



Preparation and performance of poly (vinyl chloride)/aminated poly (vinyl chloride) blend ultrafiltration membranes

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ABSTRACT

Polyvinyl chloride (PVC) was treated with aqueous solution of ethylenediamine to obtain aminated polyvinyl chloride (APVC). PVC/APVC blends ultrafiltration membranes, by phase inversion technique. Different polymer blend compositions with and without an additive, like Poly (ethylene glycol) of molecular weight 600 Da were also prepared. The blend membranes were characterized and evaluated by scanning electron microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), water contact angle, water content, pure water flux, and membrane porosity to investigate the influence of APVC on the final properties of the membranes. The presence of amine functional group was confirmed by FTIR spectrum. SEM analysis showed that the blend PVC membranes have thinner top layer and higher porosity in the sublayer. The blend membranes showed an increase in overall porosity, hydrophilicity, and water content, with increase in APVC content and in the presence of additive. The fouling resistant capability of the membranes was studied by Bovine serum albumin as the model foulant and flux recovery ratio (FRR) of the membranes was calculated. The blend membrane showed an increase in FRR indicating more fouling resistance than the pure PVC membrane

Keywords: Ultrafiltration; Aminated poly (vinyl chloride); Blend membranes; Hydrophilicity; Antifouling; SEM

1. Introduction

Membrane separation process became commercially viable after the introduction of phase inversion technique for the preparation of polymeric membranes [1–3]. Recently among all the membrane process, more interest has been shown in pressure-driven microfiltration and ultrafiltration (UF) separation process [4,5].

UF membranes that have been developed and commercialized are finding its use in the separation of extremely small suspended particles and dissolved macromolecules from fluids using synthetic asymmetric membranes [6]. However, the flux decline due to fouling on the membrane surface over a period of operation time limits its application. Current research and development are focused on drastic improvements in antifouling properties of membranes and at

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the same time maintaining high throughput during separation process [7]. Many researchers have demonstrated that increase in the hydrophilicity of membranes results in a significant reduction in the surface fouling due to lower interaction between foulant and the membrane surfaces [8,9]. Nature of polymeric material plays an important role in developing such membrane properties. Polyvinyl chloride (PVC) UF membranes have been widely used in water, waste water treatment, reverse osmosis pretreatment, and separation process in chemical and biochemical industries due to its stiffness, chemical resistance, mechanical stability, and commercial availability [10,11]. However, the application of PVC membranes as such becomes limited in UF process due to its hydrophobicity. Therefore, it is necessary to enhance the hydrophilic nature of PVC membrane to improve their antifouling properties. Blending of two different polymers offers attractive opportunity to create high membrane hydrophilicity while retaining bulk properties with required mechanical and chemical stability [12,13]. In recent years, many studies revealed about blending of PVC with other polymers such as polyacrylonitrile, poly (vinyl butyral), poly (methyl methacrylate), and poly (vinyl pyrrolidone) [14–16]. However, the most important problem in blending is that most of the polymer pair is rather immiscible.

In this study, instead of selecting a new polymer, PVC was functionalized by reacting with ethylenediamine (EDA) to obtain aminated polyvinyl chloride (APVC) [17] as second polymer for blending. It is reported that the modification of PVC with amine functional group increases the surface hydrophilicity [18]. The addition of organic or inorganic additives as the third component to the blend polymers has been one of the important techniques in the membrane preparation to control morphology and permeation performance of membranes which act as pore forming agents. Low molecular weight pore former Polyethylene glycol (PEG-600) was selected because higher molecular weight may suppress the formation of microvoids during the membrane casting [19]. The objective of this study is to develop highly permeable and antifouling UF membrane by blending PVC/APVC with and without pore forming additive PEG-600 by phase inversion technique. The effect of polymer blend composition and additive on morphology, water flux, hydrophilicity, water content, and porosity of membranes was analyzed. The composition of modifying polymer APVC was optimized to 30% to avoid phase separation. The morphology of the membrane was studied by scanning electron microscopy (SEM) and hydrophilicity of membrane by contact angle measurement. Fourier Transform Infrared

spectroscopy (FTIR) spectrum was recorded to confirm the amination of PVC. The fouling resistant capability of the membranes was studied by Bovine serum albumin (BSA) as model protein and fouling during BSA separation was calculated. Flux recovery ratio (FRR) values of PVC and PVC/APVC blend membranes were calculated and the results were discussed.

2. Experimental

2.1. Material and methods

Poly (vinyl chloride) with K value 55–57, average molecular weight $M_w = 48,000$, and density 1.4 was purchased from Sigma-Aldrich (India). PEG (600 Da) was procured from Merck (I) Ltd and used as supplied, as a non-solvent additive for the whole study. Analar grade *N-N*-Dimethylacetamide (DMAc) was procured from SRL Chemicals, India Ltd and sieved through molecular sieves (Type-5) to remove moisture and stored in dry conditions prior to use. Sodium lauryl sulfate (SLS) of analar grade was obtained from Qualigens Fine Chemicals Ltd, India and used as surfactant in a coagulation bath. Distilled water was employed for the UF experiments and for the preparation of gelation bath. Anhydrous sodium monobasic phosphate and sodium dibasic phosphate hepta hydrate were procured from SRS Chemicals Ltd, India and used for the preparation of phosphate buffer solutions for proteins analysis. Proteins, viz., BSA, $M_w = 69$ kDa; pepsin $M_w = 35$ kDa; Trypsin $M_w = 20$ kDa, were purchased from M/s. SRL Chemicals Ltd, India. Egg Albumin (EA) $M_w = 45$ kDa was obtained from CSIR biochemical centre, New Delhi, India.

2.2. Amination of PVC

In a three-necked round bottom flask equipped with a dropping funnel and a mechanical stirrer, 20 g of PVC polymer was mixed with 80% EDA solution and heated at $80 \pm 5^\circ\text{C}$ under nitrogen atmosphere with constant stirring for 1 h. Then, the PVC polymer mixture was filtered and washed in distilled water. This resulted in light yellow colored aminated PVC (APVC) which was washed with distilled water and dried in vacuum for 3 h at 45°C [17].

2.3. Preparation of solution blending

Blend solution was prepared by dissolving the two polymers PVC and APVC (Total Polymer Composition = 12.5%) in different compositions in the presence and absence of additive PEG-600 in solvent DMAc under constant mechanical stirring in a round bottom

flask for 4 h at 40–45°C. A series of such polymer solutions were prepared by varying the compositions of PVC and APVC with and without PEG-600 as shown in Table 1. The homogenous solution thus obtained was kept as such in room temperature for 6 h in an air tight condition to get rid of air bubbles. The method of preparation involved was same as that of the “phase inversion technique” method employed in our earlier works as reported by other researchers from our lab [20]. The casting conditions, namely relative humidity ($25 \pm 2\%$) and temperature ($30 \pm 1^\circ\text{C}$) were standardized and maintained for the preparation of membranes with better homogeneity, thickness, and morphology. The thickness was within the range of 0.19 ± 0.20 mm and measured with a micrometer having a precision of 0.001 mm.

2.4. Preparation of blend membrane

The membranes were cast over a smooth glass plate using doctor blade. After casting was over, the solvent present in the cast film was allowed to evaporate for 30 s and the glass plate along with the cast film was gently immersed in the gelation bath consisting of 2.0% (v/v) DMAc (solvent) and 0.2 wt.% surfactant SLS. The membranes were removed from the bath after 2 h and washed with distilled water. Finally, the membranes were stored in distilled water containing 0.1% formalin solution to prevent microbial growth.

2.5. Experimental setup

The UF experiments were carried out in a batch type, dead end cell (UF cell-S76-400-Model, Spectrum, USA) fitted with Teflon-coated magnetic paddle. The effective membrane area available for ultra filtration

was 38.5 cm^2 . The solution filled in the cell was stirred at 400 rpm using a magnetic stirrer. The permeating solution was collected from the bottom of the cell. The cell was connected to a compressor with a pressure control valve and gage through a feed reservoir. The membrane compaction experiments were carried out at $30 \pm 2^\circ\text{C}$, at 414 kPa transmembrane pressure. After compaction, the membranes were subjected to a transmembrane pressure of 345 kPa to measure the pure water flux (PWF) under steady state conditions. The PWF was calculated using Eq. (1). The PWF was measured three times and the average of it was reported for accuracy.

2.6. Membrane characterization

2.6.1. FTIR analysis

The powders of pure PVC and APVC were dried for 2 h in a vacuum drier. FTIR spectrum was obtained using BOMEM MB mid infra red spectrometer operated at 4 cm^{-1} resolution. The IR spectrum was obtained by KBr pellet method.

2.6.2. Membrane compaction

The blend and pure PVC membranes were subjected to hydraulic compaction by loading the membranes of required size into the UF test cell connected to a pressure reservoir. The compaction measurement was carried out at transmembrane pressure of 414 kPa. The water flux was measured at every hour until it leveled off after 4–5 h. The PWF (J_w) and compaction factor were determined using the following equation:

$$J_w = Q/(A(\Delta t)) \quad (1)$$

Table 1
Composition and casting conditions of PVC/APVC blend composition (w/w %)

| Blend composition | | Additive, PEG-600 (wt.%) | Solvent, DMAc (wt.%) |
|------------------------|----------------------------------|--------------------------|----------------------|
| Polyvinyl chloride (%) | Aminated poly vinyl chloride (%) | | |
| 100 | 0 | 0 | 87.5 |
| 90 | 10 | 0 | 87.5 |
| 80 | 20 | 0 | 87.5 |
| 70 | 30 | 0 | 87.5 |
| 100 | 0 | 2.5 | 85.0 |
| 90 | 10 | 2.5 | 85.0 |
| 80 | 20 | 2.5 | 85.0 |
| 70 | 30 | 2.5 | 85.0 |

Notes: Casting temperature, $30 \pm 1^\circ\text{C}$; casting relative humidity, $25 \pm 2\%$; solvent evaporation time, 30 s. Total polymer concentration at: 12.5 w/w%

where J_w is the water flux (in $\text{lm}^{-2} \text{h}^{-1}$), Q is the quantity of permeate collected (in l), Δt is the sampling time (in h), and A is the membrane area (in m^2). The compaction factor is defined as the ratio of initial PWF to steady state PWF.

2.6.3. Measurement of contact angle

The surface wetting behavior of the blending and pure membranes was measured by contact angle method to investigate the hydrophilicity of membranes. Contact angle measurements of water on the wet membrane surfaces were carried out by the sessile drop method at ambient temperature using a goniometer (Holman India). Membrane samples of size of $3 \times 3 \text{ cm}^2$ were washed thoroughly with water and mopped with a filter paper to remove the moisture content prior to the experiment. Then, they were put on a sintered glass plate with the active layer up, to study the polar interactions between the membranes—Water interfaces. The sessile drop was formed on the membrane surface by depositing $5 \mu\text{L}$ of Milli-Q water slowly and steadily onto the membrane surface with a micro syringe. The contact angle was measured at membrane—Water—Air inter phase at room temperature within 30 s of the addition of water drop. For each sample, measurements were performed in six different locations and the average was considered for accuracy.

2.6.4. Equilibrium water content (EWC)

Since the equilibrium water content (EWC) is the indicating parameter of hydrophilicity of membranes, it is considered to be a very important parameter in membranes characterization [21]. It is also related to the membrane porosity. After the surface of the membranes was mopped with a tissue paper, initial weight of membranes was taken (W_w). The wet membranes were dried in a vacuum drier for 24 h at a temperature of $50\text{--}60^\circ\text{C}$ and again weighed in dry condition (W_d). The EWC was calculated as follows [21].

$$\text{EWC (\%)} = \frac{W_w - W_d}{W_w} \times 100 \quad (2)$$

where W_w is the wet sample weight (g) and W_d is the dry sample weight (g).

2.6.5. Molecular weight cut off, porosity, and mean pore radius

Molecular weight cut off (MWCO) of all the blend membranes was estimated using PEG of different

molecular weights (4, 6, 8, 10, 12, and 15 kDa). PEG solutions were prepared individually at a concentration of 500 ppm using deionized water and the same was used as standard solution for rejection studies. UF test cell was filled with PEG solution and pressurized at a constant pressure of 345 kPa throughout the experiments. The concentration of feed and permeate was found out using a total organic carbon analyzer (Shimadzu, TOC-V CPH). The percentage of solute rejection (SR %) was calculated from the concentration of feed (C_f) and permeate (C_p) by the following equation [9].

$$\text{SR (\%)} = 1 - \frac{C_p}{C_f} \times 100 \quad (3)$$

The molecular weights (M) of all the PEG solutions were correlated with their Stokes–Einstein radii, and this was used in the calculation of mean pore radius of membranes, r [9].

$$\text{Mean pore radius } r = (0.0262 \text{ nm}) \sqrt{\text{Mg/mol}} - 0.03 \text{ nm}$$

where M is the lowest molecular weight of PEG molecules and has a rejection of more than 80% in the UF experiments. Membrane porosity and the mean pore size were measured based on the membranes dry weight. The membrane wet weight was taken after mopping the excess water on the surface. Then, the membranes were put in a vacuum drier at $50\text{--}60^\circ\text{C}$ for 24 h and measured the dry weight. The porosity of the membrane was calculated as per the following equation [22,23]:

$$\varepsilon (\%) = \frac{W_w - W_d}{\delta \rho A} \times 100 \quad (4)$$

where ε is the membranes porosity, W_w is wet sample weight (g), W_d is the dry sample weight (g), ρ (g/cm^3) is the density of pure water, A (cm^2) is the area of membrane in wet state, and δ (cm) is the thickness of the membranes in the wet state.

2.6.6. Scanning electron microscopy (SEM) analysis

The membranes morphology study was carried out by SEM (SEM, LEICA Stereoscan, and Cambridge, UK). Both cross section and the top view of PVC and PVC/APVC blend membranes were investigated. The membranes were first cleaned and immersed in liquid nitrogen for 60–90 s. These frozen membranes were

then gold sputtered for making electrically conductive. Depending upon the physical nature of the membranes, the images were obtained under high vacuum at 15 kv.

2.6.7. Anti fouling properties of blend membranes

The flux decline under consistent pressure during UF membrane was generally attributed to membrane fouling. The anti fouling properties of membranes were investigated as per the known procedure [24]. The steady state PWF (J_{W1}) of prepared membranes was first measured after compaction. BSA was selected as model feed protein solution for anti fouling experiments. The feed BSA solution of 1 g/L (in 0.1 M phosphate buffer saline with pH 7.4) was introduced in the test cell and the filtrate was collected in 0.1 MPa, until a steady state value (J_p) was attained. Later, all the membranes were washed with distilled water for 2 h in a vibrator. Then PWF of all the pure and blend membranes were measured at steady state (J_{W2}). To evaluate the antifouling property of PVC/APVC and PVC membranes, the flux decline was first calculated as per the following equation.

$$\text{Flux loss ratio (\%)} = \left[1 - \frac{J_p}{J_{W1}} \right] \times 100 \quad (5)$$

The FRR of the membranes after hydraulic cleaning is calculated as per the formula:

$$\text{FRR}_{\text{hc}} (\%) = \frac{J_{W2}}{J_{W1}} \times 100 \quad (6)$$

3. Results and discussions

3.1. Fourier transform Infrared spectroscopy (FTIR) analysis

The FTIR spectra of pure PVC and APVC powder were recorded to investigate the intermolecular interactions between PVC and APVC powder. The spectrum of pure PVC material showed the absorption band at 1,425, 1,340, 1,200, and 950 cm^{-1} as shown in Fig. 1(a). These signals corresponded to many C–C and C–H vibrations found in PVC polymer [25]. There were additional new peaks located at around 1,580–1,650 cm^{-1} as shown in Fig. 1(b), which could be explained due to the presence of primary amine groups [26]. The brand band at around 3,400 cm^{-1} is formed due to N–H valence bond [27]. The appearance of new peaks confirmed the presence of amine groups in the modified PVC.

3.2. Scanning electron microscope analysis

The SEM analysis of prepared membrane both on surface and cross section image plays a very important role in the mechanism and selectivity of the membranes. The cross sectional SEM images of the PVC and PVC/APVC blend membranes in the presence and absence of pore former PEG-600 are shown in Figs. 2 and 3 respectively. From the images, it was understood that all the membranes possessed a typical asymmetrical structure consisting of top and bottom skin layers and a finger like support layer or microvoids. This structure is obtained generally whenever the dope solution is directly immersed in the non-solvent bath [28].

Careful examination of the morphology revealed that pure PVC membranes showed an un-fully developed macrovoidal structure. However, as the APVC content was increased in the dope solution, finger like structures were observed with more pores.

The PVC membrane with pore former PEG-600 showed the development of inclined finger like structure compared to pure PVC membrane. The PVC/APVC blend membrane with pore former exhibited a porous sublayer of more sponge-like structure with more pore on the walls of sponge layer.

3.3. Effect of APVC composition on compaction of PVC/APVC blend membranes

Membranes are compressed when operated at a pressure more than the operating pressure resulting in stress relaxation. In general, the PWF was found to be decreased while compaction time increased for all the prepared membranes. Initial and final steady state values of PWF for all blend membranes with and without PEG-600 pore former were measured and reported in Table 2. It was observed that membrane prepared from 100% PVC without pore former had a flux value of 295 $\text{lm}^{-2} \text{h}^{-1}$ and almost remained constant at a value of 154 $\text{lm}^{-2} \text{h}^{-1}$ after 4–5 h compaction time. The constant value was the indication of compaction. When the PVC membrane was prepared with 2.5% PEG-600, the constant flux increased from 154 to 201 $\text{lm}^{-2} \text{h}^{-1}$. During compaction, the polymeric chains reoriented and effected a change in structure and lowered the volume of porosity and flux. Similar observations were reported by Chakrabarthy et al. [21]. As the APVC content was increased from 10 to 30% in the presence of 2.5% PEG-600 additive, the constant flux was observed to increase from 287 to 554 $\text{lm}^{-2} \text{h}^{-1}$. In the same manner, the compaction factor also was found in the increasing trend. The SEM images support the fact that the increase in flux and the number

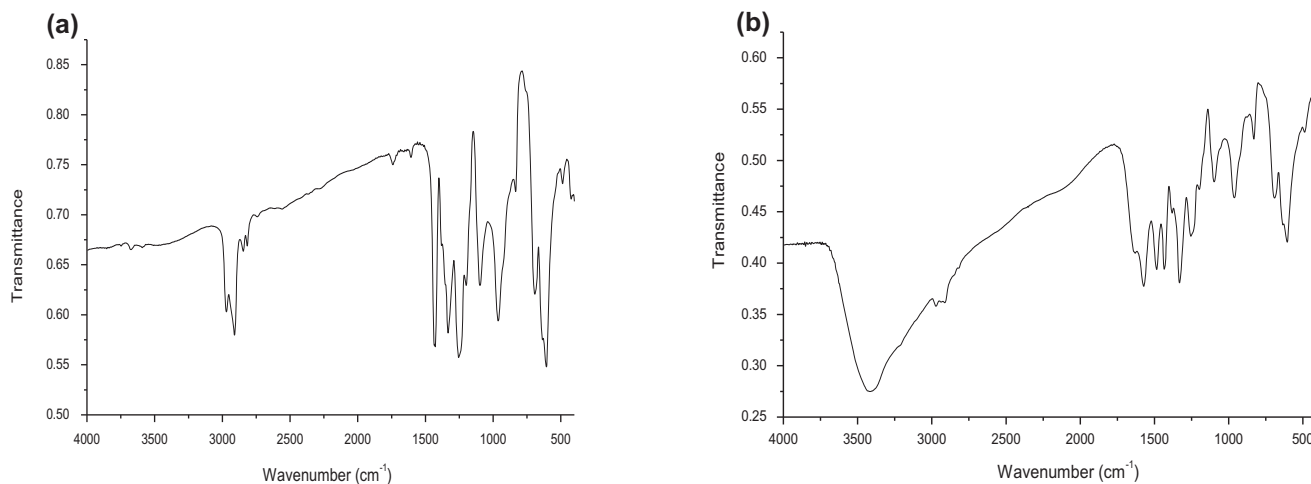


Fig. 1 FT-IR spectra of (a) PVC-base polymer and (b) Aminated PVC.

of pores with higher sizes were formed while APVC composition was increased in the presence and absence of additive.

3.4. Effect of APVC on the membrane hydraulic resistance

Membrane hydraulic resistance R_m is an indication of membrane tolerance toward hydraulic pressure. This was obtained by subjecting the membranes to various pressures from 207 to 414 kPa and measuring the PWF and the resistance offered by dense top skin layer and the surface porosity. R_m was calculated from the inverse slope of corresponding transmembrane pressure versus PWF plots and the results are reported in Table 2.

It was clear from Table 2 that the pure PVC membranes in the absence of additive PEG-600 showed a hydraulic resistance of $4.62 \text{ kPa} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ due to its low porosity. When the APVC composition was increased from 10 to 30%, in the blend membranes without additive, the hydraulic resistance was observed to decrease from 3.63 to $1.77 \text{ kPa} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. When PEG was introduced in to the casting solution of pure PVC, there was a significant decrease in the hydraulic resistance to water permeation. As explained in SEM analysis, the pore former addition in the dope solution contributed in the formation of macropores on the membrane surface due to instability in the thermodynamics which enhances the precipitation of casting solution [1,29].

3.5. Molecular weight cut off, mean pore size, porosity

The porosity, MWCO and pore radius of pure PVC and PVC/APVC blend membranes in the absence and presence of PEG-600 were studied and the results are summarized in Table 3. The pure PVC membranes

showed a MWCO of 8 kDa and increased to 10 kDa when 10% composition APVC was blended. With further increase of APVC content to 30%, the MWCO was found to be increased to 15 kDa. The mean pore size of membranes calculated from the sieving experiments also increased from 26.1 to 32 \AA with APVC content increase. It could also be observed that in the presence of PEG-600, the pore size of PVC/APVC blend membranes further increased to 37 \AA at 70/30 (wt.%) blend composition. The increase in the pore size with addition of APVC confirmed the pore forming ability of APVC. PEG-600 is well known as pore forming additive in Non Induced Phase Separation (NIPS) method due to the fact that it can diffuse from polymer-rich phase to polymer-poor phase owing to the solubility of PEG in water resulting in delay in the solidification of polymer-rich phase to form fully developed macropores [30,31].

The porosity of pure PVC and PVC/APVC blend membranes was determined and the results are presented in Table 3. Pure PVC membrane had a porosity of 44.8% and the values increased to 60.5% for 70/30 composition of blend membranes. Similarly the addition of non solvent additive further increased the porosity of the membranes as shown in our results. This could be explained by the fact that the presence of additive increased the precipitation rate of the entire system during the phase inversion which led to large pores and high porosity [21].

3.6. Contact angle, PWF and water content

The contact angle measurement of the prepared membranes was carried out to determine the hydrophilicity of the prepared blend membranes. The effects of blend composition on the contact angle are

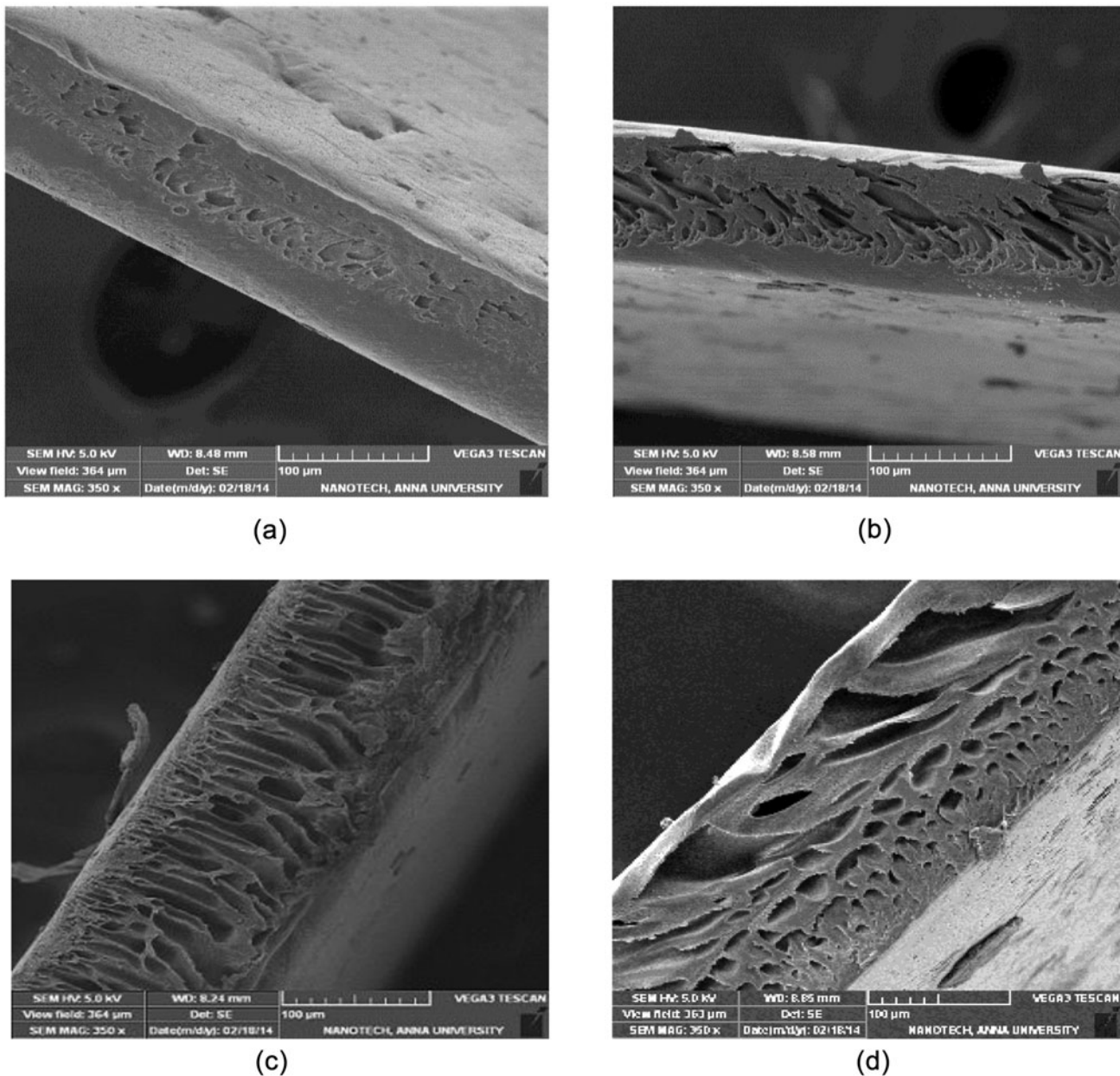


Fig. 2 Cross sectional SEM images of PVC/APVC blend membranes without additive PEG-600 (w/w): (a) 100/0, (b) 90/10, (c) 80/20, and (d) 70/30.

tabulated in Table 4. The contact angle of pure PVC membrane was 82.4° and decreased to 78.6° at 70/30 blend composition. The contact angle of amine group incorporated PVC blend membranes showed lower contact angle than the pure PVC. The decrease in the contact angle indicated the role of APVC in improving the hydrophilicity. The presence of polar amine group had a strong affinity with water and lowered the contact angle. Further, the presence of PEG in the blend membranes decreased the contact angle [32].

The PWF was measured at 345 kPa transmembrane pressure for the entire blend membranes after 30–45 min stabilization time and the results were summarized in Table 4. The pure PVC membrane showed a flux of $105 \text{ lm}^{-2} \text{ h}^{-1}$. The flux was found in increasing trend with the APVC addition from 10 to 30 wt.%. This was further increased in the presence of PEG. The flux increase was more in the case of PEG presence than in the case of PEG-600 absence. This could be attributed to the formation of more pores by

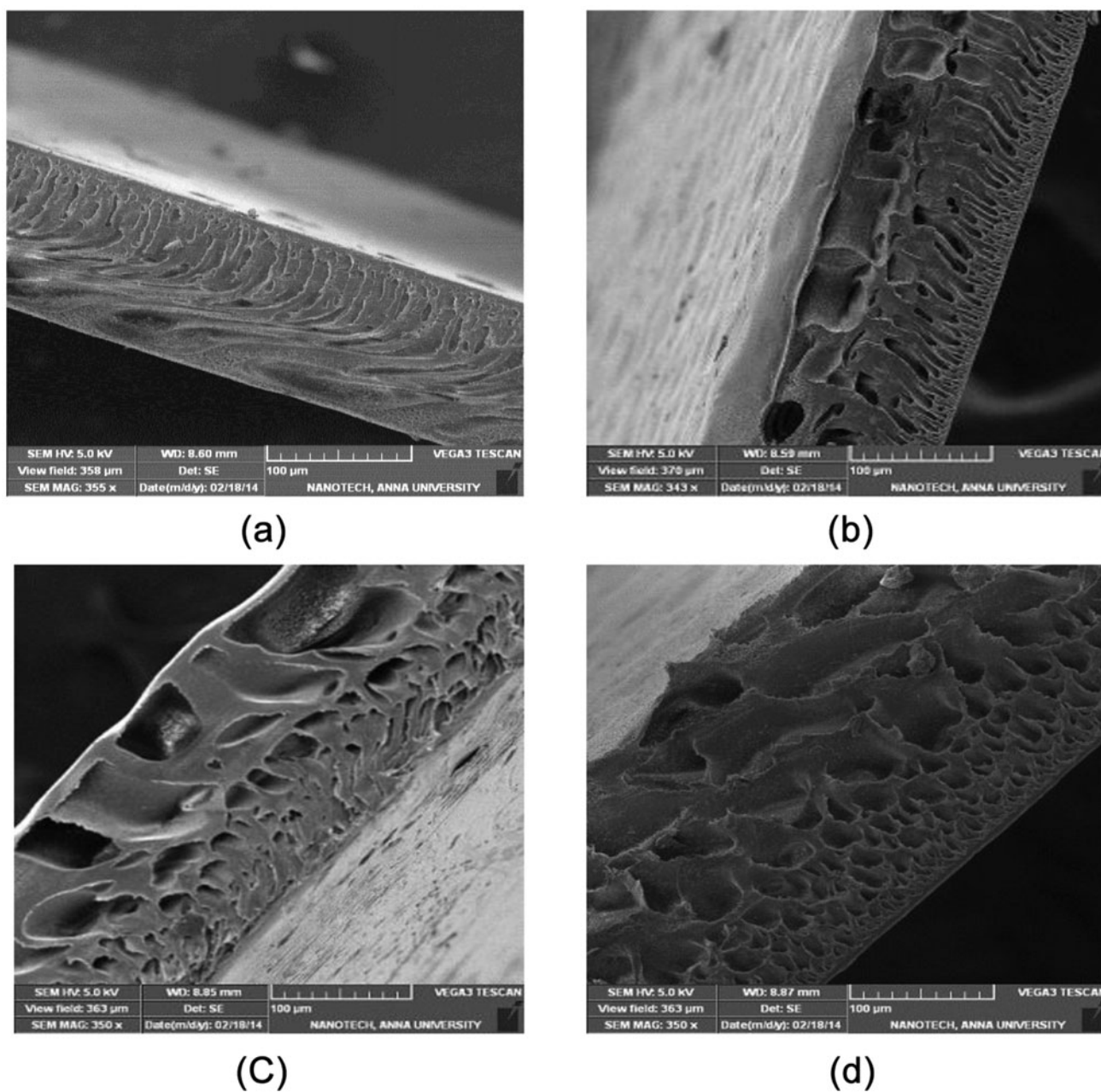


Fig. 3 Cross sectional SEM images of PVC/APVC blend membranes with additive PEG-600 (w/w): (a) 100/0, (b) 90/10, (c) 80/20, and (d) 70/30.

leaching of PEG during gelation process [33] and to the increasing immiscible phase behavior of the blend because of low molecular attractive forces between the blend components. This effect was more prominent in the presence of higher APVC content which led to increased flux due to the segmental gap between the polymer chain [34]. The SEM analysis carried out in this study also supported more pores formation. The leaching out of PEG during the gelation could be con-

firmed when the water content of blend membranes were compared. The pure PVC membranes showed water content of 52.5% which was increased to 55.4% when the PEG was introduced. The water content of blend membranes PVC/APVC was observed to increase from 66.9 to 70.6% when the APVC content was increased from 10 to 30 wt.% in the presence of PEG-600. This is due to more affinity of amine group toward water.

Table 2

Initial water flux, Final water flux, and compaction factor of PVC/APVC blend membrane

| Polymer blend composition | Additive, PEG-600 | Pure water flux at 414 KPa ($\text{l m}^{-2} \text{h}^{-1}$) | | Compaction factor | Hydraulic resistance kPa ($\text{l m}^{-2}/\text{h}^{-1}$) |
|---------------------------|-------------------|--|-------|-------------------|--|
| | | Initial | Final | | |
| 100/0 | 0 | 295 | 154 | 0.52 | 4.62 |
| 90/10 | 0 | 401 | 213 | 0.53 | 3.63 |
| 80/20 | 0 | 584 | 325 | 0.56 | 2.68 |
| 70/30 | 0 | 749 | 417 | 0.57 | 1.77 |
| 100/0 | 2.5 | 365 | 201 | 0.55 | 2.69 |
| 90/10 | 2.5 | 528 | 287 | 0.54 | 2.04 |
| 80/20 | 2.5 | 762 | 419 | 0.55 | 1.66 |
| 70/30 | 2.5 | 983 | 554 | 0.56 | 1.24 |

Table 3

Molecular weight cut off, mean pore size, and porosity of PVC/APVC blend membrane

| Polymer blend concentration (12.5%) | Additive PEG 600 (wt.%) | Mean pore size (\AA) | Porosity (%) | MWCO (kDa) |
|-------------------------------------|-------------------------|---------------------------------|--------------|------------|
| 100/0 | 0 | 23.4 | 44.8 | 8 |
| 90/10 | 0 | 26.1 | 48.7 | 10 |
| 80/20 | 0 | 28.7 | 52.0 | 12 |
| 70/30 | 0 | 32.0 | 60.5 | 15 |
| 100/0 | 2.5 | 26.1 | 50.6 | 10 |
| 90/10 | 2.5 | 28.7 | 53.8 | 12 |
| 80/20 | 2.5 | 32.0 | 57.8 | 15 |
| 70/30 | 2.5 | 37.0 | 72.8 | 20 |

Table 4

Contact angle, pure water flux, and water content of PVC/APVC blend membrane

| Polymer blend Concentration (12.5 wt.%) | Additive PEG 600 (wt.%) | Contact angle ($^{\circ}$) | Pure water flux ($\text{l m}^{-2} \text{h}^{-1}$) at 345 kPa | Water content (wt.%) |
|---|-------------------------|------------------------------|--|----------------------|
| 100/0 | 0 | 82.4 (± 0.4) | 105 | 52.5 |
| 90/10 | 0 | 79.0 (± 0.3) | 120 | 61.2 |
| 80/20 | 0 | 78.6 (± 0.5) | 159.2 | 64.7 |
| 70/30 | 0 | 74.4 (± 0.7) | 192 | 65.1 |
| 100/0 | 2.5 | 80.9 (± 0.4) | 138 | 55.4 |
| 90/10 | 2.5 | 74.1 (± 1.1) | 170 | 66.9 |
| 80/20 | 2.5 | 71.4 (± 0.8) | 182.8 | 69.2 |
| 70/30 | 2.5 | 68.9 (± 0.7) | 262 | 70.6 |

3.7. Antifouling properties of blend membranes

The modified membranes performance was investigated with respect to polymer composition and the additive concentration for the adsorptive fouling. BSA protein was taken as model feed solution. The membranes were rinsed with water and the relative flux loss ratio (FLR) and FRR were found out. The values are tabulated in the Table 5. It was generally known that lower the values of FLR, higher the antifouling

tendency of the membrane [34]. From Table 5, it is clear that FLR of PVC/APVC blend membrane decreased from 62.5% to 59.2% with increase in the APVC content from 10% to 30%. The lower retention value of BSA was attributed to formation of larger porosity. The trend clearly revealed that the PVC/APVC blend membranes showed less fouling tendency than the pure PVC. This was attributed to surface enrichment of the amine group that immobilized the available water resulting into a

Table 5

Pure water flux, steady state BSA flux, water flux after rinse, flux loss ratio, and flux recovery ratio of PVC/APVC blend membranes

| Polymer blend composition (12.5%) | Additive PEG 600 (wt.%) | Pure water flux ($\text{lm}^{-2} \text{h}^{-1}$) | Steady state BSA flux ($\text{lm}^{-2} \text{h}^{-1}$) | Pure water flux after rinse ($\text{lm}^{-2} \text{h}^{-1}$) | Flux recovery ratio (%) | Flux loss ratio (%) |
|-----------------------------------|-------------------------|--|--|--|-------------------------|---------------------|
| 100/0 | 0 | 105 | 38.7 | 63.3 | 60 | 63.1 |
| 90/10 | 0 | 120 | 45 | 82.1 | 68.3 | 62.5 |
| 80/20 | 0 | 159.2 | 62.8 | 118.0 | 74.1 | 60.5 |
| 70/30 | 0 | 192 | 78.3 | 158.5 | 82.2 | 59.2 |
| 100/0 | 2.5 | 138 | 52 | 95.0 | 68.8 | 62.3 |
| 90/10 | 2.5 | 170 | 66.4 | 126.2 | 74.1 | 60.9 |
| 80/20 | 2.5 | 182.8 | 73.2 | 154.7 | 84.2 | 59.9 |
| 70/30 | 2.5 | 262 | 108.5 | 235.4 | 89.6 | 58.6 |

hydrated layer and hindering the protein adsorption [35,36].

FRR is indicative of hydraulic cleaning efficiency and antifouling property of PVC/APVC blend membranes. Higher the value of FRR means higher the cleaning efficiency and better the antifouling property of the membranes. From the Table 5, it could be observed that PVC/APVC blend membranes showed higher FRR than pure PVC membrane. The FRR value of PVC/APVC blend membranes was 82.2% at 70/30 composition, which implies higher cleaning efficiency and higher antifouling property of membranes. The protein deposits could be easily removed by hydraulic cleaning.

4. Conclusions

In this study, PVC was aminated by EDA and novel UF membranes were prepared by blending PVC and aminated PVC with and without additive PEG-600. Effect of blend composition on compaction, water content, hydrophilicity, PWF, porosity, morphology, and antifouling behavior of PVC/APVC blend membranes were evaluated. The introduction of amine group was confirmed by FTIR spectrum. The addition of APVC increased the porosity and mean pore size compared to the pure PVC membranes and produced top and bottom sublayer with finger like support structure. The PWF was increased indicating increased hydrophilicity. The higher hydrophilicity is due to the enrichment of polar groups toward the surface of membranes. Both APVC and the addition of PEG have shown high FRR indicating enhanced antifouling property of PVC/APVC membranes. The membranes can be reused with simple hydraulic cleaning. Overall, the study results showed that the PWF, membranes morphology, water content, porosity, and hydrophilic-

ity of PVC/APVC blend membranes improved significantly by incorporation of APVC. Hence, APVC can be considered as a modifying agent for developing low energy, antifouling UF membranes.

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