

# Performance enhancement of polysulfone ultrafiltration membrane by blending with polyurethane hydrophilic polymer

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## Abstract

The aim of this work was to study the effect of two solvents such as *N,N'*-dimethylformamide (DMF) and dimethylacetamide (DMAc) used in the production of polysulfone (PSf) and polyurethane (PU) blend ultrafiltration membranes, influence permeability and selectivity. PSf/PU membranes were prepared by the phase inversion method using polymer concentrations of 100/0, 20/80 and 0/100 wt%. Permeation performance of the prepared membranes was evaluated in terms of pure water flux, water content and hydraulic resistance. It was found that the membrane composed of 20/80 wt% of PSf/PU in the presence of DMAc showed a water flux of 60.5 l m<sup>-2</sup> h<sup>-1</sup> under transmembrane pressure of 345 kPa, and the water flux of 23.5 l m<sup>-2</sup> h<sup>-1</sup> for 20/80 wt% of PSf/PU in the presence of DMF. With increasing the polarity of DMAc in the casting solution, an increase in porous layer thickness was observed, and then a good water flux of membranes can be obtained. It was found that the polar solvent caused the rapidly demixing of casting solution in coagulation bath and formed porous asymmetric membranes with defective skin layer. The permeation rates of proteins were measured with different molecular weights of the proteins.

**Keywords:** membrane preparation; permeation; polymer membrane; solvents; ultrafiltration.

## 1. Introduction

Polymeric membranes have been well recognized in an extensive variety of industrial applications [1]. Membranes are mainly prepared by a process where phase separation is induced by a non-solvent (NIPS). In a phase separation method a polymer solution loses solvent by evaporation or exchange with another liquid, called non-solvent and followed by precipitation of the polymer to form the

membrane. In the NIPS process [2, 3], the dope is made by dissolving the polymer in a mixture of solvent and non-solvent. The solvent in the film, cast on a glass surface, is allowed to evaporate under a controlled environment to control the membrane morphology. Polymer blending is a proven tool to obtain new types of materials with a wide diversity of properties intermediate between those of pure components. Blending of polymers not only modifies the properties of membrane made from single polymer but also increases the flux of the membrane [4, 5]. However, the properties of the polymer blend depend upon the compatibility of the individual polymers with each other and the method of mixing.

Polysulfone (PSf) having its superior properties such as chemical, mechanical and thermal resistance, is considered an ideal candidate in the membrane industry. However, owing to the emerging problems such as fouling, either blending with additional polymer [6] or other modification of membrane polymers has been found to be necessary. The use of PSf for aqueous phase is restricted due to its hydrophobicity and could be improved by modification of PSf through blending. The blend membranes have better permselectivity and permeability than that of membrane composed of the individual polymers. Chakrabarty et al. [7] reported increased trend of flux, number of pore number and pore area with adding hydrophilic polymer of polyvinylpyrrolidone in hydrophobic PSf polymer. Recently, Qtaishat et al. [8] prepared novel composite hydrophobic/hydrophilic membranes for membrane distillation using blended PSf with surface modifying macromolecules.

Membranes based on polyurethane (PU) have also been prepared by other researchers and were characterized for water permeability and void formation [9]. Because of their flexible permeability and diffusivity, PUs were also used for membrane preparations for gas fractionations. Thus, blending of PSf with an amorphous hydrophilic and relatively inexpensive polymer such as PU not only can reduce the cost of the finished product but also facilitate the development of new materials with the combined properties. Sivakumar et al. [10] fabricated cellulose acetate (CA) membranes by solution blending of CA with PU in *N,N'*-dimethylformamide (DMF) as solvent. In their study, they reported that hydrophilic/hydrophobic balance was altered and blend membranes showed better solute flux compared with pure CA membranes. Duarte et al. [11] produced PU/polyethersulfone composite membranes to obtain a support with low transport resistance. In their study, different non-solvents (gelation solution) were used to alter membrane morphological

structure. Because Filip and Macocinschi [12] have already investigated the effect of PSf as blend polymer with increment of 20 wt% and the effect of thermal stability and activation energy of PU membranes, we have made an attempt to study the effect of PU as a blending polymer up to 20 wt% and the effect of solvents dimethylacetamide (DMAc) and DMF in the ultrafiltration performance. Various solvents have been used for the formation of membranes. A proper selection of a solvent plays a vital role in the characteristics of membranes formed. Chakrabarty et al. [13] formed PSf asymmetric membranes using N-methyl-2-pyrrolidone (NMP) and DMAc solvents separately. In the present investigation, membrane prepared by the NIPS process on solution blending of PSf with PU and the performance of blend membranes are reported. The effect of PU composition used in the DMF and DMAc casting solution on pure water flux, water content and on hydraulic resistance of the blend membranes are discussed and compared with solvents made from PSf and PU.

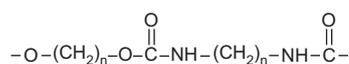
## 2. Experimental

### 2.1. Materials and methods

Commercial grade polysulfone Udel P-3500 (PSf) was supplied, as a gift sample, by Amoco Polymers Inc. (Alpharetta, GA, USA), and was used as received. Commercial grade PU ( $M_w=160$  kDa,  $T_g=23^\circ\text{C}$ ) grade no. 58311, obtained from M/s. Chemplast Ltd. (Chennai, Tamilnadu, India), was used as received. The chemical structure of PU is given in Figure 1. DMF, DMAc and sodium lauryl sulfate of analar grade were from SD Fine Chemicals (Mumbai, Maharashtra, India). Proteins, namely, bovine serum albumin (BSA) (69 kDa), from Himedia Laboratories (Mumbai, Maharashtra, India); egg albumin (EA) (45 kDa), from CSIR Biochemical Center (Delhi, Uttar Pradesh, India); pepsin (35 kDa) and trypsin (20 kDa), from SRL (Mumbai, Maharashtra, India) were also obtained.

### 2.2. Preparation of membranes

The solutions of PSf, PU at a total polymer concentration of 17.5 wt% were prepared by dissolving in three different compositions (PSf/PU: 100/0, 20/80 and 0/100 wt%), of polar solvents DMF and DMAc, under constant mechanical stirring at  $50^\circ\text{C}$  for 3 h. The membranes were cast on a glass plate using a Doctor blade (Petro-lab Instruments, Kolkata, West Bengal, India). After 30 s of solvent evaporation at 50% relative humidity, the polymer film was immersed in the gelation bath containing water and surfactants kept at  $10^\circ\text{C}$ . The thickness of spread casting solution was



**Figure 1** Chemical structure of polyurethane used for membrane formation.

controlled by manually adjusting the height of the casting blade. Thickness of the cast membranes was measured by a micrometer (Mitutoyo, Tokyo, Japan) at various parts of a particular membrane. The thickness of the membrane was maintained  $0.22\pm 0.02$  mm.

### 2.3. Characterization of membranes

The membranes were cut into circular discs with a diameter of 76 mm for setup in a stirred UF cell (UF cell-XFUFO7601-Model, Millipore India Ltd., Bangalore, Karnataka, India) fitted with Teflon coated magnetic paddle. The ultrafiltration (UF) experiments were carried out in a 400-ml feed solution and effective membrane area available for  $38.5\text{ cm}^2$ . The solution filled in the cell was stirred at 400 rpm using a magnetic stirrer. All the experiments were carried out at  $30\pm 2^\circ\text{C}$  and 345 kPa transmembrane pressure. The pure water flux was calculated by measuring the volume of permeates that penetrated the membrane per unit time. These wet membranes were dried for 12 h at  $100\pm 2^\circ\text{C}$  and weighed. From the dry and wet weights of the samples, the percent water contents were calculated using the equation given elsewhere [14]. To determine the membrane hydraulic resistance ( $R_m$ ), the pure water flux of the membranes was measured at different transmembrane pressures ( $\Delta P$ ), i.e., 69, 138, 207, 276 and 345 kPa. The variation of pure water flux was plotted as a function of pressure for all prepared membranes. The hydraulic resistances of the membranes ( $R_m$ ) were determined from the inverse of slopes using the following equation:

$$R_m = \frac{\Delta P}{J_w} \quad (1)$$

### 2.4. Morphological studies

The membranes were cut into small pieces and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20–30 s and frozen. The cross-sections of the membranes were viewed using a Jeol JSM-840A scanning electron microscope (Tokyo, Japan).

### 2.5. Protein permeation studies

Aqueous solutions of trypsin pepsin, EA and BSA were prepared at a concentration of 1000 ppm by dissolving the proteins (0.1 wt%) individually in phosphate buffer (0.5 M, pH 7.2). The experiments were performed in the order of trypsin pepsin, EA and BSA. The stirred UF cell was filled with protein solution and maintained at a constant pressure of 345 kPa. Then after UF, the permeate solutions of corresponding membranes were collected in graduated tubes and were analyzed for the concentration of protein using a UV-Visible spectrophotometer (Shimadzu, Model UV-160A, Kyoto, Japan) at  $\lambda_{\text{max}}$  of 280 nm. The percentage protein rejection was calculated from the concentration of protein in the feed and permeate using the following equation:

$$\%SR = \left[ 1 - \left( \frac{C_p}{C_f} \right) \right] \times 100 \quad (2)$$

where,  $C_p$  is the concentration of permeate, and  $C_f$  is the concentration of feed.

## 2.6. Pore size distribution studies

From the protein rejection studies, the pore size distribution (average pore radius, surface porosity and pore density) of the membranes was calculated. The average pore radius was found using Eq. (3) [15]:

$$\bar{R} = \frac{\bar{\alpha}}{\% SR} \times 100 \quad (3)$$

where  $\bar{R}$  is the average pore radius ( $\text{\AA}$ ) of the membrane;  $\bar{\alpha}$  is the average solute radius ( $\text{\AA}$ ) and is constant for each molecular weight. The average solute radii is known as 'stoke radii' and the value of  $\bar{\alpha}$  can be found from the plot between the solute radius and molecular weight of the solute as given by Sarbolouki [16] which is shown in Table 1. Assuming the membrane to be of asymmetric type, the surface porosity of the membrane was found using Eq. (4):

$$\varepsilon = \frac{3\pi\eta_w J_{w1}}{\bar{R} \times \Delta P} \quad (4)$$

where  $\varepsilon$  is the surface porosity;  $\eta_w$  is the viscosity of the deionized water ( $\text{g cm}^{-1} \text{s}^{-1}$ );  $J_{w1}$  is the pure water flux ( $\text{cm s}^{-1}$ ) and  $\Delta P$  is the applied pressure ( $\text{dyn cm}^{-1}$ ). From the values of  $\varepsilon$  and  $R$  (cm), the pore density in the membrane surface was calculated using Eq. (5).

$$n = \frac{\varepsilon}{\pi \times \bar{R}^2} \quad (5)$$

where  $n$  is number of pores  $\text{cm}^{-1}$ .

## 3. Results and discussion

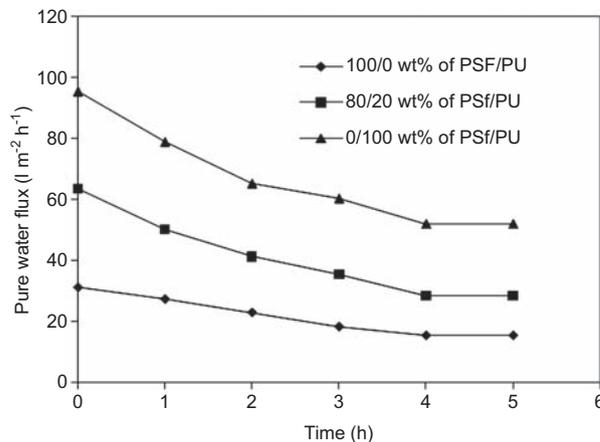
### 3.1. Effect of compaction time

The effect of compaction time on pure water flux (PWF) for all PSf, PSf/PU and PU blend membranes with DMF and DMAc is shown in Figures 2 and 3. It is seen that PWF declines gradually due to compaction with time, and after approximately 5 h of compaction it reaches a steady-state value. This is due to the fact that the walls of the pores become closer, denser and uniform resulting in reduction in pore size as well as the

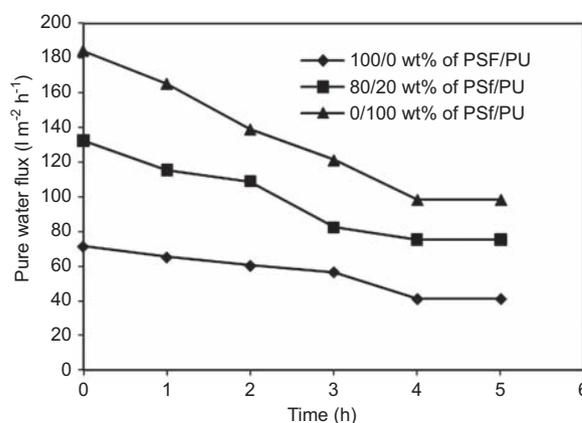
**Table 1** Average solute radius and molecular weight of the selected proteins.

Protein	Molecular weight (kDa)	Average solute radius ( $\text{\AA}$ ) <sup>a</sup>
Trypsin	20	21.5
Pepsin	35	28.5
Egg albumin	45	33.0
BSA	69	45.0

<sup>a</sup>Values given by Sarbolouki [16].

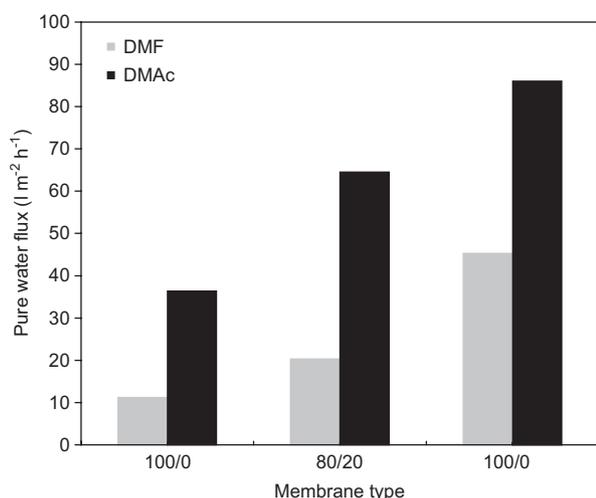


**Figure 2** Effect of compaction time on pure water flux with DMF as solvent.



**Figure 3** Effect of compaction time on pure water flux with DMAc as solvent.

flux during compaction [17]. Thus, a membrane with 100% PSf in DMAc as solvent has a flux at 414 kPa of  $71.5 \text{ l m}^{-2} \text{ h}^{-1}$  initially and this decreased to a steady-state value of  $41.2 \text{ l m}^{-2} \text{ h}^{-1}$  after 5 h of compaction, which is higher than that of membrane made in the presence of DMF (i.e.,  $15.4 \text{ l m}^{-2} \text{ h}^{-1}$ ). This could be due to diffusivities of solvents in non-solvents. The order of the above two solvent/non-solvent diffusivities was:  $\text{DMF} > \text{DMAc}$  [18]. The sublayer structure in which the size of cavity was relatively bigger and the number of cavity was smaller was then obtained in the presence of DMAc and DMF. By contrast, the mutual diffusion rate of the DMAc-water or DMF-water was relatively quicker. The creation and pore formation induced by this quicker mutual diffusion competed with each other, which resulted in the final sublayer structure of the PSf/PU membranes with DMAc and DMF. From the above discussion, it could be concluded that it was the mutual diffusion rate of the non-solvent/solvent that was controlled by solvents and membrane structure. These observations were in accordance with the effects indicated by Chakrabarty et al. [13]. The addition of PU to PSf, in the presence of both solvents, also has the same effect on pure water



**Figure 4** Effect of PU and solvents on PWF.

flux. Thus, a membrane with PSf/PU ratio as 80/20 wt% in the presence of DMAc has a constant flux value of 75.4 l m<sup>-2</sup> h<sup>-1</sup> after 5 h compaction.

### 3.2. Pure water flux and equilibrium water content

The effect of difference of solvents on PWF and water content (WC) of PSf/PU blend membranes is shown in Figure 4 and Table 2, respectively. PWF is the key specification of any membrane and must be essentially determined. For the PSf, PSf/PU blend and PU membranes, PWF was measured at 345 kPa pressure, under steady-state conditions and at a constant sampling period. All the membranes were stabilized for the PWF measurement for 30–40 min. It could be seen that the addition of PU in the dope solution increased the PWF of the membrane. The PWF of 100 wt% PSf membrane in the presence of DMF as solvent was 11.2 l m<sup>-2</sup> h<sup>-1</sup> at 345 kPa transmembrane pressure (TMP). PWF increases from 11.2 to 45.3 l m<sup>-2</sup> h<sup>-1</sup> with an increase in the concentration of PU from 0 to 100 wt% in PSf membrane. A similar observation has also been reported elsewhere [19] for polyether-polyamide blend membranes. According to Shen et al. [20], the solvent dissolution power for membrane formation ranked NMP>DMAc>DMF>DMSO. The rate of polymer precipitation became slower from cloud point data for the ternary polymer-solvent-water systems, as

could the decrease of PWF of the final membrane. As can be seen in Table 2, the water content increased with an increase of PU content, the water content of blend PSf /PU membranes with DMAc was higher than that of the PSf /PU membranes with DMF. This increasing trend confirms the presence of increasing number of pores in the membrane with the increased concentration of PU (20 wt%).

### 3.3. Membrane hydraulic resistance

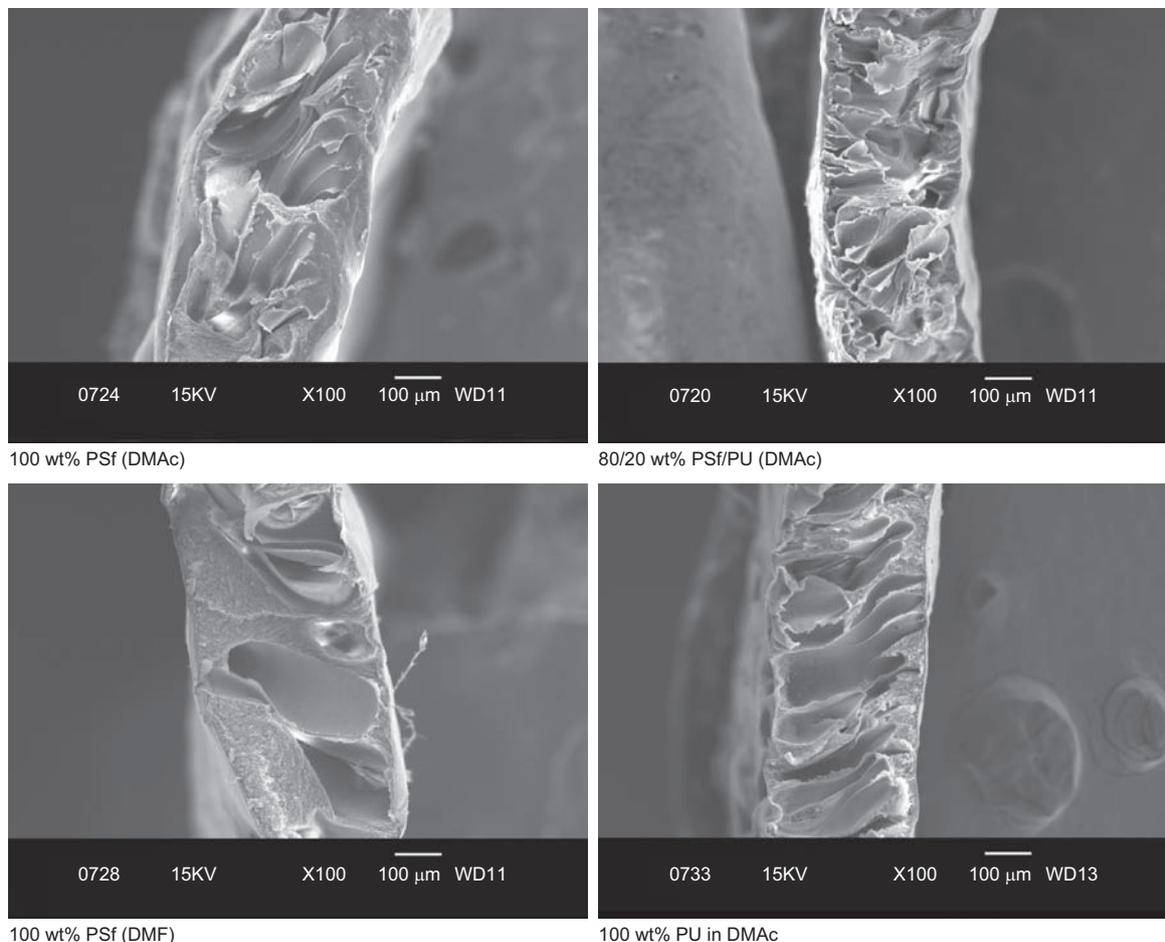
The hydraulic resistance of the membrane was calculated using Eq. (1). As can be seen in Table 2, the 100 wt% PSf in DMF exhibited membrane resistance of 12.5 kPa/l m<sup>-2</sup> h<sup>-1</sup> and membrane resistance decreases to 10.3 kPa/l m<sup>-2</sup> h<sup>-1</sup> for 100 wt% PSf in DMAc. The reduced resistance is due to the polarity and volatility of the solvents. Using DMF as the solvent, the obtained membrane contains high membrane resistance, which is due to the instantaneous liquid-liquid demixing. Using DMAc as the solvent, the lowest membrane resistance for the delayed liquid-liquid demixing was obtained. A similar trend has also been observed for blend membranes prepared from 80/20 wt% of PSf/PU blend in the presence of both solvents. Similar observations have also been observed by Malaisamy et al. [21] for PU and sulfonated PSf blend UF membranes.

### 3.4. Morphological studies

It can be seen from Figure 5 that membranes thus formed are of asymmetric structure consisting of a dense top layer and a porous sublayer. The sublayer seems to have finger-like cavities as well as macrovoid structure. The shape and structure can be related to the concentration and composition of solvents and polymer in the casting solution. The size of the skin layer increases with adding PU content in the casting solution. It should be noted that a 100 wt% of PU was enough to initiate the formation of pores in the skin layer. When comparing SEM photos, the increasing pore size and increasing finger-like voids are due to addition solvents such as DMF and DMAc. The order of the two solvent/non-solvent diffusivities was: DMF>DMAc [18]; there existed one determinable factor similar to the mutual diffusion of the solvent/non-solvent that dominated the total polyvinylidene fluoride (PVDF) membrane formation process. That is to say, in the sublayer formation process of PSf membrane,

**Table 2** Water content,  $R_m$  and pore size distribution of PSf/PU blend membranes.

Polymer composition (17.5 wt%)		DMF, wt%	DMAc, wt%	Water content, %	$R_m$ (kPa/l m <sup>2</sup> h <sup>-1</sup> )	Average pore radius, R (Å)	Surface porosity, $\epsilon \times 10^{-5}$	Pore density, number of pores/cm <sup>2</sup> , $\eta \times 10^9$
PSf, %	PU, %							
100	0	82.5	–	70	12.5	21.5	4.3	6.0
		–	82.5	75	10.3	29.0	6.5	6.8
80	20	82.5	–	78	8.3	36.3	5.4	6.5
		–	82.5	82	6.4	42.5	7.3	7.0
0	100	82.5	–	86	4.1	45.6	6.7	7.3
		–	82.5	89	1.7	53.2	7.9	7.6



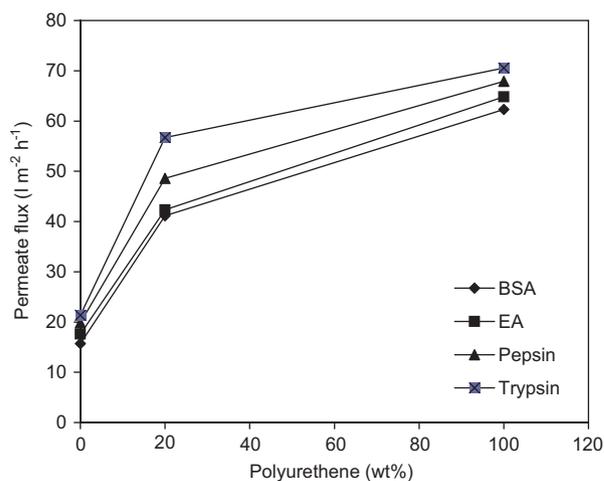
**Figure 5** Morphological view of membranes.

the mutual diffusion rate of the DMF-water or DMAc-water was relatively slower, which resulted in a slower rate of the creation of a new nucleus. The macrovoids were formed during the solidification process, also known as the nucleation process [22]. The coagulant solution diffused through the surface layer into the membrane wall and accumulated as droplets underneath the surface layer. The solvent from the surrounding polymer solutions dissolved into the droplets and contributed to the growth of the droplets in size. Phase inversion occurred during the solvent exchange process from the polymer solutions, which led to solidification of the surrounding polymer. Consequently, the space filled with coagulant and the solvent was solidified and macrovoids were formed.

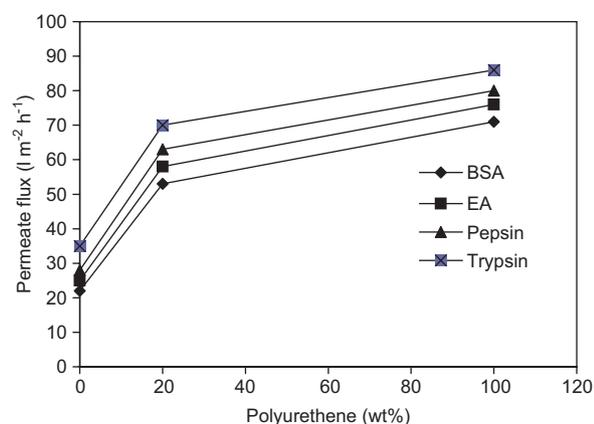
### 3.5. Pore size distribution

As seen in Table 2, the average pore radius of the PSf membrane is 21.5 Å in the presence of 82.5 wt% DMF. It is seen that adding 82.5 wt% DMAc in the PSf casting solution enhances the pore radius in the membrane to 29.5 Å due to the quicker mutual diffusion solvents and non-solvent. Surface porosity ( $\epsilon$ ) provides total pore area per unit

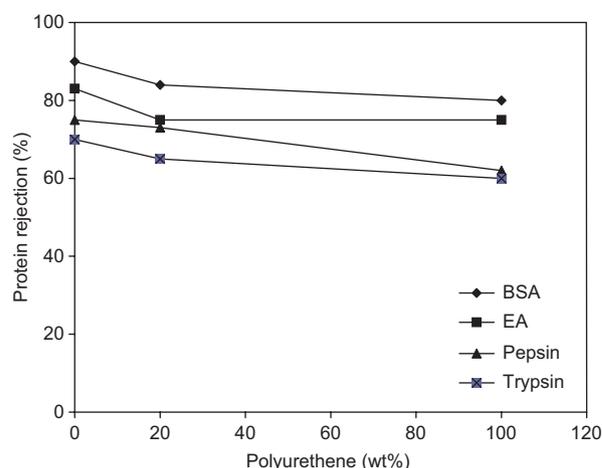
surface area of the membrane. As seen in Table 2, the value of  $\epsilon$  is found to be  $4.3 \times 10^{-5}$  for PSf hydrophobic membrane in the presence of DMF as solvent. When the hydrophilic



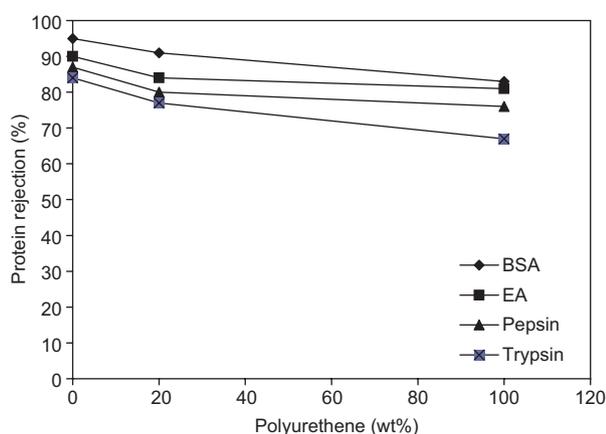
**Figure 6** Effect of PU on permeation of protein in the presence of DMF.



**Figure 7** Effect of PU on permeation of protein in the presence of DMAc.



**Figure 9** Effect of PU on protein rejection in the presence of DMAc.



**Figure 8** Effect of PU on protein rejection in the presence of DMF.

PU content was increased to 20 wt% in the PSf polymer matrix, the surface porosity increased to  $5.48 \times 10^{-5}$  in the presence of DMF as solvent. Consequently, the water flux through such porous membranes is expected to increase significantly with reduced retention. These results are in good agreement with the PWF data. Malaisamy et al. [23] obtained similar results when PU was added to sulfonated PSf blend membranes. When pure PU membrane is compared with the PSf and 80/20 wt% PSf/PU, the average pore radius, surface porosity and pore density values are enhanced. These results show the more hydrophilic character of the PU membrane, which is reported by Malaisamy et al. [23].

### 3.6. Protein permeation studies

The effect of PU composition on the protein permeate flux and rejection through 100/0, 80/20 and 0/100 wt% PSf/PU blend membranes are shown in Figures 6–9, respectively. It is apparent that the permeate flux of a given protein through

80/20 wt% blend membranes is higher than 100 wt% PSf membrane. The permeate flux of trypsin for the 80/20 wt% membrane in the presence of DMF was found to be  $56.7 \text{ l m}^{-2} \text{ h}^{-1}$ , and for the membrane prepared from casting solution with DMAc as solvent the permeate flux increased to  $70 \text{ l m}^{-2} \text{ h}^{-1}$ . As the nature of solvents present in the casting solution increases the surface porosity of the membrane also increases. Similar trends were observed for pepsin, EA and BSA protein solutions. The order of magnitude of permeate flux of protein solution was found to be trypsin>pepsin>EA>BSA for all membranes, which is due to the differences in the molecular weight. It can be observed that the rejection of trypsin for 80/20 wt% in DMF blend membrane is found to be 77%, whereas for the membranes prepared from casting solution with DMAc as solvent, the rejection decreased from 77% to 65%, respectively. Similar results were reported by Sivakumar et al. [24] for removal proteins through CA/PSf blend membrane.

## 4. Conclusions

PU was added into pure PSf casting solution as a hydrophilic polymer to enhance the permeability performance of PSf/PU blend membranes. Prepared membranes were characterized in terms of their PWF, hydraulic resistance, molecular weight cut-off and morphological properties. The solvent nature played a significant role in the performance and structure of the resulting PSf/PU blend UF membranes made from the casting solutions using DMAc and DMF solvents. The order of the PWF of these membranes was: DMAc>DMF. PWF increased and rejection for protein solution increased with the increase in PU concentration. The permeate flux of protein of the PSf/PU blend membrane was  $53 \text{ l m}^{-2} \text{ h}^{-1}$  (using DMAc) and  $41 \text{ l m}^{-2} \text{ h}^{-1}$  (using DMF), when the polymer concentration was 80/20 wt%, which indicates that PU was a little more hydrophilic than PSf while in solution.

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