Effect of Polymers Blend Ratio Binder on Electrochemical and Morphological Properties of PC/S-PVC-Based Heterogeneous Cation-Exchange Membranes

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ABSTRACT: In this research, heterogeneous cation exchange membranes were prepared by the casting-solution technique using polycarbonate (PC) and *S*-polyvinylchloride (*S*-PVC) as binders along with cation exchange resin as functional group agent. The effect of blend ratio (PC to *S*-PVC) of polymer binder on structure and electrochemical properties of the prepared membranes were elucidated. The morphology of the prepared membranes was investigated by scanning electron microscopy (SEM) and scanning optical microscopy (SOM). The images show that the addition of PC ratio in the casting solution results in formation of a membrane with more inner cavities and micro voids. The electrochemical properties and mechanical strength tests were conducted. Water content, ion exchange capacity, ion permeability, flux, current efficiency, and oxidative stability of the prepared membranes initially were decreased by increasing the PC ratio in the casting solution and then it began to increase. The blending of *S*-PVC and PC polymers results in membranes with lower mechanical strength. Membrane potential, surface charge density, perm-selectivity, cationic transport number, electrical resistance, and energy consumption were initially improved by the increment of PC ratio in the casting solution and then it decreased. The membrane with 70% PC exhibited the highest flux, maximum current efficiency, and minimum energy consumption. However, the selectivity of this membrane was low compared with the other prepared membranes. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 644–656, 2011

Key words: poly carbonate; poly vinyl chloride; binder ratio; electrochemical properties; ion exchange membrane; electro-dialysis

INTRODUCTION

In the field of separation science and technology, membrane processes are currently being studied in numerous applications with practical interests. Among them, electrically driven membrane processes using ion-exchange membranes (electro-membrane process) stand in a very special position. The progress in electro-membrane processes has closely been connected to developing modern ion-exchange membranes in the early 1950s. The membranes fulfilled more and more the basic requirements in electro-membrane processes; today they are highly perm-selective, physically strong, and have low electrical resistances.[1,2]

Electro-membrane processes are based on the selectivity of ion-exchange membranes. These cation- and anion-exchange membranes contain electrically charged groups fixed to the polymer matrix and allow permeation of ions of opposite signs through the membrane under the influence of an electric field which separates ionic species from an aqueous solution and other uncharged components.[3] In such processes, ions interact with membrane, water, and with each other in a complex fashion.[4]

Ion-exchange membranes have versatile applications from desalting of brackish water to treating industrial effluents, environmental protection, recovery and reuse of valuable compounds, as well as processing biological effluents.[5]

For different special applications, it is necessary to impart some special selective characteristics. Variation of the functional groups nature, selection of different polymeric matrices and polymers blending, their crosslink densities, nature of the surface layer, and heterogeneity of the membranes are different tools using which it is possible to achieve some special membranes. To assess the suitability of any membrane for any specific application it is necessary to evaluate two vital parameters, the main transport characteristics of the membrane and its structural properties.[6] In such applications of electro-membrane processes two limiting effects must be taken into consideration: the competition in the membrane transports between the organic and inorganic ions in one hand and the poisoning of the membrane

Compositions of Casting Solution for the Preparation of Heterogeneous Ion Exchange Membrane

Membrane	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Polymers binder (PC : S-PVC), (w/w)	0 : 100	30 : 70	50 : 50	70 : 30	100 : 0
Solvent (THF : Binder), (v/w)	20 : 1	20 : 1	20 : 1	20 : 1	20 : 1
Resin particle (Resin : binder), (w/w)	50 : 50	50 : 50	50 : 50	50 : 50	50 : 50

material by charged organic compounds on the other hand. Several authors have studied the influence of hydrophobic or amphiphilic ions on the membrane properties. Generally, an increase in electric resistance and a loss in perm-selectivity of ion-exchange membranes were observed depending on the nature and concentration of organic ions present in the solution.[7–13] Ion-exchange membranes both the homogeneous and heterogeneous, being unique in their nature supersedes each other in one way or another. Homogeneous membranes have good electrochemical properties but lack in their mechanical strengths, whereas heterogeneous membranes with very good mechanical strength are comparatively poor in their electrochemical performances.[14] Early references on heterogeneous ion-exchange membranes reveal that they may be made by mechanical incorporation of powdered ion-exchange resin into sheets of rubber, PVC, acrylonitrile copolymers or some other extrude able or mold able matrices. Such membranes can be prepared either by (i) calendaring ion-exchange particles into an inert plastic film or (ii) dry molding of inert film forming polymers and ion-exchange particles and then milling.[2]

S-PVC is a flexible and durable polymer with suitable biological and chemical resistance. PC is also a polymer with appropriate temperature and impact resistance properties. Moreover PC has a good adsorption property due to its structure which provides high electrostatic interaction. Membranes with improved properties can be produced by blending of these polymers. In this research heterogeneous ion exchange membranes were prepared by blending of PC/S-PVC as binders. Moreover the changes in electrochemical and morphological properties of the prepared membranes were studied as a function of blend ratio of binders (PC to S-PVC). Membrane characterization was conducted using sodium chloride solutions to determine the nature of membranes performance.

MATERIALS AND METHODS

Material

S-polyvinylchloride (S-PVC), supplied by BIPC, Iran, grade S-7054, Polycarbonate (PC) supplied by DSM (Xantar®), Tetrahydrofuran (THF) as solvent and cation-exchange resin (Ion exchanger Amberlyst® 15, strongly acidic cation exchanger, H^+ form- more than 1.7 milli equivalent/g) by Merck were used to prepare the membranes. All other chemicals were supplied by Merck Inc. Distilled water was used throughout the study.

Preparation of membranes

For the preparation of membranes, particle resin were dried in oven (BEHDAD Co., Model: oven 5) at 30°C for 48 h, then powdered in a ball mill (Pulverisette 5, FRITSCH CO.) and sieved to desired mesh size. Ion exchange resin with desired particles size (−300 + 400 mesh) was used for the preparation of membranes. The membranes were prepared by dissolving the polymer binder (S-PVC or PC or the mixture of S-PVC and PC) in THF solvent in a glass reactor equipped with a mechanical stirrer (Model: Velp Sientifica Multi 6 stirrer) for more than 4 h. This was followed by dispersing a specific quantity of particle resin and casting on a glass plate. The membranes were dried at ambient temperature (25°C) and immersed in twice distilled water. At the final stage, membranes were pretreated by immersing in HCl and NaCl solutions just before using. The membranes thicknesses were measured by a digital caliper device (Electronic outside Micrometer, IP54 model, OLR) to maintain the membrane thickness around 80–120 μm. The composition of casting solution is depicted in Table I.

Test cell

The test cell used for measuring transport number, specific electrical resistance, ion diffusion, and other electrochemical properties is shown in Figure 1. As shown in the apparatus, cell consists of two cylindrical compartments vessels from Pyrex glass separated by the membrane which was fixed between rubber rings.

Each vessel has a volume of 150 cm³. One side of each vessel was closed by Pt electrode that supported with a piece of Teflon (Poly tetra fluoro ethylene) and the other side equipped with a piece of porous medium to support the membrane. At the top of each compartment there are two orifices for feeding and sampling. To minimize the effect of boundary layers on the membranes during the experiments witch makes concentration polarization on the membrane surface, both sections were stirred
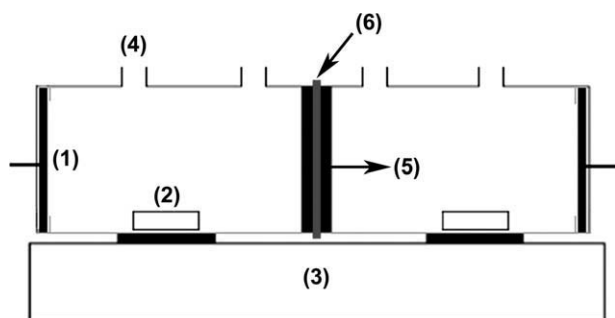
Figure 1 Schematic diagram of test cell: (1) Pt electrode, (2) magnetic bar, (3) stirrer, (4) Sampling orifice, (5) rubber ring, (6) Ion exchange membrane.

vigorously by magnetic stirrers. All experiments were carried out using a membrane area of 13.85 cm^2 square centimeters.

Characterization of prepared membranes

Morphological studies

The structures of prepared membranes were examined by scanning electron microscope (Philips, Model XL30, Netherlands), scanning optical microscopy (Olympus model IX 70) and Differential scanning calorimetry (METLER DSC 30 instrument). To obtain good membrane SEM images, the samples were frozen in liquid nitrogen and fractured. After sputtering with gold, they were viewed under microscope. Also in these experiments, optical microscopy was used in transmission mode with light going through the membrane for scanning purposes.

Water content

Measurement of water content was undertaken according to mass differences between the dried and the swollen membranes. The membranes were immersed in distilled water for 24 h, and then taken out and its surface wiped by filter paper and weighed (Mettler Toledo Group, Model: AL204). The wet membranes were dried at fixed temperature (50°C) for 4 h until constant mass as dry-membrane achieved. The water content can be calculated from the following equation[15–19]:

$$\text{Water content \%} = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100 \quad (1)$$

Contact angle measurements

To study the surface wetting characteristics of prepared membranes, the contact angles between water and membrane surface were measured using a contact angle measuring instrument [G10, KRÜSS, Germany]. This test was performed for evaluation of membrane surface hydrophilicity. The deionized

water was used as the probe liquid in all of the measurements. To minimize the experimental error, the contact angle was measured at five random locations for each sample and then the average was reported (with 1–2.6% Standard division). All experiments have been done in the ambient conditions.

Ion exchange capacity and fixed ion concentration

Ion exchange capacity (IEC) is defined as milliequivalent of ion exchange group included in a 1g dry membrane.[15,16] The IEC was determined through titration. To measure the ion exchange capacity of membranes, a sample membrane is left at first in a 1M HCl solution for 24 h, to convert the exchange group to an H type, and then it is washed with water sufficiently and is kept in it for 24 h until the washed water does not exhibit acidity recognized by the reaction with methyl red. Next, the membrane is immersed in a 1M NaCl solution for 24 h and is washed sufficiently with water. The immersed solution and washed water are collected and finally H$^+$ ions dissolved into the collected solution are analyzed with a 0.01M NaOH and a phenolphthalein indicator (A meq). Finally, the membrane is wiped with filter paper and dried in oven at 50°C for 4 h and then weighed (W g). The IEC can be calculated from the following equation[15–17]:

$$\text{IEC} = \left(\frac{A}{W}\right) \quad (2)$$

By the use of relationship between the IEC and water content, the effect of these parameters can be optimized. The fixed ion concentration or the equivalent of functional group per absorbed water content can be used for this purpose. The high fixed ion concentration in the prepared membranes can control the channels for counter ions transport in the membrane and therefore increases the ion selectivity. The fixed ion concentration (F.I.C) can be calculated by[15]:

$$\text{F.I.C} = \left(\frac{\text{IEC}}{\text{Water content}}\right) \quad (3)$$

Donnan equilibrium's law

In the evaluation of ions equilibrium condition in membranes, the Law of Donnan equilibrium was considered in NaCl solution. A sample membrane is taken in 0.5M NaCl solution. According to the chemical potential equations and the mass conservation, the relations are established as follows[19,20]:

$$\bar{C}_{\text{Na}^+} \times \bar{C}_{\text{Cl}^-} = KC_{\text{Na}^+} \times C_{\text{Cl}^-} \quad (4)$$

where, $\bar{C}$ is the ion concentration in membrane and C is the ion concentration in solution. For cationic membrane:

$$\bar{C}_{Na^+} = \bar{C}_{Cl^-} + (F.I.C) \tag{5}$$

And for the solution:

$$C_{Na^+} = C_{Cl^-} = C_s \tag{6}$$

Therefore from the combination of equations:

$$\frac{\bar{C}_{Cl^-}}{\bar{C}_{Na^+}} = K \left[\frac{C_s^2}{(\bar{C}_{Cl} + (F.I.C))^2} \right] \tag{7}$$

The analysis of the quadratic equation [Eq. (7)] can be used to evaluate membrane permselectivity.

Membrane potential, permselectivity and transport number

When both surfaces of an ion exchange membrane are in contact with a solution of different concentration, an electrical potential would be developed across the membrane due to the tendency of the oppositely charged ions to move with various velocities and mobility. The magnitude of this parameter depends on the electrical characteristic of the membrane along with the nature and concentration of the electrolyte solution used.[21–23] The membrane potential is as algebraic sum of two Donnan potentials and diffusion potential, determined by the partition of ions into the pores as well as the mobilities of ions within the membrane phase compared with the external phase.[21] The membrane potential is measured using a two-cell glassy apparatus as show in Figure 1 in which an equilibrated circular membrane with 13.85 cm^2 effective area is embodied between the cells. At ambient temperature (25°C), an electrolyte solution with concentration of $C_1 = 0.1M$ and a solution with $C_2 = 0.01M$ are poured into the cells compartments on either side of the membrane. Both sections were stirred vigorously by magnetic stirrers to minimize the effect of boundary layers on the membrane's surface. After 10 min the developed potential difference across the membrane is measured by connecting both compartments and saturated calomel electrode through KCl bridges and with the help of a digital auto multi-meter (DEC, Model : DEC 330FC, Digital Multimeter, China). The measurement was repeated for 5 min meanwhile potential was measured in every one minute until the value constant ($E_{measure}$) was reached.

The membrane potential generated between the solutions contacting with both membrane surfaces is expressed by the Nernst equation[15,19,21,24,25] that used for calculation of transport number of ions as follows:

$$E_{Measure} = (2t_i^m - 1) \left(\frac{RT}{nF} \right) \ln \left(\frac{a_1}{a_2} \right) \tag{8}$$

Where t_i^m is the transport number of ions (cationic or anionic) in the membrane phase, R is the gases

constant, T is the temperature, n is the electrovalence of counter-ion and a_1, a_2 are the electrolyte activity in the solutions in contact with both membrane surfaces determined by Debye-Huckel limiting law.

Ion selectivity of membranes is quantitatively expressed in terms of permselectivity based on the migration of counter-ion through the ion-exchange membrane as follows[21,25]:

$$P_s = \frac{t_i^m - t_0}{1 - t_0} \tag{9}$$

Where, t_0 is the transport number of these ions in solution phase.[26]

In fact, permselectivity is a measure of the characteristic difference in the membrane permeability of counter-ions and coions that confirmed the Law of Donnan equilibrium.

Concentration of fixed charge on membrane surface

The homogeneity and uniform distribution of functional groups on the membranes surface can provide more conducting regions on membranes surface and improves the electrochemical properties of them. The existence of more conducting regions on the membrane surface also can strengthen the intensity of uniform electrical field around the membrane and decreases the concentration polarization phenomenon. The concentration of fixed charge on membrane surface (Y) has been expressed in terms of permselectivity as follows[21,23,27]:

$$Y = \frac{2C_{Mean}P_s}{\sqrt{1 - p_s^2}} \tag{10}$$

Where P is the permselectivity and C_{Mean} is the mean concentration of electrolytes.

Conductivity and permeability

The conductivity and cation permeability were determined via the test cell. The apparatus consists of two compartments that separated by the membrane, which was fixed between rubber rings. A 0.1M electrolyte solution was placed on one side of the cell (Anodic section) and 0.01M solution was placed on the other side as diffusion cell. A DC electrical potential (DAZHENG, DC power supply, Model : PS-302D) with constant voltage (10 V) was applied across the cell with platinum electrodes placed at the end of compartments and the conductivity changes versus time was measured using a digital conduct-meter (JENWAY, Model: 4510). During the experiment, ions permeate through the membrane into the permeation section. Therefore, the conductivity of this section increases with time. The

solutions of both compartments were stirred vigorously between two successive measurements to ensure the return of equilibrium condition in two solution-membrane interfacial zones and to minimize the effect of boundary layers on the membrane's surface that causes concentration polarization.

The permeation of ions through the membrane phase can be calculated from the variation of conductivity measurement. According to Fick's law and electrical potential, flux (N) through the membrane can be expressed as follows,[19,24]:

$$N = P \frac{C_1 - C_2}{d} \quad (11)$$

Where P is the coefficient permeation of ions, d is the membrane thickness and C_1, C_2 are the ion's concentration in the compartments.

The boundary conditions are:

$$C_1^0 = 0.1M, \ C_2^0 = 0.01M, \ C_1 + C_2 = C_1^0 + C_2^0 = 0.11M \quad (12)$$

Therefore:

$$N = -\frac{V}{A} \times \frac{dC_1}{dt} = P \frac{C_1 - C_2}{d} \quad (13)$$

Where A is the membrane surface area,

$$\ln\left[1 - \frac{2C_2 - 2C_2^0}{C_1^0 - C_2^0}\right] = -\frac{2PAt}{Vd}, \quad \frac{2C_2 - 2C_2^0}{C_1^0 - C_2^0} << 1 \quad (14)$$

$$Q_2 = KC_2 \Rightarrow Q_2 = \frac{KPAt(C_1^0 - C_2^0)}{Vd} + KC_2^0 \quad (15)$$

and Q is the conductivity.

On the basis of the final equation the diffusion coefficient of ions in the membrane can be determined from the slope of the straight line of $Q-t$.

Electrical resistance

The electrical resistance has practical importance due to its indirect relation with energy consumption in the process.[15] The resistance is measured in the test cell. The measurement is carried out in $0.5M$ NaCl solution. For the purpose, a membrane sample is immersed in a $0.5M$ NaCl solution for 24 h, then taken out and washed with distilled water. Then it was embodied in the cell. A $0.5M$ NaCl solution is supplied in the compartments of cell which is left in $25°C$ thermostat. Electrical resistance (R_1) is measured using alternating current bridge with frequency of 1500 Hz (Audio signal generator, Electronic AFZAR AZMA CO. P.J.S). Next the membrane sample is taken away; the apparatus is re-integrated

without a membrane, and electric resistance (R_2) is measured again. The membrane resistance is calculated by the resistance of cell subtracting the resistance of electrolyte solution ($R_m = R_1 - R_2$). The specific resistance is expressed as follows[15,16]:

$$r = \left(\frac{RA}{d}\right) \quad (16)$$

Where r is specific resistance, A is surface area of membrane, and d is its thickness.

Current efficiency and energy consumption

The current efficiency (C.E) was calculated via following equation[24]:

$$\text{C.E} = \frac{F \times Z_i \times \Delta n}{\int\limits_{t=0}^{t=t} I dt} \quad (17)$$

And for the energy consumption (E):

$$E = \frac{\int\limits_{t=0}^{t=t} I \times V \times dt}{\Delta n \times M_w} \quad (18)$$

Where, Z_i is the valance of ion, Δn is transport number of moles, V is voltage, F is faraday constant, I is the current intensity, and M_w is the molar mass of ions.

Tear resistance

Tear resistance as a mechanical property of the prepared membranes was tested according to ASTM1922-03 in Iran Polymer and Petrochemical institute. All samples were cut to the standard shape in the ambient conditions ($28.6°C$, relative humidity of 28%) before testing. For each test, three samples were used and the average values were reported.

Membrane oxidative stability

The prepared heterogeneous membranes samples were immersed into 3% H_2O_2 aqueous solution containing 4ppm Fe^{3+} at $25°C$ for up to 60 h. The mass of dried samples (drying at $50°C$ for 4 h) before and after the experiment were compared.

RESULTS AND DISCUSSION

Morphological studies

The SEM images of the surface and cross section of the prepared membranes are presented in Figures 2–4. These images show nonconducting area (binder) and
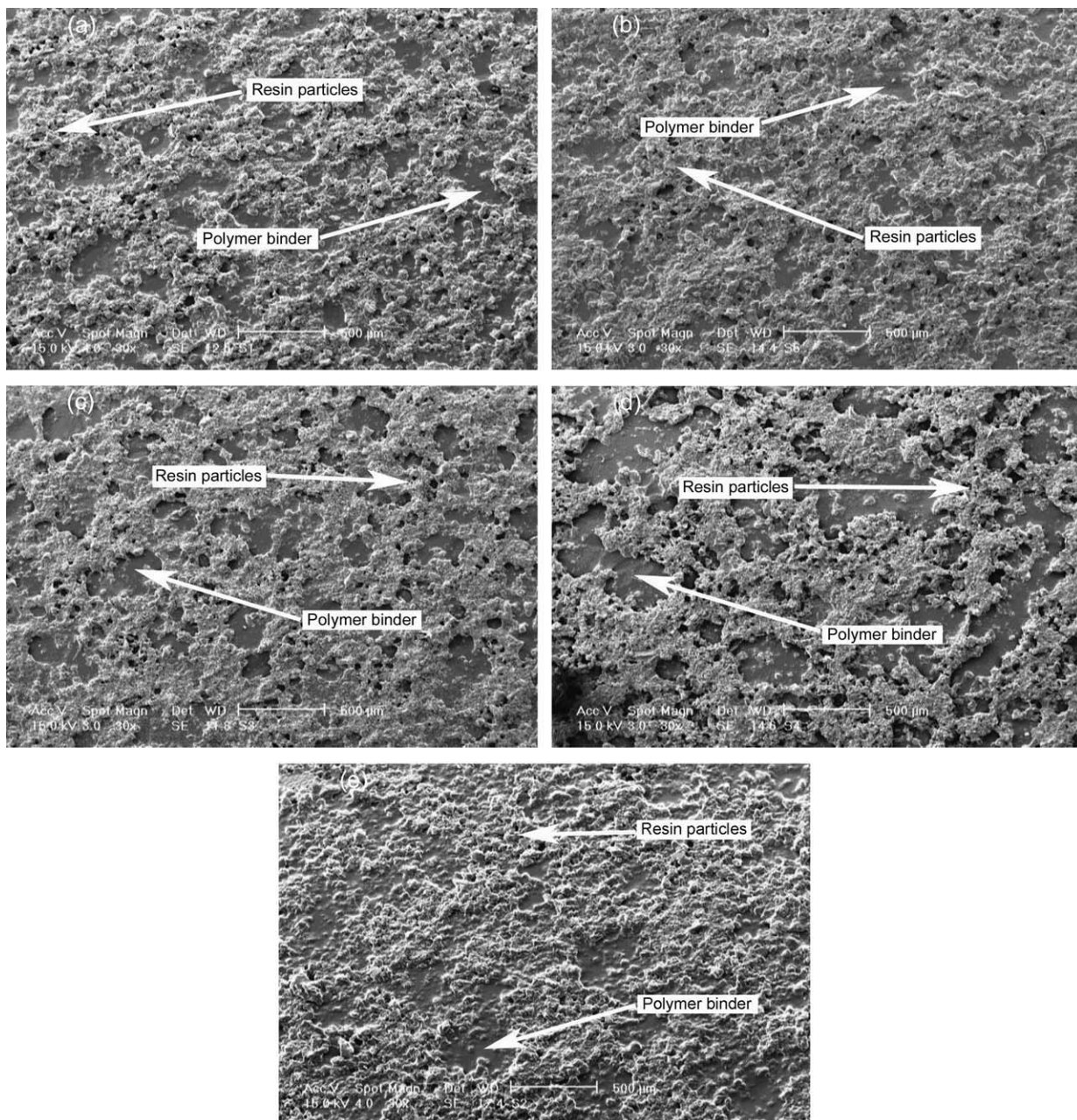
Figure 2 SEM surface images (30X magnification) for prepared membranes with various polymer binder ratio (PC: SPVC): a-(0 : 100), b-(30 : 70), c-(50 : 50), d-(70 : 30), e-(100 : 0).

conducting ion exchange areas (resin particles) on the surface and in the bulk of the prepared membranes. As the heterogeneous membranes swell in water, the cracks and fissures open and the fraction of conductive area is increased.[28] These cracks are shown in Figure 5. The most important feature in the SEM studies is the absence of clear polymer-polymer phase separation in the solidified materials. This feature may indicate a good interpenetration of PC and S-PVC chains in the membrane.

Also the miscibility of PC with S-PVC blends was examined by differential scanning calorimetry (DSC). The thermal behavior analysis of prepared membranes with various ratios of polymer binder was investigated by DSC test in a temperature range of 20–300°C at heating rate of $10°C$ min^{-1} under nitrogen. The obtained thermal analysis results showed only one Glass transition point for each membrane. This is attributed to the absence of polymer-polymer phase separation in the membrane matrix due to a good interpenetration of PC and S-PVC polymer chains.[29,30] The DSC results (Glass transition) are presented in Table II.

With increase of blend ratio of polymer binder (PC to S-PVC), free spaces in the membrane matrix decreased due to lower space rotation in PC chains
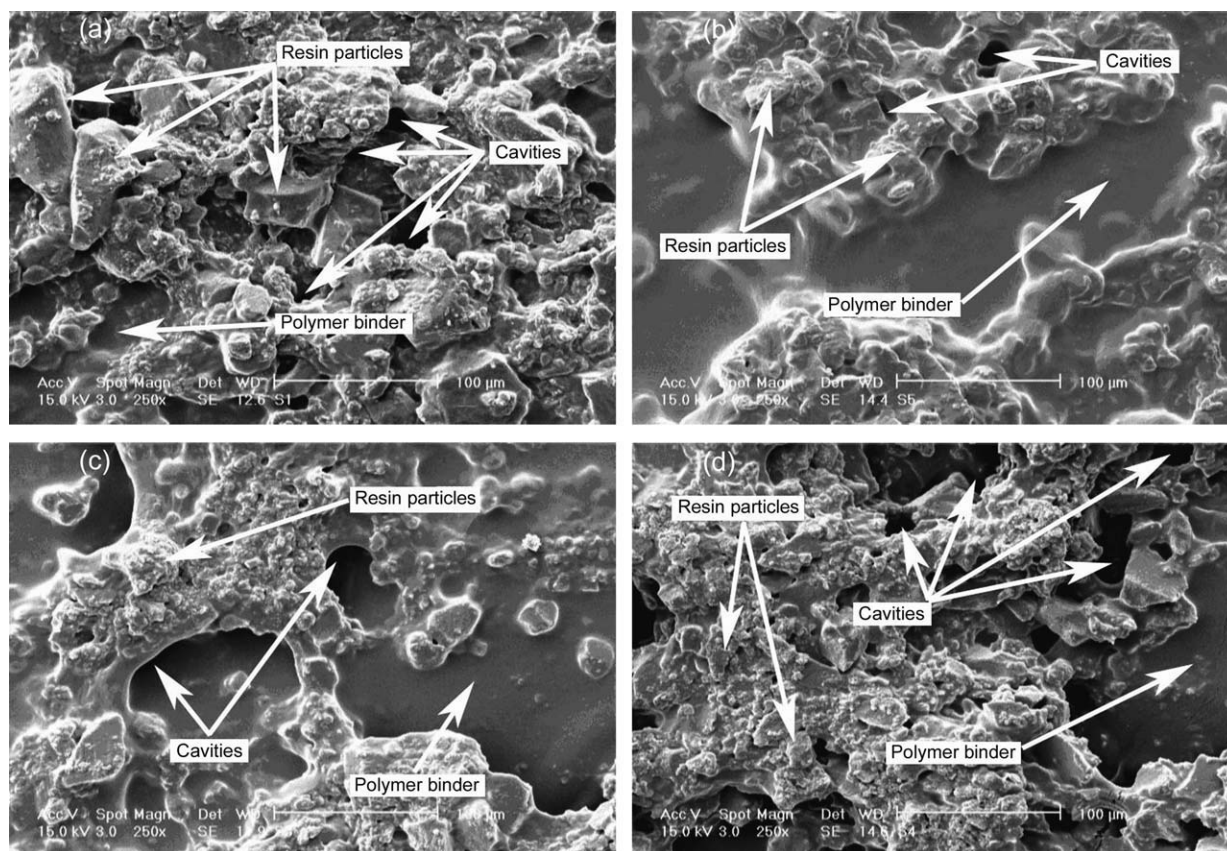
Figure 3 SEM surface images (250X magnification) for prepared membranes with various polymer binder ratio (PC: SPVC): a-(0 : 100), b-(30 : 70), c-(50 : 50), d-(70 : 30), e-(100 : 0).

compared with *S*-PVC chains (Table III)[31] that makes less inner cavities and void in the bulk of membrane. With more increment of blend ratio of polymer binder, the inner cavities and void were increased again probably due to discontinuity of polymer's chains. However, it was decreased again for PC membrane.

The SOM was used in the evaluation of extended area of the prepared membranes. The images in transmission mode with light going through the membrane are shown in Figure 6. The prepared membranes appeared as relatively uniform surfaces. The resin particles are seen as a dark spots. Resin particles are distributed uniformly all over the area. The uniform distribution of functional groups can provide more conducting region in the membrane's surface and therefore would improve the electrochemical properties of the prepared membranes.

Water content and contact angle measurements

Increasing the blend ratio (PC to *S*-PVC) of polymer binder initially decreases water content of the prepared membranes (Fig. 7). This may be attributed to the variation of inner cavities and void in the bulk of membrane as shown in SEM images. Water content was increased afterwards. In fact, with increment

of blend ratio (PC to *S*-PVC) of polymer binder, the polymer's binder micro-phase will be discontinued which causes more swelling of the membrane and higher water absorption. Water content of *S*-PVC based membranes was higher than PC based membranes which may be due to the existence of higher free spaces among the polymer's chains in *S*-PVC membrane matrix because of higher free space rotation in *S*-PVC chains compared with PC chains that makes more cavities, void, and tortusity in the bulk of the membrane. In fact, the existence of benzene rings and methyl branches in PC structure prevents the free rotation of PC chains which results in fewer cavities in PC membranes (Table III).

Also the contact angles were measured to evaluate the hydrophilicity and surface properties of the prepared membranes (Fig. 7). The results indicate that the surface of PC membrane is more hydrophilic compared to *S*-PVC membrane. This can be ascribed by the higher hydrophilic polar groups of PC polymer as shown in Table III. In fact, the hydrogen bonds of water molecules with oxygen atoms in polycarbonate are stronger than similar bonds with chloride groups in *S*-PVC polymers.[32]

Moreover, the results reveal that increasing the blend ratio (PC to *S*-PVC) of polymer binder, firstly increases the contact angle of the prepared
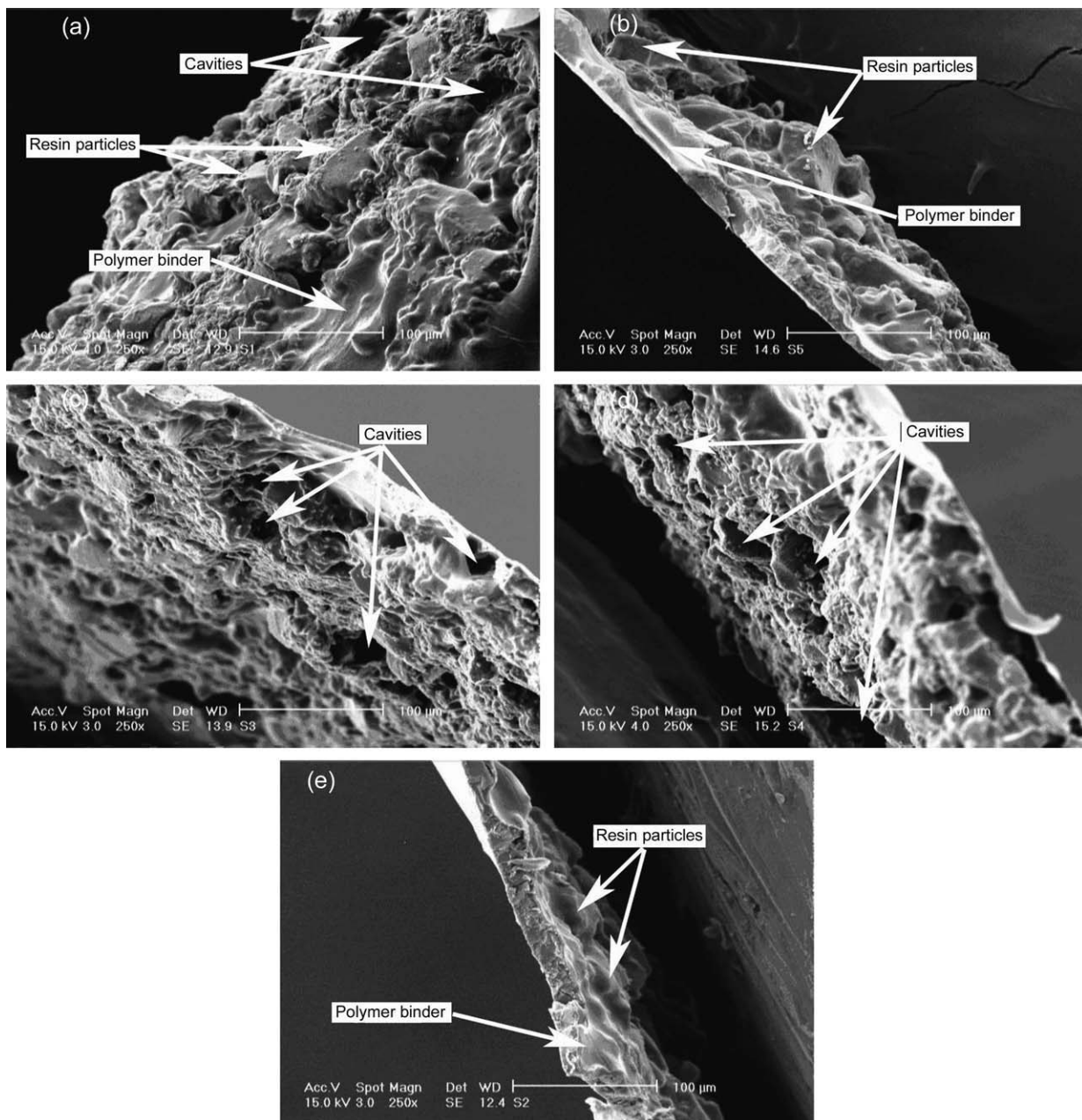
Figure 4 SEM cross section images (250X magnification) for prepared membranes with various polymer binder ratio (PC: SPVC): a-(0 : 100), b-(30 : 70), c-(50 : 50), d-(70 : 30), e-(100 : 0).

membranes due to the decrease of the cavities on the membrane surface. This was followed by a reduction in contact from (30 : 70) to (70 : 30) blends ratio binder. The results may be due to higher hydrophilicity of PC compared with S-PVC[32] and also enhancement of cavities and voids on the surface of membranes as seen in SEM images.

Ion exchange capacity and fixed ion concentration

According to Figure 8, with the increment of polymer binder ratio (PC: S-PVC) the ion exchange capacity of the prepared membranes is initially decreased because of the existence of less free space between the polymer's chains in PC membranes that can decrease the cavities and voids in the membrane bulk. In fact, free spaces in S-PVC can prevent the isolation of functional group by the polymer binder and leads to increment of ion exchange capacity. With higher increment of polymer binder ratio (PC: S-PVC) from (30 : 70) to (70 : 30), the ion exchange capacity was increased again. This may be attributed to more formation of inner cavities and void in the bulk of membrane due to discontinuity of polymer's chains which makes more void spaces. However, this was decreased again for PC membrane because
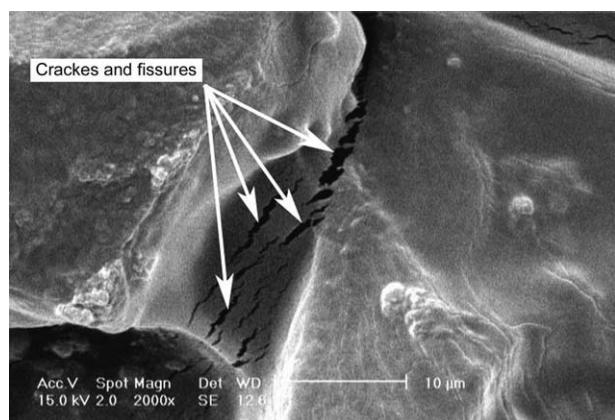
Figure 5 Formation of cracks and fissures in matrix of membrane.

of lower space rotation in PC chains. The functional groups in membranes with less free spaces in fact are isolated with binder in the membrane matrix and are partially not accessible to ion exchange which leads to IEC decline.

The high fixed ion concentration in the prepared membranes can control the channels for counter ions transport in the membrane and therefore increases the ion selectivity. In fact, this factor indicates the ion selectivity of the prepared membranes. The PC cation exchange membranes possess a higher fixed ion concentration compared to the S-PVC membranes (Fig. 9) due to less water content.

Donnan equilibrium's law

To evaluate the equilibrium condition of cations versus anions in the prepared membranes as a function of polymer binder, the Law of Donnan equilibrium was considered in 0.5M NaCl solution. The ratio of entered counter to co ions in the membrane matrix can be used in qualitative evaluation of membrane's selectivity. As Figure 9 shows, based on the Donnan equilibrium law, with increment of polymer binder ratio (PC: S-PVC), initially the membrane selectivity to Na$^+$ ions is increased and then it is decreased by increment of binder ratio from (30 : 70) to (70 : 30). As was expected, ion selectivity was increased again for PC membrane due to higher fixed ion concentration.

TABLE II
The Thermal Analysis Results (DSC-Glass Transition) of Home-Made Membranes with Various Blend Ratios of Polymer Binders (PC to S-PVC)

Membrane	Glass transition (T_g), K
Sample 1, (0 : 100)	364.55
Sample 2, (30 : 70)	355.45
Sample 3, (50 : 50)	351.65
Sample 4, (70 : 30)	358.75
Sample 5, (100 : 0)	354.35

TABLE III
Chemical Structures of Used Polymers

Polymer	Chemical structure
Polycarbonate (PC)	
S-polyvinyl chloride (SPVC)	

## Membrane potential, surface charge density, permselectivity, and transport number

The results show that initially the membrane potential will increase with the increment of binder ratio (PC: S-PVC) (Fig. 10). This may be attributed to increment in the membrane surface charge density due to highly uniform distribution of resin particles as shown in SEM and SOM images. This leads to enhanced Donnan exclusion and is responsible for the increment of membrane potential. The homogeneity and uniform distribution of functional groups can provide more conducting region in membrane surface and generate easy flow channels for the counter-ions and therefore improve the electrochemical properties of the membranes. Membrane potential was decreased again from (30 : 70) to (70 : 30) ratio due to lower fixed ion concentration and membrane surface charge density (Fig. 10).

Figure 11 indicate that the perm-selectivity and transport number are initially increased with the increment of binder ratio (PC: S-PVC) resulted from an increment in the fixed ion concentration which can control ions pathways due to existence of high ionic functional groups. Membrane perm-selectivity was decreased again from (30 : 70) to (70 : 30) ratio due to the decrease of fixed ion concentration.

The PC based membranes exhibited superior selectivity and transport number in comparison to S-PVC membranes because of higher fixed ion concentration. Additionally the lower transport number and perm-selectivity of S-PVC based membranes can be explained by higher swelling which facilitates the diffusion of counter and coions through the membrane.[24]

Conductivity and permeability

During the experiment, ions permeate through the membrane and conductivity is increases with time (Fig. 12). As shown in Figures 12 and 13, Sample 4 with the highest ion permeability has the maximum flux. The selectivity of this sample is low compared to the other membranes. Sample 2 with the highest
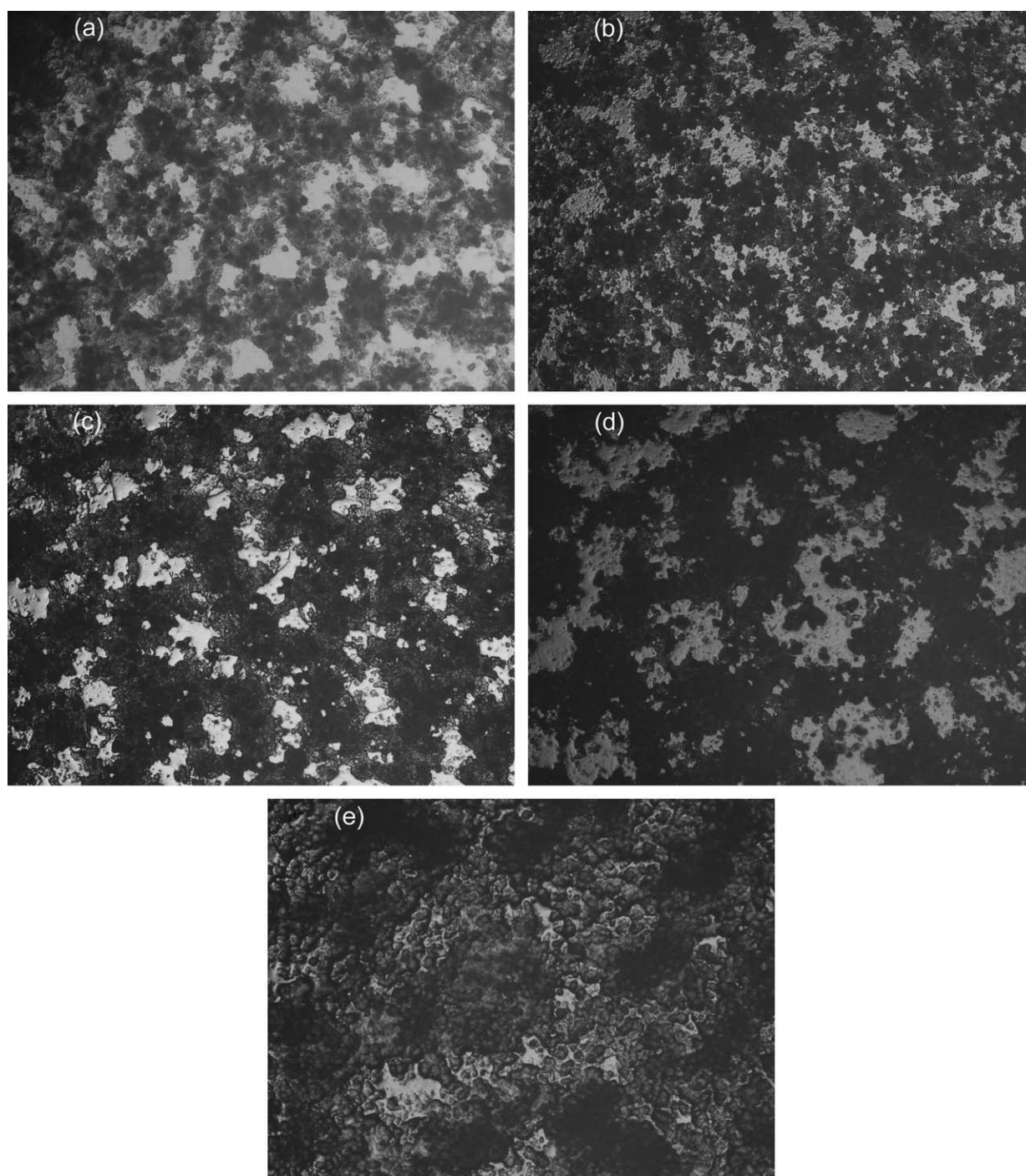
Figure 6 Scanning Optical Microscopy images of prepared membranes with various polymer binder ratio (PC: SPVC): a-(0 : 100), b-(30 : 70), c-(50 : 50), d-(70 : 30), e-(100 : 0).

perm-selectivity among the prepared membranes exhibit minimum ion permeability and flux.

Electrical resistance

The electrical resistance of prepared membrane (Fig. 14) was initially increased with increment of binder ratio (PC: S-PVC). This may be attributed to decreasing of the ion exchange capacity and water content in the membrane as shown in Figure 7. The membrane resistance was decreased again from (30 : 70) to (70 : 30) ratio (PC: S-PVC) due to the increase of water content and IEC. The low electrical resistance of PC membrane may be attributed to high surface charge density of this membrane.

**Current efficiency and energy consumption**

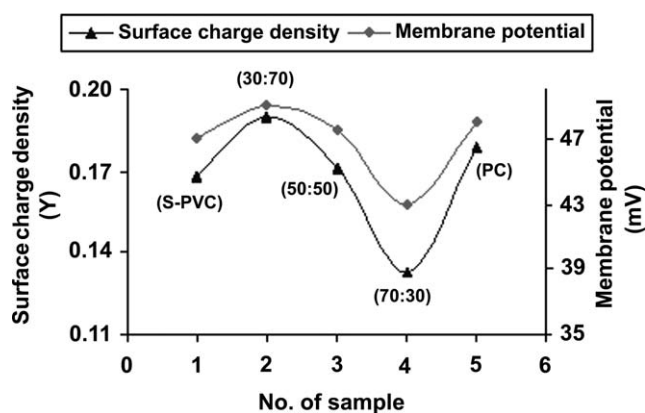According to Figure 15, Sample 4 with the highest ionic flux and permeability showed maximum current
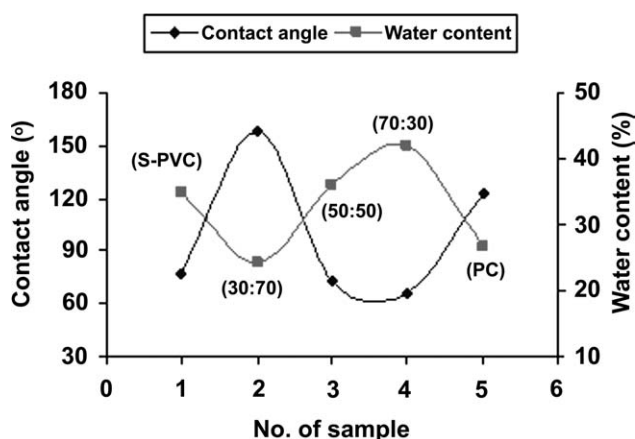
Figure 7 The effect of polymer binder ratio (PC: SPVC) on water content and surface hydrophilicity of prepared membranes.
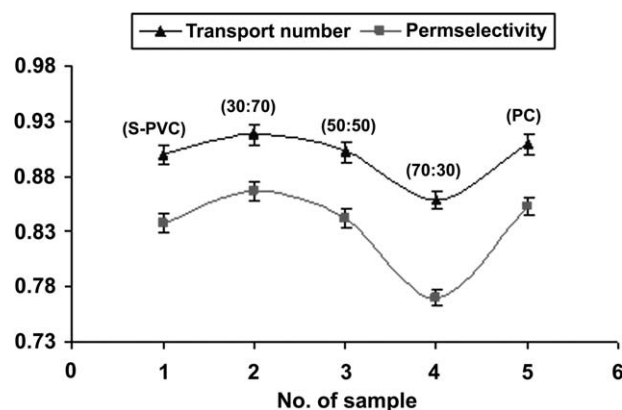

Figure 10 The effect of polymer binder ratio (PC: SPVC) on membrane potential and membrane surface charge density.

efficiency and minimum energy consumption in comparison with other prepared membranes in this research. However, its selectivity was low compared with others.

Mechanical properties

The loss of solvent due to evaporation introduces micro voids between the resin particles and binder region.[33] These micro voids are sufficient to accommodate solvent molecules for the solvation of ionic species in the resin. However, the swelling evaluation of prepared membranes showed that variations of membranes thickness, width and length at swelled membranes were negligible.

The results show that mechanical strength is decreased with the increase of blending ratio of PC to S-PVC (Fig. 16) because the PC binder being more brittle in nature compared with the S-PVC,[31,34] and lower space rotation in the PC chains compared to the S-PVC chains (Table III).

Figure 8 The effect of polymer binder ratio (PC: SPVC) on ion exchange capacity of prepared membranes.
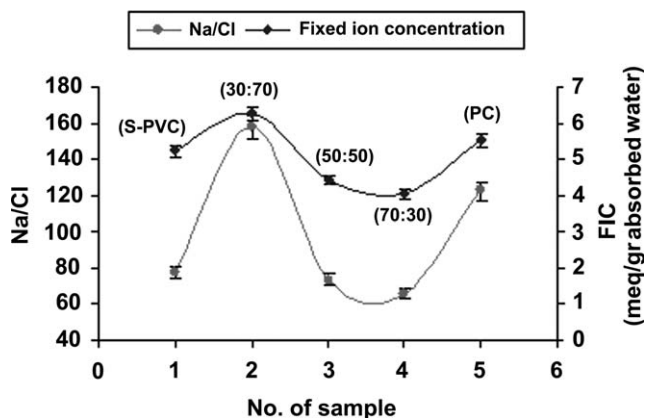
Figure 9 The effect of polymer binder ratio (PC: SPVC) on fixed ion concentration and selectivity based on Donnan equilibrium's law (Sample 1 (0 : 100), Sample 2 (30 : 70), Sample 3 (50 : 50), Sample 4 (70 : 30), Sample 5 (100 : 0)).

Figure 11 The effect of polymer binder ratio (PC: SPVC) on transport number and membrane's permselectivity.
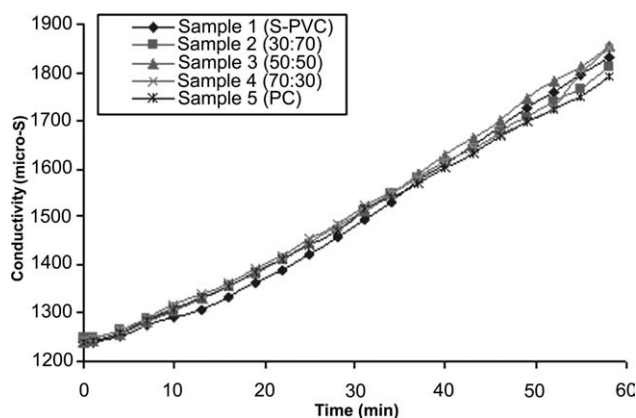
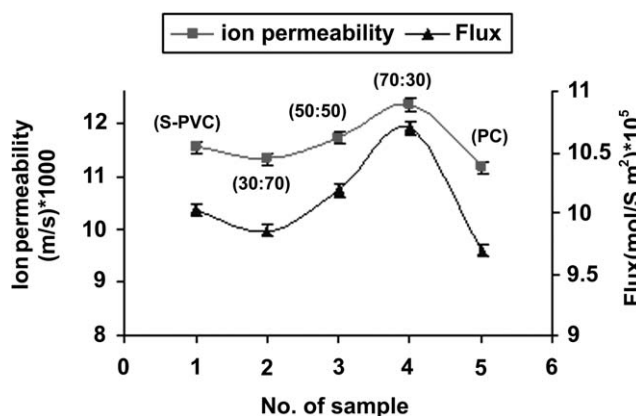Figure 12 The variation of conductivity with time in permeate section for prepared membranes.

Membrane oxidative stability

The prepared membranes samples were immersed in an oxidant aqueous solution for oxidative stability measurements.
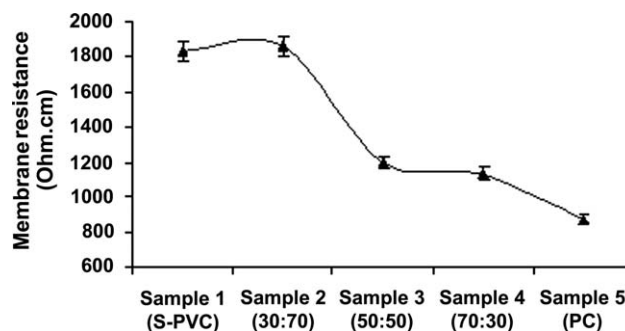
As shown in Figure 16, the oxidative stability of the prepared membrane was initially increased with the increment of binder ratio (PC: S-PVC) due to the decrease of water diffusion in the membrane matrix. The oxidative stability was decreased again for the prepared membranes due to the higher water diffusion and lower stability of PC compared to S-PVC[31] as was achieved in the experiments. The Sample 2 was more stable compared to the other prepared membranes.

CONCLUSION

The ion exchange membranes were prepared by the phase inversion technique with PC and S-PVC as binders and resin particle as ionic sides. A good interpenetration of PC and S-PVC chains into the membranes was observed. A relatively uniform sur-


Figure 14 Membrane resistance of prepared membranes with various polymer binder ratios (PC: SPVC).

face was obtained for the prepared membranes. The results show that with the increase of blend ratio (PC to S-PVC) of polymer binder, water content and ion exchange capacity of the prepared membranes are initially decreased and then increased. The uniform distribution of functional groups can provide more conducting region in the membrane surface and therefore improve the electrochemical properties of the prepared membranes. The high fixed ion concentration in the prepared membranes can control the channels for counter ions transport in the membrane and therefore increases the ion selectivity. The selectivity of Sample 2 was superior compared to the other prepared membranes. The PC cation exchange membranes possess a higher fixed ion concentration compared to the S-PVC membranes. The membrane potential was decrease from (30 : 70) to (70 : 30) ratio binder (PC: SPVC) due to lower fixed ion concentration and membrane surface charge density. Sample 4 with the highest ion permeability has the maximum flux, but the selectivity of this sample was low compared to the other membranes. The Sample 2 with the highest perm-selectivity among the prepared membranes has suitable ion permeability and flux. The membrane resistance was

Figure 13 Flux of ions and ion permeability for prepared membranes with various polymer binder ratios (PC: SPVC).
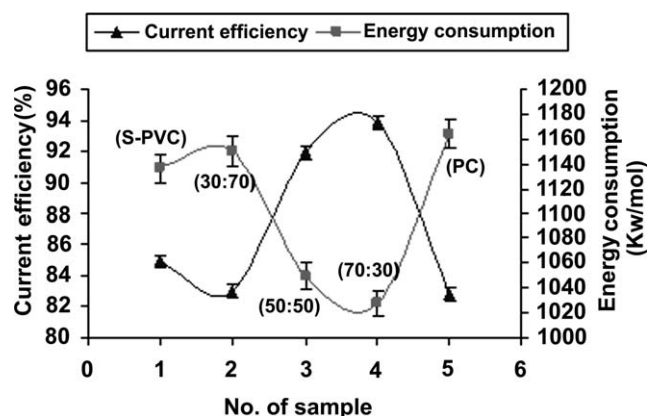
Figure 15 Energy consumption and Current efficiency of prepared membranes with various polymer binder ratios (PC: SPVC).
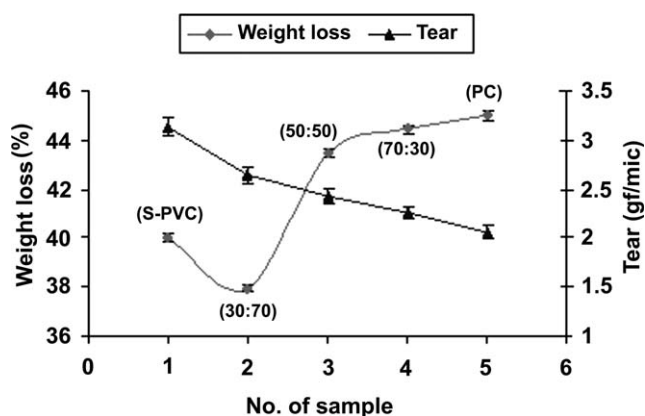
Figure 16 Oxidative stability (weight loss) and tear of prepared membranes with various polymer binder ratios (PC: SPVC).

also decreased from (30 : 70) to (70 : 30) binder ratio (PC: *S*-PVC). Sample 4 with the highest flux showed the maximum current efficiency and minimum energy consumption. The results indicate that mechanical strength was decreased with increasing the blending ratio of PC to *S*-PVC. In addition, the oxidative stability test shown that sample 2 was more stable compared with the other prepared membranes.

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