bands at 1541 and 1510 cm^{-1} .

The ¹H-NMR and ¹³C-NMR spectrum are shown in Figures 4 and 5. The characteristic peaks of the ¹H-NMR are as follows: CH₂ between the phenyl groups of MDI (3.768 ppm), CH₂ (DEG) adjacent to the urethane bond (3.648 ppm), CH₂ (DEG) adjacent to the ether bond (4.172 ppm), aromatic hydrogen (MDI and HBS) (7.08–7.335 ppm), aromatic hydrogen (HBS) (6.48–6.829 ppm), and urethane NH (8.53 and 9.63 ppm).

The characteristic peaks of the ¹³C-NMR are as follows: CH₂ between the phenyl groups of MDI (38.12–39.37 ppm), CH₂ (DEG) adjacent to the urethane bond (63 ppm), CH₂ (DEG) adjacent to the ether bond (68.03 ppm), aromatic C (MDI+HBS) (118, 128.3 ppm), quaternary aromatic C (135–137 ppm), and carboxylic C (152.1, 153 ppm). The chemical name of the cSMM is poly(4,4'-diphenylene methylene methoxyethylene-urethane) both end capped by HBS.

Effect of cSMM on PWF, WC, and R_m of PEI Membranes

After initial compaction of the membranes for 5 h at 414 kPa, the TMP was maintained at 345 kPa for further characterization. All the membranes were washed thoroughly with deionized water and loaded on to the UF kit. The PWF were measured by subjecting them to a pressure of 345 kPa using deionized water as the feed. For pure PEI membranes, the PWF of $6.36\text{ L m}^{-2}\text{ h}^{-1}$ was observed. When cSMM additive content was increased from 1 to 5 wt % in the blend, there was an increase in the flux of the membranes, from 10.65 to $60.38\text{ L m}^{-2}\text{ h}^{-1}$, as shown in Figure 6. It is evident that the permeate flux of all blend (PEI/cSMM) membranes exhibited higher flux values compared to pure PEI membranes. This linear trend with an increase in cSMM additive composition may

Table I. Water Content, Contact Angle, and Adhesion Work of PEI/cSMM Blend Membranes

Blend composition (wt %)		Solvent (wt %)	Water content (%)	Contact angle, (θ)	Adhesion work (mN m ⁻¹)
PEI	cSMM	NMP			
17.5	0	82.5	61.00	93.4	67.7
17.5	1	81.5	66.50	77.3	87.8
17.5	3	79.5	69.41	66.1	101.2
17.5	5	77.5	73.60	61.0	106.9

be due to the higher hydrophilic nature of cSMM leading to the formation of cavities in the sub layer, which gives way to the mobility of the water molecules.²⁸

WC is correlated with hydrophilicity of the membrane.²⁹ It was determined by the measurement of the change in mass before and after hydration. Pure PEI and PEI/cSMM blend membranes prepared at various compositions were subjected to WC studies. Table I showed that the virgin membrane has a lower WC 61.0%. The addition of cSMM in the casting solution resulted in blend membrane with 5 wt % and the WC was found to be 73.6%. Thus, for higher WC with the enhancement of cSMM additive concentration implied the increased hydrophilicity by the additional sulfonic groups from the cSMM.

R_m is an indication of the tolerance of membranes toward hydraulic pressure during UF. In our case, the R_m was measured by placing the membranes to various TMP from 69 to 414 kPa to observe the value of PWF. Thus, all the membranes such as pure PEI and PEI/cSMM were subjected to PWF measurement study. The R_m was determined from the inverse of the slope of the corresponding TMP versus PWF plots as presented in Figure 7.

It is seen from figure that the pure PEI membrane exhibited a higher R_m due to its low porosity and closed pores as explained in SEM analysis. In the blend membranes, as the cSMM additive concentration was increased from 1 to 5 wt %, the R_m decreased gradually from 52.63 to 5.21 kPa L⁻¹ m⁻² h⁻¹. This may be explained by the fact that an increase in the

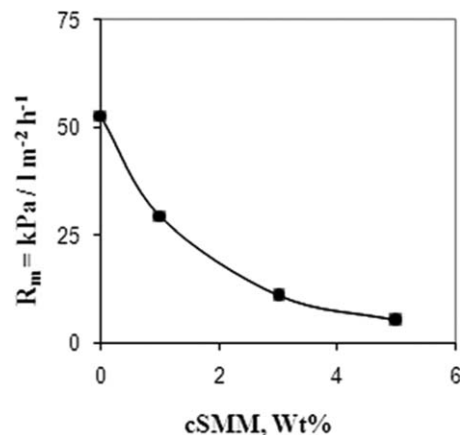


Figure 7. Hydraulic resistance of the membranes.

Table II. Performance of PEI/cSMM Blend Membranes

Blend composition (wt %)		Solvent (wt %)	Flux decline rate, R_{fd} (%)	Protein permeate flux ($L m^{-2} h^{-1}$)	% SR	MWCO (kDa)
PEI	cSMM	NMP				
17.5	0	82.5	67.0	2.1	94.6	<69
17.5	1	81.5	64.32	3.8	92.5	<69
17.5	3	79.5	63.13	10.47	90.3	<69
17.5	5	77.5	55.10	27.12	87.1	<69

composition of cSMM enhances the size of pores to a great extent due to larger segmental gap between polymer chains which leads to the decrease in the value of R_m resulting in the formation of macrovoids on the membrane surface due to thermodynamical instability.³⁰

Effect of cSMM on MWCO, BSA Rejection, and Permeate Flux of PEI Membranes

All prepared membranes showed a MWCO of <69 kDa because of their smaller pore size, which is due to the molecular weight of BSA solutes larger than the MWCO of a membrane. This is well agreement with the pure water permeability and higher % SR of the membranes. The resultant MWCO of blend membrane is listed in Table II.

All membrane prepared in the present study were subjected to the rejection study of BSA buffer solution (pH = 7.2). The composition of the casting solution plays a crucial role in the separation of protein. Pure PEI membrane subjected to separation of BSA was found to be a higher rejection 94.6%, as shown in Table II. From the rejection values it can be noted that as cSMM additive content increased from 1 to 5 wt % in PEI blend membrane, the % SR decreased to 87.1%. This may be due to the higher cSMM additive concentration that created a mixed casting solution uneven and inhomogeneity resulting in the formation of larger pores within the membranes. The larger pores at higher cSMM concentration were also confirmed by observing macroporous in SEM.

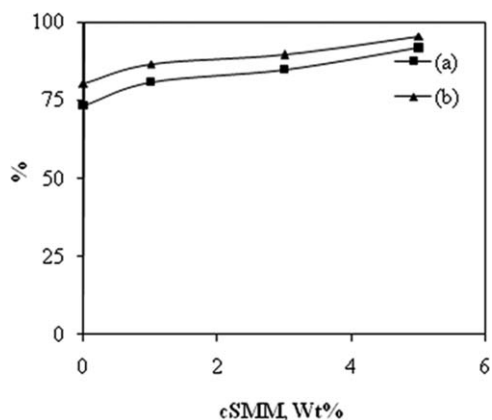
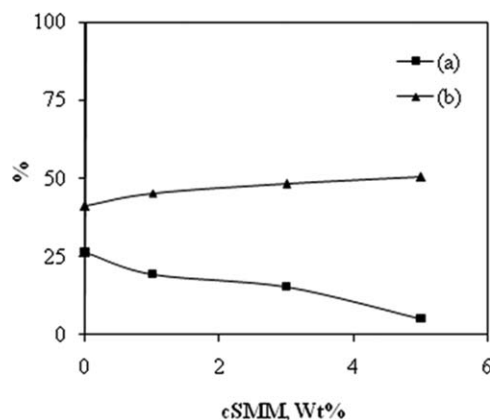
The permeate protein flux is the measure of product rate of the membrane for the given protein solutions. The permeate flux of

proteins (BSA) of pure PEI was found to be $2.1 L m^{-2} h^{-1}$. Furthermore, the 5 wt % of cSMM content in the PEI membrane, the protein permeate flux increased to $27.12 L m^{-2} h^{-1}$ as shown in Table II. From the table it was observed that when the cSMM additive content in the blend membrane was increased, the flux also increased to a significant level due to higher hydrophilicity and swelling behavior of cSMM.

Effect of cSMM on Fouling Properties of PEI Membranes

The effect of cSMM additive concentration on the protein solution permeate flux was carried out to analyze the fouling properties of pure PEI and PEI/cSMM blend membranes. The R_{fd} value is introduced to reflect the antifouling ability of the membrane; the lower value of R_{fd} means the highest fouling resistant of membrane.³¹ The R_{fd} of pure PEI membrane showed a result of 67.0%, when the cSMM content was increased from 1 to 5 wt %, the R_{fd} values are decreased to 64.32, 63.13, and 55.1%, respectively, as shown in Table II. It indicates that the ability of fouling resistant increases with an addition of cSMM in casting solution. This may be due to the hydrophilic nature of sulfonic groups from cSMM which can migrate to the top and enrich the membrane surface with sulfonic groups, which lower the surface energy between protein and membrane surface.³²

FRR after water cleaning of pure PEI membrane showed a result of 73.1%. As the cSMM content in the casting solution was increased from 1 to 5 wt %, the FRR values are 80.8, 84.8, and 95.1%, respectively, as shown in Figure 8(a). The pure PEI membrane, exhibited low FRR after alkali cleaning value of 80.2%. Increasing cSMM content from 1 to 5 wt %, the flux

**Figure 8.** Effect of cSMM on PEI membranes: (a) flux recovery ratio after water cleaning and (b) flux recovery ratio after alkali cleaning.**Figure 9.** Effect of cSMM on PEI membranes: (a) irreversible fouling rate and (b) reversible fouling rate.

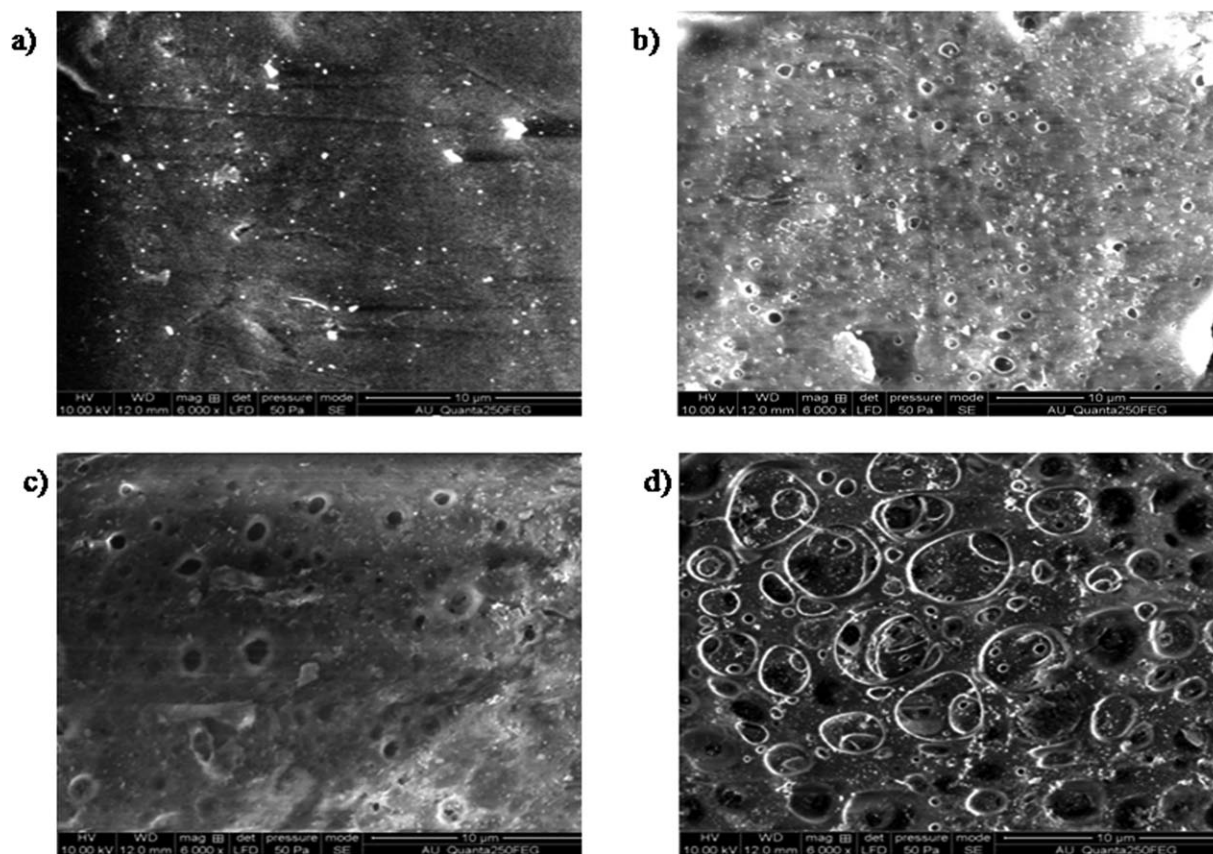


Figure 10. The scanning electron micrographs of top surface of PEI/cSMM blend membranes with different cSMM additive: (a) 0 wt % cSMM, (b) 1 wt % cSMM, (c) 3 wt % cSMM, and (d) 5 wt % cSMM.

recovery values are 86.4, 89.4, and 97.1%, respectively, as shown in Figure 8(b). The increase in the FRR after water and alkali cleaning with cSMM content could be explained as the following. Generally that protein adsorption decreases with increasing hydrophilicity of the membrane surface. The increasing hydrophilicity of membranes weakened the interaction between surface of membrane and proteins, because protein and many other foulants are hydrophobic in nature.³³ So that protein foulants can be easily washed away from the modified membranes as result of, flux recoveries after water and alkali cleaning was higher, which indicates that the surface-modified membranes have better fouling resistance behavior.

The advanced detail about fouling resistant characteristic, the irreversible and reversible fouling rate of the pure and PEI/cSMM blend membranes were discussed. The irreversible fouling rate of pure PEI membrane was found to be 26.1%, when an increase in cSMM content from 1 to 5 wt % the values are 19.3, 15.1, and 5.0%, respectively, as shown in Figure 9(a). It was observed that the irreversible fouling value of the pure PEI membrane was higher than that of PEI/cSMM blend membranes and main flux decline was because of irreversible fouling. From this it was noted that PEI/cSMM blend membranes has a better ability to resist the membrane fouling than pure PEI membrane due to the presence of sulfonate groups on the membrane surface. The existence of sulfonate groups in cSMM on the PEI membrane surface enhances the hydrophilicity and

further reduced proteins adsorption and deposition.³⁴ Furthermore, the reversible fouling rate of Pure PEI membrane was found to be 40.8%. Increasing cSMM content from 1 to 5 wt % the corresponding values are 45.1, 48.0, and 50.1% as shown in Figure 9(b). This increasing trend may be due to the surface fouling on membrane surface, which can be removed by water washing because surface fouling was reversible.³⁵

Surface Morphology

A SEM was used to observe top surface of the membranes. From Figure 10(a), it can be observed that the smooth membrane surface was formed in the dense top layer for pure PEI membranes. With increasing cSMM concentration within the casting solution, dispersed pores increase proportionally and a rough membrane surface can be found in the skin of the PEI/cSMM blend membranes. It is possible that an increase in cSMM concentration probably caused the thermodynamic membrane-forming system unstable so that it accelerated the precipitation rate in the coagulation bath and the formation of porous membranes.³⁶ From Figure 10(b-d), we can see that upon increase of 5 wt % cSMM in the blend polymer caused the formation of more pores on the PEI membrane surface compared to that of pure PEI membranes. This is mainly due to the leaching process of the additive during the gelation.³⁷

The CA and the membrane ω_A are listed in Table I. The table shows that the decrease in WC and the increase in the ω_A were

observed by increasing cSMM additive content in PEI blend membranes. Both trends of the CA and ω_A indicate the hydrophilicity of the PEI/cSMM blend membrane increases with the increase in cSMM concentration. Similar results have also been observed for UF membranes from poly(ether sulfonamide)/PEI blends by Blicke et al.³⁸

CONCLUSIONS

The synthesized cSMM contains charged sulfonic groups and it was confirmed by FT-IR and NMR spectroscopy. The prepared cSMM was blended into the casting solution of PEI with different composition by phase inversion technique. SEM and CA study reveals that the addition cSMM led to an increase in pore size and surface hydrophilicity of the membrane, which results in higher PWF and WC in blend membranes. Permeate flux of BSA increased to $27.12 \text{ L m}^{-2} \text{ h}^{-1}$ and rejection decreased to 87.1% when the cSMM concentration increases from 1 to 5 wt %. In comparison to the unmodified PEI membranes, the cSMM blended membranes exhibited lower R_{fd} and high FRR due to their higher hydrophilicity and bigger pore size. As a result, the incorporation of cSMM into the PEI membrane improves the performance of UF membranes significantly and promises us to develop superior antifouling membranes for different proteins in future.

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