Protein Separation by Cellulose Acetate/Sulfonated Poly(ether imide) Blend Ultrafiltration Membranes

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ABSTRACT: A process for purifying aqueous solutions containing macromolecular proteins such as bovine serum albumin (BSA), egg albumin (EA), pepsin, and trypsin has been investigated. Protein removal from food and biorelated industrial waste streams are gaining increased visibility due to environmental concern and saving precious materials. Ultrafiltration (UF) processes are largely being applied for protein separation from aqueous streams. In this work, an attempt has been made to separate the valuable proteins using cellulose acetate (CA)/sulfonated poly(ether imide) (SPEI) blend UF membranes prepared in the absence and presence of the additive, polyethyleneglycol (PEG600) in various compositions. The blend membranes were subjected to the determination of pore statistics and molecular weight cut-off (MWCO). Porosity and pore size of the membranes increased with increasing concentrations of SPEI and PEG600 in the casting solution. Similarly, the MWCOs of the blend membranes ranged from 20 to greater than 69 kDa, depending on the various polymer blend compositions. Surface morphology of the blend membranes were analyzed using scanning electron microscopy. Studies were carried out to find the rejection and permeate flux of proteins. On increasing the concentration of SPEI and PEG600, the rejection of proteins is decreasing, whereas the permeate flux has an increasing trend. The effect of hydrophilicity of SPEI on fouling of protein for CA/SPEI blend membranes was also discussed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2047–2057, 2008

Key words: cellulose acetate; sulfonated poly(ether imide); blend membranes; protein separation; pore statistics

INTRODUCTION

Effective effluent treatment of industrial waste streams is essential for protecting human health and the environment. Efficient separation and recovery of macromolecular proteins from industrial waste streams is gaining more and more importance because of the increasing demand for high purity products.[1] Food and biorelated industrial wastes are generally incinerated or put into landfill or discharged into sewer, in which case, valuable proteins were not recovered. In addition, incineration of organic waste often gives toxic emission whose distribution degree is even higher than that of organic solid waste. Furthermore, effluents containing proteins generate biochemical oxygen demand and chemical oxygen demand (COD) in surface water. The waste load equivalents of 1 kg protein is 1.36 kg COD in dairy effluents.[2]

Ultrafiltration (UF) and reverse osmosis (RO) have become standard procedures for the separation of macromolecular solutions. Separation of colloidal suspensions by UF can be achieved by permselective membranes, which allow the passage of solvent and small solute molecules but retain macromolecules.[3,4] Intensive research has been carried out by several researchers on the transmission and rejection of proteins using cellulose acetate (CA) and polysulfone membranes, and it has been concluded that membrane UF is a reliable process for macromolecular separations.[5–7]

Modified and unmodified polysulfone UF membranes have been used for the fractionation of egg protein solution.[8] The modified membranes had increased water flux because of their hydrophilic carboxyl and sulfonic groups. Furthermore, the pore-forming additive plays a key role in the formation of pore sizes in the asymmetric membranes. On leaching the pore former and casting solvent during gelation, the gel is stabilized to form the membrane. The choice of pore former will depend upon polymers.[9,10] PEG200 has been used as a pore-forming additive in the preparation of polyetherimide asymmetric membranes, and the results reveal that increasing the amount of PEG200 in the polymer solution used to prepare the membrane drastically improved the solute rejection rate.[11]

Traditionally, CA membranes are used in UF and RO-membrane processes. The performance of CA

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membranes can be improved by blending it with appropriate polymers in view of the fact that polymer blends have provided an efficient way to fulfill new requirements for material property.[12] CA-polysulfone blend UF membranes using polyvinylpyrrolidone (PVP) as an additive have been prepared and applied to the separation of proteins, achieving more than 90% separation.[13] Separation of proteins and metal ions by modified CA membranes with PEG600 and PVP has been attempted.[14] Recently, CA/poly (ether imide) (PEI) blend UF membranes have been prepared and applied to the rejection of proteins and metal ions.[15]

Furthermore, membrane fouling is a main drawback during the separation of proteins by UF membranes.[16] It is generally agreed that increasing hydrophilicity can reduce the fouling properties of the membrane. In the present investigation, CA-based UF membranes were prepared by blending CA with sulfonated poly (ether imide) (SPEI) and PEG600 in various compositions. The prepared membranes were used for the protein-rejection studies. The main objective of this work is to study the effect of CA/SPEI blend composition and concentration of the polymeric water soluble additive PEG600 in the casting solution on the rejection and permeate flux of proteins such as bovine serum albumin (BSA), egg albumin (EA), pepsin, and trypsin. The surface properties such as morphology, molecular weight cut-off (MCWO), average pore size, and porosity were estimated using aqueous solutions of proteins of different molecular weight as feed. Surface morphology of CA/SPEI blend membranes were characterized by scanning electron microscopy (SEM). The fouling properties of CA/SPEI blend membranes were evaluated using BSA as model protein.

EXPERIMENTAL

Materials

Commercial grade MYCELL cellulose diacetate CDA5770 (acetyl content 39.99 wt %) was procured from Mysore Acetate and Chemicals Company, India, and used after reprecipitation from acetone and vacuum dried at 25°C for 12 h. Polyetherimide (Ultem® 1000) supplied by GE Plastics, India, as a gift sample. It was dried at 150°C for 4 h before use. *N*-Methyl-2-pyrrolidone (NMP), 1,2-dichloroethane (DCE), isopropanol, *N*,*N*-dimethylacetamide (DMAc), acetone, and sodium lauryl sulfate (SLS) of analar grades from SD Fine Chemicals, India, were used as such without further purification. Anhydrous sodium monobasic phosphate and sodium dibasic phosphate heptahydrate were procured from CDH Chemicals (Mumbai, India) and used for the preparation of phosphate buffer solutions in the protein analysis. Proteins, viz., BSA (69 kDa), are from Himedia Laboratories, India; EA (45 kDa), from CSIR Biochemical Centre, India; pepsin (35 kDa) and trypsin (20 kDa) are from SRL Chemicals Limited, India, and were used as received. Chlorosulfonic acid was procured from Merck (I) (Mumbai, India) and used as such for the preparation of sulfonated PEI. Deionized and distilled water was used for the UF experiments and for the preparation of gelation bath.

Sulfonation of PEI

Polyetherimide (Ultem 1000) was sulfonated by chlorosulfonic acid as the sulfonating agent as reported earlier.[17] Twenty grams of PEI dissolved in 100 mL of DCE at 60°C and subsequently the PEI solution was kept at 30°C was placed in a three-necked round-bottomed flask. The solution was stirred using a mechanical stirrer under nitrogen atmosphere. Then 10 mL of chlorosulfonic acid, diluted with 200 mL of DCE, was slowly added drop wise to the PEI solution by using a dropping funnel within 1 h with vigorous stirring. After being reacted for 3 h, the reaction product, which precipitated in the reaction medium, was dissolved in DMAc at 50°C, coagulated with excess isopropanol, filtered, washed with isopropanol, and dried at 40°C in a vacuum oven. The sodium salt form of the product was obtained by soaking it in excess 0.1 mol/L NaOH aqueous solution for 2 days.

Preparation of blend membranes

The blend solutions based on CA and SPEI (total polymer concentration = 17.5 wt %) were prepared by dissolving the two polymers with different compositions of 100/0, 95/5, 85/15, and 75/25 wt % in presence and absence of additive PEG600 (0–10 wt %) in a solvent, NMP (72.5–82.5%) under constant mechanical stirring at 30 rpm in a round-bottomed flask for 4 h at 40°C. The homogeneous solution that was obtained was allowed to stand at room temperature for 1 day in an airtight condition to get rid of air bubbles.

The method of preparation involved is the same as that of the "phase inversion" method used in earlier works as reported by other researchers.[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°C ± 1°C and a relative humidity of 50% ± 2%. 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] Before casting, a 2-L gelation bath, consisting of 2.5% (v/v) NMP solvent (to reduce the rate of liquid-liquid demixing and

macrovoids) and 0.2 wt % surfactant, SLS (to reduce surface tension at the polymer-nonsolvent interface) in distilled water (nonsolvent) was prepared and kept at 20°C ± 1°C. The membranes were cast over a glass plate using a doctor blade. After casting, the solvent present in the cast film was allowed to evaporate for 30 s, and the cast film along with the glass plate was gently immersed in the gelation bath. After 1–2 h of gelation, the membranes were removed from the gelation bath and washed thoroughly with distilled water to remove all NMP and surfactant from the membranes. The membrane sheets were subsequently stored in distilled water, containing 0.1% formalin solution to prevent microbial growth.

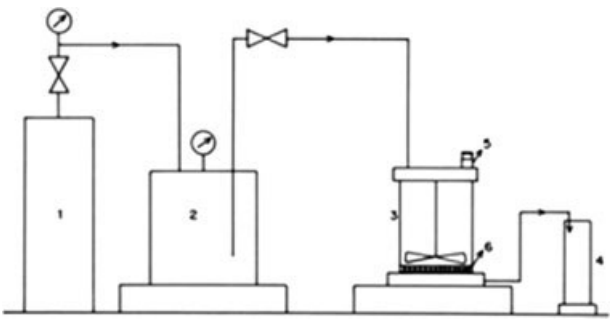

Figure 1 Schematic diagram of ultrafiltration testkit. (1) Compressor, (2) feed tank, (3) UF cell, (4) permeate collector (5) pressure relief valve, and (6) membrane.

Experimental setup

The UF experiments were carried out in a batch type, dead end cell (UFcell-S76-400-Model, Spectrum, USA) with a diameter of 76 mm, fitted with Teflon-coated magnetic paddle (as shown in Fig. 1). This cell was connected to a compressor with a pressure control valve and gauge through a feed reservoir.

Fouling studies

BSA solution (0.1 wt %) was prepared with phosphate buffer (0.5*M*, pH 7.2) and used as feed solution. The permeate BSA concentration was determined spectroscopically at 280 nm using an UV–vis spectrophotometer (SL 164, Elico, India). Each membrane was first compacted for 15 min, and the deionized water flux was measured. The flux of the membrane was calculated by the following equation:

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

where J_w is the water flux ($m^3\ m^{-2}\ s^{-1}$), Q is the quantity of permeate collected (in m^3), A is the membrane area (in m^2), and Δt is the sampling time (in s).

After 1 h of water filtration, the process was stopped, and the cell is emptied. The BSA solution was added to the cell, and the flux was collected over measured time intervals. The flux during protein filtration was recorded until the constant flux is reached, which is called J_p. The flux decline rate (R_{FD}) was calculated by the following equation[20]:

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

Morphological studies

The top surfaces and cross sections of the CA/SPEI blend membranes in the presence and absence of additive, PEG600 was studied using SEM (LEICA Stereoscan, Cambridge, UK). The membranes were cut into pieces of various sizes and mopped with a filter paper. These pieces were immersed in liquid nitrogen for 20–30 s and frozen. Frozen bits of the membranes were broken and kept in a desiccator. These dry membrane samples were used for SEM studies. The samples were gold sputtered for producing electrical conductivity, and photomicrographs of the samples were taken under very high vacuum conditions operating between 15 and 25 kV, depending on the physical nature of the sample. Various SEM images were taken for top surface and cross section views of the polymeric membranes.

Pore size and porosity

The average pore size and surface porosity were determined by the UF of protein solutions of different molecular weights. From protein removal studies as described below, the molecular weight of the solute (protein) that has a solute rejection (%SR) above 80% was used to evaluate the average pore size, $\bar{R}$, of the membranes by the following equation[21,22]:

$$\bar{R} = 100\left(\frac{\alpha}{\%SR}\right)$$

where $\bar{R}$ is the average pore size (radius) of the membrane (Å) and α is the average solute radius (Å). The average solute radii, also known as the Stoke radii, were obtained from the plot of solute molecular weight versus solute radius in aqueous solution, which was developed by Sarbolouki.[22]

The surface porosity, ε, of the membrane was calculated by the orifice model given below assuming that only the skin layer of the membrane is effective in separation[23]

$$\varepsilon = \frac{3\pi\mu J_W}{\Delta P \bar{R}}$$

where μ is the viscosity of the permeate water in (Pa s), J_w the pure water flux of the membrane in ($m^3\ m^{-2}\ s^{-1}$),

$\bar{R}$ the average pore radius in (Å), and ΔP is the transmembrane pressure in (Pa).

Molecular weight cut-off and protein rejection

Molecular weight cut-off (MWCO) is an attribute of pore size of the membranes and is related to the rejection of a spherical solute of given molecular weight. The MWCO has a linear relationship with the pore size of the membrane.[24] In general, the MWCO of the membrane is determined by identifying an inert solute of lowest molecular weight that has a solute rejection of 80–100% in steady state UF experiments.[21] Thus, the proteins of different molecular weights such as trypsin (20 kDa), pepsin (35 kDa), EA (45 kDa), and BSA (69 kDa) were chosen for the estimation of MWCO. All the protein solutions were prepared individually at a concentration of 0.1 wt % in phosphate buffer (0.5*M*, pH 7.2) using deionized and distilled water and used as standard solutions and filtered through each membrane individually. The permeate protein concentration, collected over measured time intervals, was estimated using UV–visible spectrophotometer (Hitachi, Model U-2000) at a wavelength of 280 nm. The percentage solute rejection (%SR) was calculated from the concentration of the feed (C_f) and the concentrate of the permeate (C_p) with the following equation:

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

where C_p and C_f are the concentrations of permeate and feed solutions, respectively.

RESULTS AND DISCUSSION

UF membranes based on CA and SPEI with various compositions were prepared. The composition of SPEI in blend solution was varied from 0 to 25 wt % of the 17.5 wt % polymer concentration in the casting solution. A further increase in SPEI content in blend, that is, beyond 25%, resulted in phase separation of the blend, due to incompatibility between CA and SPEI. This means that the composition enters into the unstable region quickly. Hence, the composition of SPEI in the blend-casting solution studies was restricted up to 25 wt % of the 17.5 wt % of polymer concentration in the casting solution. Thus, compositions of 0–25 wt % SPEI in CA were selected for further studies. Furthermore, the hydrophilic polymeric additive, pore former, PEG 600 concentrations in the polymer-casting solution were varied from 2.5 wt % in an increment of 2.5 wt % for all the polymer blend solutions, and the maximum compatible additive concentration was found to be

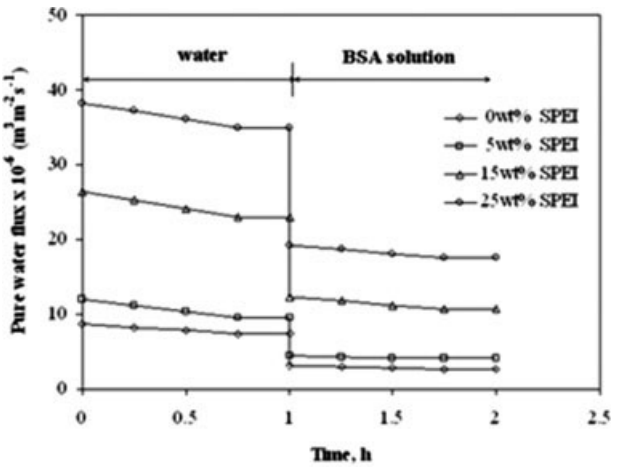

Figure 2 Effect of SPEI concentration in casting solution on the flux of the CA/SPEI blend membranes.

10 wt %. Beyond this concentration, all the polymer blend solutions exhibited incompatibility with the additive as soon as solution blending was mechanically arrested. Hence, the maximum additive concentration in the present system was restricted to 10 wt %. The effects of CA/SPEI blend composition and concentration of polymeric additive PEG600 in the casting solution on the rejection and permeate flux of proteins such as BSA, EA, pepsin, and trypsin were discussed. The surface properties such as fouling, morphology, MWCO, average pore size, and porosity of blend membranes were also reported.

Fouling studies

Effect of SPEI concentration in casting solution on the protein solution permeate flux was carried out to study the fouling properties of pure CA and CA/SPEI blend membranes. Figure 2 shows the effect of SPEI concentration on flux of pure CA and CA/SPEI blend membranes, respectively. It can be seen that the pure water fluxes (J_w) before UF of the BSA solution change little during filtration. The flux decreased dramatically at the initial operation of BSA solution UF due to protein adsorption or convective deposition. It is proposed that some protein molecules in the feed will deposit or adsorb on the membrane surface (cake formation), causing a drop in flux in the 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 this work, the concentration polarization was minimized, because there was rigorous stirring near the membrane surface and the high molecular weight of BSA molecules. Therefore, the membrane fouling mostly caused the flux decline of the membranes.

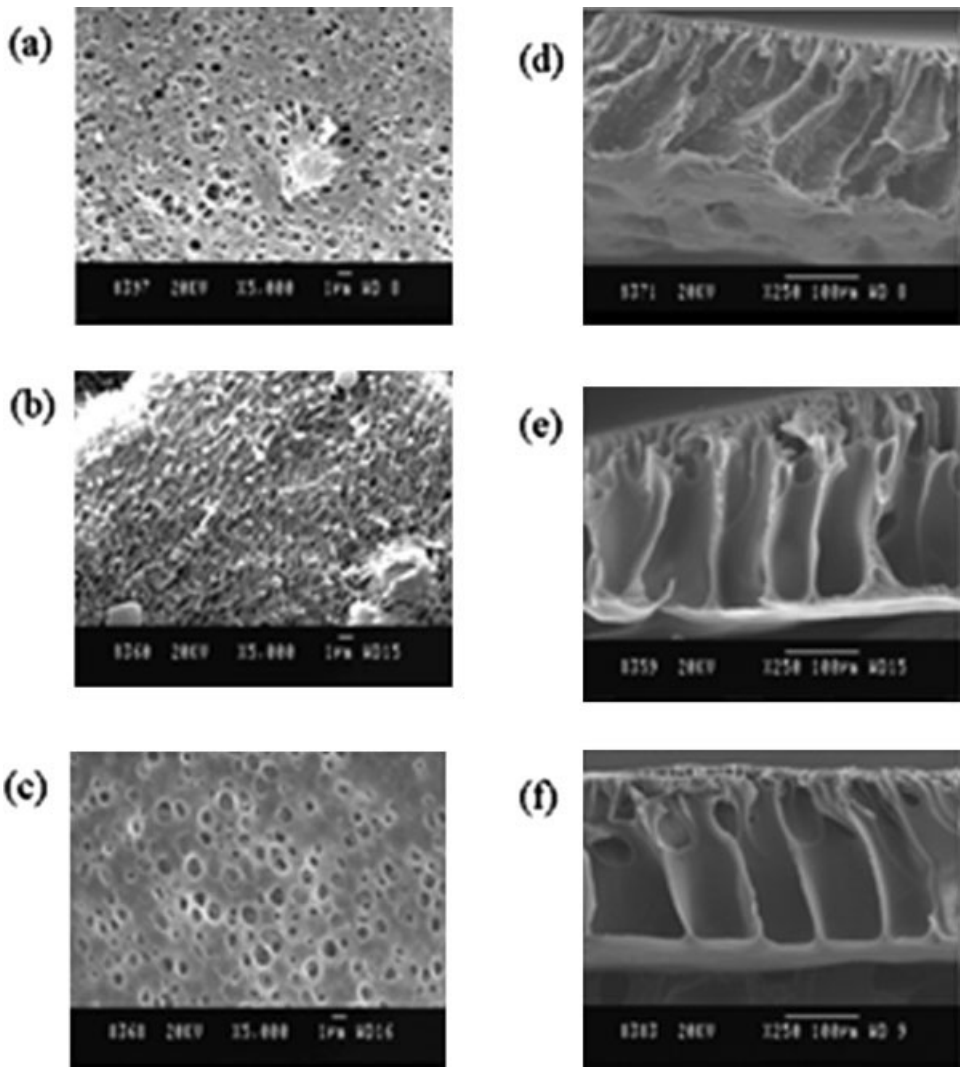

Figure 3 SEM micrographs of CA/SPEI (75/25 wt %) blend membranes with different concentrations of additive, PEG 600. Top surface (5000×): (a) 0 wt %; (b) 5 wt %; (c) 10 wt %, cross section (250×); (d) 0 wt %; (e) 5 wt %; (f) 10 wt %.

The membrane fouling in the UF was due to the deposition of protein on the membrane surface by adsorption and aggregation, which blocked membrane pores to some extent.

R_{FD} value is introduced to reflect the resistant fouling ability of the membrane; the lower value of R_{FD} means the higher resistant fouling ability of the membrane. For the CA/SPEI blend membranes, the R_{FD} values were 63.9%, 57.4%, 53.7%, and 49.9% when the concentrations of SPEI in the blend membrane were 0, 5, 15, and 25 wt %, respectively. It indicates that the ability of fouling resistance increases with an addition of SPEI in casting solution. This is due to more hydrophilic sulfonic groups get enriched at membrane surface, which is well agreed with water content of CA/SPEI blend membrane surfaces.[25]

Morphological studies

The protein rejection and protein solution permeate flux of CA/SPEI blend membranes in the absence and presence of PEG600 additive are shown in Figures 4–7. When the concentration of PEG600 additive increases in CA/SPEI blend membranes, protein rejection decreases and protein solution permeate flux increases as shown in Figures 5 and 7. To understand the permeation results, the top surface and cross section morphologies of the blend membranes prepared were carefully studied with SEM. The micrographs of the top surfaces and cross sections of CA/SPEI (75/25 wt %) blend membranes in the presence and absence of PEG600 additive are shown in Figure 3(a–f).

In the SEM observations and permeation properties measured, when the PEG600 additive increases

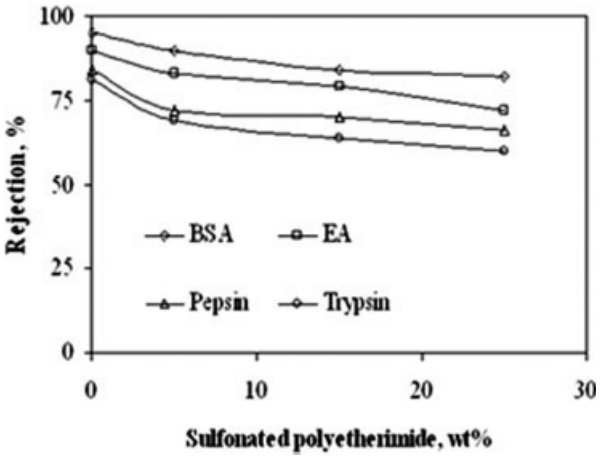

Figure 4 Effect of concentration of SPEI on percent rejection of proteins for CA membranes.

from 0 to 10 wt %, the pore size of the top surface becomes bigger, and the distance from the top surface to the starting point of the macrovoid formation becomes larger. The macrovoid formation in the cross section is suppressed by increasing the concentration of PEG600 additive. The SEM observations also illustrate that the decrease in protein rejection and increase in protein solution permeate flux are largely influenced by the increase in the pore size of the top surface and the porosity of the top layer. The membrane morphologies and permeation results in Figures 3–7 agree well with early studies on the role of various additives: the pore-forming agents enhancing permeation properties. The results appear to suggest that the change of PEG600 concentration may be used to prepare the desire membrane for UF.

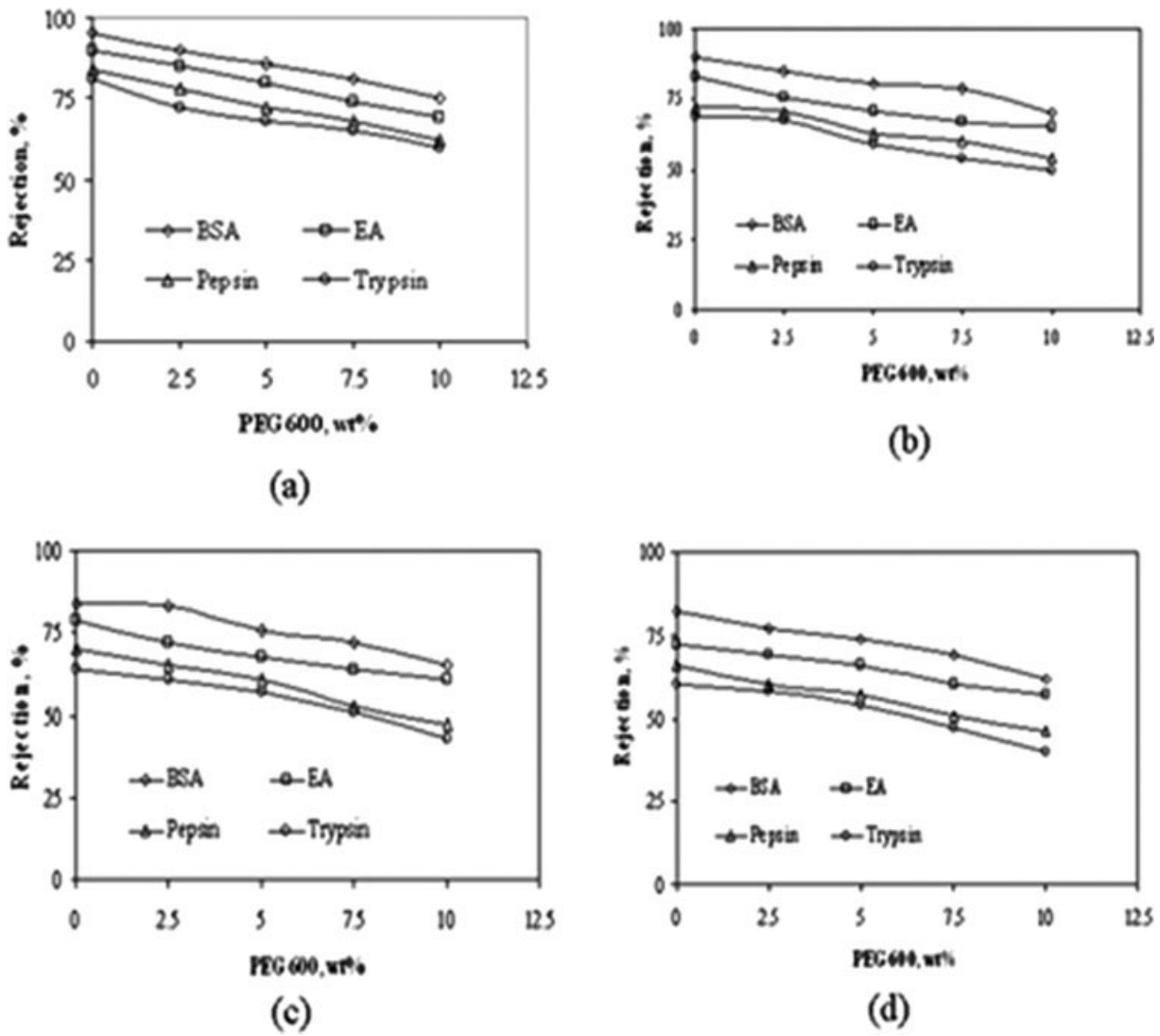

Figure 5 Effect of concentration of PEG600 on percent rejection of proteins: (a) pure cellulose acetate, (b) 95/5 wt % CA/SPEI, (c) 85/15 wt % CA/SPEI, and (d) 75/25 wt % CA/SPEI.

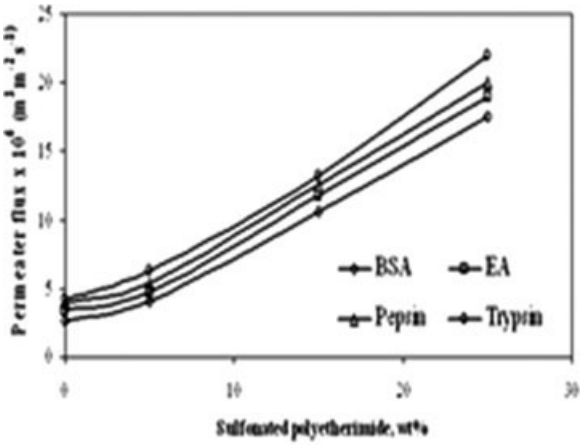

Figure 6 Effect of concentration of SPEI on permeate flux of proteins for CA membranes.

It has been generally accepted as a common rule that thermodynamically less stable membrane-forming systems can make more porous membranes.[26–28] Membrane morphologies in this study may apparently seem to follow the common rule. The increase in the pore size and the porosity of top layer observed in this study can be explained quantitatively by the ratio of nonsolvent inflow to solvent outflow suggested by Young et al.[29,30] With increasing ratio of PEG600 to NMP, nonsolvent (water) inflow and outflow of solvent (NMP) of the top layer is changed greatly. With the existence of a larger amount of PEG600 disturbs the aggregation of the polymer molecules in the top layer resulting in the same effect as when the ratio of nonsolvent inflow to solvent outflow increases, thus yielding a

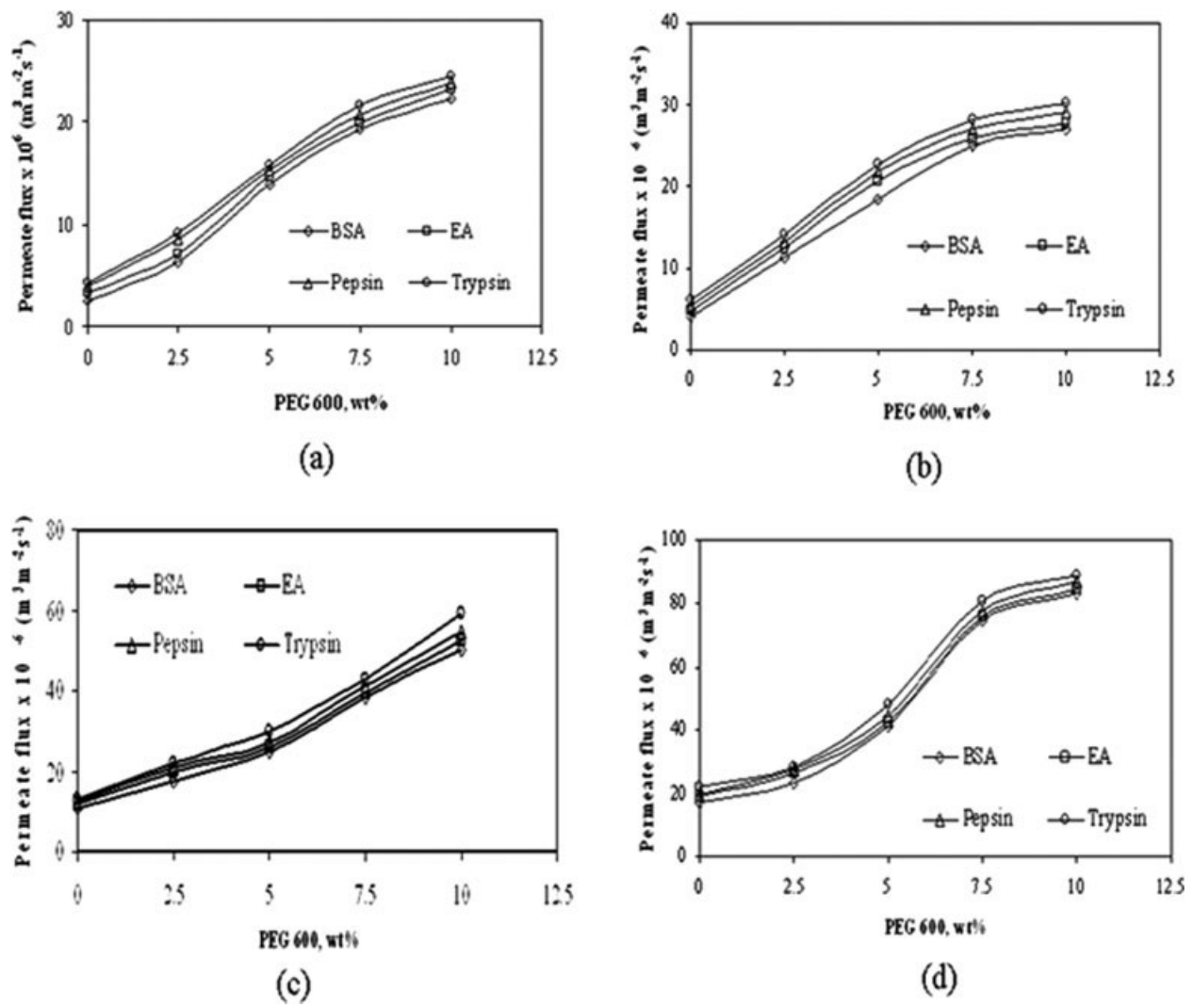

Figure 7 Effect of concentration of PEG600 on permeate flux of proteins: (a) pure cellulose acetate, (b) 95/5 wt % CA/SPEI, (c) 85/15 wt % CA/SPEI, and (d) 75/25 wt % CA/SPEI.

TABLE I
Average Pore Size and Surface Porosity of CA/SPEI Blend Membranes

Polymer composition (17.5 wt %)		Additive	Solvent				
CA (wt %)	SPEI (wt %)	PEG600 (wt %)	NMP (wt %)	% SR	MWCO (kDa)	Pore radius R (Å)	Porosity ε (%)
100	0	0	82.5	81	20	34.57	0.033
95	5	0	82.5	83	45	48.19	0.042
85	15	0	82.5	84	69	64.29	0.045
75	25	0	82.5	82	69	65.85	0.073
100	0	2.5	80	85	45	47.06	0.041
95	5	2.5	80	85	69	58.82	0.053
85	15	2.5	80	83	69	64.46	0.073
75	25	2.5	80	77	>69	69.48	0.093
100	0	5	77.5	86	69	56.98	0.067
95	5	5	77.5	81	69	65.43	0.076
85	15	5	77.5	76	>69	68.42	0.099
75	25	5	77.5	74	>69	70.27	0.160
100	0	7.5	75	81	69	65.43	0.080
95	5	7.5	75	79	>69	65.82	0.104
85	15	7.5	75	72	>69	72.22	0.144
75	25	7.5	75	69	>69	75.36	0.270
100	0	10	72.5	75	>69	69.33	0.088
95	5	10	72.5	70	>69	74.29	0.099
85	15	10	72.5	65	>69	80.00	0.172
75	25	10	72.5	62	>69	83.87	0.271

membrane with more porous top layer and possibly, more porous sublayer.

Molecular weight cut-off

Effect of concentration of SPEI

Pure CA membrane without additive, PEG 600, had the MWCO of 20 kDa. It is also evident from Table I that the MWCO values are dependent on the polymer composition. Thus, in the CA/SPEI blend membranes, in absence of additive, as the sulfonated PEI content was increased from 5 to 25 wt %, the MWCO value also increased from 45 to 69 kDa. This increase in MWCO value may be due to the formation of a segmental gap and the partial phase separation upon proportionately increasing the concentration of SPEI in the blend. Similar results have been observed for CA and SPEEK blend membranes, with various blend compositions and found successful in protein-rejection applications.[31]

Effect of concentration of PEG 600

The MWCO values had a change in magnitude when additive was added into the casting solution of CA/SPEI blend membranes. Thus, for pure CA (100%) membranes, when the additive concentration was increased, from 2.5 to 10 wt %, the MWCO values enhanced from 45 to greater than 69 kDa. Various additive concentrations have significant effect on MWCO of the CA/SPEI blend membranes. It is evident from Table I that for a given blend composition, an increase in the additive concentration increased the MWCO linearly. Similar observations were also observed for the other two blend compositions. Furthermore, for a given additive concentration of 2.5 wt %, as the sulfonated PEI content in the blend was increased from 5 to 25%, the MWCO also increased from 69 to greater than 69 kDa. The membranes with other additive concentrations such as 5, 7.5, and 10 wt % also exhibited similar behavior, as shown in Table I. The increase in MWCO with increasing PEG600 may be due to fast rate of leachability of PEG600 during gelation process, which leaves a large pore on membrane surface as evidenced from SEM results (Fig. 3). This is in good agreement with the trend observed for pore size studies carried out for CA/SPEI blend membranes. Similar results have also been observed for CA/SPSf blend membranes by Malaisamy et al.[21]

Pore size and porosity of the membranes

Effect of concentration of SPEI

In the CA/SPEI blend membrane system, the increase in SPEI composition from 5 to 25 wt % yielded changes in pore statistics. The pore size and porosity of the membranes determined from the protein rejection studies are shown in Table I. It is evident from these results that the pure CA (100%)

membrane prepared in the absence of SPEI has relatively smaller pore size and porosity. Addition of 5–25 wt % SPEI into the casting solution induced the formation of bigger pore size. Increase in the pore size and porosity, in principle, would lead to the increase in the permeate flux of the membrane. This is in good agreement with the results obtained in this study. Further additions of SPEI resulted in the increase of the pore size and porosity. It should be noted that the porosity and pore size increased to a maximum of 0.073% and 65.85 Å, respectively, for a 25 wt % of SPEI content. Although bigger pore size will favor high permeate flux, the solute rejection will drastically fall.

Effect of concentration of PEG 600

The addition of PEG600 to the CA/SPEI blend membranes has changed the pore statistics to a substantial level. The effect of variation of PEG600 on porosity and pore size of blend membranes are shown in Table I. The porosity increases from 0.053 to 0.099%, and the pore size increases from 58.82 to 74.29 Å with increase in the concentration of the pore-forming additive, PEG600 from 2.5 to 10 wt % in 95/5 wt % CA/SPEI blend membrane. The membranes with 85/15 and 75/25 wt % CA/SPEI blend composition also exhibited similar trend. Similarly, for a given additive concentration, for example, 2.5 wt %, when the SPEI content was increased from 5 to 25 wt % in the membrane, the porosity and pore size were found to increase from 0.053 to 0.093% and 58.82 to 69.48 Å, respectively. The membranes with other additive concentrations such as 5, 7.5, and 10 wt % also exhibited similar behavior, as shown in Table I. This was due to the leaching of the additive from the membrane surface during gelation. This is in good agreement with the trend observed for proteins permeate flux studies carried out for CA/SPEI blend membranes. Similar results have also been observed for PU/SPSf and CA/LCD PSf blend UF membranes.[32,33]

Protein rejection

Effect of concentration of SPEI

The composition of the polymer blend membrane had the effect of altering the protein-rejection efficiency. Thus, when the SPEI content in the blend membrane was increased from 5 to 25 wt % in the absence of additive, the percentage rejection of BSA reduced from 90 to 82% as shown in Figure 4. Rejection of all other proteins also decreased with increase in the SPEI content in the blend membranes. The rejection decreased in the order BSA > EA > pepsin > trypsin. This may be due to the fact that the higher SPEI content creates inhomogeneity between polymer matrices resulting in the formation of pores in the membrane. Similar results, showing low protein rejection, were observed for modified polysulfone membranes.[8] For all of the above membranes, BSA exhibited a higher separation and trypsin exhibited a lower separation, which is due to the higher molecular weight of 69 kDa and lower molecular weight of 20 kDa of the respective proteins. Thus, the size of the solute played a major role in the separation performance.

Effect of concentration of PEG 600

The effect of concentration of PEG600 on the protein rejection behavior of pure CA and CA/SPEI membranes are shown in Figure 5(a–d), and it was observed that pure CA membranes exhibited a decrease in rejection behavior from 90 to 75% when the additive concentration was increased from 2.5 to 10 wt % for BSA as shown in Figure 5(a). In CA/SPEI blend membranes of 95/5 wt % composition, for BSA, as the additive concentration was increased from 2.5 to 10 wt %, the rejection decreased linearly from 85 to 70% as shown in Figure 5(b). A similar trend was observed for other proteins. The membranes with 85/15 and 75/25 wt % CA/SPEI blend composition also exhibited similar trend toward all the protein molecules as shown in Figure 5(c,d). This may probably be due to the increase in size of the pores at higher end of additive concentration due to leaching during gelation. The pure water flux studies carried out for these membranes exhibited a similar trend. Comparable results have also been obtained by other researchers.[34]

Similarly for a given additive concentration, for example, 2.5 wt %, when the SPEI content was increased from 5 to 25 wt % in the membrane, the rejection of BSA was found to decrease from 85 to 77%. The membranes with other additive concentrations such as 5, 7.5, and 10 wt % also exhibited similar behavior. Furthermore, in all the above studies, BSA exhibited a maximum rejection of 85% by CA/SPEI blend membrane with 95/5 wt % composition and at 2.5 wt % additive concentration, whereas trypsin exhibited the lowest rejection of 40% by the membranes with 75/25 wt % composition with 10 wt % additive concentration. The higher percentage rejection of BSA and lower percentage rejection of trypsin are obviously due to their molecular sizes. Similar results were reported for CA/polyethersulfone/PEG 600 blend membranes by Mahendran et al.[35]

Protein solution permeate flux

Effect of concentration of SPEI

The permeate flux of the proteins BSA, EA, pepsin, and trypsin by the 100/0, 95/5, 85/15, and 75/25 wt %

CA/SPEI blend membranes in the absence and presence of additive is shown in Figures 6 and 7(a–d). The pure CA (100%) membrane, in the absence of additive, showed the lowest permeate flux of 2.60×10^{-6} m^3 m^{-2} s^{-1} for BSA. The other proteins, EA, pepsin, and trypsin, showed comparatively higher fluxes with the pure CA membranes. For the CA/SPEI blend membranes, without additive, for a given protein molecule (e.g., BSA), when the SPEI content in the blend was increased from 5 to 25%, the flux also increased from 4.03 to 17.50×10^{-6} m^3 m^{-2} s^{-1} as shown in Figure 6. A similar trend was observed for other proteins. This trend may be due to the hydrophilic SPEI, which could reduce fouling of protein thereby enhancing the product rate.

Effect of concentration of PEG 600

The presence of additive in the casting solution has a significant role in the morphology and, in turn, on flux, of resulting membranes. Thus, the pure CA membrane for a given protein molecule had an enhanced flux when the additive was increased from 2.5 to 10 wt %, as shown in Figure 7(a). In the pure CA (100%) membrane, BSA had a flux of 6.36×10^{-6} m^3 m^{-2} s^{-1} for 2.5 wt % PEG 600 and 22.22×10^{-6} m^3 m^{-2} s^{-1} for 10 wt % PEG 600. The other proteins also exhibited a similar trend. For the 95/5% CA/SPEI blend membrane, the increase of additive from 2.5 to 10 wt % increased the protein permeate flux from 11.42 to 27.00×10^{-6} m^3 m^{-2} s^{-1} for BSA, as shown in Figure 7(b). All of the other blend compositions also exhibited similar behavior when the additive was increased from 2.5 to 10 wt %, as shown in Figure 7(c,d). A similar trend was also observed for the other proteins. This may have been due to the formation of macrovoids in the membrane, due to the faster rate of leaching out of the additive during gelation. In all the membranes, regardless of the additive concentration and polymer blend composition, the order of protein flux was trypsin > pepsin > EA > BSA. The reason for this trend may be explained by the fact that the permeate flux of the proteins was inversely proportional to their size.

CONCLUSIONS

In this work, protein separation has been studied using modified CA membranes prepared by blending CA with SPEI in the presence and absence of hydrophilic polymeric additive, PEG600 in different concentrations. In general, all the modified membranes exhibited improved permeate flux for protein separation compared to the pure CA membranes. Permeate flux increases as a function of concentration of SPEI and PEG600. However, increasing concentrations of SPEI and PEG600 in the membrane-casting solution resulted in decreased rejection of proteins. The MWCO and pore statistics results obtained from protein-rejection studies and pure water flux demonstrate that the MWCO, pore radius, and porosity show significant increases with increasing concentration of SPEI and PEG600 in the casting solution. SEM analysis showed that in the blend membranes, the pore size increased with increasing SPEI content in the casting solution. It has also been concluded that the mixture of SPEI into the blend system changes the morphology of the membranes extensively. The fouling property of CA/SPEI blend membrane reduced considerably due to the increased sulfonic group concentration at the surface of membranes with an increase of SPEI concentration in the membrane-casting solution.

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