Preparation, Structure, and Transport Properties of Ultrafiltration Membranes of Poly(vinyl chloride) (PVC), Carboxylated Poly(vinyl chloride) (CPVC), and PVC/CPVC Blends

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ABSTRACT: Ultrafiltration (UF) membranes were prepared from poly(vinyl chloride) (PVC), carboxylated poly(vinyl chloride) (CPVC), and PVC/CPVC blends by the phaseinversion method. The physical structure of the membranes was characterized by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The fouling characteristics of all the three membranes and acrylamide (AA)-grafted PVC membranes were characterized by ultrafiltration of bovine serum albumin (BSA) solution over a range of pH and of salt concentrations. Maximum adsorption of the protein on the membrane occurred near the isoelectric point of BSA and in the presence of the salts. The charge on BSA appears to be a dominant factor in determining the fouling. The UF results are explained in terms of nature of the membrane polymer, and effect of different ionic environments on the conformational changes of the protein. The ultrafiltration fluxes are correlated by a model based on the membrane resistance and the time-dependent resistance of the concentration polarization layer of the protein. The values of a mass transfer coefficient and concentration polarization were determined. Zeta potential of the membranes were also determined before and after the UF. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1117-1130, 1999

Key words: ultrafiltration membranes; poly(vinyl chloride) (PVC); carboxylated poly-(vinyl chloride) (CPVC); PVC/CPVC blend; DSC; SEM analysis; AFM analysis; BSA; zeta potential

INTRODUCTION

The feasibility of a membrane separation process depends mainly on the characteristics of the membrane. If a polymer of desired properties is not available, then two or more different polymers can be combined to obtain blends with desirable features. Over the years, numerous membrane materials, based on the chemical combinations of monomers in graft or block or by copolymerization, have been developed.^{1,2} Blends of similar cellulose esters have been known as membrane materials since 1969,³ but the first real blends of different polymers were reported by Cabasso et al.^{4,5} followed by several other workers.^{6–8} The most common and practically important miscible polymers owe their miscibility to specific interactions, for example, hydrogen bonding, electrostatic interactions, etc., between different groups on the polymeric structure of the components. For example, a weak hydrogen bond is postulated be-

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tween halogen-containing polymers and oxygencontaining polymers,⁹ as shown below.



This type of interaction is responsible for the miscibility of various polyesters,¹⁰ polyacrylates,¹¹ and vinylacetate copolymers with poly(vinyl chloride) (PVC).⁹ We have selected carboxylated PVC for blending with PVC, and we expect that the interaction between the two PVCs and the similar chemical nature would be sufficient to give a suitable blend as a membrane material.

In this work, preparation, structure, and transport properties of ultrafiltration (UF) membranes made from poly(vinyl chloride) (PVC), carboxylated poly(vinyl chloride) (CPVC), and PVC/CPVC blends will be discussed.

It is also demonstrated that the PVC membrane characteristics can be changed by a controlled grafting reaction.¹² Even a small number of hydrophilic groups such as —OH or —COOH should be sufficient if they were situated on the walls of the pores.¹² The membranes were then prepared from acrylamide (AA)-grafted PVC, and their fouling characteristics were compared with those of the PVC, CPVC, and PVC/CPVC blend membranes.

MATERIALS AND EXPERIMENTAL METHODS

PVC resin was obtained from Reliance Industries Ltd. with a K value 57.01, CPVC was purchased from Aldrich Chemicals (MW 220,000) and bovine serum albumin (BSA), (MW 68,000, V-fraction >97% pure) was obtained from Loba Chemie and was used as such without any purification.

The thermal behavior of the polymer blends was determined using a differential scanning calorimeter (Perkin-Elmer, DSC-7). The sample (≈ 5 mg) encapsulated in a platinum pan was heated from 20–350°C at a rate of 10°C/min under nitrogen atmosphere to measure glass transition temperature (T_{σ}).

The membranes were prepared by the phaseinversion method. The method consists of casting a film from the polymer solution using an additive having a concentration of 10-12%, which was then gelated in a nonsolvent. The casting solution was kept at the casting temperature ($60-65^{\circ}C$) for dissolution. The membranes were made by pouring the solution of the polymer in dimethyl formamide (DMF) on a glass plate, and drawing a blade across it to form a thin film. After a predetermined evaporation time period the film was immersed in a coagulation bath. The coagulation bath temperature was $10-15^{\circ}$ C, and the time between film casting and the beginning of the coagulation was 5 to 240 s for PVC, CPVC, and PVC/ CPVC blend membranes. After coagulation time, the membranes were removed from the glass plate and leached overnight in running water to remove any traces of solvent.

By changing the concentration of the polymer in the DMF solution, membranes with various properties were prepared. The membranes were prepared from 10 to 12% (w/v) polymer solutions in DMF and were denoted as PVC-10, PVC-11, and PVC-12 for PVC, and CPVC-10, CPVC-11, and CPVC-12 for CPVC. Blend membranes were cast from PVC 10% + CPVC 1%, PVC 9% + CPVC 2%; PVC 8% + CPVC 3%; PVC 7% + CPVC 4%; PVC 6% + CPVC 5%; and PVC 5% + CPVC 6% solutions in DMF, respectively. All the above compositions are in w/v unless otherwise stated. Acrylamide (AA) grafted PVC was prepared by radical polymerization using azo-bis-isobutyronitrile (AIBN) as the initiator.¹³ The grafting efficiency was found to be 0.12%. The membranes were cast by the same method as for the PVC membranes.

The physical structure of the membranes was determined by analyzing the photographs made by means of a JSM-35 Scanning Electron Microscope (JOEL, Japan) and an Atomic Force Microscope (AFM) at the Tata Institute for Fundamental Research (TIFR), Mumbai. For SEM, the membranes were carefully dehydrated by inserting them successively in water-ethanol mixtures, pure ethanol, an ethanol-hexane mixture, and then in pure hexane. After careful dehydration of the membranes, they were fractured in liquid nitrogen and then covered with metallic gold to obtain an adequate contrast of the membrane fracture. For AFM analysis, the membranes were cast on a nonwoven polyester fabric and subsequently coagulated. From this membrane, a small section $(1 \times 1 \text{ cm}^2)$ was cut from the center of the membrane sheet for the analysis. This small section was placed in pure ethanol for 10 s and then exposed to air for 10 min to allow the excess of ethanol on its surface to evaporate. The membrane was placed in ethanol before examination



Figure 1 Plot of relative viscosity vs. polyblend composition for PVC/CPVC polyblends. Solvent, DMF; temperature: 300 K.

because this approach improved the resolution of the AFM image. $^{\rm 14}$

The performance of the membranes was tested by ultrafiltration (UF) experiments, in a flat sheet module with an effective membrane area of 112 cm² and 0.4 cm channel height. The transport properties of the membrane with reference to water and 0.75 g \cdot lit⁻¹ BSA solution were tested at a constant temperature (303 K), pressure (98 kPa), and flow rate (14 lit. m⁻² \cdot h⁻¹), unless otherwise stated. All the membranes were pressurized at 48 kPa for 30 min prior to the UF experiment. The water flux was obtained using distilled water.

The zeta potential of the membrane was measured by the Dip cell method.¹⁵ The membrane was placed in a cell dipped in an electrolyte medium with the active layer facing the bottom platinum electrode. The medium was 0.01 *M* KCl, with conductivity of 1.71×10^{-3} S \cdot cm⁻¹; the dielectric constant of the solution was taken as 78. The electro-osmotic flux was measured by weight gain on an electronic balance. Measurements were made over only initial 10 min to avoid heating of the solution. A fresh solution was used for each measurement. All measurements were carried out in duplicate and averaged.

The porosity of the membranes was determined via the gravimetric method by measuring the water content in the membrane sample.¹² A membrane of definite diameter was cut, and the excess water on the membrane surface was wiped off using a tissue paper. The weight of the wet membrane was noted. The membrane was then dried to a constant weight in an oven. The change in the weight was used to estimate the porosity of the membrane.

RESULTS AND DISCUSSION

For efficient use of blends, compatibility of blend components is an essential requirement. A simple viscometric technique can be employed to check the polymer-polymer compatibility.^{16,17} To characterize the compatibility of PVC and CPVC polymers, measurement of viscosity of their solution in DMF with varying compositions was carried out. The relative viscosity is plotted as a function of blend composition in Figure 1. The plot is linear, indicating good compatibility between the two polymers. In the case of incompatibility, a sigmoidal plot would have resulted, which is a characteristic of a two-phase system.^{16,17} The compatibility of CPVC and PVC probably arises because of the same chemical nature of the two polymers and/or due to specific interactions between C=O and Cl-C-H groups.⁹

The glass transition temperature (T_g) , which characterizes the segmental motion of polymers, also can be used to verify the compatibility of the different polymers. For an immiscible multiphase system, each phase possesses its own T_g . The observation of single T_g in the polymer blend is usually taken as proof of miscibility of the poly-



Figure 2 DSC analysis of PVC, CPVC, and blend membranes.

| Membrane Type | Porosity (%) | Pure Water Flux (Lit. $m^{-2} h^{-1}$) | Flux of BSA Solution (Lit. $m^{-2} h^{-1}$) | Rejection of BSA (%) | |
|------------------|-----------------|---|--|-------------------------|--|
| PVC-10 | 62.64 | 219.64 | 70.35 | 93.93 | |
| PVC-11 | 54.13 | 156.54 | 56.54 | 97.05 | |
| PVC-12 | 49.36 | 147.32 | 54.02 | 97.70 | |
| CPVC-10 | 96.40 | 964.28 | 80.35 | 89.00 | |
| CPVC-11 | 91.20 | 830.36 | 71.42 | 98.11 | |
| CPVC-12 | 85.00 | 739.28 | 70.34 | 98.26 | |

Table I Characteristics of PVC and CPVC Membranes

mer mixture.¹⁸ From heat flow vs. temperature plots as shown in Figure 2, PVC, CPVC, and blend polymers have single T_g values. The blend material differs by only 1°C from the pure materials. However, there is a considerable difference in their melting temperatures and heats of fusion (ΔH). CPVC showed a low ΔH value (39.05 J/g) compared to PVC (124.38 J/g) and the blend (82.9 J/g), suggesting that CPVC is more amorphous in nature.

Membranes were cast at different concentrations of the polymers PVC and CPVC, in DMF. The characteristics and performance of the membranes as a function of the casting conditions are given in Table I. The concentration of the polymer in the casting solution exerts a considerable influence on the characteristics of the membrane such as porosity, and thus, on permeability of water during ultrafiltration. The membranes obtained from solutions with a lower concentration of the polymer showed a greater porosity, as shown by the pure water flux through the membrane. The gelation rate is slower in the case of membranes obtained from higher concentration solutions. With an increase in the concentration of the polymer in the casting solution, the polymer chains prohibit solvent molecules from diffusing through the phase-separated polymer solution. The membranes prepared from 11% casting solutions of PVC and CPVC showed 97–98% rejection efficiency for macromolecules. A further increase in concentration to 12% shows reduction in flux by 6%, but no improvement in the rejection efficiency. The reproducibility in the flux for membranes prepared under identical conditions was within 4–5%. The high porosity, which contributes to much higher water fluxes in the case of CPVC, may be because of the repulsive forces between carboxylic acid groups of the polymer in the solution as well as in the gelation media, giving highly porous membranes.

The effect of the PVC/CPVC ratio on the performance of blend membrane is shown in Table II. As the CPVC content was increased, the rejection efficiency varied between 89–96%. At 1% CPVC content, the flux increased substantially, probably because of the higher porosity, but further increase in CPVC content in the blend decreases the flux as well as the rejection efficiency for BSA. With the increasing CPVC content of the blend, the distance between the macromolecules is possibly reduced, owing to the intermolecular interactions. To have a compromise between the flux rejection efficiency for protein, the CPVC content in the casting solution was selected at 1% for all further studies with blends.

| PVC : CPVC Content | Flux of Water (Lit. $m^{-2} h^{-1}$) | Flux of BSA (Lit. $m^{-2} h^{-1}$) | % Rejection of BSA |
|-----------------------|---------------------------------------|-------------------------------------|-----------------------|
| 11% + 0% | 156.54 | 56.54 | 97.05 |
| 10% + 1% | 207.68 | 94.85 | 96.82 |
| 9% + 2% | 191.39 | 90.21 | 92.02 |
| 8% + 3% | 165.00 | 88.92 | 89.56 |
| 7% + 4% | 129.64 | 80.36 | 89.52 |
| 6% + $5%$ | 120.42 | 80.35 | 92.23 |
| 5% + $6%$ | 110.16 | 76.54 | 93.12 |

 Table II
 Effect of CPVC Ratio on Membrane Performance

| Membrane | Additive (10% v/v) | Flux of Water (Lit. $m^{-2} h^{-1}$) | Flux of BSA (Lit. $m^{-2} h^{-1}$) | Rejection of BSA (%) |
|----------|-----------------------|---------------------------------------|-------------------------------------|----------------------|
| PVC | Methanol | 180.64 | 65.00 | 91.46 |
| | Ethanol | 157.54 | 58.14 | 92.47 |
| | Butanol | 174.32 | 61.23 | 89.35 |
| | Cyclohexanol | 142.34 | 51.34 | 86.54 |
| | Ethyl acetate | 139.43 | 56.36 | 91.32 |
| CPVC | Methanol | 652.45 | 89.28 | 92.57 |
| | Ethanol | 739.46 | 94.64 | 91.68 |
| | Butanol | 741.34 | 66.54 | 91.35 |
| | Cyclohexanol | 803.36 | 76.50 | 94.64 |
| | Ethyl acetate | 821.32 | 79.45 | 93.28 |
| 10% PVC | Methanol | 236.54 | 96.34 | 90.63 |
| + 1% | Ethanol | 241.00 | 95.47 | 91.00 |
| CPVC | Butanol | 207.68 | 76.42 | 94.43 |
| Blend | Cyclohexanol | 213.14 | 82.13 | 93.22 |
| | Ethyl acetate | 204.50 | 78.34 | 89.42 |

Table III Effect of Various Additives on the Membrane Performance

The effect of certain additives as nonsolvents of polymers in the casting solution was also studied at 10% (v/v) loading in DMF. These additives are expected to reduce the solvency of the solvent and, therefore, change the pore structure of the membrane.²⁰ The membrane performance with different additives is given in Table III. The flux of BSA solution and rejection were the highest when the lower molecular weight alcohols such as methanol were used as additives.

The membranes were also prepared at different evaporation times with the optimum polymer compositions and additives. The membranes obtained with the shorter evaporation time exhibit a more asymmetric structure,¹² whereas the structure of membranes with longer evaporation times is compact and homogeneous. This leads to a compromise situation between the active layer thickness and the width of the pore that controls permeability and rejection. Evaporation time was optimized at 5–15 s for all the membranes.

The relationship between membrane morphology and kinetic effects suggests that mass transfer of gelation medium plays an important role in

| Membrane | Additive to Gelation Medium (5% v/v) | Flux with Water $(L \cdot m^{-2} \cdot h^{-1})$ | Flux with BSA $(L \cdot m^{-2} \cdot h^{-1})$ | Rejection of BSA (%) |
|----------------|---|---|---|-------------------------|
| PVC | Water | 156.54 | 56.5 | 97.0 |
| | 5% Methanol | 150.00 | 64.1 | 92.5 |
| | 5% Ethanol | 182.42 | 65.0 | 89.2 |
| | 5% NaCl | 139.28 | 58.7 | 91.2 |
| | 5% DMF | 210.46 | 58.5 | 90.0 |
| CPVC | Water | 830.36 | 71.4 | 98.1 |
| | 5% Methanol | 739.28 | 85.7 | 90.0 |
| | 5% Ethanol | 642.85 | 75.0 | 92.8 |
| | 5% NaCl | 728.57 | 92.8 | 94.1 |
| | 5% DMF | 852.31 | 79.4 | 96.1 |
| PVC/CPVC Blend | Water | 207.68 | 92.8 | 90.8 |
| (10% + 1%) | 5% Methanol | 233.00 | 97.8 | 91.2 |
| | 5% Ethanol | 203.57 | 71.4 | 90.7 |
| | 5% NaCl | 219.64 | 71.4 | 90.7 |
| | 5% DMF | 241.56 | 99.4 | 94.5 |

Table IV Effect of Gelating Media on Membrane Performances

Normal gelating medium = water.







Figure 3 (a)–(f) The surface characteristics of PVC, CPVC, and PVC/CPVC blend ultrafiltration membranes obtained by SEM before and after UF experiments.

determining the structure of the membrane. Mass transfer mainly occurs at the interface between the polymer solution and the gelation medium by diffusion process. Exchange of the solvent and nonsolvent across the interface introduces a phase separation, leading to various asymmetric structures.²⁰

Table IV shows that the flux increased and the rejection of BSA decreased by the addition of some salts or organic solvents into the coagulation bath. These additives affect the transfer rate of the solvent into the gelation medium, thereby resulting in a change in the membrane properties. The rejection efficiency of membrane produced from water alone was highest (98%), while the addition of alcohols gave more porous but less efficient membranes (rejection efficiency \approx 90%).

Physical Structure of the Membranes

The surface of the membranes obtained from the PVC, CPVC, and PVC/CPVC blend was characterized by SEM before and after the UF experiments. Analysis of the photographs [Fig. 3(a)-(f)] shows that the membranes from the PVC/CPVC blend have a smoother surface and a uniform pore structure and are less fouled than the PVC membranes.

The Atomic Force Microscope (AFM) is an effective tool to investigate the surface topography and to measure the pore dimensions of the ultrafiltration membranes. Samples can be examined by AFM without preparative procedures that can alter the membrane structure such as high-vacuum gold coating. The structures of the surface of the PVC, CPVC, and PVC/CPVC blend membranes, as revealed by the atomic force microscopy, are shown in Figure 4(a)–(c). These figures are top-view images of the surfaces of the PVC, CPVC, and PVC/CPVC blend membranes, respectively, showing an area of $1.5 \times 1.5 \ \mu m^2$. The bar at the right side of the image denotes the vertical deviation in the samples, with the white regions indicating the highest points and the dark regions indicating the depressions.

The AFM permits the measurement of the distance variations in the sample's surfaces, as seen in the Figure 5(a)–(c). These lines yield profiles of surface structures. Distance variations along these profiles are determined by the measurement of the horizontal and the vertical distances between the pair of cursors, which are also shown in Figure 5(a)–(c). These measurements indicate that the pore diameters are in the range of 1.5–17 Å for PVC, 2.4–7.6 Å for CPVC, and 2.3–21.2 Å for blend membranes, which are suitable for ultrafiltration.¹⁵

The samples can also be viewed at a perpendicular to the horizontal plane, as shown in Figure 6(a)–(c). These structures result from portions of impinging assemblies of nodule aggregates that constitute the surface of UF membranes.¹⁵

Electrostatic Characteristics of the Membranes

The zeta potentials of each membrane were determined before and after UF using the Smoluchowski equation¹⁵ (Table V). The fouled mem-







Figure 4 (a)–(c) A top view image of PVC, CPVC, and PVC/CPVC blend ultrafiltration membrane surfaces taken with an AFM with the bar at the right indicating the vertical deviation.



Figure 5 (a)–(c) A vertical displacement profile of PVC, CPVC, and PVC/CPVC blend membrane surfaces from a diagonal line across insert image by AFM with cursor pairs more readily identified.

branes show lower negative zeta potentials than the fresh membranes. Because the fouling layer of protein decides the zeta potential of the fouled surface, the measured value essentially indicates zeta potential of the fouling layer. These zeta potentials, obtained for the fouled membranes, may correspond to surface potential of the BSA molecule.²²

Ultrafiltration (UF) Characteristics

The effect of transmembrane pressure at three different values (49, 98, and 196 kPa) was studied with PVC, CPVC, the PVC/CPVC blend, and AAg-PVC membranes. The schematic diagram of ultrafiltration setup is shown in Figure 7.

The permeation rate (J) in UF is limited by the formation of an adsorbed protein layer as well as the concentration polarization layer on the membrane surface, and can be expressed as follows

$$J(t) = \frac{P - \sigma \Delta \Gamma}{\mu (R_m + R_a + R_p)} \tag{1}$$

where R_m is the membrane resistance, R_a is the resistance offered by the adsorbed protein layer, and R_p is the resistance of the accumulated pro-



Figure 6 (a)–(c) A three-dimensional surface of image of a PVC, CPVC, and PVC/CPVC blend ultrafiltration membranes at $1.5 \times 1.5 \ \mu m^2$.

| | Zeta Potential (mV) | | |
|----------|---------------------|----------|--|
| Membrane | Before UF | After UF | |
| PVC | -23.49 | -6.8 | |
| CPVC | -16.74 | -7.1 | |
| Blend | -15.81 | -7.5 | |

Table VZeta Potentials of the Membranesbefore and after UF

tein in the concentration polarization layer. The adsorbed protein resistance, (R_a) , can be obtained from water flux through the fouled membrane, and σ is the rejection coefficient. The total amount of protein accumulated near the membrane surface (Mt) can be obtained by the mass balance on the feed and retentate streams for the protein.

$$Mt = \int_{0}^{t} \{ (V_{0}C_{b}) - C_{r}(V_{0} - JA_{m}) - C_{p}JA_{m} \} dt$$
(2)

where C_b is the feed concentration, C_r is the retentate concentration, C_p is the permeate concentration, A_m is the active membrane area of the membrane, and V_0 is the volumetric flow rate through the unit. The complete schematic diagram of ultrafiltration process is shown in Figure 8.



Figure 7 Schematic flow diagram of the experimental setup.



Figure 8 Schematic diagram of ultrafiltration process.



Figure 9 Normalized permeate fluxes at different pressures with PVC and CPVC membranes. Flow rate = 14 Lit. $m^{-2} h^{-1}$, pH ≈ 6.5 .

Table VI Experimentally Determined Membrane Resistances, Concentration Polarization, and Mass Transfer Coefficient for PVC, CPVC, PVC/CPVC Blend, and AA-gr-PVC Membranes with BSA at Different Pressures.

| Membrane | Pressure (kPa) | $R_m 	imes 10^{-11} \ ({ m s}^2/{ m m}^2)$ | $R_a 	imes 10^{-11} \ ({ m s}^2/{ m m}^2)$ | $\begin{array}{c} C_m \times 10^3 \\ (\text{kg/lit}) \end{array}$ | $k 	imes 10^5 \ m (m/s)$ |
|-----------|-------------------|--|--|--|---------------------------|
| PVC | 49 | 1.08 | 0.21 | 1.08 | 2.62 |
| | 98 | 1.12 | 1.23 | 1.20 | 3.48 |
| | 196 | 1.09 | 2.26 | 1.29 | 4.73 |
| CPVC | 49 | 0.47 | 0.010 | 1.16 | 2.36 |
| | 98 | 0.48 | 0.036 | 1.25 | 3.03 |
| | 196 | 0.49 | 0.069 | 1.30 | 3.78 |
| Blend | 49 | 2.35 | 0.88 | 1.13 | 2.64 |
| | 98 | 2.35 | 1.07 | 1.20 | 2.95 |
| | 196 | 2.33 | 2.86 | 1.23 | 4.2 |
| AA-gr-PVC | 49 | 1.56 | 2.24 | 1.03 | 2.66 |
| | 98 | 1.57 | 2.86 | 1.17 | 2.79 |
| | 196 | 1.57 | 3.37 | 1.21 | 6.94 |

 $C_b = 0.75$ g lit, flow rate = 14 Lit/m²/h, pH = 6.5, and $D = 6.33 \times 10^{-11}$ m²/s.

The following flux equation can be used to correlate the membrane surface concentration with the bulk phase concentration of the protein.

$$J = k \ln\left(\frac{C_m}{C_r}\right) \tag{3}$$

If C_m is assumed to be constant, eq. (3) predicts a linear plot of J vs. $\ln C_r$ with a slope equal to -k and an intercept equal to $\ln C_m$. The resistance of the membranes to pure water (R_m) , concentration polarization (C_m) , and mass transfer coefficient (k) and fouled layer resistance (R_a) were calculated for all the membranes and are given in Table VI. Because the C_m is very low in most of the cases, the osmotic pressure difference $(\Delta \pi)$ in eq. (1) can be neglected.

The normalized flux is defined as

Normalized Flux =
$$\frac{\text{Flux of solute}}{\text{Flux of pure water}}$$
 (4)

Figures 9 and 10 show the normalized fluxes of all the membranes. In general, flux at a constant pressure reduces to as low as 5-10% of the initial value, while C_m and k values increase with pressure for all the four membranes.

The pressure has a compacting effect on the adsorbed protein layer, as shown by the higher values of Ra for the membranes (Table VI). The CPVC membranes showed lower normalized fluxes, but it also has a much weaker fouling tendency compared to other membranes. Figures 11 and 12 indicate the effect of pressure on the protein layer resistance that increases with accumulated protein layer (Mt) and reaches a constant value after some time. If the concentration polarization layer were to remain unchanged with time, one would expect a linear relation between these two quantities. But the highly nonlinear variation, which is also dependent on the operating pressure, indicates probably changes in the polarization layer with time.

Figure 13 shows the effect of temperature on UF performance of the blend membrane. The flux increased with an increase in the temperature. The viscosity of the BSA solution decreases from 0.041 Poise at 288 K to 0.0065 Poise at 318 K. The dispersion of protein molecules from the polarization layer on the membrane surface is assisted by this decrease in viscosity at higher temperatures. A similar trend was observed in the case of the PVC, CPVC, and AA-g-PVC membranes. It was observed that the fouling resistance and polarized layer resistance also decrease with an increase in the temperature for all the membranes. But the resistance was an order of magnitude lower in the case of the CPVC membrane compared to the other three membranes $(R_a \text{ values for PVC},$ CPVC, blend, and AA-g-PVC membranes are 3.84 \times 10¹¹, 0.57 \times 10¹¹, 2.32 \times 10¹¹, and 3.3 \times 10¹¹ s^2/m^2 under identical conditions at 288 K). The repulsive interaction between carboxylate groups on the surface of the membrane and -ve charge



Figure 10 Normalized permeate fluxes at different pressures with PVC/CPVC blend and AA-g-PVC membranes. Flow rate = 14 Lit. $m^{-2} h^{-1}$, pH ≈ 6.5 .

on the protein surface reduces the adsorption of the protein on the CPVC membrane surface. The trend remains the same, even at the higher temperatures.

Figure 14 shows the flux at different pH in the absence of an electrolyte. It was observed that at pH 2.5 and 9.0, membranes show higher permeation flux. At these pH values away from the isoelectric point of the protein (pI 4.8), the BSA molecules acquire significant net charge, and thus, enlarge due to electrostatic repulsion. These effects would yield a more permeable deposited layer, resulting in a higher permeation flux of water through the UF membrane.

The effect of addition of salt (NaCl) to BSA solution at pH 2.5 with the blend membrane showed a significant effect on permeate flux (Fig.

15). The flux dropped immediately compared to the gradual decline in the absence of the salt. Further increase in the salt concentration causes additional drop in the flux. The fouling resistance (R_a) was lowest for the acrylamide-grafted PVC membrane compared to other membranes at pH 2.5 $(R_a \text{ values for PVC}, \text{ blend}, \text{ and } \text{AA-}g\text{-PVC} \text{ are } 1.98 \times 10^{11}, 3.44 \times 10^{11}, \text{ and } 1.2 \times 10^{11} \text{ s}^2/\text{m}^2)$. Similar effects were also observed at pH 9.0, where the fouling resistance was lower for the blend membrane $(R_a \text{ values for PVC}, \text{ blend}, \text{ and } \text{AA-}g\text{-PVC} \text{ are } 2.08 \times 10^{11}, 1.5 \times 10^{11}, \text{ and } 3.35 \times 10^{11} \text{ s}^2/\text{m}^2 \text{ at pH 9.0}$.

At pH \approx 9, the BSA molecules acquire significant –ve charge and enlarge due to electrostatic



Figure 11 Variation of R_p and Mt with pressure for PVC and CPVC membranes.





Figure 12 Variation of R_p and Mt with pressure for the PVC/CPVC blend and AA-g-PVC membranes.

repulsion. These effects would give a better permeable deposited protein layer, which results in a slightly higher flux. The added salt reverses the effect by shielding the charge effect, causing molecular contraction, thereby decreasing the permeability. The flux drop at pH 2.5 and 9.0 follows the same trend for all other three membranes.

Figure 16 shows the decline in the flux on addition of the salt to BSA solution at the isoelectric point of BSA (4.8) with the blend membrane. A similar trend was observed in the case of PVC, blend, and AA-g-PVC membranes. At the isoelectric point all the membranes showed maximum fouling tendency. However, blend and AA-g-PVC



Figure 13 Effect of temperature on flux decline for the PVC/CPVC blend membrane. Pressure 98 kPa, flow rate = 14 Lit. $m^{-2} h^{-1}$, $pH \approx 6.5$.

membrane showed marginally lower fouling resistances (R_a values for PVC, blend, and AA-g-PVC are 3.77×10^{11} , 2.43×10^{11} , and 2.73×10^{11} s²/m² at pH 5.2). At the isoelectric point, in the absence of the salts, the protein molecule is in its compact state and has no net charge, and this provides the least permeable layer. The presence of the salt can make the hydrophobic effects stronger and a more compact protein state, and thus decreases the flux further.



Figure 14 Effect of pH on flux decline for the PVC/ CPVC blend membrane. Pressure 98 kPa, flow rate = 14 Lit. $m^{-2} h^{-1}$.

CONCLUSIONS

The performance of PVC, CPVC, and the PVC/ CPVC blend as a membrane material for ultrafiltration was verified under various conditions. The concentration of the PVC and CPVC polymers in casting solution was optimized at 11%, while for the blends the CPVC content was optimized at 1%. The addition of methanol and ethanol to the casting solution gives membranes with a higher flux and similar rejection efficiency for BSA. The evaporation time was optimized 5–15 s for all the three membranes. The blend membrane gave a higher flux (85–95 lit/m² \cdot h) and comparable rejection efficiency (94%) compared to PVC and CPVC membranes alone. The pore size of the membranes in the range of 2 to 21 Å was also found suitable for ultrafiltration.

The fouling resistance increases with an increase in the pressure and decreases with an increase in temperature, which is also decided by the pH of the solution. The pH influences the interaction between the membrane and BSA. The UF flux is minimum at pH 5.2, which is close to the isoelectric point of BSA. The variation in flux can be explained on the basis of conformational changes of the BSA molecules at different pH, the nature of the membrane material, and the hydrophobic and electrostatic interactions among BSA molecules and between the membrane and BSA.



 $\label{eq:Figure 15} \begin{array}{l} \mbox{Effect of salt concentration on flux decline} \\ \mbox{for the PVC/CPVC blend membrane. Pressure 98 kPa,} \\ \mbox{flow rate} = 14 \mbox{ Lit. } m^{-2} \mbox{ } h^{-1}, \mbox{ pH} \approx 2.5. \end{array}$



Figure 16 Effect of salt concentration on flux decline for the PVC/CPVC blend membrane. Pressure 98 kPa, flow rate = 14 Lit. $m^{-2} h^{-1}$, $pH \approx 5.2$.

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