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R. Mahendran[a]; R. Malaisamy[a]; D. Mohan[a]
[a] Department of Chemical Engineering Membrane Laboratory, Anna University, Chennai, India

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CELLULOSE ACETATE AND EPOXY RESIN BLEND ULTRAFILTRATION MEMBRANES: PREPARATION, CHARACTERIZATION, AND APPLICATION

R. Mahendran, R. Malaisamy, and D. Mohan*

Membrane Laboratory, Department of Chemical Engineering,
Anna University, Chennai 600 025, India

ABSTRACT

Membranes based on cellulose acetate used in ultrafiltration applications lack good, chemical, mechanical and thermal resistance. In order to prepare membranes with improved properties, modification of cellulose acetate with epoxy resin through solution blending was attempted. In the present work, the membrane casting solutions with different polymer blend compositions of cellulose acetate and diglycidyl ether of bisphenol-A (DGEBA) were prepared at $30 \pm 2^{\circ}C$. The maximum percent compatibility of the two polymers, cellulose acetate and diglycidyl ether of bisphenol-A, was estimated to be 60/40%. Ultrafiltration blend membranes based on various blend compositions were prepared, characterized in terms of compaction, pure water flux, water content, membrane hydraulic resistance and molecular weight cut-off. The application of these membranes, in rejection of proteins of various molecular weights, are discussed.

Key Words: Ultrafiltration; Blend membranes; Proteins separation; Modified membrane

*Corresponding author. E-mail: mohantarun@yahoo.com

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INTRODUCTION

Cellulose acetate was one of the first membrane polymers that has been used for aqueous based separation and used as both reverse osmosis (RO) and ultrafiltration (UF) membranes.[1] The requirement of more aggressive cleaning and sanitizing agents and more chemical and mechanical resistant membranes, led to the necessity of modifying cellulose acetate based membranes.[2] The hydrophilic/hydrophobic balance, as well as the physicochemical properties, of a membrane system can easily be changed if the membrane is prepared from multi-component polymer mixture/blends.[3]

The application of cellulose acetate membrane may be enhanced to processes with increasingly diversified macromolecular components through the modification of cellulose acetate with balanced hydrophilic-hydrophobic moiety. Cellulose acetate has been blended with polyurethane in different compositions, using DMF solvent as to prepare membranes and applied for the rejection of proteins and metal ions.[4] Further, CA has been found as a successful blend component with polysulfone and sulfonated polysulfone, in preparing ultrafiltration membranes.[5,6] In addition, CA has been blended with natural polymeric derivative, chitosan in trifluoro acetic acid solvent, and found compatible.[7] Reports on cellulose diacetate and cellulose triacetate blends in pure water flux and solute transport have been identified.[8] Similarly, diglycidyl ether of bisphenol-A, is being used as a successful composite material due to its superior qualities. These material also possesses high porosity, good resilence character, abrasion resistance and oil resistance. The hydrophilic nature of the resin, is expected to yield membrane of better performance in terms of pure water flux and hence, product rate in rejection studies. Similar investigations on membrane preparation and wettability studies of epoxidized polyurethane have been carried out and highlighted the effect of epoxy group on performance.[9] The DGEBA, the simple epoxy resin (ER) can be blended with cellulose acetate to introduce hydrophilicity in the resultant blend membrane and optimum membrane performance can be achieved in terms of better solute rejection and flux. Further, separation of proteins by membrane was found to be advantageous due to the non-destructive nature and limiting denaturation of proteins of the process.[10] As the ER is hydrophilic in nature, the blending of ER with CA, would substantially reduce the fouling behavior of the resulting membranes. Earlier studies have shown that the increase in hydrophilicity will reduce the fouling behavior and increase the flux.[11,12] Furthermore, blending would enhance chemical stability of the membrane due to the epoxy resin.

Hence, in the present investigation, cellulose acetate was blended with epoxy resin in polar medium and the membrane compaction, pure water flux, water content, membrane resistance (R_m), molecular weight cut-off (MWCO) and protein rejection were determined and the results are discussed.

EXPERIMENTAL

Materials

Cellulose acetate (CA) was procured from Mysore Acetate & Chemical Co. Ltd, India; Epoxy resin (ER) LY 556 (DGEBA) was procured from Ciba-Geigy; solvent N,N-dimethyl formamide (DMF) (AR) was obtained from CDH Ltd, India. Sodium monobasicphosphate anhydrous and sodium dibasicphosphate heptahydrate were procured from CDH Chemicals Ltd., India and used for the preparation of phosphate buffer solutions in protein analysis. Proteins viz., BovineSerum Albumin (BSA), $\bar{M}_w = 69\,kDa$, Pepsin, $\bar{M}_w = 35\,kDa$, Trypsin, $\bar{M}_w = 20\,kDa$ were purchased from SRL Chemicals Ltd., India and used as received. Egg Albumin (EA), $\bar{M}_w = 45\,kDa$ was obtained from CSIR Bio-Chemical Centre, New Delhi, India. Deionized and distilled water was employed for the preparation of protein solutions and also used for the preparation of gelation bath.

Preparation and Characterization of the Membrane

Cellulose acetate and epoxy resin were blended in different proportions (Table 1) using DMF as solvent by thoroughly mixing for 4 h at $30 \pm 2°C$. The casting solutions were kept standing for an hour in order to eliminate the air bubbles. The casting solution was poured over a glass plate and the membranes were cast using a stainless steel casting blade with an oily sheet attached with desired thickness of the membranes. The casting was carried out at $24 \pm 2°C$ and the relative humidity was kept at 50–55%. The membranes were gelled in non-solvent (H_2O) as reported earlier.[13] The thickness

Table 1. Characteristics of CA/ER Blend Membranes

Polymer Blend Composition (17.5 wt%)		PWF ($l.m^{-2}\ h^{-1}$) (345 kPa)	Water Content (Wt%)	R_m ($kPa.lm^{-2}\ h^{-1}$)	MWCO (kDa)
CA (%)	ER (%)				
100	0	13.4	78.3	0.25	35
95	5	19.3	81.3	0.25	–
90	10	20.5	81.3	0.24	35–45
85	15	25.2	82.3	0.20	–
80	20	28.4	83.3	0.15	45
75	25	35.3	83.5	0.10	–
70	30	49.2	84.3	0.08	45
65	35	54.7	84.1	0.07	–
60	40	63.8	84.4	0.06	69

of the membrane maintained in this work was 0.22 ± 0.02 mm as followed in earlier studies with blend membranes.[4,14]

Compaction

The membranes prepared were cut in to necessary size, to use in the ultrafiltration kit of 38.5 cm^2 effective membrane area and initially pressurized with distilled water at 414 kPa for 4 h. The water flux was measured at every one hour interval. The pre-pressurized membranes were used in subsequent ultrafiltration experiments at 345 kPa.[1]

Pure Water Flux

Membranes after compaction were subjected to pure water flux at transmembrane pressure of 345 kPa. The permeate water was collected under steady state flow and the flux was determined as follows:

$$J_W = \frac{Q}{A \cdot \Delta T}$$

where

J_W = Water flux, l m^{-2} h^{-1}
Q = Quantity of permeate, l
A = Membrane area, m^2
ΔT = Sampling time, h

Water Content

Water content of the membranes was measured as follows.[15] The membranes were soaked in water for 24 h and weighed after mopping with blotting paper. These wet membranes were placed in a drier at 60°C for 48 h and the dry weights were determined. From the two values the percent water content was derived as follows.

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

W_w = Wet sample weight
W_d = Dry sample weight

Membrane Hydraulic Resistance (R_m)

Membrane hydraulic resistance is an important parameter, which reflects the tolerance of membranes towards hydraulic pressure.[16] It would be more useful to apply the membrane for a particular environment and to identify the suitability of the membranes for a particular membrane process. Membrane hydraulic resistance (R_m), was evaluated by measuring pure water at different transmembrane pressures such as 69, 138, 207, 276, and 345 kPa after compaction. The resistance of the membrane was evaluated from the slope of the transmembrane pressure difference (ΔP) vs. water flux (J_W) using the following equation.

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

Molecular Weight Cut-Off (MWCO)

Molecular weight cut-off of the membrane was determined by identifying an inert solute, which has the lowest molecular weight and has solute rejection of 80–100%, in steady state UF experiments.[17] Thus, the proteins of different molecular weights such as, Bovine Serum Albumin (69 kDa), Egg Albumin (45 kDa), Pepsin (35 kDa) and Trypsin (20 kDa) were taken for rejection studies for the membranes with 100/0, 90/10, 80/20, 70/30 and 60/40%, CA/ER compositions. The permeate concentrations were analyzed using UV-spectrophotometry, at $\lambda_{max} = 280$ nm.

APPLICATION STUDIES

Protein Rejection

After mounting the membrane in the UF cell, the chamber was filled with individual protein solution and immediately pressurized under nitrogen atmosphere to the desired level (345 kPa) and maintained constant throughout the run. Proteins such as BSA, EA, Pepsin and Trypsin were dissolved (0.1 wt%) in phosphate buffer (0.5 M pH 7.2) and used as standard feed solutions. For all experiments, the concentration of feed solution was kept constant. Permeate was collected over measured time intervals in graduated tubes and the tube contents were analyzed for protein concentration, by UV-Spectrophometry (Hitachi, model U-2000) at λ_{max} 280 nm. The percent protein rejection was calculated from the concentration of feed and permeate using equation:[17]

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

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

Upon completion of run, the ultrafiltration cell was emptied, the membrane was removed and washed gently with pure water to remove adherent protein solution, and then reinserted in the clean cell for re-measurement of its pure water flux.

RESULTS AND DISCUSSION

The blend membranes were found to be compatible up to a composition of 60/40% of CA/ER in DMF. These membranes were subjected to characterization and solute rejection studies and the results have been discussed as follows with respect to the effect of polymer blend composition.

Membrane Compaction

The compaction was aimed to make membranes with rigid pore structure and size, which could further yield reproducible results in characterization and performance evaluation. At constant operating pressure (414 kPa), the pure water flux of CA/ER blend membranes upon compaction was measured every hour. During compaction, for all the membranes, initially the pure water flux was found to be high and declines gradually and reaches a steady state after 3 h of compaction, as shown in Fig. 1. This initial decline in flux may be due to the fact that the membrane pores are being compacted leading to uniform pore size and steady state water flux. Both the pure and blend membranes, exhibited similar trend upon compaction, irrespective of the composition.

Pure Water Flux

Membranes after compaction, were subjected to a transmembrane pressure of 345 kPa for the measurement of pure water flux. The flux was measured under steady state flow.[18] The values of pure water flux are presented in the Table 1. The values show that in the blend membranes, as the concentration of the epoxy resin increases from 5 to 40%, the water flux also increases from 13.4 to 63.8 $l \cdot m^{-2} \cdot h^{-1}$. This linear trend due to the increase in epoxy content in the blend may be due to the hydrophilic nature of the epoxy group present in the membrane. The result is supported by the similar results

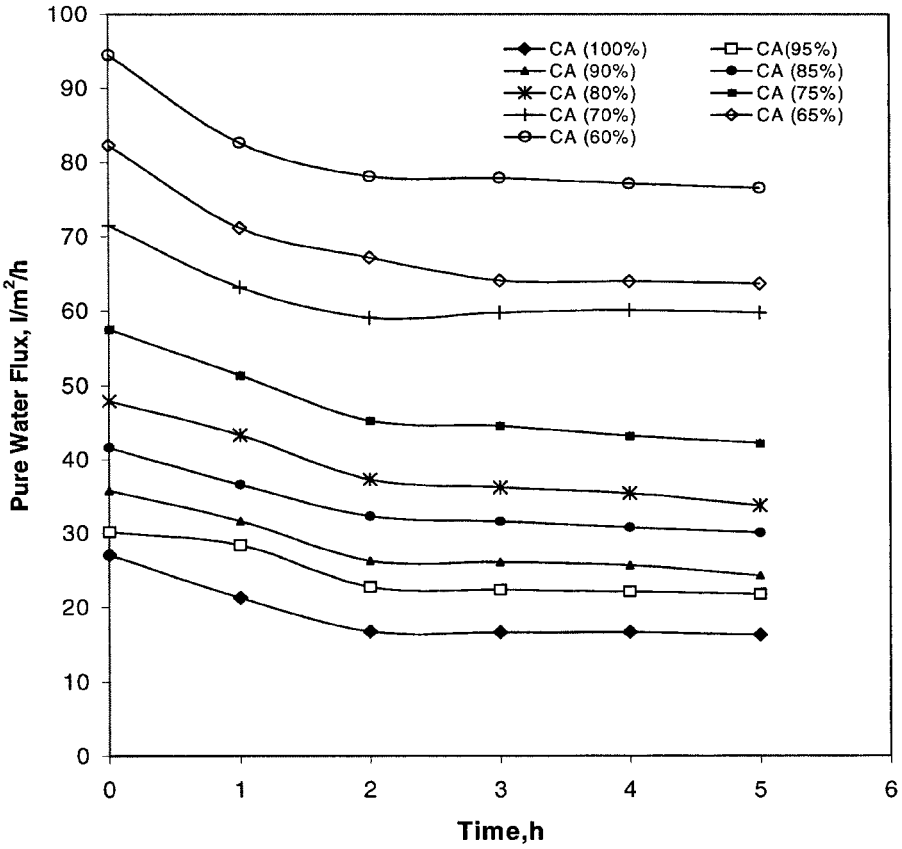

Figure 1. Compaction studies of CA/ER blend membranes with different compositions of epoxy resin.

obtained from the epoxidation of polyurethane and wettability studies carried out earlier.[9]

Water Content

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. Variation in the concentration of epoxy resin from 5 to 40 wt% in the blend membranes resulted in an increase in the water content of the membranes from 78.3 to 84.4% as shown in Table 1. This increase in percent water content may be due to the presence of hydrophilic epoxy group in the blend membrane, as compared with pure cellulose acetate membrane. The water uptake of membranes are significant in identifying the hydrophilic nature and available internal surface area of a polymeric membrane matrix.

Membrane Hydraulic Resistance (R_m)

Resistance of the membrane was calculated from the slope of the straight line obtained from the plot of transmembrane pressure vs. water flux (Fig. 2). The effect of concentration of epoxy resin on R_m, has been explained on the results obtained from the figure and the values are depicted in the Table 1. From the values, it is obvious that as the concentration of the epoxy resin in the blend system was increased, the membrane resistance has decreased. The reason may be, the increase in void volume, with respect to increase in ER content in the blend. Further, the values are inversely proportional to the water flux of the respective membranes.

Molecular Weight Cut-Off (MWCO)

Based on the rejection values of the globular proteins and the procedure followed by Sarbolouki[17] the MWCO of the CA/ER blend membranes was

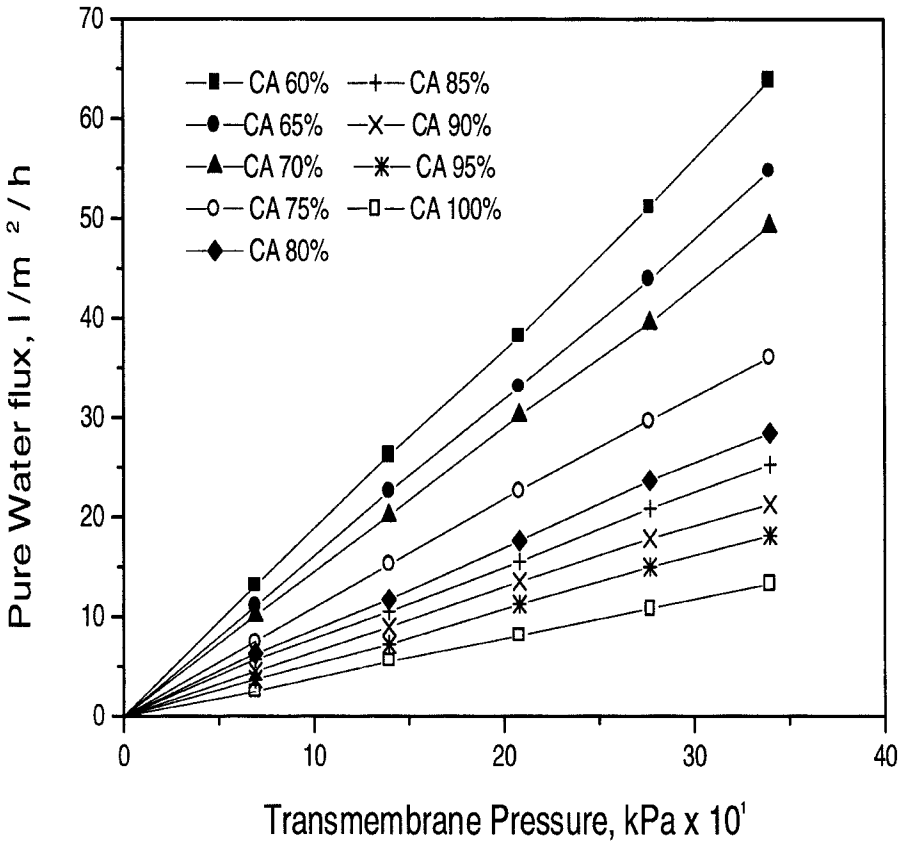

Figure 2. Pure water flux of CA/ER blend membranes at different transmembrane pressures.

determined and is reported in Table 1. It can be explained that pure CA membrane (100/0%), has the lowest MWCO value of 35 kDa, as the membrane has yielded 84% rejection for pepsin (35 kDa). The MWCO value has increased upon an increase of ER content in the blend and thus, at 40% ER content, the MWCO was found to be 69 kDa. This increase in MWCO value, may be due to formation of a segmental gap, due to the partial phase separation upon proportionately increasing the concentration of ER, in the blend. It can also be interpreted that there has been no possibility of interaction between the polymers CA and ER at various compositions. Similar results have been observed for CA and PU blend membranes, with various blend compositions and found successful in rejection applications.[14] These MWCO values show that, all the membranes fall in ultrafiltration range and are perfectly suitable for molecular level rejection studies.

APPLICATION

Protein Rejection Studies

The rejection of proteins viz., BSA, EA, Pepsin and Trypsin were carried out using CA/ER (100/0, 90/10, 80/20, 70/30, and 60/40%) membranes. The pH of the feed solution was kept constant at 7.2, since, the change in pH may increase the adsorptive fouling of the membranes.[19] Further, intermolecular forces between protein molecules and membranes will predominate and affect the efficiency of membranes, if pH of the solution changes.[20]

Role of Polymer Blend Composition

The rejection of proteins, such as BSA, EA, Pepsin and Trypsin by 100/0, 90/10, 80/20, 70/30, and 60/40% CA/ER blend membranes, is shown in Fig. 3. Pure cellulose acetate, when subjected to separation of BSA, EA, Pepsin and Trypsin, offered a higher separation of 98, 95, 84, and 76%, respectively as shown in Fig. 3. For CA/ER blend membranes, as the ER content was increased, the separation has decreased for all proteins as evidenced from Fig. 3. Thus, for 90/10%, CA/ER blend membranes, BSA has exhibited a rejection of 96%, and reduced to 82% for 60/40% blend membrane. A similar trend has been observed for other proteins as well. The difference in percent rejection of the proteins is due to the different solute sizes. The blend membranes with other compositions have also exhibited similar trend as that of 90/10% CA/ER. This may be explained by the fact that, the increase in ER content enhances the size of pores due to extended segmental gap between polymer chains.[21]

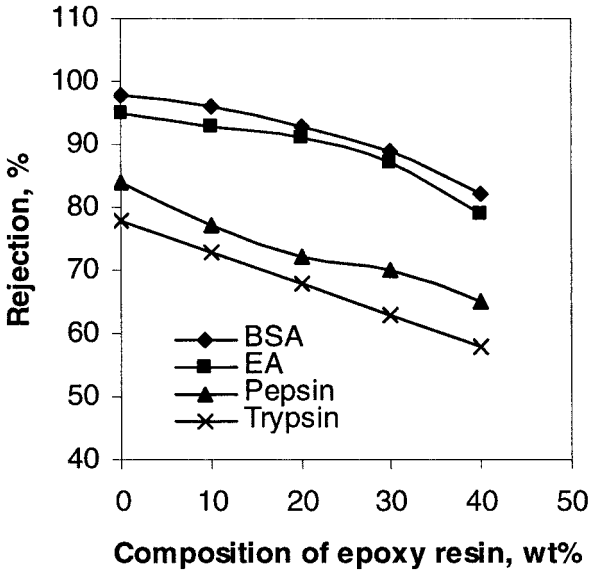

Figure 3. Effect of epoxy resin composition in CA/ER blend membranes on rejection of proteins.

CONCLUSION

A new type of polymeric blend membrane material based on cellulose acetate and diglycidyl ether of bisphenol-A, epoxy resin has been identified. The extent of their blend compatibility with various compositions using N,N-dimethyl formamide as solvent has been determined to be 60/40% of cellulose acetate and epoxy resin. The membranes prepared were characterized for their compaction, pure water flux, water content, membrane resistance, and molecular weight cut-off. These blend ultrafiltration membranes with different composition, were subjected to the separation of proteins such as BSA, EA, Pepsin and Trypsin. The membranes showed higher pure water flux and good resistance towards hydraulic pressure as compared with pure cellulose acetate membranes. The MWCO value falls in between 35 and 69 kDa, based on the composition of ER in the blend. The rejection of proteins was found to be maximum for BSA (98%) and minimum for trypsin (58%), for the blend membranes. The composition of the blend, plays a major role in determining the characteristics and performance of the membranes.

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