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Studies on Cellulose Acetate/Low Cyclic Dimmer Polysulfone Blend Ultrafiltration Membranes and their Applications

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Abstract: Flat sheet ultrafiltration membranes from cellulose acetate (CA)/low cyclic dimer polysulfone (LCD PSf) were prepared by a phase inversion method. N, N′-Dimethyl formamide and different molecular weight of polyethylene glycol (PEG 200, PEG 400, and PEG 600) were used as solvent and pore-forming additive, respectively. The membranes were characterized in terms of pure water flux, water content, porosity, membrane hydraulic resistance, and morphology. The pure water flux was found to reach the highest value of 181.82 $\mathrm{Lm^{-2}h^{-1}}$ at 5 wt.% PEG of 600 molecular weight and 10 wt.% LCD PSf content in the blended solution for membrane preparation. SEM micrographs indicated that the addition of PEG into the CA/LCD PSf solution changes the inner structure of the membrane. The influence of filtration time and applied pressure on membrane permeability was examined by copper/polyethylenimine complex rejection studies. With increase in filtration time, the rejection of the copper/polyethylenimine complex decreased and the results were discussed.

Keywords: Ultrafiltration, blend membranes, molecular weight of PEG, metal ion separation, Cu/PEI complex ion rejection

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INTRODUCTION

Ultrafiltration (UF) today is considered as a basic unit operation with significant potential for the solution of separation problems related to various industrial processes. UF membranes are prepared by a phase inversion technique, which are of increasing importance in the field of membrane material preparation (1). Cellulose acetate (CA) is one of the popular membrane materials for reverse osmosis and ultrafiltration applications. The modification of CA polymer by means of blending with other polymers is a convenient and effective method to improve hydrophilicity and the physical properties for practical utilization (2). In our previous work, membranes blended from various compositions of CA/Sulfonated poly (ether ether ketone) (SPEEK) were prepared in N, N′−dimethyl formamide (DMF) as a casting solvent (3). It has also been reported that the hydrophilic property of CA can be modified by blending with polysulfone (PSf), sulfonated polysulfone (SPSf) in different compositions, using DMF as a solvent and PEG as an additive to yield membranes with excellent characteristics (4, 5).

CA/PSf blend membranes have been preferred for applications involving water and wastewater purification and desalination using reverse osmosis and ultrafiltration (6). During the phase inversion technique, the casting solution of polymers in solvent should be a clear and a viscous solution, however, they may become cloudy over a period of time, as in the case of CA/PSf in DMF. This cloudiness is due to the presence of crystalline cyclic dimer of polysulfone containing two repeat unit of polysulfone (7), normally produced during the manufacturing of polysulfone. Solvay Advanced Polymers *LLC* has introduced a modified polysulfone called UDEL P-3500, a low cyclic dimer polysulfone (LCD PSf) (8). LCD PSf was designed specifically for membrane production and Solvay says that it offers a number of economic advantages for manufacturers. The advantages are attributed to the lower level of cyclic dimer present in the polymer. LCD PSf also improves the stability and shelf life of the dope solution used during processing, which may translate into greater efficiencies in the overall fabrication process. In addition, LCD PSf offers a number of technical advantages such as higher fiber strength (for fewer fiber breakages), and more consistent filtration.

Polymeric additives are widely used for the control of membrane structure by altering their pore size. Pore-forming agents such as PEG and polyvinylpyrrolidone (PVP) have been used in the polymer blends for the fabrication of ultrafiltration and microfiltration membranes (9, 10). PEG is a nontoxic material widely used for biotechnical applications. Since, PEG is miscible with membrane materials and is well−soluble in water as well as in organic solvents, it has been chosen as an additive in this study. The molecular weight of PEG plays an important role in the formation of the structure of CA membranes. The pore size of cellulose acetate blend membranes increases due to the increase in molecular weight of PEG (11, 12).

Hence, in the present investigation, a novel membrane has been prepared by blending of CA and LCD PSf in DMF as a solvent with a different molecular weight of PEG. The prepared membranes have been characterized in terms of pure water flux, water content, porosity, membrane hydraulic resistance, morphology, and rejection of copper/polyethylenimine complex. In this study, copper ion has been selected due to their economic and environmental importance. The polyethylenimine (PEI) has been used as a chelating agent, which has an appropriate molecular weight and affinity to copper (13, 14).

EXPERIMENTAL

Materials

Commercial grade MYCEL cellulose acetate CDA 5770 was purchased from Mysore Acetate and Chemicals Company Ltd., India and used after recrystallization from acetone. UDEL P-3500 LCD polysulfone was supplied by Solvay Advanced Polymers LLC of Alpharetta, Georgia, USA. Three kinds of Polyethylene glycol (PEG 200, PEG 400, and PEG 600) with a weight-average molecular weight of 200, 400, and 600 were procured from Merck (I) Ltd., and used as a non-solvent additive. DMF and Sodium lauryl sulfate (SLS) were obtained from Qualigens Fine Chemicals, Glaxo India Ltd., India, which were of analytical grade. DMF was sieved through molecular sieves (Type-4 A°) to remove moisture and stored in dried conditions prior to use. Acetone (AR) was procured from Sisco Research Laboratories Pvt. Ltd., India. Polyethyleneimine ($M_w = 600-1000$ kDa) was procured from Fluka Chemie AG, Steinheim, Switzerland and used as 1 wt.% aqueous solution for the studies. Copper (II) sulphate 5-hydrate (AR) was procured from Merck (I) Ltd., and used as such for the preparation of aqueous metal ion solutions. Deionized double distilled water was employed for the preparation of gelation bath and aqueous solutions of copper/polyethylenimine (Cu/PEI) complex of 1 wt.% PEI concentration.

Membrane Preparation

The casting solution was prepared by blending CA and LCD PSf with different molecular weight of PEG at various compositions as shown Table 1 using DMF as a solvent under constant stirring for 3 h at 60°C. The homogenous solution was kept in air for at least 1 h to get rid of air bubbles. CA and LCD PSf blend membranes were made by a phase inversion technique (15). The prepared homogeneous solutions were

Table 1. Membrane formulations

	Polymer (17.5 wt.%)		Additive (wt.%)			
Membrane	CA (%)	LCD PSf (%)	PEG 200	PEG 400	PEG 600	Solvent DMF (wt.%)
M-000	90	10	—	—	—	82.5
M-200	90	10	5	—	—	77.5
M-400	90	10	—	5	—	77.5
M-600	90	10	—	—	5	77.5

poured onto a glass plate and formed a film of thickness of 0.22 ± 0.02 mm using a Gardner knife. Membrane evaporation was done in a controlled atmosphere (humidity: $52 \pm 2\%$ and temperature: $24 \pm 1°C$) for 30 s to degas the solvent, and then immersed in the coagulation medium (2 L of solution consisted of 2.5% (v/v) DMF and 0.2 wt.% SLS and remaining distilled water) for 1.5 h with temperature of $10 \pm 2°C$. Finally, the prepared membranes were dipped in distilled water for 20 min and stored in 0.1% (v/v) of formalin solution to prevent microbial growth over the surface of the membranes.

Membrane Characterization

Ulrafiltration Set Up

Experiments of permeation under a pressure gradient were carried out in a batch type, dead end cell (UF cell-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 pressure control valve and gauge through a feed reservoir.

Hydraulic Compaction

The Hydraulic compaction of fresh membranes was carried out by loading the membranes in necessary size, in the UF cell connected to the pressure reservoir with pure water at a pressure of 414 kPa. The initial pure water flux (PWF) was taken 15 min after the pressurization of the test cell. The PWF was also taken at every 1 h time interval till it leveled off after 6 to 7 h (16). The compaction factor was calculated from Eq. (1) (17).

$$\text{Compaction factor} = \frac{\text{Initial pure water flux}}{\text{Steady state pure water flux}} \tag{1}$$

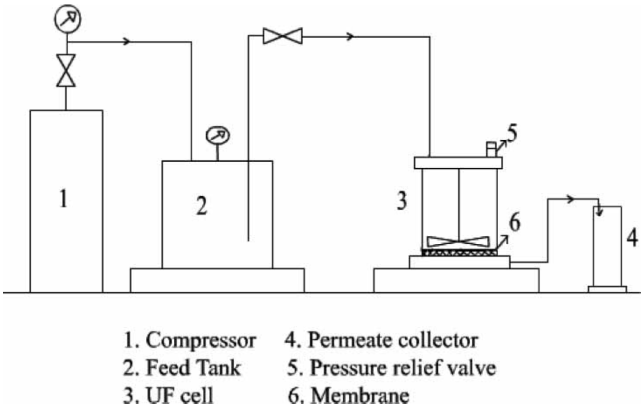

Figure 1. Schematic representation of UF experimental set-up.

The pre-pressurized membranes were used in subsequent UF experiments at 345 kPa applied pressure.

Pure Water Flux

The thoroughly washed membranes after compaction were loaded in UF cell. The flux was measured under steady-state flow with applied pressure of 345 kPa. From the measured values, the PWF was determined from Eq. (2) (18).

$$J_w = \frac{q}{A \cdot \Delta T} \tag{2}$$

where, J_w = Pure water flux ($Lm^{-2}h^{-1}$); q = Quantity of water permeated (L); A = Effective membrane area (m^2); ΔT = Sampling time (h).

Water Content

The wet membranes were placed in a vacuum oven at 85°C for 48 h and the water content as the weight fraction of water in the wet membrane at ambient temperature was calculated by Eq. (3) (19).

$$\text{Water content} = \frac{W_1 - W_2}{W_1} \times 100 \tag{3}$$

where, W_1 and W_2 are the weight of the membranes in the wet and dry states.

Porosity

After the membrane was equilibrated in water, the volume occupied by water and the volume of the membrane in the wet state was determined according to

Chen et al. (20). The membrane porosity was obtained by Eq. (4).

$$\text{Porosity} = \frac{(W_1 - W_2)}{\rho_{\text{water}} \times V_T} \tag{4}$$

where, V_T is the apparent volume of the membrane in the wet state (m^3) was calculated by using the following formula,

$$V_T = \frac{(W_1 - W_2)}{\rho_{\text{water}}} + \frac{W_2}{D_p} \tag{5}$$

where, ρ_{water} is the density of pure water at 25°C (kg/m^3) and D_P is the density of dry state membrane (kg/m^3).

Membrane Hydraulic Resistance

To determine membrane hydraulic resistance (R_m), the PWF of membranes were measured at applied pressures viz., at 69, 138, 207, 276, 345, and 414 kPa, after compaction. The R_m was evaluated from the slope obtained by plotting PWF versus pressure difference (ΔP), using the Eq. (6) (21, 22).

$$R_m = \frac{\Delta P}{J_w} \tag{6}$$

Scanning Electron Microscopy

The morphologies of the top and the cross–section of the membranes were examined using scanning electron microscopy (SEM). The membranes were freeze dried, then frozen in liquid nitrogen and fractured to expose the cross-sectional areas. The dried sample was gold–coated and viewed with SEM (LEICA Stereoscan, Cambridge, UK).

Application Studies

The characterized CA/LCD PSf blend membranes were used for copper ion rejection studies at 345 kPa. Aqueous solution of copper ion has been prepared with 1000 ppm of PEI complex in distilled water. For all experiments, the concentration of the feed solution was maintained as constant. The pH of these aqueous solutions were adjusted to 6 ± 0.25 by adding a small amount of either 0.1 M HCl or 0.1 M NaOH. Solutions containing PEI and individual copper ions were thoroughly mixed and left standing for 5 days to complete binding (23–25). After mounting the membrane in the UF cell, the chamber was filled with a known volume of copper solution and immediately pressurized to the desired level (345 kPa) and maintained constant throughout the run. The permeate was collected under stirred (200 rpm) UF cell over measured time intervals in graduated tubes and the tube contents were analyzed for copper content by UV-Visible

Spectrophotometry (Hitachi, model U-2000) at $\lambda_{\max} = 620\,\text{nm}$ (25, 26). The percentage copper/polyethyleneimine (Cu/PEI) complex rejection (%R) was calculated (27) from the concentration of feed and permeates using Eq. (7).

$$\%R = \left[\frac{C_f - C_P}{C_f}\right] \times 100 \tag{7}$$

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

RESULTS AND DISCUSSION

Preparation of membranes through modification of CA by blending is expected to improve the performance of the resultant membranes. In this study, CA has been modified by blending with LCD PSF. An attempt was also made to prepare a flat-sheet membrane with improved permeability by introducing various molecular weight of PEGs as pore-forming additive in the CA/LCD PSf casting solution. The prepared membranes were characterized in terms of PWF, porosity, membrane resistance etc. The applicability of the membranes for copper ion removal from the aqueous phase in the presence of a macromolecular complexing agent was examined. Due to a stronger tendency of branched PEI to form complexes with divalent metal ions through amino groups (23, 24), PEI has been chosen as the macromolecular chelating agent in comparison to other binding/complexing agents such as polyacrylic acid, polyvinyl alcohol, polydiallyldimethylammonium chloride etc. Further, the effects of the molecular weight of PEG on *%R* and permeate flux with respect to applied pressure and filtration time was investigated and discussed.

Hydraulic Compaction

A typical PWF *vs* time curve of blended UF membranes were started with a rapid initial drop, followed by a long-term gradual decrease and ended with steady state, as shown in Fig. 2. The steady state flux can only be attained after a long time (7 h) operation and the feed concentration is low like pure water. The M-000 CA/LCD PSf blend membrane of 90/10% composition in the absence of PEG was found to have very low flux at the initial hours of compaction. For M-000 membrane, the steady state was attained within 6 to 7 hours of compaction and the value was found to be 93.5 $\text{Lm}^{-2}\text{h}^{-1}$ at 414 kPa as shown in Fig. 2. During compaction, the polymer molecules were slightly reorganized and their structure is changed, which results in low volume porosity, increased membrane hydraulic resistance, and eventually low flux (28). For the CA/PSf blend membrane, the steady state value of pure water flux was

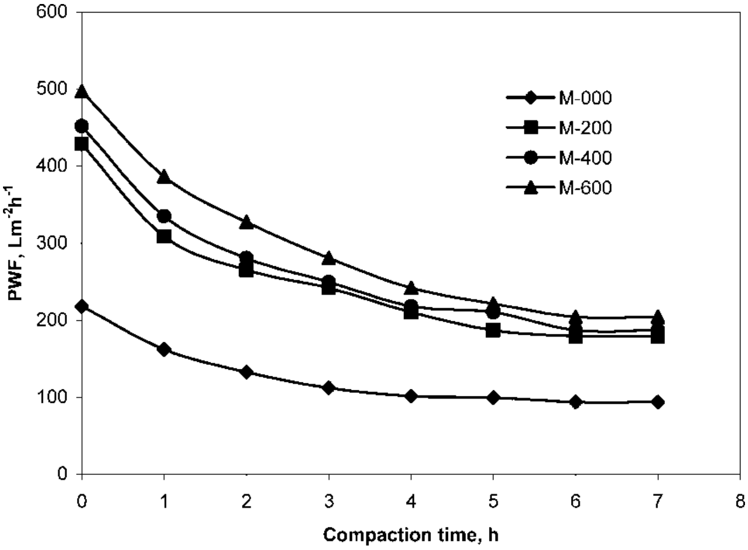

Figure 2. Effect of compaction time on PWF for CA/LCD PSf blend membranes with different molecular weight of PEG.

74.5 Lm^{-2}h^{-1} (29), demonstrating that the use of the LCD PSf in place of the normal PSf improves the compaction of the membrane.

Additives are chosen to improve the pore statistics and morphology of the membranes. Thus different molecular weight of PEGs like PEG 200, PEG 400, PEG 600 were added to the CA/LCD PSf casting solutions at 5 wt.% composition. The increase in flux upon increase in the molecular weight of PEGs at 5 wt% level may be due to the formation of large voids in the internal structure of membrane (30). However the CA/LCD PSf blend membrane of 90/10% composition, with 5 wt.% PEG 200 was subjected to the study and the initial flux was found to be 428.6 Lm^{-2} h^{-1}. Similarly, the flux value increased to 450 and 501 Lm^{-2} h^{-1} for the molecular weight of PEG 400 and 600 respectively.

Compaction factors for prepared membranes were plotted in Fig. 3, which indicated that a large pore size membrane (M-600) has a high tendency of compacting under pressure. Because of the large void space created by PEG 600, the internal structural reorganization is more in M-600, which leads to a high compaction factor of 2.44.

Pure Water Flux

Pure water flux is one of the main specifications describing the performance of the membrane. After compaction, membranes were subjected to a

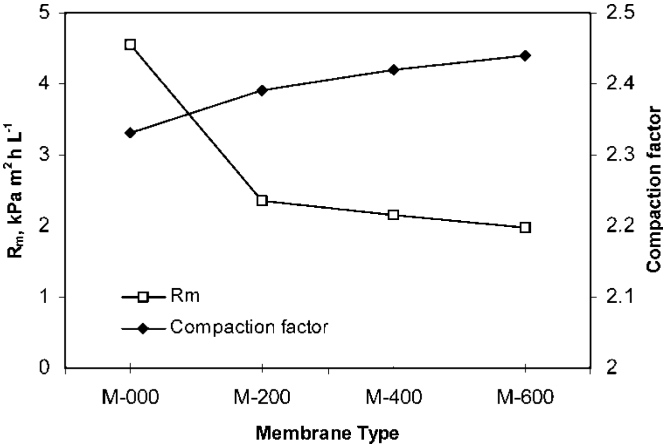

Figure 3. Effect of molecular weight of PEG on compaction factor and membrane hydraulic resistance for CA/LCD PSf blend membranes with PEG.

transmembrane pressure of 345 kPa for the measurement of PWF. The flux was measured under steady state conditions. All the membranes were stabilized for the PWF measurement by placing the compacted membranes in deionized water for 30 to 40 min.

The effect of the molecular weight of PEG from 200 to 600 at polymer composition (90/10%) on pure water flux was studied, and the results are shown in Fig. 4. When there is no PEG added, the PWF is 62 $Lm^{-2}h^{-1}$, which is higher than that reported for the CA/PSf blend membrane in the same composition (29). For 90/10% blend membrane, the molecular weight

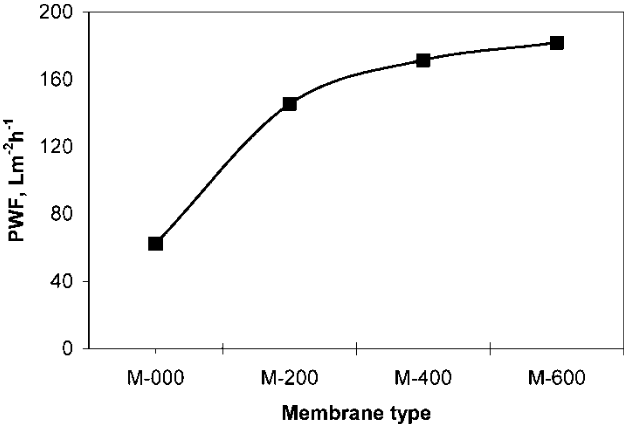

Figure 4. Effect of molecular weight of PEG on PWF for CA/LCD PSf blend membranes with PEG.

of PEG increases from 200 to 600, and the PWF also increased from 145.45 to 181.82 $Lm^{-2}h^{-1}$, respectively. This increment of flux might be due to the high molecular weight PEG that would create a large vacant space inside the membrane during the leaching process. The same trend was observed by Kim et al. (31) for the polysulfone membrane prepared with N-methylpyrrolidone as a solvent in the casting solution.

Water Content

The water content of the membranes is an indirect indication of the hydrophilicity and flux behavior of membranes. Membranes were thoroughly washed with distilled water before the estimation of the water content. The prepared blend membranes were subjected to water content and the results were shown in Fig. 5. In the CA/LCD PSf polymer blend, as the absence of an additive, the water content was found to be 72.15%. Further, the water content increased with increasing the molecular weight of PEG with blending composition of 90/10% CA/LCD PSf. Since the water content is also dependent on the porosity it has been used as one of the structural parameters of the membranes.

Porosity

A good porous membrane should exhibit high permeability and selectivity. In order to receive higher permeate flux in the UF process, the surface porosity of

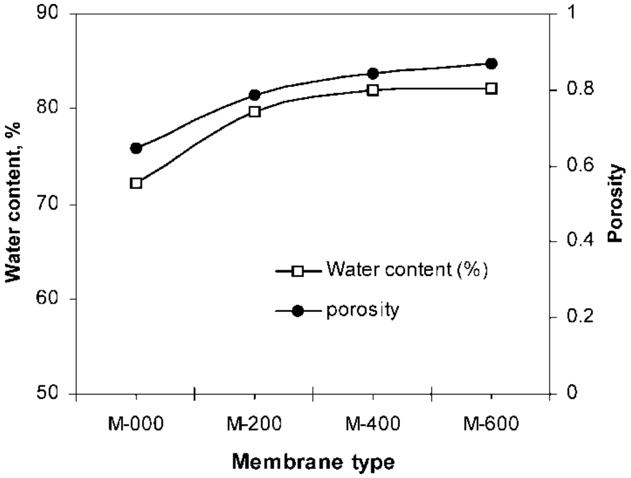

Figure 5. Effect of molecular weight of PEG on water content and porosity for CA/LCD PSf blend membranes with PEG.

the hydrophilic membrane must be in a suitable range (20). From Fig. 5, for the CA/LCD PSf blend membrane, when the PEG 200 concentration was increased from 0 to 5 wt.%, the membrane porosity increased from 0.65 to 0.78 respectively. A high molecular weight PEG content is usually associated with the membrane of a large pore size at its surface, and that large pore size and porosity favor the membrane wettability and make against the membrane strength.

Membrane Hydraulic Resistance (R_m)

R_m is a parameter that indicates the hydraulic pressure withstanding capability of membranes. Both the dense top "skin" layer and the porosity offer the hydraulic resistance. R_m was calculated from the initial slope of the corresponding pressure vs. pure water flux plots (Fig. 6) (32). Figure 6 is the pressure variation against water flux graphs, for CA/LCD PSf membrane with 5 wt% PEGs. From the figure we observe that the flux is linear, and the resistance values have been determined from this narrow range. The determined values shown in Fig. 3, the blend membrane of CA/LCD PSf in the absence of the additive (M-000), exhibited a higher membrane hydraulic resistance of 4.55 kPa m^2hL^{-1} due to its low porosity (33). When the molecular weight of PEG was increased from 200 to 600 in the casting solution of CA/LCD PSf, there was a corresponding

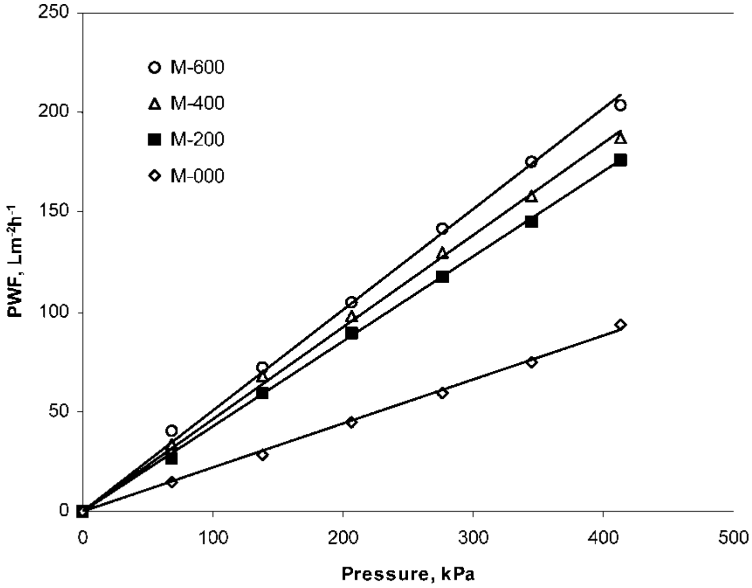

Figure 6. Effect of applied pressure on PWF for CA/LCD PSf blend membranes with different molecular weight of PEG.

decrease in the resistance of the membrane from 2.35 to 1.98 kPa m^{2}hL^{-1}. Malaisamy et al. (29) reported that pure water flux and the water content increased with increasing concentration of PEG 600 (2.5 to 10 wt%) with pure CA, but the membrane hydraulic resistance decreased.

Scanning Electron Microscopy

Membrane morphology is a powerful tool to investigate the structure of polymeric integrally skinned membrane. To develop high performance polymeric membranes, it is essential to design the morphological structures of the membranes for their specific applications. Figure 7 shows the cross–sectional view of the membranes viz., M-000, M-200, M-400, and M-600. This cross–section shows an asymmetric structure consisting of the typical finger-like macrovoids enclosed in a continuous polymer matrix.

Figure 7a shows that the blend membrane has an asymmetric structure consisting of a two-skin layer and a finger-like support layer. As the molecular weight of the PEG content increases, the internal porous structure changes, as shown in Fig. 7b–d. In addition, spherical shaped pores were observed at the wall structure of the blend membrane. Finally, membranes have an irregular pore structure while adding higher molecular weight PEG

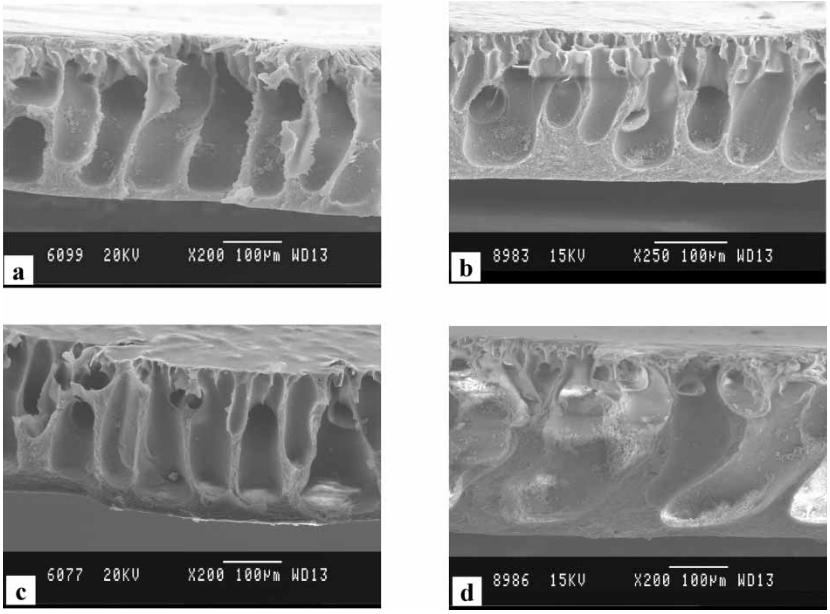

Figure 7. SEM Micrographs of cross section of CA/LCD PSf blend membranes with different molecular weight of PEG. (a) M-000 (b) M-200 (c) M-400 (d) M-600.

to their blend solution. But, Yang et al. (30) suggested that phase separation might start to occur, with an increase in the molecular weight of the PEG in the blend membrane. In addition, the 90/10% of CA/LCD PSf have a regular structure with obvious pores, while the pore size became irregular with the increase in the molecular weight of the PEG content.

Application Studies

The rejection of Cu/PEI complex is one of the criteria for the evaluation of the performance of membranes. The effect of molecular weight of PEG as an additive on membrane performance was shown in Figs. 8–11 and it indicated that these permeate flux values are low compared to PWF values presented in Fig. 3. The reason is due to the high resistance to flow that was offered by Cu/PEI complex ions deposited at the surface of the membrane and the viscosity of the solution.

Effect of Applied Pressure

The effect of applied pressure from 69 to 345 kPa on Cu/PEI complex ion rejection and permeate flux for different membranes were reported in Figs. 8 and 9. Figure 8 clearly shows that the M-000 membrane exhibits a higher value of Cu/PEI complex rejection (78.6%) at 345 kPa and this rejection

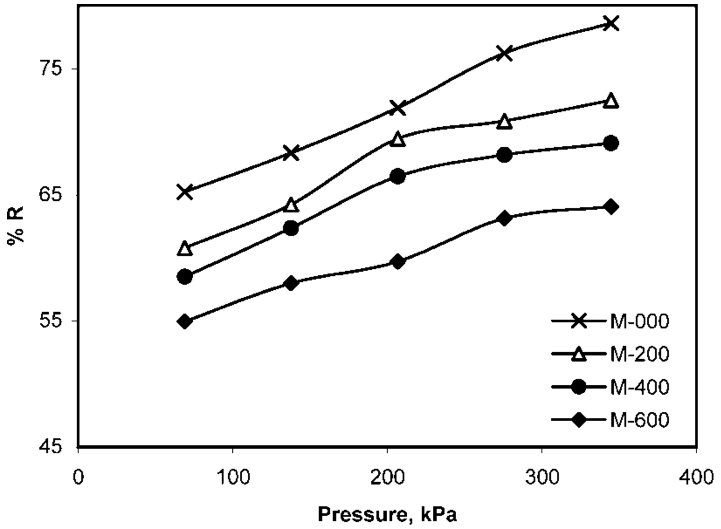

Figure 8. Effect of pressure on Cu/PEI complex ion rejection for CA/LCD PSf blend membranes with different molecular weight of PEG.

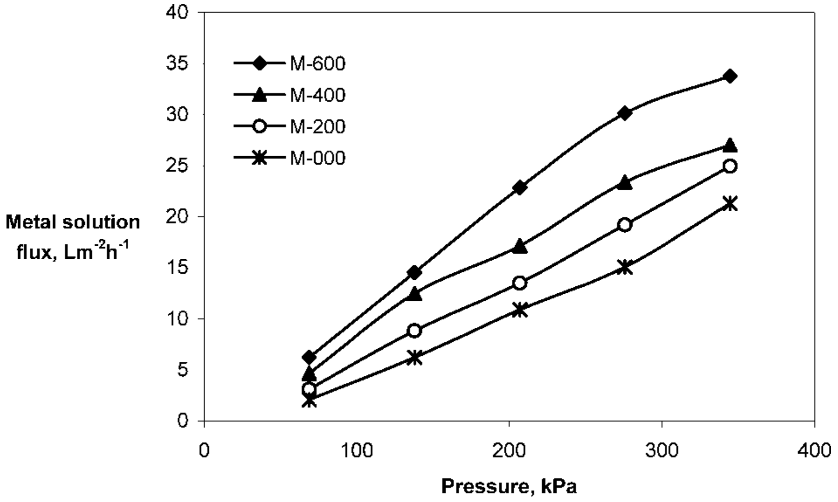

Figure 9. Effect of pressure on metal solution flux for CA/LCD PSf blend membranes with different molecular weight of PEG.

increases significantly with increasing pressure. An increase in pressure can enhance the convective flow of the particle towards the membrane, which subsequently enhances the polarization, and deposition of particles. The molecular weight of PEG has also played a significant role on Cu/PEI

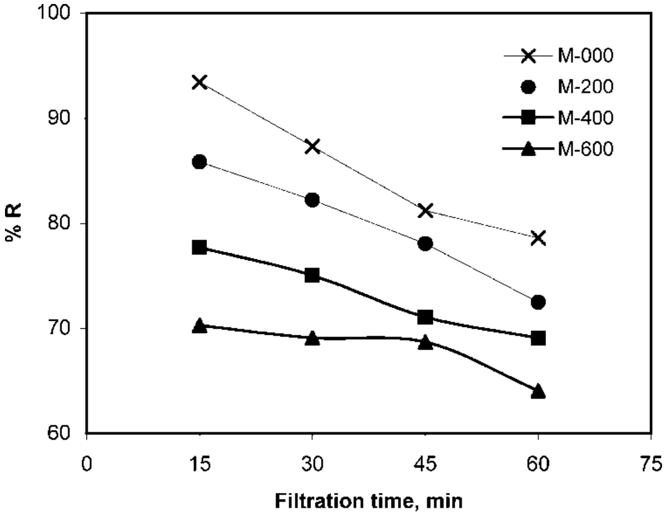

Figure 10. Effect of filtration time on copper ion rejection for CA/LCD PSf blend membranes with different molecular weight of PEG.

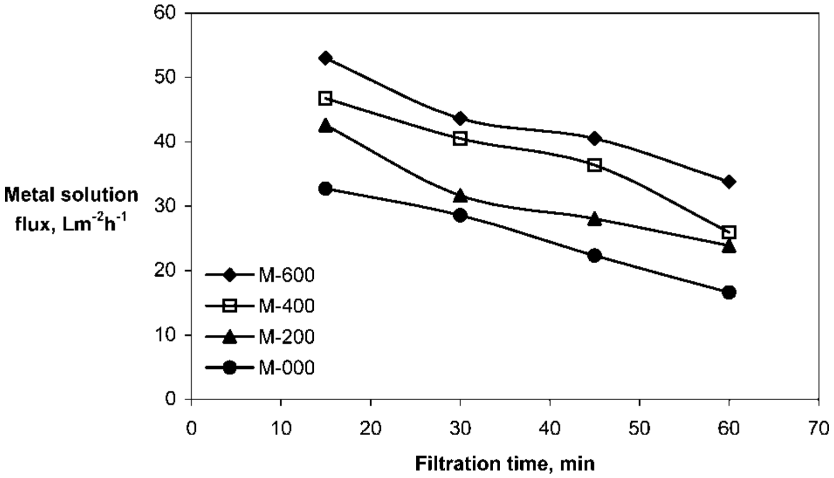

Figure 11. Effect of filtration time on metal solution flux for CA/LCD PSf blend membranes with different molecular weight of PEG.

complex rejection at constant pressure. From Fig. 8, when the molecular weight of PEG is increased from 200 to 600 in the blend solution, the Cu/PEI complex rejection decreases from 72.5 to 64.07% at 345 kPa respectively. This occurs because of the fact that the pore size of the blend membrane increased, while increasing additive molecular weight.

Figure 9 indicates the significant flux variation with respect to the applied pressure. At 345 kPa, the Cu/PEI product rate for the CA/LCD PSf membrane without any additive is 21.3 Lm^{-2} h^{-1}. It has been reported that the Cu/PEI product rate was 1.8 Lm^{-2} h^{-1} using CA/PSf blend membrane (29), indicating that the replacement of PSf with LCD PSf improves the metal ion separation. It has been observed that membrane M-000 has the lowest flux compared to the other three membranes viz., M-200, M-400, M-600 at various applied pressures, which is due to an increase in the number of pores in the membranes, which is consequent of the addition of PEG. Moreover from Fig. 9, the permeate flux at all pressure values is lower than the pure water flux, which is due to the fouling of the membrane. Figure 9 also indicates clearly that the PEG molecular weight has also a significant role to play on flux measurement studies. When the molecular weight of PEG was increased from 200 to 600, there was a corresponding increase in flux from 24.9 to 33.8 L m^{-2} h^{-1} at 345 kPa.

Effect of Filtration Time

The effect of filtration time on %R and permeate flux, for prepared membranes at constant applied pressure of 345 kPa are shown in Figs. 10 and 11, respectively. The increase in filtration time, results in a significant decrease in the Cu/PEI complex rejection (34). Also, when the molecular weight of PEG is increased from 200 to 600, there is a corresponding decrease in Cu/PEI complex rejection of membranes from 72.5 to 64.07% at 60 min filtration time as depicted in Fig. 10. From Fig. 11, it is seen that there is always a substantial decline in the permeate flux due to the irreversible binding and convection induced deposition of Cu/PEI complex ion to the membrane surface and a continuous increase of the Cu/PEI complex ion concentration in the retentate by Meireles et al. (35) They also indicated that flow decline depends on the pore and molecule size distributions of the prepared membranes.

CONCLUSIONS

In this work, cellulose acetate and low cyclic dimer polysulfone were blended with different molecular weight of PEGs by means of the phase inversion method. The addition of different molecular weight PEGs in a CA/LCD PSf casting solution influences the membrane properties and morphology remarkably. With a 5 wt% of PEGs, the hydrophilicity of the blend membrane was increased. Experiments show that the increase in molecular weight of PEGs (200, 400, and 600) in casting solution resulted in the increase of the pure water flux, the water content and the porosity. Scanning electron micrographs illustrate that the morphology of CA/LCD PSf blend membranes changed with increase in the molecular weight of PEGs. From metal ion separation experiments, it is found that the percentage rejection of Cu/PEI complex decreased with increasing the molecular weight of PEGs but the metal solution flux increased. The higher molecular weight PEG 600 in CA/LCD PSf membrane showed the highest solution flux compared with all other CA/LCD PSf blend membranes. In comparison with the results reported earlier on CA/PSf blend membranes, the substitution of PSf with LCD PSf categorically improved most of the membrane performances.

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