Cellulose Acetate and Sulfonated Polysulfone Blend Ultrafiltration Membranes. I. Preparation and Characterization

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ABSTRACT: Modification of polymeric membrane materials by incorporation of hydrophilicity results in membranes with low fouling behavior and high flux. Hence, Polysulfone was functionalized by sulfonation and ultrafiltration membranes were prepared based on sulfonated polysulfone and cellulose acetate in various blend compositions. Polyethyleneglycol 600 was employed as a nonsolvent additive in various concentrations to the casting solution to improve the ultrafiltration performance of the resulting membranes. The total polymer concentration, cellulose acetate, and sulfonated polysulfone polymer blend composition, additive concentration, and its compatibility with polymer blends were optimized. The membranes prepared were characterized in terms of compaction, pure water flux, membrane resistance, and water content. The compaction takes place within 3–4 h for all the membranes. The pure water flux is determined largely by the composition of sulfonated polysulfone and concentration of additive. Membrane resistance is inversely proportional to pure water flux, and water content is proportional to pure water flux for all the membranes. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1749–1761, 2002

Key words: ultrafiltration; membrane characterization; membranes; separation techniques

INTRODUCTION

Membranes are being used in various industries such as chemical, food, pharmaceutical, and metal-finishing industries for concentration purposes.[1]

In aqueous separations, among various types of membrane separation techniques, ultrafiltration (UF) has been found to be a suitable process for macromolecular solute separations. Though several methods are available for the preparation of ultrafiltration membranes, phase inversion has been found to be a versatile technique for asymmetric ultrafiltration membrane preparation, because the casting solution and the conditions of formation can be varied widely to get desired pore structures.

Cellulose acetate membranes have been prepared by many membrane researchers and characterized for their compaction, hydraulic permeability, and osmotic permeability properties.[2,3] Cellulose acetate and its derivatives are suitable as membrane materials, because of advantages such as moderate flux, high salt rejection properties, relatively easy manufacture, cost effectiveness, renewable source of raw material, more hydrophility than polysulfone and nontoxicity.

Similarly, in view of their chemical, mechanical, thermal, and hydrostatic stability, polysulfone polymers are of practical interest as membrane materials for a wide variety of ultrafiltration applications. However, as polysulfone is uncharged and hydrophobic in nature, research on improvement of its flux and retention behavior started early in the 1980s. To improve structure and performance of the membrane, polysulfone was added with low molecular weight organic additives having different functional groups.[4–7] Polysulfone, widely used for ultrafiltration applications,[5] has certain drawbacks such as hydrophobicity, strict membrane casting conditions and relative low rejection, etc. To circumvent the above problems, sulfonation of polysulfone was believed to offer better results.[8–10]

Sulfonated polysulfone has its usage as membrane, and researchers have prepared and studied its water, salt permeability, and water regain properties.[11,12] The structure and performance of the membranes, prepared based on sodium salt of sulfonated polysulfone, were found to be dependent on the composition of the original casting solution and the composition of the nascent membrane at the instant of gelation.[12] Modified polysulfone membranes have been found to possess less fouling behavior than their unmodified analogs, and their tolerance has been extended to a wide range of retentate pH values.[13]

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Further, sulfonated polysulfone has been blended with polysulfone recently, and the effects of the formulation of casting solutions and membrane forming conditions on membrane performance have been investigated.[14] This has paved the way for usage of sulfonated polysulfone as a blend component with other polymers.

Homopolymers, due to a variety of drawbacks, are limited in the range in ultrafiltration membrane applications. Thus, cellulose acetate suffers from drawbacks such as a fairly narrow temperature range of usage (maximum 30°C), a narrow pH range, restricted to pH 2–8, poor chlorine resistance, greater compaction susceptibility, which reduces membrane lifetime, and high biodegradability, which greatly limits its usage. Similarly, although polysulfone was considered as the best candidate for ultrafiltration and reverse osmosis membrane preparations, as a homopolymer, polysulfone also possesses certain undesirable qualities such as hydrophobic behavior and strict casting conditions.

Hence, to circumvent the drawbacks of the membranes, cellulose acetate has been blended with polysulfone, and better results have been observed.[15,16] However, because polysulfone is a hydrophobic polymer, the product efficiency was not enhanced to a significant level, even though coupled with cellulose acetate. Hence, to improve the product effiiciency and the hydrophilic/hydrophobic balance of the membrane system, it was proposed to carry out functionalization of polysulfone by sulfonation. Further, the presence of a suitable hydrophilic additive was expected to result in a membrane with the desired flux behavior and, hence, an attempt has been made to prepare membranes in presence of additives also. Various additives were employed, and a suitable additive was chosen for the investigation. The effect of polymer blend composition and additive concentration on compaction, pure water flux, water content, and membrane hydraulic resistance was investigated, and the results are discussed. The molecular weight cutoff, pore statistics, and morphologic properties are reported in the second part of the present investigation.[17]

EXPERIMENTAL

Materials

Commercial-grade MYCEL cellulose acetate CDA 5770 (acetyl content 39.99 wt %) was procured from Mysore Acetate and Chemicals Company Ltd., India, and was used after recrystallization from acetone. The glass transition temperature, T_g, and molecular weight of recrystallized polymer are 219°C and 115 kDa, respectively.

Commercial-grade polysulfone Udel P-3500, supplied by Amoco Polymers Inc., USA, was used as received (M_w = 77 kDa, T_g = 195°C) for the preparation of sulfonated polysulfone. The T_g and degree of substitution of the prepared sulfonated polysulfone was found to be 234°C and 0.38, respectively.

Polyethylene glycol 600 was procured from Merck (I) Ltd., and was used as such, as a nonsolvent additive for the whole study. Molecular sieves of type 4 Å was procured from SRL Chemicals Ltd., Mumbai, India, and used for drying solvent N,N'-Dimethylformamide, DMF.

The solvent, N,N'-Dimethylformamide (DMF) ("ExcelaR") grade from M/s.Qualigens Fine Chemicals Ltd., India, was used for casting solution preparations. Other solvents of analar grade such as acetone, 1,2-dichloroethane and methanol from Qualigens Fine Chemicals Ltd., India, were used. Sodium lauryl sulphate (SLS) of AR grade was obtained from Qualigens Fine Chemicals Ltd., India and used as surfactant. Chlorosulfonic acid (AR) was procured from E. Merck Ltd., Germany, and used as sulfonating reagent. Sodium methoxide of AR grade was procured from Fluka AG, Buchs, stored in a sealed plastic container, and used for the preparation of sodium salt of sulfonated polysulfone.

Deionized and distilled water was employed for the ultrafiltration experiments and for the preparation of gelation bath.

Preparation and characterization of sulfonated polysulfone

Polysulfone (Udel P-3500) was sulfonated by using chlorosulfonic acid as the sulfonating agent as reported earlier.[14] The solid sodium salt of sulfonated polysulfone obtained was precipitated in ice-cold water followed by washing with ethanol and dried in vacuum for 1–2 h at 70°C.

The purified sample was further characterized for functional group determination by an FTIR spectrophotometer (Perkin-Elmer, model-Spectrum RX1), degree of substitution by a ^{1}H-NMR spectrophotometer (Varion Unity Inova, 400 MHz, with wide bore magnet), glass transition temperature (T_g) by a Differential Scanning Calorimeter with a heating rate of 10°C/min (Dupont 2000, model DSC 2910), and temperature of degradation by a thermogravimetric analyzer with a heating rate of 10°C/min (Mettler, model TA 3000 with TG 50 thermo balance).

Preparation of solution blending of polymers

The blend polymers based on cellulose acetate and sulfonated polysulfone (17.5 wt %) were prepared by blending the two polymers in different compositions (Tables I and II) in the presence and in the absence of the additive, PEG 600, in a polar solvent, DMF, under constant mechanical stirring in a three-necked round-

TABLE I
Effect of Compaction Time on Pure Water Flux of CA/SPS Blend Membranes

Blend composition (%) 17.5 wt %		Pure water flux ($l/m^{-2}.h^{-1}$) at 414 kPa		
CA	SPS	Initial	Final	Ratio of final/inital
100	0	26.8	16.1	0.60
95	5	29.8	19.7	0.66
90	10	34.2	21.8	0.91
85	15	52.4	39.4	0.93
80	20	89.3	52.9	0.59
75	25	111.3	66.4	0.59
00	100	285.7	97.4	0.34

Casting solution temperature = 40 ± 2°C; casting relative humidity = 50 ± 2%; casting temperature = 23 ± 3°C; solvent evaporation time = 30 s.

TABLE II
Effect of Compaction Time on Pure Water Flux of CA/SPS Blend Membranes with Different Additive Concentrations

Blend composition (%) 17.5 wt %			Pure water flux ($l/m^{-2}.h^{-1}$) at 414 kPa		
CA	SPS	PEG 600 wt %	Initial	Final	Ratio of final/initial
100	0	2.5	90.6	48.5	0.53
95	5	2.5	120.5	54.0	0.44
90	10	2.5	134.0	62.3	0.46
85	15	2.5	141.5	66.4	0.46
80	20	2.5	155.8	72.7	0.46
75	25	2.5	113.2	68.4	0.60
00	100	2.5	386.5	152.7	0.39
100	0	5.0	111.5	61.2	0.54
95	5	5.0	129.8	72.7	0.56
90	10	5.0	137.1	87.2	0.63
85	15	5.0	145.4	116.3	0.79
80	20	5.0	205.7	154.8	0.75
75	25	5.0	199.4	132.4	0.66
00	100	5.0	397.4	171.4	0.43
100	0	7.5	147.5	91.4	0.61
95	5	7.5	205.7	105.4	0.51
90	10	7.5	245.1	124.6	0.50
85	15	7.5	313.7	157.9	0.50
80	20	7.5	326.2	176.6	0.54
75	25	7.5	238.9	139.5	0.58
00	100	7.5	468.8	230.6	0.49
100	0	10.0	178.7	99.7	0.55
95	5	10.0	259.7	128.8	0.49
90	10	10.0	423.8	174.5	0.41
85	15	10.0	435.3	199.4	0.45
80	20	10.0	443.6	230.6	0.51
75	25	10.0	413.5	192.2	0.46
00	100	10.0	514.3	233.8	0.45

Casting solution temperature = 40 ± 2°C; casting relative humidity = 50 ± 2%; casting temperature = 23 ± 3°C; solvent evaporation time = 30 s.

bottom flask for 3 h at 40°C. The homogeneous solution obtained was allowed to stand for 1 h in air-tight conditions to get rid of the air bubbles.

Pure polysulfone (100%) with different concentrations of additive, PEG 600, in solvent, DMF, was prepared by mechanically stirring at 90°C for 4 h (Table III). Pure cellulose acetate and sulfonated polysulfone (Tables I and II) casting solutions with different concentrations of additive PEG 600 were also prepared individually using DMF as solvent, by stirring mechanically at room temperature. All the above casting solutions were also kept for 1 h, in air-tight conditions, to get rid of the air bubbles, before casting.

Membrane preparation

The preparation method involved is the same as that of the phase inversion method employed in our earlier work and as reported already by other researchers.[18–21] The casting environment viz., relative humidity and temperature, were standardized for the preparation of membranes with better physical properties such as homogeneity, thickness, and smoothness. The relative humidity was maintained between 48–50% and temperature was kept at 23 ± 3°C for all the casting experiments.

Casting and gelation conditions maintained for the blend systems were also applied for all the pure individual polymeric solutions. However, for polysulfone, the casting relative humidity was kept between 18 ± 2% and temperature at 34 ± 2°C, to avoid precipitation of polysulfone by absorbing moisture from environment. The thickness of the membranes was maintained at 0.22 ± 0.02 mm and measured with a micrometer having a precision of 0.01 mm. These casting and gelation conditions were maintained constant throughout, because the thermodynamic conditions

would largely affect the performance of the resulting membranes.[22]

Prior to casting, a gelation bath of 2 L, consisting of 2.5% (v/v) DMF (solvent) and 0.2 wt % surfactant,

TABLE III
Effect of Compaction Time on Pure Water Flux of Pure PSf Membranes with Various Additive Concentrations

Composition (%) 17.5 wt %	PEG 600 wt %	Pure water flux ($l/m^{-2} \cdot h^{-1}$)		
		Initial	Final	Ratio of final/initial
PSf (100%)	0	131.94	38.05	0.28
	2.5	141.47	54.28	0.38
	5.0	164.93	72.59	0.44
	7.5	185.06	94.06	0.50
	10.0	192.20	101.29	0.52

Casting solution temperature = 85 ± 2°C; casting temperature = 34 ± 2°C; casting relative humidity = 18 ± 2%; solvent evaporation time = 30 s.

sodium lauryl sulphate (SLS) in distilled water (non-solvent), was prepared and kept at $20 \pm 1°C$.

Characterization

The prepared membranes were cut into an effective membrane area of 38.5 cm² for use in the UF stirred batch cell having 450 mL capacity and 10 mL hold up volume supplied by M/S.Spectrum Inc., USA, and characterized as follows.

Compaction

The compaction of fresh membranes were carried out by loading the thoroughly washed membranes in the UF test cell connected to the pressure reservoir with water and subjected to compaction at a pressure of 414 kPa. The water flux was measured every 1 h.

Pure water flux (PWF)

Membranes after compaction, were subjected to a trans-membrane pressure of 345 kPa to measure PWF. The flux was measured under steady state conditions. From the observed flux, the PWF was estimated from the expression,

$$J_w = \frac{Q}{A.\Delta T}$$

where, J_w is water flux (L/m² · h), Q, the quantity of water collected (l), ΔT the sampling time (h), and A, the membrane area (cm²).

Water content

Water content of the membranes was obtained by soaking the membranes in water for 24 h and weighing after mopping with blotting paper. These wet membranes were placed in a vacuum drier at 50°C for 24 h and the dry weights were determined. From these two values, the percent water content was derived as below.[23]

% Water content

$$= \frac{\text{Wet sample weight} - \text{Dry sample weight}}{\text{Wet sample weight}}$$

$$\times 100$$

Membrane resistance (R_m)

To determine membrane resistance (R_m), the pure water flux of membranes was measured at different transmembrane pressures (ΔP) viz., at 69, 138, 207, 276, and 345 kPa, after compaction. The resistance of

the membrane, R_m, was evaluated[24] from the slope of water flux (J_w) vs. transmembrane pressure difference (ΔP) using the equation

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

RESULTS AND DISCUSSION

Preparation of a membrane through modification of polysulfone by sulfonation was expected to support the objective of the present investigation, which envisaged the preparation of membranes with improved performance. Hence, polysulfone was modified to incorporate hydrophilicity by sulfonation and the resultant sulfonated polysulfone was used for blending with cellulose acetate. Thus, membranes were prepared from the above blend polymers and the effects of polymer composition and additive concentration on various membrane characteristics were analyzed and are discussed.

Sulfonation of polysulfone

The sulfonation of polysulfone in the investigation was confirmed by the presence of a peak, assigned to the sulfonic group at 1028 cm⁻¹ by FTIR (Fig. 1). The degree of sulfonation was estimated using ¹H-NMR and was found to be 0.38 (Fig. 2). The degree of sulfonation was determined from the measurement of the area of the peak for the H-atom α to the —SO₃H group, which shifted in absorption of radiation from its original position. The amount of absorbance at the shifted position is proportional to that of the —SO₃H group incorporated in the polysulfone skeleton. The differential scanning calorimetric and thermogravimetric analyses of sulfonated polysulfone have established the enhancement in both glass transition temperature, T_g (234°C) and thermal resistance of polysulfone upon sulfonation (Figs. 3 and 4).

Optimization of polymer, additive, solvent, and their concentrations in membrane preparation

Because the performance of blend polymer membranes promised to be higher than membranes prepared from individual polymers, sulfonated polysulfone was blended with cellulose acetate in polar solvent, i.e., N,N'-dimethylformamide. To prepare sulfonated polysulfone-based ultrafiltration blend membranes, concentration of the sulfonated polysulfone, SPS, in the casting solution was first optimized by studying the effect of polymer wt % in casting solution on pure water flux. Thus, the SPS wt % was varied from 15 to 20 wt % in the casting solution using DMF as the solvent, and as the concentration of SPS
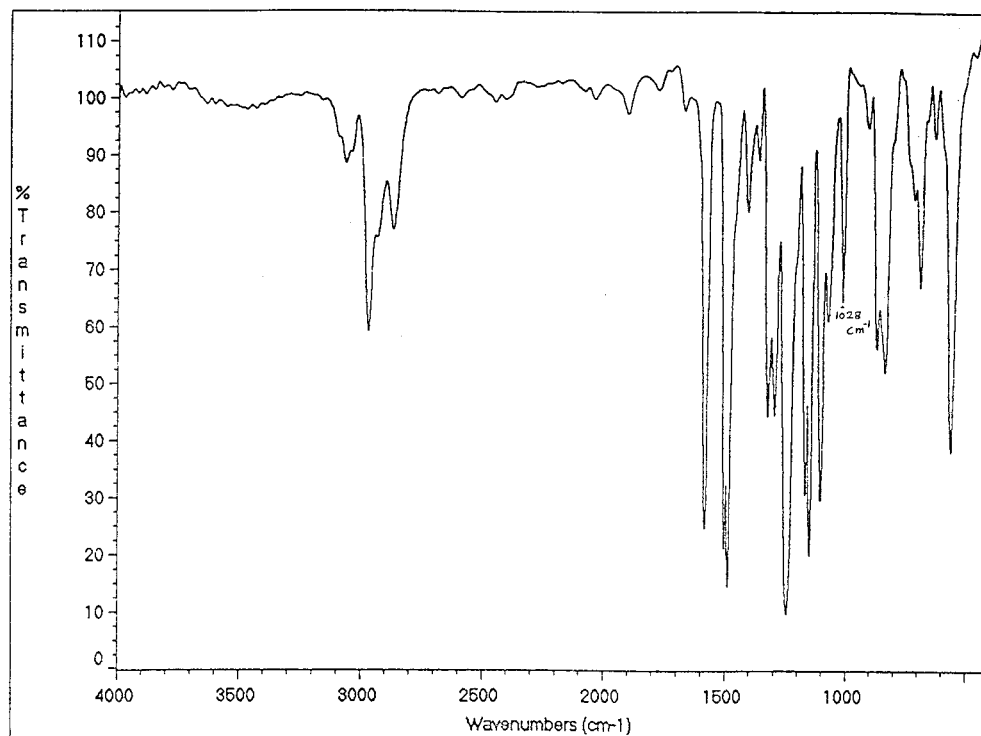
Figure 1   Infrared spectrum of sulfonated polysulfone.

was increased, the flux decreased as shown in Table IV. From the data, the total polymer concentration in all the casting solution was maintained at an optimum value of 17.5 wt %, to give a membrane associated with solute rejection of practical significance with relatively higher flux.

Further, to standardize the blend compatibility of the cellulose acetate–sulfonated polysulfone system, cellulose acetate was blended with sulfonated polysul-

fone at various proportions (CA/SPS) from 100/0% to 75/25%, in DMF. A further increase in sulfonated polysulfone content in blend, i.e., beyond 25%, resulted in phase separation of the blend, due to incompatibility between cellulose acetate and sulfonated polysulfone. This means that the composition enters into the unstable region quickly. Hence, in all further blend systems, the SPS content was confined to a maximum of 25% in CA/SPS, and accordingly, the
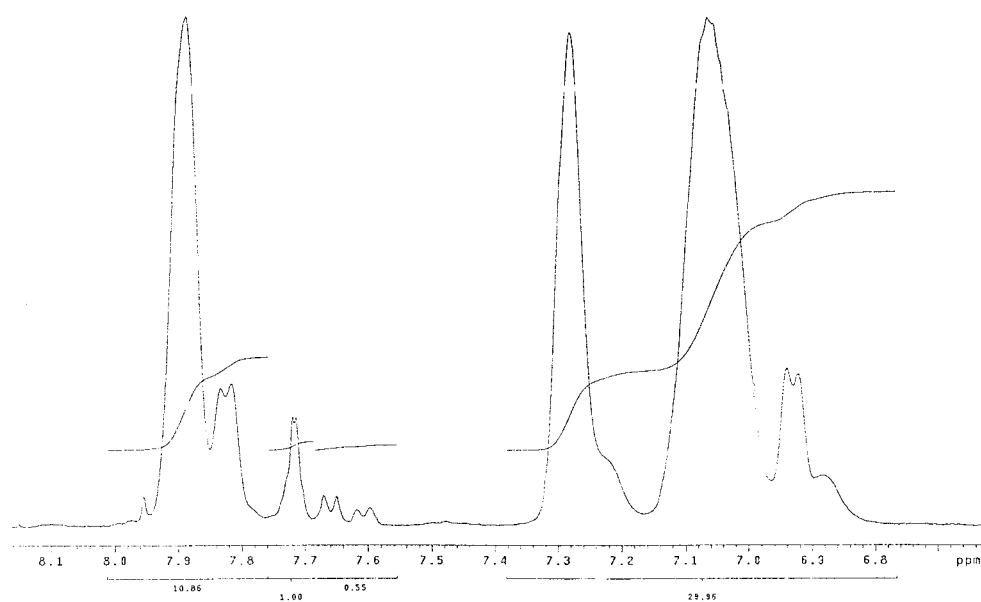
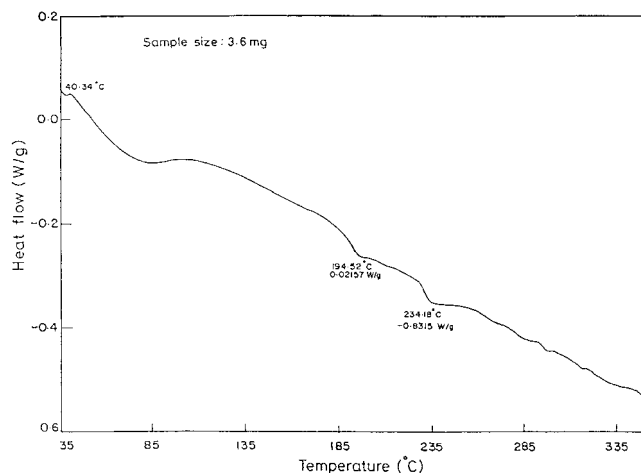**Figure 2**   NMR spectrum of sulfonated polysulfone.

Figure 3 DSC thermogram of sulfonated polysulfone.

blend membranes were prepared from different polymer compositions, viz., 95/5, 90/10, 85/15, 80/20, and 75/25%, with a total polymer concentration of 17.5 wt %.

Further, to improve and control the pore size of membranes, various nonsolvent additives such as polyethyleneglycol 600, maleic acid, and methyl cellosolve were used in separate experiments as pore formers in the casting solution of pure sulfonated polysulfone. The role of the above additives on pure water flux of the sulfonated polysulfone membrane is shown in Table V, and it has been inferred that the membranes with THE polymeric additive PEG 600 yielded the highest flux, due to its relative larger size. Further,
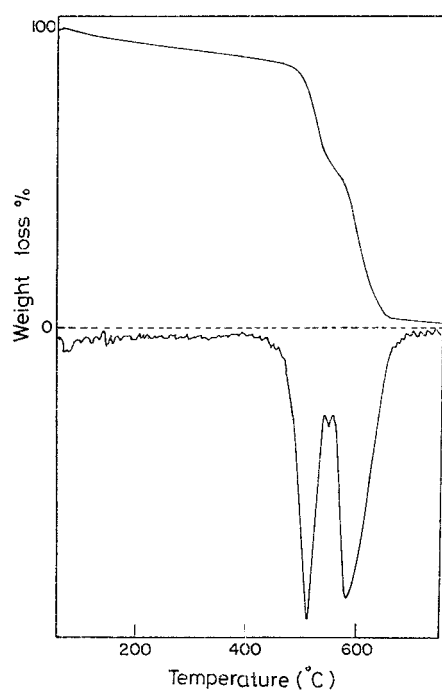
Figure 4 TGA curve of sulfonated polysulfone.

TABLE IV
Effect of Polymer Concentration on Pure Water Flux of SPS (100%) Membranes

SPS, wt %	DMF, wt %	Pure water flux ($l/m^{-2} \cdot h^{-1}$)
15.0	85.0	83.16
17.5	82.5	80.52
20.0	80.0	76.45

PEG has acted as a good compatibilizer in many systems, including the present blend system.[25–28]

The 600 molecular weight PEG was chosen, because casting solutions prepared with higher molecular weights are thermodynamically less stable and coagulation values become much lower.[29] The solvent DMF was chosen for all the studies, because DMF is a suitable solvent for SPS and other polymers and is advantageous for the gelation process, because of its hydrophilicity.[30]

Based on the above results, the total polymer blend concentration was maintained at 17.5 wt %, the rest being the additive PEG 600 and solvent in the present investigation.

Effect of compaction time on flux

Role of polymer blend composition

The compaction study was aimed to make the pores of the membranes uniform, rigid, and to get steady state flux. Further, during compaction, any trace quantity of additive or surfactant present inside the pores would also be eliminated.[6] Permeability results at the initial and at steady state are shown in Table I.

From Table I it is observed that in the case of pure cellulose acetate membrane, pure water flux decreased from 26.8 $L \cdot m^{-2} \cdot h^{-1}$, with increasing the time of compaction, and almost remains constant, i.e., at 16.1 $L \cdot m^{-2} \cdot h^{-1}$ after a definite time viz., between 3 to 4 h, indicating the completion of compaction. During compaction of polymeric membranes under pressure, the thickness of the membrane and pore sizes decrease by reorganization of polymeric chains, which in turn, lowers the porosity. This leads to an increase in the hydraulic resistance offered by the membrane as a result of the dense structure of the membrane, and consequently lowers the flux. Similar observations have been reported by other researchers.[31,32]

TABLE V
Effect of Different Additives on Pure Water Flux of Pure SPS Membranes

Additives	wt %	PWF ($l/m^{-2}h^{-1}$)
PEG 600	5.0	155.84
Maleic acid	5.0	93.72
Methyl cellosolve	5.0	97.56

When SPS was introduced in the blend system, from 5 to 25%, the initial water flux also increased from 29.8 $L \cdot m^{-2} \cdot h^{-1}$ to 111.3 $L \cdot m^{-2} \cdot h^{-1}$, as evidenced from Table I. This increase in flux upon increase in SPS composition may be due to the increase in the hydrophilic nature of the blend membranes.[14] The steady-state water flux was attained within 3 to 4 h of compaction, and the water flux was found to be considerably higher, i.e., 66.44 $L \cdot m^{-2} \cdot h^{-1}$ for a membrane having 25% SPS in the blend polymer, than the pure cellulose acetate.[33]

However, the pure SPS (100%) membranes yielded a relatively higher flux of 97.40 $L \cdot m^{-2} \cdot h^{-1}$ (Table I) after compaction at steady state, due to higher hydrophilicity of the sulphonated polysulfone. The CA/SPS blend membranes with high SPS composition have higher PWF than polysulfone membranes (Table III).

Role of additive concentration

The hydrophilic polymeric additive and pore former PEG 600 concentration in the polymer casting solution was varied, from 2.5 wt % in increments of 2.5 wt % for all the polymer blend solutions, and the maximum compatible additive concentration was found to be 10 wt %. Beyond this concentration, all the polymer blend solutions exhibited incompatibility with the additive, which may be due to the solutions reaching lower coagulation values.[34] The pure water flux on compaction at every hour for 5 h for all the CA, CA/SPS, and SPS membranes with different PEG 600 concentrations was measured, and the initial and steady-state values are reported in Table II.

Thus, a membrane with 100% CA in the presence of 2.5 wt % PEG 600 as an additive has a flux of 90.6 $L \cdot m^{-2} \cdot h^{-1}$ initially, and the flux decreases to a constant value of 48.5 $L \cdot m^{-2} \cdot h^{-1}$ after 3–4 h of compaction. It has a higher flux compared to a membrane made in the absence of PEG 600 (i.e., 16.1 $L \cdot m^{-2} \cdot h^{-1}$). Results are shown in Table II. Further, an increase in pore former concentration to 5 wt % increases the flux from 48.5 to 61.2 $L \cdot m^{-2} \cdot h^{-1}$, and this trend continued for the 10 wt % PEG 600 concentration. Thus, the presence of PEG 600 in the pure cellulose acetate casting solution has acted as a pore former and has proportionately increased the flux. Similar trends have also been observed for casting solutions with inorganic as well as organic additives.[7,35,36]

Further, for CA/SPS blend membranes of any particular composition, as the additive was increased, the water flux also increased and attained steady state within 3–4 h of compaction. This increase in flux upon increase of additive concentration may be due to the leaching out of additive during gelation, which leads to pore formation. Also, the steady-state behavior of flux after 3–4 h of compaction is due to the pores attaining uniform shape upon hydraulic compaction.

On the other hand, for a particular additive concentration, for example 2.5 wt %, when the SPS composition was increased in the blend from 0 to 20 wt %, an increase in flux from 48.5 $L \cdot m^{-2} \cdot h^{-1}$ to 72 $L \cdot m^{-2} \cdot h^{-1}$ was observed (Table II). The increase in flux behavior with an increase in SPS content may be due to the hydrophilic nature of the SPS. However, beyond 20% SPS in the blend, a decline in the steady-state flux to 68.4 $L \cdot m^{-2} \cdot h^{-1}$ was observed, which may be accounted for by the aggregation of SPS with PEG 600, known as nodular aggregates, giving a solution with different viscosities and a membrane with relatively fewer pores. The SEM images of CA/SPS membranes support these observations that at 10 wt % PEG 600 concentration, the membrane with 20% SPS composition has higher pore size and more numerous, than with the 25% SPS composition [Fig. 5(a)–(c)]. A similar trend has been observed for the polyethersulfone membrane with diethylene glycol as the nonsolvent additive.[37] Similarly, for 5, 7.5, and 10 wt % PEG 600 concentrations, the same trend has been observed (Table II).[33] The relative increase in flux may be due to the formation of higher and larger pores due to leaching out of additives in the gelation bath from the membrane at a higher rate. Irrespective of the amount of additive and SPS content in blend membranes, the steady state was attained after 3–4 h of compaction.

Similarly, for pure SPS membranes with all the additive concentrations, relatively higher PWF values were observed, and shown in Table II. However, the flux values of CA/SPS blend membranes with higher SPS content are higher than PSf membranes (Table III). The SEM pictures of pure PSf membranes at 0 and 10 wt % PEG 600 concentrations stand as evidence for the observed trend that, at 0 wt % PEG 600, the compaction phenomenon is greater and the compaction behavior decreases with an increase in additive concentration [Fig. 6(a) and (b)]. This may be due to the physical nature of hydrophobic polysulfone polymer, which does not undergo greater compaction although the pores are more open.

### Effect of polymer blend composition and additive concentration on pure water flux

The pure water fluxes of compacted CA, CA/SPS, and SPS membranes were measured at a constant sampling period under steady-state conditions, after 30–45 min of stabilization at 345 kPa transmembrane pressure.
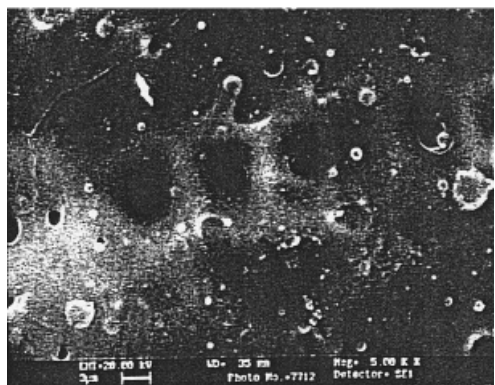
Role of polymer blend composition

The pure cellulose acetate (100%) membrane, prepared in the absence of the additive PEG 600, and SPS exhibited a low value of PWF due to its crystalline
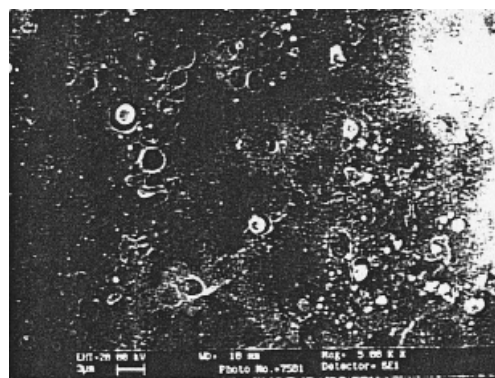
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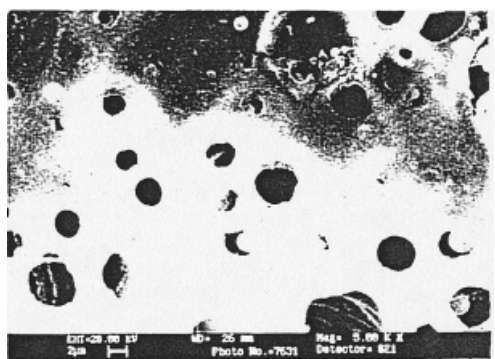
b

c

Figure 5 SEM micrographs of top surface of CA/SPS blend membranes with various blend compositions at 10 wt % additive concentration. (a) 95/5% CA/SPS; (b) 80/20% CA/SPS; (c) 75/25% CA/SPS.

nature, and the value was found to be 13.5 L · m^{-2} · h^{-1} (Fig. 7) at 345 kPa.

As SPS was increased to 5% cellulose acetate, an increase of flux to 14.54 L · m^{-2} · h^{-1} was observed (Fig. 7). This enhancement in flux may be due to the increase in the hydrophilicity of the blend membranes due to incorporation of hydrophilic SPS in the blend

system. The PWF of the blend membrane at 25% of SPS was found to be 55.06 L · m^{-2} · h^{-1}. Thus, the increase in flux is a direct consequence of the presence of SPS in the blend system. The increase in flux is not only due to the hydrophilicity but also due to the increasing immiscible phase behavior of the blend, due to low molecular attractive forces between the blend components.[38] This effect was more prominent in the presence of higher SPS content and led to increased flux, as reported.[39]

Further, the pure SPS membranes also resulted in a higher water flux of 80.51 L · m^{-2} · h^{-1} (Fig. 8). The water flux values of blend membranes with high SPS content are, however, obviously higher than that of pure PSf membranes (Fig. 8).
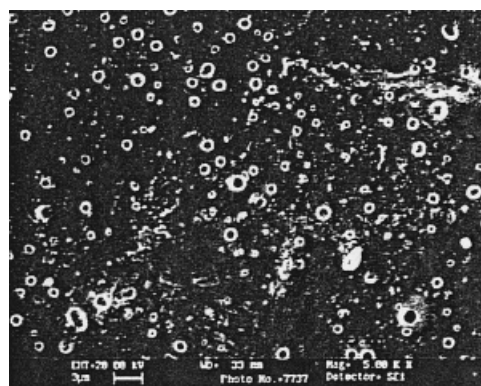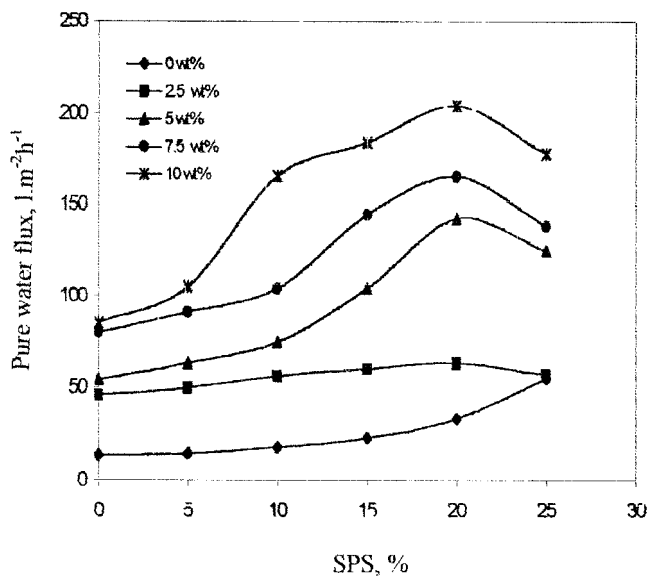

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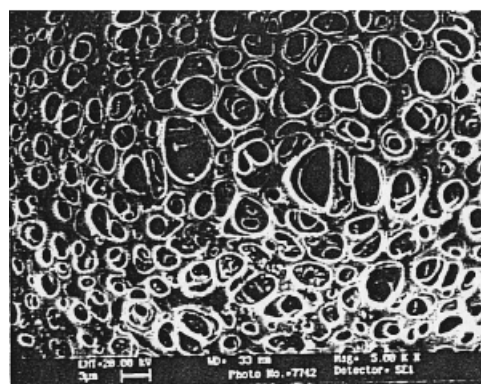
b

Figure 6 SEM micrographs of top surface of PSf (100%) membranes with different additive concentrations. (a) 0 wt % PEG 600; (b) 10 wt % PEG 600.
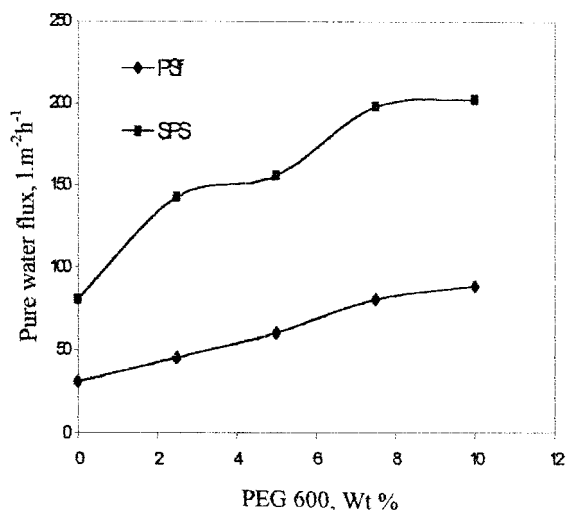
Figure 7 Effect of SPS composition on pure water flux–CA/SPS blend membranes with different additive concentrations.
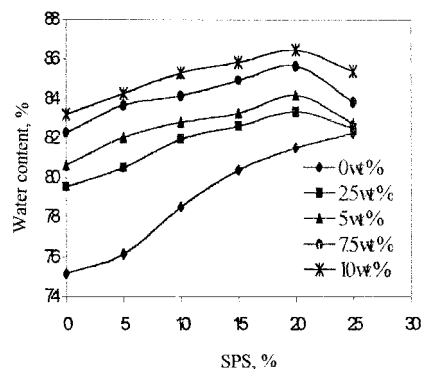
Role of additive concentration

The effect of the additive concentrations from 0 to 10 wt % at all polymer compositions on pure water flux was studied, and results are shown in Figure 7. For 100% CA membranes, as the additive concentration was increased from 0 to 10 wt %, there was an increase of PWF, from 13.5 to 85.19 $L \cdot m^{-2} \cdot h^{-1}$.

Similarly, for all the CA/SPS polymer blends from 95/5% to 75/25%, an increase in additive concentration increased the flux considerably. This trend indicates the leachability of the water soluble additive leading to the formation of larger pores.

On the other hand, for a given additive concentration viz., 2.5 wt %, an increase in SPS blend composi-

Figure 8 Effect of PEG 600 concentration on pure water flux–PSf (100%) and SPS (100%) membranes.

tion in the blend increases the flux only up to 20% of SPS composition in the blend. However, a further increase of SPS in the blend did not increase the flux; on the other hand, it decreased the PWF, as shown in Figure 7. Similar observations were also made for all additive concentrations viz., 5 to 10 wt %. This may be due to the interaction of the additive PEG 600 molecules with SPS at a concentration equal to or more than 25%, which slows down the precipitation of the polymer, resulting in the formation of a "sponge" type structure. The SEM pictures show the top surface of the membranes with different SPS compositions, and are evidence for this trend [Fig. 5(a)–(c). Similar results have also been observed by other researchers for blend membranes with PEG as an additive.[29]

However, a continuous increase in water flux was observed for SPS membranes with PEG pore former at 2.5 to 10 wt % (Fig. 8) and higher than the pure CA due to the hydrophilic nature of SPS. However, the values of CA/SPS blend membranes with high SPS content are higher than PSf membranes (Fig. 8).

Effect of polymer blend composition and additive concentration on water content

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 water content.

Role of polymer blend composition

The cellulose acetate membrane, in the absence of both SPS and PEG 600, was found to have a water content of 75.15%, as shown in Figure 9.

The SPS composition in the blend system was increased from 5 to 25% in absence of an additive, and its effect on water content is depicted in Figure 9. In the CA/SPS polymer blend, as the SPS content was increased, the water content also increased, and at 25%

Figure 9 Effect of SPS composition on water content–CA/SPS blend membranes with different additive concentrations.
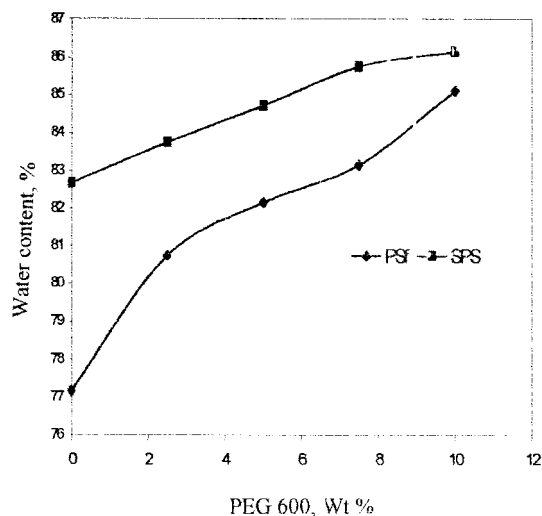
Figure 10 Effect of PEG 600 concentration on water content–PSf (100%) and SPS (100%) membranes.

of SPS, the water content was found to be 82.24%. This linear trend is due to the inherent water uptake of sodium ions, in the sodium salt of sulfonated polysulfone.

Further, this is confirmed by the fact that in the absence of an additive, the pure SPS membrane was found to have a water content of 82.67% (Fig. 10), which is comparatively higher than that of pure PSf membranes (Fig. 10). Similar results have also been observed for sodium salt of the sulfonated polysulfone membrane.[11]

Role of additive concentration

The pore former PEG 600 was added to the casting solution of CA, the CA/SPS blend, and SPS, and its influence on water content of membranes was studied. Thus, the pore former concentration in the casting solution of CA was increased from 0 to 10 wt % and the resulting water contents are shown in Figure 9. The addition of PEG 600 to the casting solution of pure CA enhanced the water content of the membranes. Thus, at 0 wt % PEG 600, the water content was found to be 75.15%, and attained a maximum of 83.19% at 10 wt % PEG 600.

It is also evident from the table and figure that in all the blend membranes, as the concentration of PEG was increased to 2.5 wt %, the water content also increased. This increase in water content, irrespective of the polymer blend composition, may be due to the addition of PEG 600 to the casting solution, which gets leached out upon gelation leading to pore formation, which becomes the domain of water molecules.[40] A further increase in the PEG 600 to 5, 7.5, and 10 wt % in the casting solution, also resulted in membranes with increasing water content. The above reason con-

firms the PEG 600 activity in the formation of membranes.

However, for a given additive concentration of 2.5 wt %, an increase in SPS composition in the blend increased the water content only up to 20% of SPS. Beyond this SPS composition, the increase in SPS content in the blend decreased the water content. A similar trend has also been observed for all the additive concentrations in the blend. This trend of passing through a maximum may be due to reduced pore formation in the membranes, and the subsequent lower water content may be due to the formation of network or aggregation of the polymer chain in view of the interaction between SPS and PEG at a higher concentration in the presence of CA.[28]

On the other hand, a continuous increase in water content was observed for pure SPS membranes when the pore former concentration was increased from 2.5 to 10 wt % (Fig. 10). The water content values of CA/SPS blend membranes at a higher SPS content are comparatively higher than PSf membranes (Fig. 10).

Effect of polymer blend composition and additive concentration on hydraulic resistance

Membrane hydraulic resistance, R_m, an indication of the tolerance of a membrane towards hydraulic pressure, was measured by subjecting the membranes to various pressures from 69 to 414 kPa and measuring the pure water flux. Thus, all the membranes, such as pure CA, CA/SPS, and SPS, prepared both in the absence and in the presence of additive PEG 600, were subjected to a pure water flux study. R_m was calculated from the inverse of the initial slope of the corresponding pressure vs. pure water flux plots (Figs. 11 and 12), and are presented in Table VI. Figures 11 and 12 are the pressure variation against water flux graphs, for pure the CA membrane and the CA/SPS membrane with 5 wt % PEG 600, and are representatives of these experiments. From the figures we observe that the flux is linear only up to >200 kPa, and the resistance values have been determined from this narrow range. Also, for some of the membranes, even at higher pressures, the plots appears to become more linear, and the hydraulic resistance may be similar, which may be due to the fact that once the compaction is stabilized, the hydraulic resistance is similar for various membranes. However, the nonlinearity observed in certain membranes may be due to the fact that the compaction proceeds further at higher operating pressures. However, this trend can be explained by the exponential model followed by Kinzer et al.[12] in our later studies.

Role of polymer blend composition

It is evident from Table VI that the pure CA membrane, in absence of additive and PEG, exhibited a
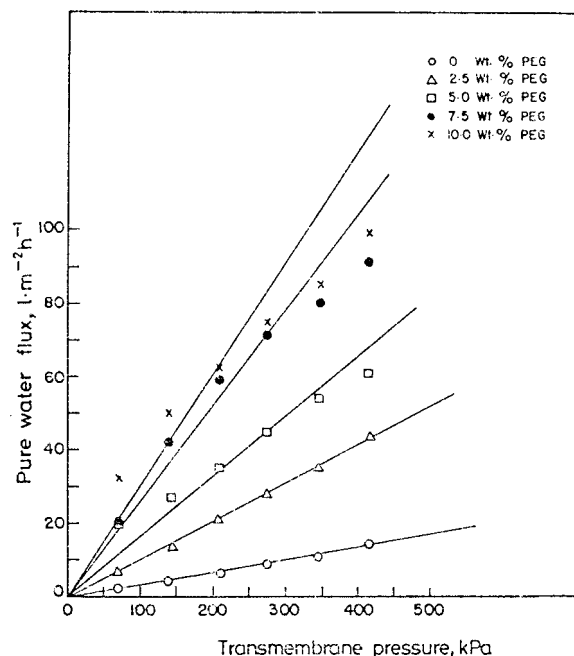
Figure 11 Effect of transmembrane pressure on pure water flux–CA (100%) membranes with different additive concentrations.

higher membrane resistance of 2.90 kPa/L $\cdot$ m^{-2} $\cdot$ h^{-1} due to its low porosity. Thus, from Figure 11 it is observed that, at low PEG 600 concentrations, due to low porosity, the compaction has been found to be negligibly less. In the blend membranes in the absence
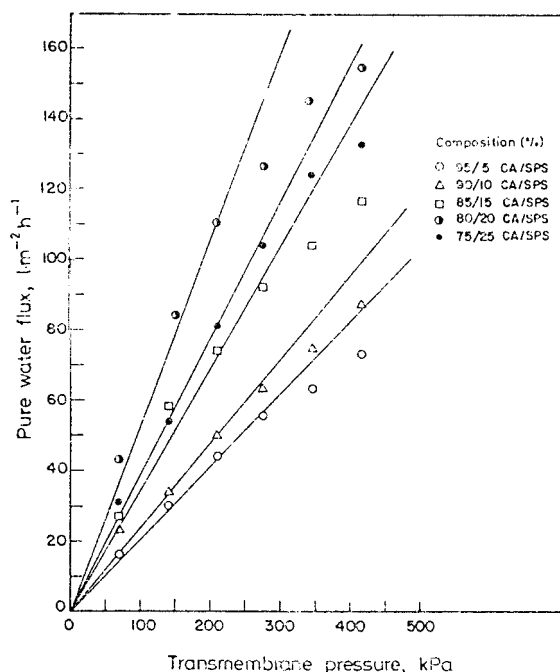
Figure 12 Effect of transmembrane pressure on pure water flux–CA/SPS blend membranes with 5 wt % additive concentration.

TABLE VI
Membrane Hydraulic Resistance of CA/SPS Blend Membranes

Blend composition (%) (17.5 wt %)		Membrane hydraulic resistance, R_m, (kPa/l/m^{-2} h^{-1})				
		PEG 600 Concentration, wt %				
CA	SPS	0	2.5	5.0	7.5	10.0
100	0	2.90	0.96	0.60	0.37	0.34
95	5	2.85	0.68	0.50	0.35	0.33
90	10	1.92	0.62	0.41	0.31	0.20
85	15	1.50	0.55	0.28	0.21	0.15
80	20	1.11	0.52	0.19	0.19	0.12
75	25	0.73	0.60	0.26	0.34	0.18
0	100	0.38	0.26	0.18	0.15	0.13

of an additive, as the SPS composition was increased from 5 to 25%, the hydraulic resistance decreased gradually from 2.85 kPa/L $\cdot$ m^{-2} $\cdot$ h^{-1} to 0.73 kPa/l $\cdot$ m^{-2} $\cdot$ h^{-1}. This may be explained by the fact that an increase in the composition of SPS not only increases the amorphous nature of membranes, but also enhances the size of pores to a greater extent due to extended segmental gap between polymer chain, which leads to a decrease in the value of R_m.[32]

For pure SPS membranes, the R_m value was found to be 0.38 kPa/L $\cdot$ m^{-2} $\cdot$ h^{-1}, which may be due to the higher hydrophilicity and larger pores observed in the SPS membrane. In general, membrane resistance of CA/SPS blend membranes (Table VI) is lower than that of pure PSf membranes (Table VII) due to the enhanced hydrophilicity of CA/SPS blend membranes.

Role of additive concentration

The presence of an additive in the casting solution has a considerable effect on the membrane resistance. Thus, when the PEG concentration was increased from 2.5 to 10 wt % in the casting solution of pure CA there was a corresponding decrease in resistance of membrane, from 0.96 to 0.34 kPa/L $\cdot$ m^{-2} $\cdot$ h^{-1} and the results are depicted in Table VI.

Similarly, for a given blend composition, when the additive concentration was increased, the R_m decreased linearly. Membranes, with all the blend com-

TABLE VII
Membrane Hydraulic Resistance, R_m, of Pure PSf Membranes

Composition (%) polymer weight 17.5 wt %	Membrane hydraulic resistance, R_m,(kPa/l/m^{-2}h^{-1})				
	PEG 600 concentration, wt %				
	0	2.5	5.0	7.5	10.0
PSf (100%)	1.15	0.79	0.73	0.43	0.40

positions, exhibited the same trend. This may be due to the fact that the addition of pore former in the casting solution results in the formation of macrovoids on the membrane surface due to thermodynamical instability, which enhances precipitation and porous nature.[41] This can also be supported by the observation that an increase in PEG content has increased the flux due to higher and larger pore formation, thereby reducing the membrane resistance.

For a given additive concentration, as the SPS content was increased, the R_m decreased due to the reasons discussed earlier. However, this trend was not followed when the SPS content was increased to 25% in the blend system because of the formation of a dense structure of the polymer–PEG 600 matrix and reduction in pore formation (Table VI), and due to hindrance in formation of voids due to the presence of a higher concentration of additive and its hydrophilicity.[42]

For pure SPS membranes, and all additive concentrations studied, the hydraulic resistance was comparatively low (Table VI). The resistance of CA/SPS membranes is lower than PSf membranes (Table VII).

Factors influencing the observations

From these studies, the important factors found to influence the characteristics of the blend membranes are (1) the hydrophilicity of the sulfonated polysulfone, and (2) membrane morphology with respect to various polymer and additive compositions. In this present investigation, and also from work of earlier researchers on modification of polysulfone and development of sulfonated polysulfone, it has been confirmed that the presence of the sulfonic group, which is hydrophilic in nature, is responsible for the change in properties of the resulting membranes, such as T_g, pure water flux, and water content.[8,14] Similarly, the presence of hydrophilic additives and their concentration, in the present case PEG 600, are important factors for changing porosity, pore volume, pore size, and subsequently the water flux, water content, and membrane resistance of the resulting membranes.[29,40]

CONCLUSION

Sulfonated polysulfone was prepared and found to be compatible with cellulose acetate and polyethylene glycol 600 at various compositions. The extent of compatibility of sulfonated polysulfone and cellulose acetate was found to be 75/25%, and the additive compatibility was found to be 10 wt %. It was found that polymer composition and additive concentration had a major influence on the ultrafiltration characteristics of membranes such as pure water flux, membrane resistance, and water content.

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