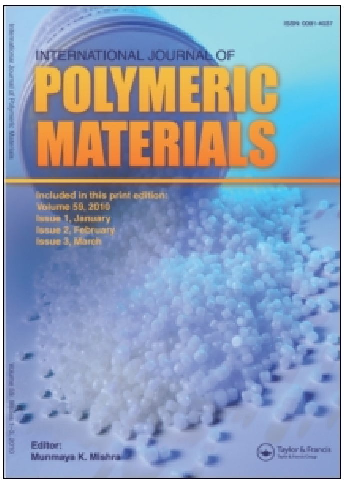

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Studies on Cellulose Acetate/Aminated Poly(ether imide) Blend Ultrafiltration Membranes

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Poly(ether imide) (PEI) was functionalized by amination. Ultrafiltration (UF) membranes were prepared from blends based on cellulose acetate (CA) and aminated poly(ether imide) (APEI) at various blend compositions. It was observed that the surface hydrophilicity of the CA/APEI blend membranes was enhanced remarkably with increase of APEI content. The pure water flux and percent water content of CA/APEI blend membranes increased from 46.7 to 90.0 $lm^{-2}h^{-1}$ *and 79.6 to 82.4 whereas the hydraulic resistance decreased from 15.67 to 4.81* $kPa/lm^{-2}h^{-1}$*, when the concentration of APEI increased from 5 to 30 wt%. The molecular weight cut-off (MWCO) of the blend membranes were found to vary from 19 to 150 kDa, for various blend compositions. The fouling resistance and strength of the blend membranes were improved considerably with an increase of APEI content. Morphology of the blend membranes were analyzed with scanning electron microscopy (SEM).*

Keywords: aminated poly(ether imide), BSA separation, cellulose acetate, dextran, hydrophilicity, ultrafiltration

INTRODUCTION

Membrane technology has been found to be an alternative approach for separation techniques because the process is faster, energy efficient and does not involve any phase change [1]. Ultrafiltration (UF) is a powerful technique that can be used to concentrate or fractionate protein solutions. Cellulose acetate (CA), an environment-friendly product from sustainable resources [2], became an interesting polymer with regard to its low price, moderate chlorine resistance, good biocompatibility and

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high hydrophilicity [3]. However, CA is not suitable for more aggressive cleaning, has low oxidation and chemical resistances, and poor mechanical strength. Hence the modification of CA gains importance.

Poly(ether imide) (PEI) is a versatile high performance polymer and gained particular interest in the fabrication of both UF and Nanofiltration (NF) membranes [4–6]. Kim and Lee [5] prepared integrally skinned uncharged PEI asymmetric NF membranes by dry/wet phase inversion method. The aromatic imide units provide high performance properties such as considerable mechanical strength, thermal stability, and chemical resistance, while the flexible ether linkages provide good processability. PEI has been successfully used in the preparation of asymmetric membranes for gas separation and oil-water separation [7,8]. PEI has certain drawbacks such as strict membrane casting conditions, relative low rejection and low gas permeability. The use of PEI for aqueous phase is restricted due to its hydrophobicity. Hence, it is desirable to make the PEI membrane hydrophilic when PEI is used in aqueous-based ultrafiltration applications. The hydrophilicity and permeability of PEI may be increased by amination. Many researchers have focused on the hydrophilization of hydrophobic ultrafiltration membrane materials [9,10].

Physical blending of polymers has been a long-standing, yet simple tool to modify properties of polymeric materials. In the field of ultrafiltration membranes, polymer blending has been investigated to modify properties such as mechanical strength, hydrophilicity coupled with water permeability, molecular weight cut-off and surface morphology [11–13]. Blends of PEI with several other polymers, such as cellulose acetate, polycarbonate, poly(ethylene terephthalate), poly(ether ether ketone) [14–18], have been studied in recent years. In addition, incorporation of functional group into the polymer backbone increases the hydrophilicity of blend membranes. Membrane fouling is a main drawback of UF membranes in the protein separation [19]. It is generally agreed that increasing hydrophilicity can improve the antifouling property of the membrane. It was reported that when PEI was sulfonated with chlorosulfonic acid, the sulfonated poly(ether imide) (SPEI) blend membranes were found to be hydrophilic in nature [20]. Shen et al. have prepared the PEI/SPEI blend UF hollow fiber membranes, and studied the effect of SPEI on the membrane morphology and their properties [21]. Richard Bowen et al. prepared PEI and sulfonated poly(ether ether ketone) (SPEEK) blend membranes with improved hydrophilic and permeability properties [22]. PEI membranes were also modified with brominated polyvinylpyrrolidone by Albrecht et al. [23]. Preparation of aminated microfiltration membranes by degradable functionalization using plain PEI membranes with various morphologies were also reported [24].

To improve the permeation and separation properties of CA membranes, many attempts have been carried out by our research group [25–27]. The present study deals with the preparation of aminated poly(ether imide) (APEI) and CA/APEI blend ultrafiltration membranes. The CA/APEI blend membranes have been characterized in terms of compaction, pure water flux, membrane hydraulic resistance, percentage water content, contact angle measurement, mechanical strength, molecular weight cut-off (MWCO) and surface morphology. The antifouling properties of CA/APEI blend membranes were also evaluated using bovine serum albumin (BSA) as a model protein.

EXPERIMENTAL

Materials

Commercial grade cellulose acetate was procured from Mysore Acetate and Chemical Co. Ltd., Mysore, India. CA was reprecipitated from acetone and then dried in a vacuum oven at 70°C for 24 h prior to use. Poly(ether imide) (Ultem® 1000) was supplied by GE Plastics, India as a gift sample. It was dried at 150°C for 4 h before used. Analytical grade N,N′-dimethylformamide (DMF) and N-methylpyrrolidone (NMP) obtained from SRL Chemicals, India, sieved through 4 Å molecular sieves to remove moisture and stored in dried condition, were used as solvents. Acetone and sodium lauryl sulphate (SLS) of analytical grades from SRL Chemicals, India, were used as received. Dextran of molecular weights 19 kDa, 42 kDa, 77 kDa and 150 kDa was procured form Sigma-Aldrich Company, USA. Sulphuric acid and phenol were procured from SRL Chemicals Ltd., India and used as received. Sodium citrate procured from BDH Ltd., India and sodium sulphate procured from E. Merk Ltd., Germany, were used as received for analysis of dextran. Bovine serum albumin (BSA) (69 kDa), anhydrous sodium monobasic phosphate and sodium dibasic phosphate heptahydrate were procured from Himedia Laboratories, India and CDH Chemicals, Ltd. (Mumbai, India), respectively, and used for the preparation of phosphate buffer solutions in the BSA rejection studies. Double-distilled water was employed for all the ultrafiltration experiments.

METHODS

Physical Measurements

The Fourier transform infrared (FTIR) measurements were performed on a Nicolet Impact 410 spectrometer. The NMR spectra were obtained from BRUKER 300 MHz spectrometer at 298 K with deutarated chloroform ($CDCl_3$) as a solvent and tetramethylsilane (TMS) as the standard. Differential scanning calorimetry (DSC) measurement was employed using a DSC Q200 (model Universal V4.4A TA system). The measurements were made from 20 to 250°C, at a heating rate of 10°C min^{-1} in N_2 atmosphere. The temperature of degradation was obtained by thermogravimetric analyzer with heating rate of 10°C min^{-1} (Mettler, Model TA 3000) with TG 50 thermo balance under N_2 atmosphere. Contact angle measurement was performed by using a DST Dynamic Surface Tensiometer. Mechanical properties were studied by using Instron 4500 model tensile testing system at an extension rate of 2 mm/min. The cross and surface morphologies of the membranes were viewed using Jeol JSM-840A scanning electron microscope.

Preparation of Aminated Poly(ether imide)

In a 500 ml three-necked flask, 30 g of PEI were dissolved in 100 ml of 2,2-dichloromethane. A mixture of trioxane, hydrochloric acid and zinc chloride was added [28]. The reaction mixture was stirred for 6 h and precipitated using ethanol. The resultant product is chloromethylated poly(ether imide).

The viscous white product was dissolved in NMP. Triethyl amine was added and the reaction mixture was constantly stirred for 12 h and poured into ethanol and washed repeatedly with hot ethanol followed by deionized water until inorganic salt and solvent were removed thoroughly. The purified polymer was then dried in a vacuum oven at 100°C for 48 h. The authenticity of chloromethylation and amination of polymer backbone were confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques.

Preparation of Membranes

Casting solution was prepared by stirring (300 rpm) CA/APEI in DMF for 3 h at room temperature. The casting solution was kept standstill for 3 h for de-aeration to get rid of air bubbles. The solution was cast on glass plate using a doctor's blade, allowed for 30 sec evaporation and immersed at 18°C in gelation bath containing 2 L of water (nonsolvent), 0.2 wt% of sodium lauryl sulphate and 2 wt% DMF. The gelation time was maintained constant (1 h) for all membranes that were stored in 0.1% formalin solution to prevent microbial growth.

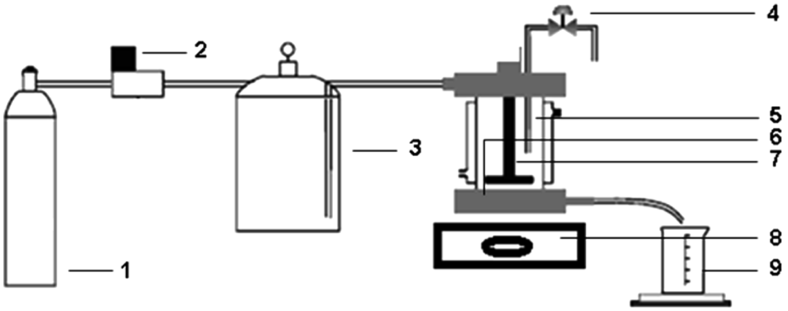
Ultrafiltration Experiments

Ultrafiltration experiments were carried out using a stirred Spectrum (Model No. S 76–40, USA), which had a volume capacity of 450 ml. Schematic representation of ultrafiltration kit is shown in Figure 1. The effective area of membrane was 38.5 cm^2. All the ultrafiltration experiments were carried out at a stirring speed of 450 rpm. Each membrane was first compacted for 5 h at 414 kPa in the cell to get steady-state flux. The pressure was then lowered to 345 kPa and the flux was measured under steady-state flow, i.e., after every 1 h for 4 h. The pure water flux of the membrane was calculated by Eq. 1 [29], where V (l), A (m^2) and Δt (h) are the volume of permeated solution, the membrane area and the permeation time, respectively. Each run was carried out in triplicate, and the average values were taken for all flux experiments.

$$J = \frac{V}{A\Delta t} \tag{1}$$

To determine membrane hydraulic resistance (R_m), the pure water flux of membranes were measured at different transmembrane pressures (ΔP) of 69, 138, 207, 276, and 345 kPa, after compaction. The resistance of the membrane, R_m was evaluated from the slope of water flux vs. transmembrane pressure difference (ΔP) using the following equation [30]:

$$Jw = \frac{\Delta P}{R_m} \tag{2}$$



1. Compressor 2. Pressure controller 3. Feed reservoir 4. Pressure release valve
5. Feed solution 6. Membrane 7. Stirrer 8. Magnetic stirrer 9. Permeate

FIGURE 1 Schematic representation of ultrafiltration kit.

Percent water content of the membranes was obtained after soaking membranes in water for 24 h, followed by mopping each with blotting paper and the membranes were weighed.

The wet membranes were placed in a vacuum oven at 100°C for 5 h and the dry weights of the membranes were determined. From the wet and dry weights, percent water content was determined by

$$\%\text{Water content} = \frac{(\text{Wet membrane weight}) - (\text{Dry membrane weight})}{\text{Wet membrane weight}} \times 100 \qquad (3)$$

Molecular weight cut-off of the membrane was determined by identifying the molecular weight of an inert solute which has solute rejection (SR), of 80–100% in steady-state ultrafiltration experiments. Thus, the carbohydrate dextran with molecular weights 19 kDa, 42 kDa, 77 kDa, and 150 kDa were chosen and their percent rejections were determined using UV-visible spectrophotometer in the frequency range, $\lambda_{max} = 485$ nm. The colorless dextran was complexed with copper sulphate and analyzed according to the reported literature [31].

After compaction, 1 mg/ml BSA concentration at pH 4.0 an with an acidic phosphate buffer solution was used as ultrafiltration solution. The flux was collected over measured time intervals. Protein concentration was determined spectroscopically at 280 nm using an UV-visible spectrophotometer (SL 164, Elico, India). The flux during protein filtration was recorded until the constant flux was reached (J_p). Flux decline ratio (R_{FD}) value was calculated to reflect the fouling resistance ability of the membrane by the following equation [32]:

$$J_{FD} = \left(1 - \frac{J_p}{J_w}\right) \times 100\% \qquad (4)$$

Solute retention R was calculated as follows

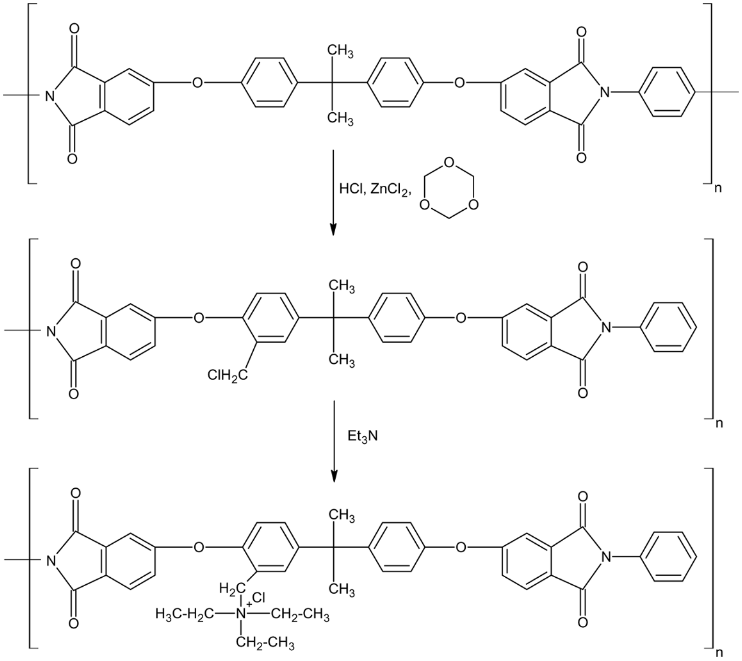
$$SR(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (5)$$

where C_p and C_f (mg/ml) were protein concentrations of permeate and feed solutions, respectively.

RESULTS AND DISCUSSION

Amination of Poly(ether imide)

Amination of poly(ether imide) was carried out by two steps, that is chloromethylation followed by amination as shown in Scheme 1. The



SCHEME 1 Amination procedure.

authenticity of the functionalization was ascertained through FTIR, ^{1}H-NMR and ^{13}C NMR spectroscopy. FTIR analysis of chloromethylated poly(ether imide) (CMPEI) shows the presence of a strong absorption band at 738 cm^{-1}, which is the characteristic absorption band for C-Cl. This absorption band is absent in the FT-IR spectrum of PEI and APEI. Further, the presence of absorbance band at 1722–24 cm^{-1} in PEI, CMPEI and APEI FT-IR spectra confirms the presence of imide group. The ^{1}H NMR spectrum (Figure 2a) for chloromethylated poly(ether imide) exhibits resonance at $\delta = 3.09$ due to the presence of CH_2, indicating the incorporation of chloromethyl group onto the polyetherimide backbone. Furthermore, resonances between $\delta = 7.02$–7.88 are attributed to the aromatic proton resonances of the poly(ether imide). The ^{13}C NMR spectrum (Figure 2b) for chloromethylated poly(ether imide) exhibits resonance at $\delta = 42.57$ due to the presence of CH_2 and $\delta = 31.02$, 43.5 are due to methyl group and tertiary carbon on the polymer backbone, respectively. Figure 3a shows the ^{1}H NMR spectrum of aminated poly(ether imide). The peaks between 7.02–7.89 are assigned to the protons of aromatic rings of the polymer backbone. The integral value of these peaks indicates that there are about

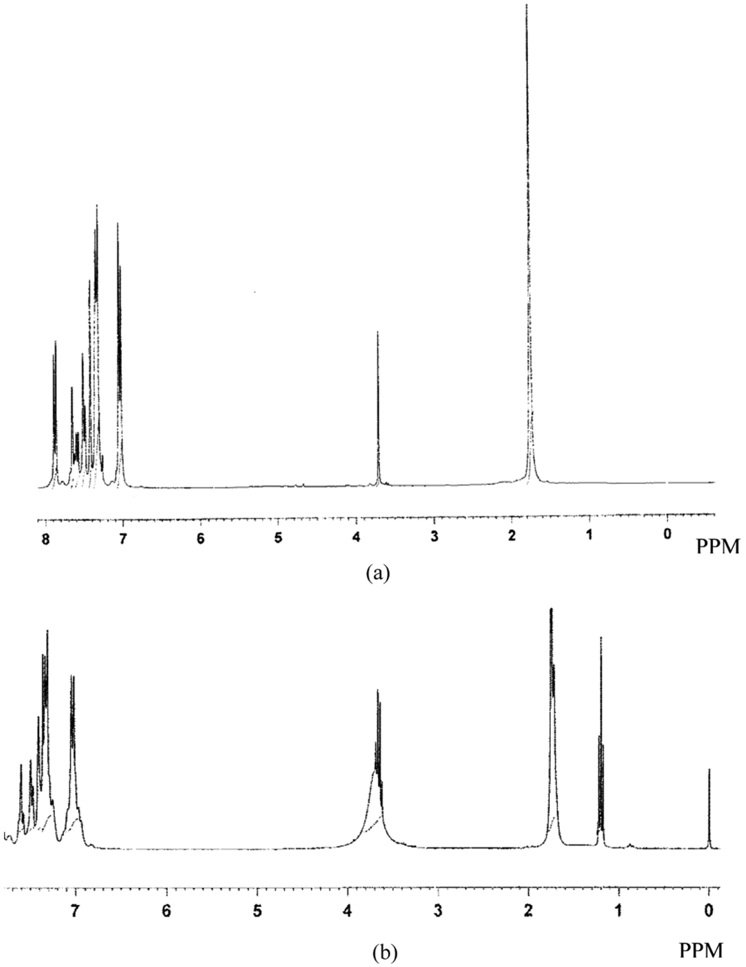
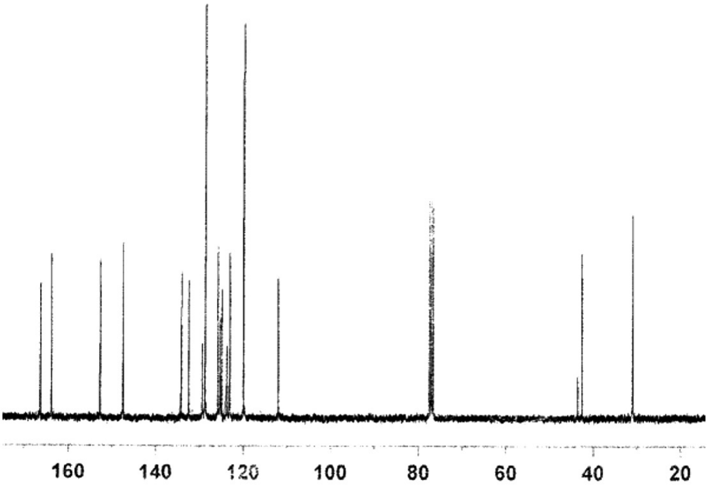
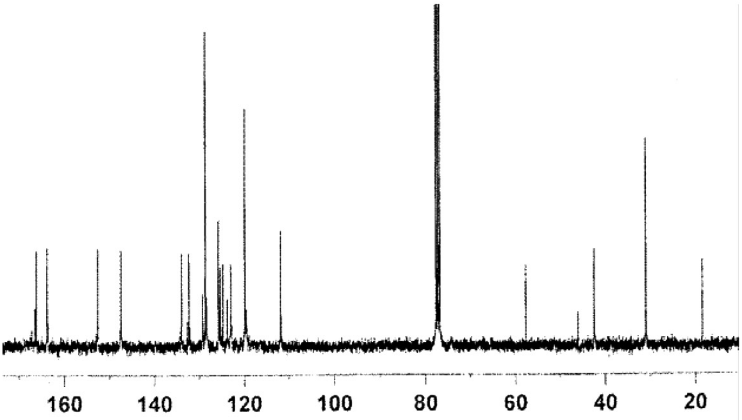


FIGURE 2 (a) 1H-NMR spectra of chloromethylated polyetherimide; (b) 1H-NMR spectra of aminated polyetherimide.

17 protons in the aromatic rings of the APEI repeat unit, as against 18 protons in the aromatic rings of the PEI repeat unit. It is obvious that the trimethyl amine group was attached to the aromatic rings of the PEI molecule. The resonance at $\delta = 1.12$(t, $-CH_3$), $\delta = 3.5$[m, $-CH_2$ (aliphatic)], $\delta = 3.6$(s, $-CH_2$ (benzylic)) and isopropylidene (6H) at $\delta = 1.7$(s) was detected for aminated poly(ether imide). On comparison with the integration of the quaternary amine ethyl groups with the isopropylidene signal (6H), the degree of substitution was obtained.



(a)



(b)

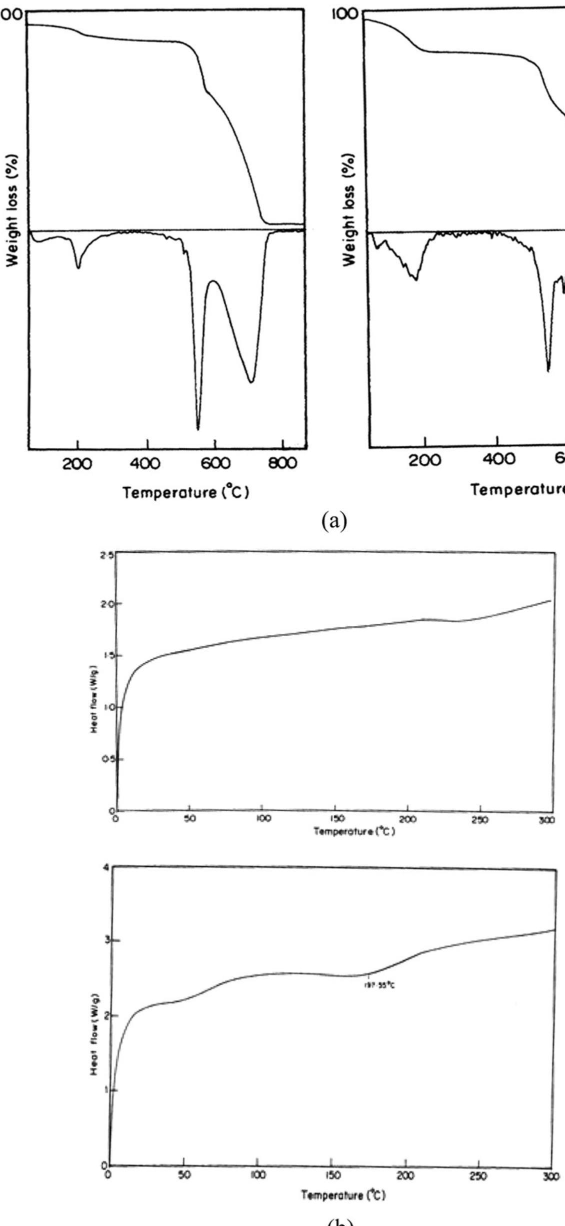
FIGURE 3 (a) ^{13}C-NMR spectra of chloromethylated polyetherimide; (b) ^{13}C-NMR spectra of aminated polyetherimide.

The degree of substitution was found to be 0.40. The ^{13}C NMR spectrum for aminated poly(ether imide) is shown in Figure 3b. Chloromethylated poly(ether imide) exhibits resonances at $\delta = 18.31(-CH_3)$, $\delta = 57.72$ [$-CH_2-$ (methylene)], $\delta = 42.46$ [$-CH_2-$ (benzylic)]. Tertiary carbon at $\delta = 46.06$ and isopropylidene carbon at $\delta = 30.90$ were detected. Through the above investigation, we can conclude that the PEI can be aminated by the method described in this work.

The attachment of amine groups to the PEI chains leads to a large modification of its solubility. The physical and chemical properties of APEI depend on the concentration of amine groups in the polymer backbone. Amination modifies the chemical character of PEI, reduces the crystallinity and affects solubility. Thermal decomposition of PEI started above 450°C and proceeded via two thermal decomposition steps. Its residual weight was above 50% even at 700°C. The thermal stability of chloromethylated and aminated PEI was investigated by TGA. The TGA and DTG curves of chloromethylated PEI and APEI are shown in Figure 4a. It is seen that three weight-loss steps are observed for chloromethylated PEI and APEI, which is reflected by three sharp peaks in the DTG curve in three separate temperature ranges. The first weight-loss peak in chloromethylated PEI and APEI is believed to be due to the splitting of chloromethyl and triethylamine, respectively. The chloromethyl and triethylamine decomposition was found to occur at 192°C and 177°C in the TGA/DTG for the chloromethylated and aminated PEI sample. From the DSC analysis of chloromethylated PEI and APEI are reported in Figure 4b, it is easy to see that the introduction of amine groups into PEI significantly decreases its thermal stability. The glass transition temperatures of chloromethylated PEI and APEI are found to be 220°C and 197°C, respectively.

Compaction

Compaction of membrane during the ultrafiltration process is an important issue in the commercial application. The membranes prepared from various blend compositions were washed thoroughly with deionized water and were compacted at 414 kPa for 5 h. Changes in the membrane performance with operating time were explored with membranes prepared from the casting solutions of CA/APEI are depicted in Figure 5. It is evident from Figure 5 that the pure water flux of membranes decreases with increasing compaction time in the initial 3 h for all polymer blend compositions. Further increase in the compaction time does not change the pure water flux significantly. This indicates that complete compaction of the blend membrane occurred in the first 3 h. The decline in the pure water flux in the early stages of compaction can be attributed to the reduction in the porosity volume due to closer rearrangement of polymer segments and chains. Similar trends have also been reported elsewhere [25–27]. Furthermore, an increase in APEI in the casting solution of blend polymer from 5 to 30 wt% of total polymer increases the flux from 68.6 to 105.9 $lm^{-2} h^{-1}$. The increase in flux upon the increase in the APEI may stem from partial compatibility due to higher free energy of



(a)

(b)

FIGURE 4 (a) TGA curve of chloromethylated and aminated polyetherimide; (b) DSC curve of chloromethylated and aminated polyetherimide.

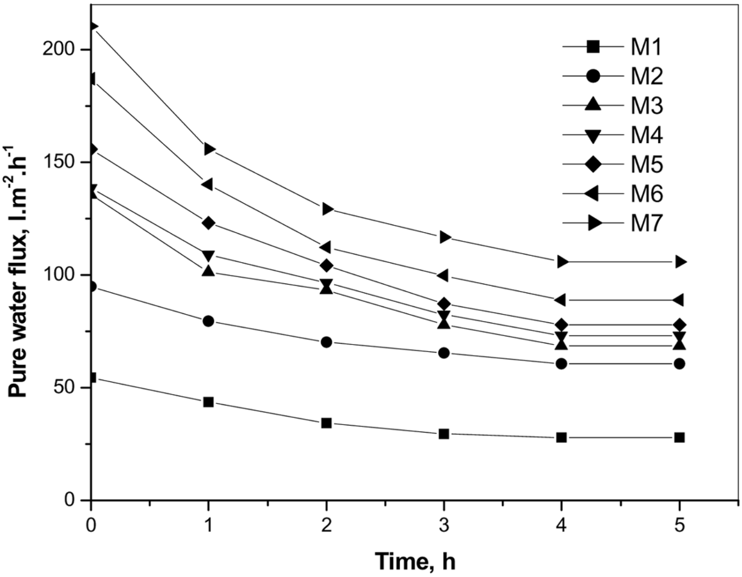


FIGURE 5 Effect of compaction time on pure water flux CA and CA/APEI blend membranes.

mixing of blends, which leads to a larger polymer chain segmental gap between CA and APEI. In addition, hydrophilic amine moiety present in the polymer backbone may also influence the enhancement of pure water flux by continuous increment of APEI in the blend composition.

Pure Water Flux

Pure water flux is one of the main specifications describing the performance of the membrane. Pure water flux was measured for all blend membranes using an applied pressure 345 kPa and is shown in Table 1. Pure CA membrane (M1) had very low water permeability of 14.9 $lm^{-2} h^{-1}$. The addition of APEI results in a remarkable increase in the water flux. When 5 wt% [M2] APEI was introduced into the membrane, pure water flux sharply increased to almost threefold. When the percentage of APEI changed from 5 to 10 wt% [M3], the pure water flux increased from 46.7 to 51.4 $lm^{-2} h^{-1}$. The pure water fluxes of CA/APEI blend compositions of 85/15(M4), 80/20(M5), 75/25(M6), and 70/30(M7) are 56.0, 65.4, 76.3 and 90.0 $lm^{-2} h^{-1}$, respectively. This enhancement in flux may be attributed to the fact that the presence of a higher amount of two polymeric components results in phase separation and inhomogeneity, leading to the

TABLE 1 Blend Composition of CA/APEI Blend Ultrafiltration Membranes

Membrane	CA (wt%)	APEI (wt%)	DMF (wt%)	PWF, $lm^{-2}h^{-1}$ At 345 kPa	R_m, $kPa/lm^{-2}h^{-1}$	MWCO
M1	100	0	82.5	14.90	15.67	19–42
M2	95	05	82.5	46.74	7.99	42
M3	90	10	82.5	51.41	7.21	42
M4	85	15	82.5	56.09	7.14	42–77
M5	80	20	82.5	65.44	6.77	77
M6	75	25	82.5	76.34	5.56	77
M7	70	30	82.5	89.96	4.81	77–150

formation of cavities in the sublayer which enhances the mobility of water molecules. A higher flux was observed for CA/APEI than for CA/PEI blend membranes [14]. This may be due to the incorporation of hydrophilic triethyl amine moiety in the polymer backbone. It has been generally agreed that increasing the hydrophilicity could improve the water permeability of the membranes.

Membrane Hydraulic Resistance

In order to determine the hydraulic resistance, the prepared membranes were subjected to different transmembrane pressures (TMP) from 69 to 414 kPa, and the corresponding pure water fluxes measured. The plot of the pressure vs. pure water flux gives a linear relationship and the inverse of the slope is the membrane hydraulic resistance. From Figure 6, it is evident that the pure water flux increased with increased operating pressure. Table 1 shows the membrane hydraulic resistance of pure CA and CA/APEI blend membranes. The higher R_m exhibited by 100% CA membrane (M1) compared with other blend membranes [M2-M7] may happen because CA is more crystalline and hydrophobic than the CA/APEI blends [33]. As the APEI concentration was increased from 5 to 30 wt% the hydraulic resistance decreased from 15.67 to 4.81 $kPa/lm^{-2}h^{-1}$. The decrease in membrane resistance may be due to the presence of APEI in the blend.

Water Content and Contact Angle Measurement

Water content is considered to be an important parameter for membrane characterization, since the pure water flux of the membrane can be predicted based on these results. The cellulose acetate membrane in the absence of APEI was found to have a water content of

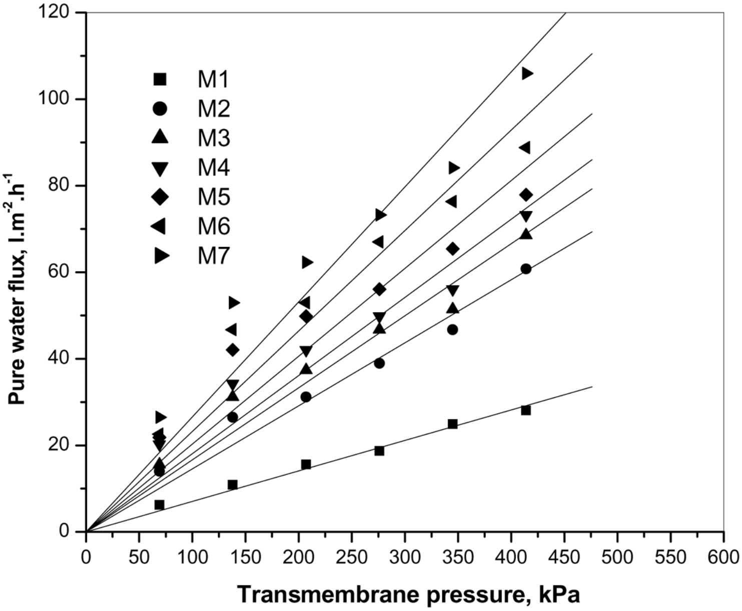


FIGURE 6 Effect of transmembrane pressure on pure water flux CA and CA/APEI blend membranes.

78.5%. Variation in the concentration of APEI from 5 to 30 wt% (M2-M7) in the blend membranes resulted in an increase in the water content of the membranes from 79.6 to 82.4% as shown in Figure 7. This may be due to the fact that hydrophilicity is being imparted. Contact angle measurement was performed on CA/APEI films using a DST Dynamic Surface Tensiometer. The change in the contact angle of the films was measured by dipping the membrane in distilled water for 10 mm depth. As shown in Figure 7, the CA membrane (M1) had the highest contact angle (58°), corresponding to the lowest hydrophilicity. The contact angle decreases with the increase of aminated PEI in this blend. The decrease in the water contact angle of modified membranes implies that a polar surface was obtained by increasing the amine group and the hydrophilicity of CA/APEI membranes was improved by increasing the average polarity of the blend. As expected, the introduction of trimethyl amine (TMA) group in the polymer unit increased the hydrophilicity of the CA/APEI membranes. Therefore, it was proposed that the aminated membranes absorb more permeate into the membrane and thus enhances the flux rate. A similar trend was observed for PES/DMMSA-BMA (polyethersulfone/N,N-dimethyl-N-(3-sulfopropyl)-butylmethacrylate) blend membranes

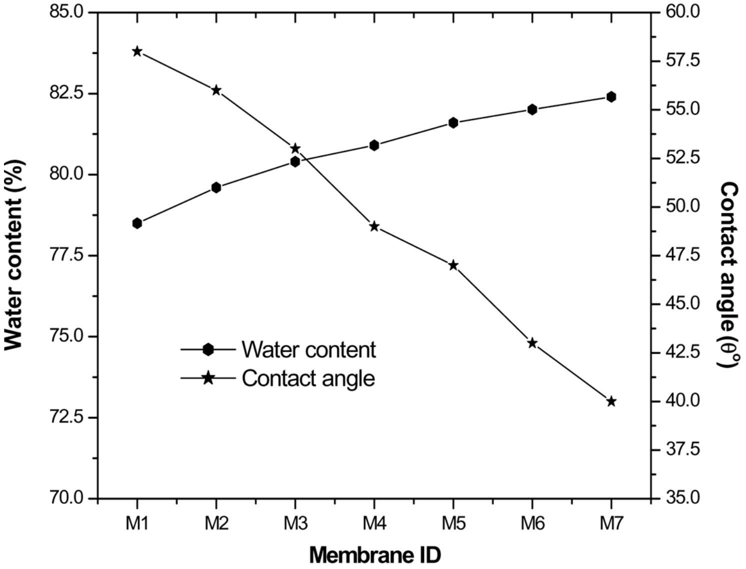


FIGURE 7 Water content and water contact angles of CA and CA/APEI blend membranes as a function of APEI concentration in casting solution.

by T. Wang et al. [31]. Effect of contact angle on poly(ether sulfone) by increasing sulfonated polycarbonate was also reported by Y. Wang et al. [34]. Zhu et al. have reported the improved hydrophilic blend membranes by blending PES with SMA (poly(styrene-maleic anhydride)), decreasing the contact angle with increasing the SMA concentration [35].

Molecular Weight Cut-off

The choice of membrane is usually guided by its nominal molecular weight cut-off (NMWCO), which is typically defined as the equivalent molecular weight of the smallest dextran that would exhibit 80% rejection. That value is usually referred to as R80. Although this choice is arbitrary, it has been adopted by most of the UF community [36]. The earliest UF membranes were characterized by filtering solutions of individual proteins covering the molecular weight range of interest. However, the resulting data can be difficult to analyze due to differences in adsorption, conformation, and electrical charge between proteins. The idea of using neutral polymers like dextrans to characterize UF membranes dates back more than 25 years [37,38]. Dextrans were chosen because they do not interact with most membranes, are well-characterized, and are available inexpensively in large quantities [39]. The percentage rejection of various molecular weights of dextran for pure CA and CA/APEI blend membranes were determined. The results are shown in Table 1. From the experiments, it has been found that the pure cellulose acetate membrane had the MWCO in between 19–42 kDa. It is also evident from Table 1 that the MWCO values depend on the polymer composition. Thus, in the CA/APEI blend membranes, as the APEI content was increased, the MWCO value also increased from 42 kDa for 5 wt% APEI (M2) and 10% APEI (M3). However, when APEI content in the blend was increased to 15 wt%, the MWCO value lies between 42 and 77 kDa (M4). For CA/APEI blend membranes with 80/20 wt% (M5) and 75/25 wt% (M6) composition, the MWCO value was found to be 77 kDa. For membrane with 70/30 wt% CA/APEI blend composition, the MWCO value lies between 77 and 150 kDa (M7).

Mechanical Properties of CA/APEI Blend Membranes

The mechanical properties of blend membranes were another major concern for the practical application purpose. Here, the tensile strength and break elongation ratio of the membranes were examined. Two dumb-bell-shaped specimens of 5 mm width and 20 mm length were punched out of the membrane film. Tensile strength and break elongation ratio tests were carried out using an Instron 4500 model tensile testing system at an extension rate of 2 mm/min.

Tensile strength and break elongation ratio of CA (M1) and CA/APEI (M2-M7) blend membranes are shown in Table 2. Tensile strength of the CA/APEI blend membranes increased significantly in comparison with the CA control membrane due to the intrinsic

TABLE 2 Mechanical Properties of CA and CA/APEI Blend Ultrafiltration Membranes

Membrane	Tensile strength (N/mm^2)	Break elongation ratio (%)
M1	1.56	7.23
M2	1.76	10.16
M3	2.10	13.07
M4	2.32	16.46
M5	2.77	24.24
M6	2.89	26.82
M7	1.26	8.69

mechanical strength of APEI. The strength increases with the increase of APEI concentration up to 25 wt% of APEI in comparison with CA membrane (M1). Tensile strength and break elongation ratio reach a peak value of 2.89 N/mm^2 and 26.8% respectively, then decline upon further increase of APEI concentration. The decline in strength of (M7) may be due to formation of macrovoids in the sublayer. SEM pictures also support this observation. Similar observations are reported elsewhere [40,41].

Membrane Morphology

The surface and cross-section structure of flat sheet ultrafiltration membrane is the most critical part in helping to identify the role of the membrane in the mechanism of permeation and rejection. Hence, the morphological studies of the pure cellulose acetate and blend (CA/APEI) membranes were made by using SEM. The micrographs of the top surfaces of pure cellulose acetate (M1) and CA/APEI, (M3), (M5) and (M7) blend membranes are shown in Figure 8. From Figure 8, it can be seen that the pores are smaller and widely distributed in pure cellulose acetate membrane. It was observed that bigger

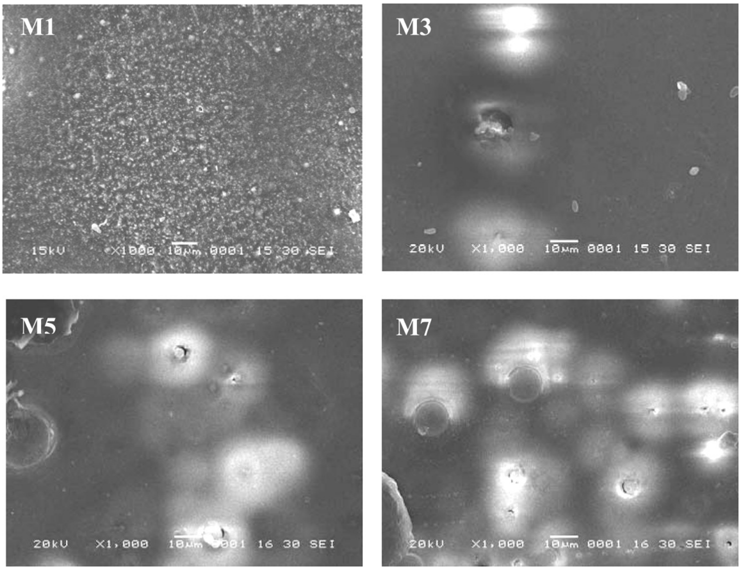


FIGURE 8 Surface—SEM images of CA (100 wt%)(M1) and CA/APEI blend membranes with APEI concentration of (M3) 10 wt%, (M5) 10 wt%, (M5) 20 wt% and (M7) 30 wt%.

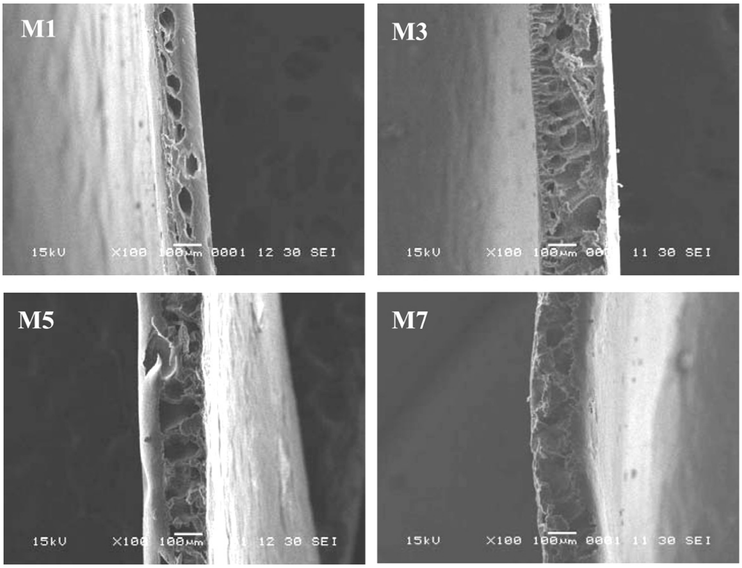


FIGURE 9 Cross—sectional SEM images of CA (100 wt%) (M1) and CA/APEI blend membranes with APEI concentration of (M3) 10 wt%, (M5) 20 wt%, and (M7) 30 wt%.

pore sizes and a higher number of pores are present in of pores CA/APEI blend membranes than in pure cellulose acetate membranes. The cross-sectional views of CA and CA/APEI above-mentioned blend compositions are displayed in Figure 9, where finger-like structures commonly found beneath the skin layer of UF membranes are seen. This may be attributed to the distribution of individual domains of APEI and CA with their respective morphologies.

Rejection Studies

The percentage rejection of BSA by membranes cast from pure CA and CA/APEI (M1-M7) were analyzed and the results are illustrated in Figure 10. The pure CA (M1) membrane exhibits 98% rejection of BSA. The rejection of BSA was reduced from 98 to 94% by the addition of 5 wt% of APEI content in the membrane. For other blend membranes, the percent rejection were 91, 87, 79, 76 and 72% when the concentration of APEI in the blend membranes were 10(M3), 15(M4), 20(M5), 25(M6) and 30(M7) wt% respectively. This is due to increased pore size due to the partial miscibility of CA and APEI. The increase in pore size of blend

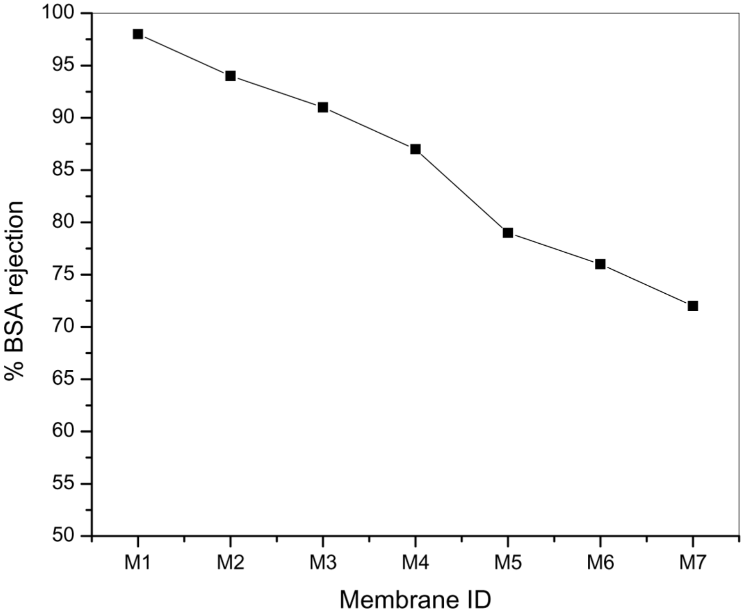


FIGURE 10 Effect of APEI concentration in casting solution on the rejection of BSA of the CA and CA/APEI blends membranes.

membranes with increasing APEI content in the blend membranes was also confirmed by SEM.

Antifouling Properties

Figure 11 shows the effect of APEI concentration in casting solution on the protein flux of the CA/APEI blend membranes. Compacted CA/APEI membranes were employed for ultrafiltration of the BSA solution. Before ultrafiltration of BSA solution, the blend membranes were cleaned with pure water for an hour, which shows that there is no significant change in the pure water flux, as shown in Figure 11. The flux decreased dramatically at the initial operation of BSA solution ultrafiltration due to protein adsorption or convective deposition. It is proposed that some protein molecules in the feed deposit or adsorb on the membrane surface (cake formation), causing a drop in the first few minutes of operation. Under constant pressure, the effects of membrane fouling and concentration polarization are usually observed by considerable decline in permeate flux with time. In the present work, the concentration polarization was minimized because of high molecular weight BSA molecules and rigorous stirring near the membrane

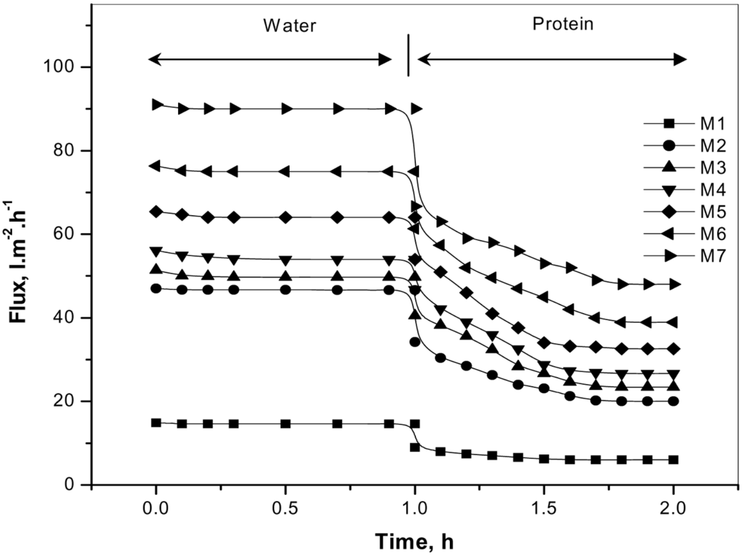


FIGURE 11 Effect of APEI concentration in casting solution on the flux of the CA and CA/APEI blends membranes.

surface. Therefore the flux decline of the membranes was mostly caused by membrane fouling.

Flux decline ratio (R_{FD}) value is introduced to reflect the fouling resistance ability of the membrane; a lower value of R_{FD} means a higher fouling resistance ability of the membrane. For the CA and CA/APEI blend membranes, the R_{FD} values were 59.73, 57.21, 54.5, 52.39, 50.18, 49.04 and 46.6 when the concentrations of APEI in the blend membrane were 0, 5, 10, 15, 20, 25 and 30 wt% (M1-M7) (Figure 11) respectively. It indicates that the fouling resistance increases with an addition of APEI in the casting solution. This is due to a more hydrophilic amine group enrichment of the membrane surface, which is consistent with contact angle measurements of blend membrane surfaces.

CONCLUSIONS

Modified ultrafiltration membranes based on CA/APEI of various compositions were prepared. Blending of CA with APEI resulted in blend membranes with enhanced ultrafiltration membrane characteristics such as lower hydraulic resistance coupled with higher water flux and water content. The addition of APEI altered the molecular weight cut-off (MWCO), membrane structure and the mechanical properties of the membranes. The improved surface hydrophilicity, due to surface enrichment of amine content, endowed the CA/APEI blend membranes with significantly enhanced protein adsorption-resistance. We conclude that the incorporation of the hydrophilic moiety (APEI) in blend membranes plays a major role in improving the flux and performance characteristics of membranes.

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