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Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

Ultrafiltration Application of Cellulose Acetate and Aminated Polyethersulfone Blend Membranes

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ABSTRACT: Fouling–resistant cellulose acetate (CA) membranes were prepared by the phase inversion technique using hydrophilic aminated polyethersulfone (APES) as the modification agent. In the presence of polyethylene glycol 600 as a pore forming agent, were blended in 100/0,90/10,80/20,70/30% compositions using N,N'- dimethylformamide as solvent. The cellulose acetate/aminated polyethersulfone membranes were applied for proteins separations. The performance of the blend membranes of various blend polymer compositions were compared with that of membranes prepared from pure cellulose acetate and blends of cellulose acetate and aminated polyethersulfone. The hydrophilic blend ultrafiltration membranes showed better performance compared to pure cellulose acetate.

KEYWORDS: Cellulose acetate, Aminated polyethersulfone, Polyethyleneglycol 600, Ultrafiltration, Proteins.

I. INTRODUCTION

Polymeric materials and their blends have played an important role in many separation applications such as ultrafiltration (UF), microfiltration, and nanofiltration [1,2,3]. UF is usually applied to a membrane separation process where the solute dimensions are significantly larger than the solvent dimensions. UF has been widely used for product recovery and pollution control in the chemical, electrocoating, electronic, metal refining as well as in the food, pharmaceutical, and biotechnological industries [4,5]. Indeed, UF is a membrane technique commonly used to separate and concentrate high molecular weight species present in solution [6]. The use of membrane separation process in the treatment of wastewater and groundwater containing toxic metal ions is an attractive and suitable technique, since it offers concentration and separation of metals or valuable chemicals without a change of state and without the use of chemicals or thermal energy [7,8]. However, application of cellulose acetate membrane to processes with increasingly diversified macromolecular components requires the modifcation of cellulose acetate with balanced hydrophilic-hydrophobic moiety [9]. Since aminated polyethersulfone show high porosity, low weight to volume ratio, good resilience character, abrasion resistance and oil resistance, they can be incorporated in cellulose acetate to introduce balanced hydrophilicity in the resultant blend membrane and hence achieve optimum membrane performance in terms of better rejection and flux. Hence, in the present investigation, cellulose acetate was blended with aminated polyethersulfone (APES) in polar medium and the results are discussed in terms of separation of proteins and permeate flux studies.

II. EXPERIMENT

Commerical grade MYCEL cellulose acetate CDA 5770 (acetyl content 39.99 wt%) procured from Mysore Acetate and Chemicals Company Ltd., India and commercial grade polyethersulfone (Gafone 3300) obtained, as a gift sample, by Gharda Chemicals Pvt Ltd., India were used as supplied. Analar grade N,N-Dimethyl formamide (DMF) from Qualigens Fine Chemicals, Glaxo India Ltd. was sieved through molecular sieves (Type-4A°) to remove moisture and stored in dry conditions prior to use. Other solvents of analar grade such as acetone and methanol from Qualigens Fine Chemicals Ltd., India were used as supplied. Sodium lauryl sulphate (SLS) of analar grade was obtained from

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Qualigens Fine Chemicals Ltd., India and was used as surfactant. Polyethylene glycol 600 (PEG 600) was procured from Merck (I) Ltd., and was used as supplied, as a non-solvent additive for the whole study. Proteins, namely, bovine serum albumin (Mw=69 kDa), pepsin (Mw=35 kDa), trypsin (Mw=20 kDa) were purchased from SRL Chemicals Ltd., India and used as received. Egg albumin (Mw=45 kDa) was obtained from CSIR Bio Chemical Centre, New Delhi, India.

III. PREPARATION OF SOLUTION BLENDING OF POLYMERS AND MEMBRANES

Preparation of solution blending of polymers

The blend solutions based on cellulose acetate and aminated polyethersulfone polymers at a total polymer concentration of 17.5 wt%, were prepared by dissolving the two polymers in different compositions (Table 1) in presence and absence of additive, PEG 600 in a polar solvent, DMF, under constant mechanical stirring at a moderate speed of rotation in a round bottom flask for 3–4 hr at 40°C. The homogeneous solution obtained was allowed to stand for at least 3 hr in an air tight condition to get rid of air bubbles.

Membrane preparation

The method of preparation involved is the same as that of the "phase inversion" method employed in earlier works as reported by other researchers [10]. 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±1°C and a relative humidity of 50±2%.The total polymer concentration was maintained at 17.5wt% 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 [11]. Prior to casting, a 2L gelation bath, consisting of 2.5% (v/v) NMP solvent (to reduce the rate of liquid–liquid demixing and macrovoids) and 0.2wt% surfactant, SLS (to reduce surface tension at the polymer–nonsolvent interface) in distilled water (nonsolvent) was prepared and kept at 20±1°C.

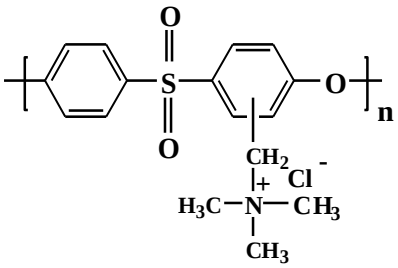

Fig. 1. Aminated polyethersulfone

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 sec, 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.

Protein rejection studies

The rejection of the proteins BSA, EA, pepsin, and trypsin were attempted individually with the blend Membranes. The CA/APES blend membranes with compositions of 90/10, 80/20, and 70/30% in the presence and absence of different additive concentrations of PEG 600 were used for the rejection of proteins under a nitrogen atmosphere, and the results were compared with the rejection by the pure CA membranes[12]. Initially, a protein of low molecular weight, trypsin,

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was used for the ultrafiltration experiments because we expected the use of a high-molecular- weight protein at the beginning would spoil the originality of the pores for the separation and comparison of low-molecular-weight proteins. Thus, the rejection of proteins were performed in the order trypsin, pepsin, EA, and BSA. The percentage solute rejection (% SR) was calculated from the concentration of the feed (Cf) and the concentrate of the permeate (Cp) with the following equation:

IV. RESULTS AND DISCUSSION

The different compositions of cellulose acetate/aminated polyethersulfone blend membranes were prepared both in the presence and absence of different concentrations of additive PEG 600. The membrane with polymer composition 80/20 (CA/APES) which gave the best results was chosen for further studies. The effect of different concentrations of additive, PEG 600 on the performance of CA/APES blend membranes are discussed.

The rejection of proteins

The proteins BSA, EA, pepsin, and trypsin by the 100/0, 90/10, 80/20, and 70/30% CA/APES blend membranes in the absence of the additive is shown in Figures 2and 3.

Role of the polymer blend composition and additive

The composition of the polymer blend membrane had the effect of altering the protein rejection efficiency. The pure CA membrane exhibited rejections of 97% for BSA and 76% for trypsin.
The higher rejection of BSA may have been due to the larger size of the BSA compared with trypsin. As the APES composition was increased from 10 to 30% in the CA/APES blend in the absence of any additive, the percentage rejection decreased. This may have been because the higher APES content created inhomogeneity between the polymer matrices, resulting in the formation of aggregate pores in the membranes[13,14]. For the 80/20% blend composition, the percentage rejection values were 94, 88, 70, and 66 % for BSA, EA, pepsin, and trypsin, respectively. The decrease in rejection may have been the decrease in the solute size of the proteins in the aforementioned order.

The effects of the additive (PEG 600) concentration on the rejection of the blend membranes is shown in Table I. The additive concentration was increased, from 2.5 to 10 wt %, in each blend composition, and the percentage rejection decreased. For the 100% CA membrane with 2.5 wt % additive, the BSA rejection was 94%, and it decreased to 82% with the increase of the additive concentration to 10 wt %. A similar trend was also observed for other proteins, with varying magnitudes. This may have been due to the leaching out of the additive (PEG 600) from the membranes during gelation, which created pores proportionately on the membrane. In the CA/APES blend membranes also, for a given polymer composition, when the additive concentration was increased, from 2.5 to 10 wt %, the separation efficiency decreased. All of the blend membranes with various additive concentrations showed similar trends for all of the protein molecules. The higher percentage rejection of BSA and the lower percentage rejection of trypsin was obviously due to their molecular sizes.

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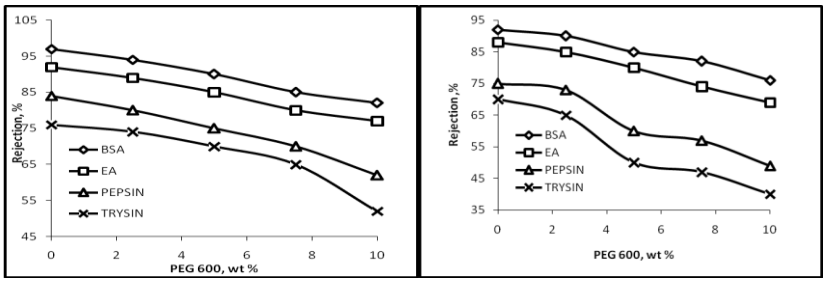
TABLE I
% SR by CA/APES Blend Membranes

Blend Composition		Additive	Percent rejection of Proteins			
CA	APES	PEG 600	BSA	EA	Pepsin	Trypsin
100	0	0	97	92	84	76
90	10	0	92	88	75	70
80	20	0	94	88	70	66
70	30	0	85	84	68	60
100	0	2.5	94	89	80	74
90	10	2.5	90	85	73	65
80	20	2.5	90	85	68	60
70	30	2.5	80	80	65	58
100	0	5	90	85	75	70
90	10	5	85	80	60	50
80	20	5	85	78	55	50
70	30	5	75	71	50	50
100	0	7.5	85	80	70	65
90	10	7.5	82	74	57	47
80	20	7.5	75	70	51	46
70	30	7.5	67	62	45	45
100	0	10	82	77	62	52
90	10	10	76	69	49	40
80	20	10	71	65	42	39
70	30	10	60	58	40	40



(a) (b)

Fig. 2. (a) Rejection of proteins CA (100 wt%) membranes (b) Rejection of proteins CA /APES (90/10 wt%) membranes

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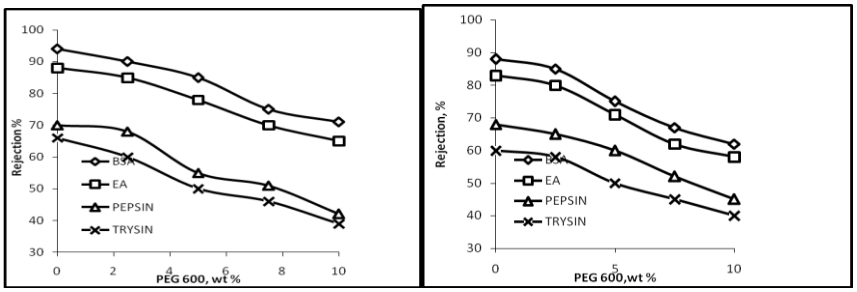
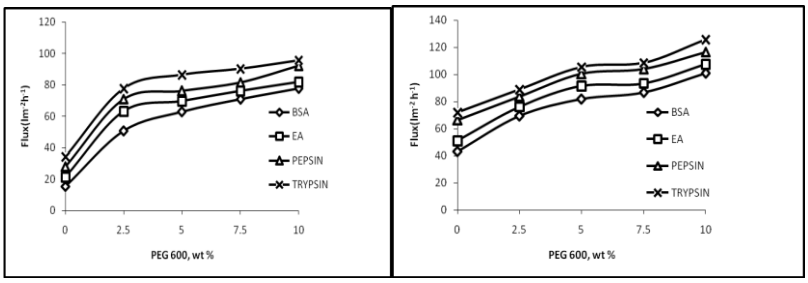


(c) (d)

Fig. 3 (c) Rejection of proteins CA /APES (80/20 wt%) membranes (d)Rejection of proteins CA /APES (70/30 wt%) membranes

Protein flux studies

The permeate protein flux is the measure of the product rate of the membrane for the given protein solutions. Role of the polymer blend composition and additive concentration on the product rate efficiency of the proteins. The permeate flux of the proteins BSA, EA, pepsin,and trypsin by the 100/0, 90/10, 80/20, and 70/30% CA/APES blend membranes in the absence of the additive is shown in Figures 4 a,b. The pure 100% CA membrane, in the absence of additive,



(a) (b)

Fig. 4. (a) Flux of proteins CA (100 wt%) membranes (b)Flux of proteins CA /APES (80/20 wt%) membranes

showed the lowest permeate flux of 17.3 $lm^{-2}h^{-1}$ for BSA as shown in Figure 4a and 4b. The other proteins, EA, pepsin, and trypsin, showed comparatively higher fluxes with the pure CA membranes. For the CA/APES blend membranes, without additive, for a given protein molecule (e.g., BSA), when the APES content in the blend was increased, from 10 to 30%, the flux also increased from 24.4 to 59.3 $lm^{-2}h^{-1}$. A similar trend was observed for all of the proteins. This trend may have been due to the hydrophilic APES, which could have reduced the fouling of protein, thereby enhancing the product rate efficiency. The presence of additive in the casting solution had a significant role in the morphology and, in turn, on the flux of the 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 %.

In the 100% CA membrane, BSA had a flux of 50.6 $lm^{-2}h^{-1}$ for 2.5 wt % PEG 600 and 78.5 $lm^{-2}h^{-1}$ for 10 wt % PEG 600. The other proteins also exhibited a similar trend[15]. For the 80/20% CA/APES blend membrane , the increase of additive from 2.5 to 10 wt % increased the protein permeate flux from 74.2 to 100.9 $lm^{-2}h^{-1}$ for BSA as shown in Figures 3a and 3b. All of the other blend compositions also exhibited similar behaviour when the additive was increased from 2.5 to 10 wt %,.. 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 of 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 flux of the proteins was inversely proportional to their size.

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V. CONCLUSION

In this work, protein separation has been studied using modified CA membranes prepared by blending CA with APES 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 APES and PEG600. However, increasing concentrations of APES and PEG600 in the membrane casting solution resulted in decreased rejection of proteins. The fouling property of CA/APES blend membrane reduced considerably due to the increased amine group concentration at the surface of membranes with an increase of APES concentration in the membrane-casting solution.

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