Research Paper

Preparation of Heterogeneous Cation- and Anion-Exchange Membranes by Eco-Friendly Method: Electrochemical Characterization and Desalination Performance

Jaydevsinh M. Gohil [1,*], Paramita Ray [2,*]

[1] School for Advanced Research in Polymers - Advanced Polymer Design and Development Research Laboratory (SARP-APDDRL), Central Institute of Plastics Engineering & Technology (CIPET), Hi Tech Defence and Aerospace Park (IT Sector), Jala Hobli, Bengaluru – 562 149, Karnataka, India
[2] Membrane Science and Separation Technology Division, CSIR-Central Salt & Marine Chemicals Research Institute, G. B. Marg, Bhavnagar-364002, Gujarat, India
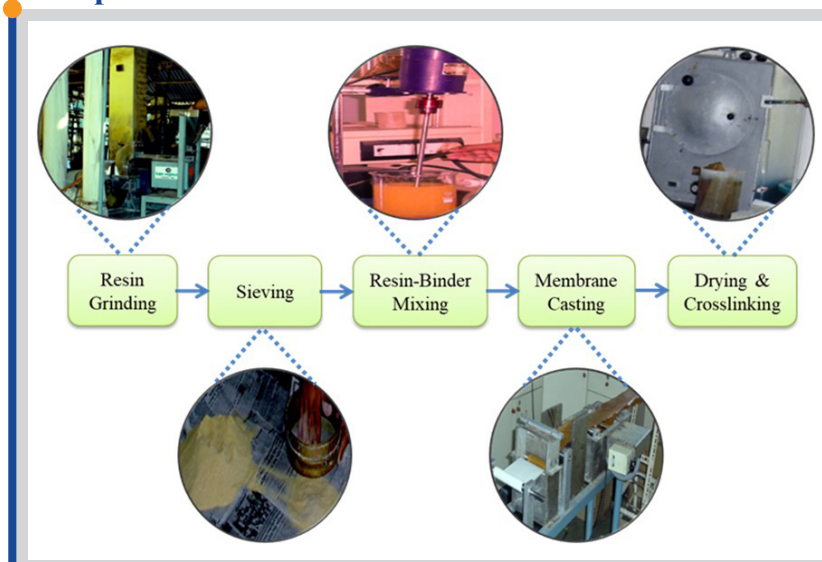
Article info

Keywords

Highlights

- Reporting eco-friendly method for the membrane preparation
- Properties of HIXMs depend on resin content and types of binder
- Membranes have low electrical resistance and homogeneous morphology
- Membrane shows high salt rejection and current efficiency using ED

Graphical abstract

Abstract

This paper emphases on the preparation, characterization and application of heterogeneous cation- and anion-exchange membranes. Membranes were made by solution casting method from the blends comprises of ion-exchange resins and eco-friendly polymer binder polyvinyl alcohol (PVA). Dimensional stability of membranes in water was controlled by crosslink density of binder. Physicochemical and electrochemical characteristics of ion-exchange membranes such as ion-exchange capacity (IEC), swelling (%), water uptake (%), surface electrical resistance, and transport number have been optimized by varying the resin:binder ratio. Thermal properties of the membranes were studied using the thermogravimetric analysis and differential scanning calorimetry to evaluate the thermal degradation pattern/stability and transition temperature, i.e., Tg of ionic membranes. The morphology of membrane samples were studied using scanning electron microscope. Heterogeneous ion-exchange membranes (HIXM) prepared from the water soluble binder showed superior electrochemical properties and homogeneous morphology compared to HIXMs prepared using the organic solvent based polymer binder polyvinyl chloride (PVC) and when used for desalination in Electrodialysis stack exhibits 85.5% salt reduction.

1. Introduction

Based on inclusion of ion-exchange functional groups to polymer materials or their chemical-bonding characteristics, ion-exchange membranes (IEM) are categorized into homogeneous, interpenetrating polymer network (IPN) and heterogeneous membranes [1]. Most of the practical IEMs are rather homogeneous and composed of either hydrocarbon or fluorocarbon polymer film hosting the fixed charges to their structure and the charged groups are uniformly distributed through the whole membrane matrix. Full-IPN membrane comprises of two or more polymer networks which are at least partially interlaced on a polymer scale but not covalently bonded to each other, while in semi-IPN membranes one of the polymers remains in network

form while the other linear polymer interlaced into the first network and form a single polymer network. However, heterogeneous ion-exchange membranes (HIXM) have more than one phase, where very fine ion-exchange resin powder is evenly dispersed in the binder. In such membranes, the ion-exchange groups remain in the clustered form and mostly unevenly dispersed throughout the membrane matrix. The binder provides the structural stability and imparts mechanical strength to the membrane. All these types of ionic membranes are extensively employed in the electrochemical membrane separation related to electrodialysis (ED) like brackish water desalination and production of ultrapure water; chloralkali production; preparation, demineralization and concentration of organic acids and salts as well as electrical energy generation by fuel cells and batteries [2-6].

Polymer materials that carry strong ion-exchange functional groups lack in film-forming characteristics and processibility, which are highly required for homogeneous membrane preparation. However, such ion-exchange materials can be molded into HIXM by casting method using the blend of ion-exchange resins and polymer binder [1,7]. Blending is carried out in dry powder, melt, latex, slurry or solution form or in-situ polymerization while the membrane forming is carried out by compression molding, calendaring, extrusion, spray coating, solution casting or phase inversion into shape of a flat sheet membrane. Customarily HIXMs prepared in these ways are low in their cost and have good mechanical properties but possesses inadequate electrochemical properties. Such membranes generally have higher electrical resistance as the mobile ion has to traverse a comparatively longer pathway due to heterogeneous structure of the membrane and lower permselectivity as the water filled domains in the membrane matrix become responsible for the leakage of co-ions. This is contrary to homogeneous type membranes that exhibit good electrochemical properties although have low mechanical strength. Electrochemical properties of HIEM in turn depend on the content of ion-exchange resin and morphology of membrane. Preparation of HIXM of a high ionic conductivity while retaining interfacial homogeneity between polymer binder and ionomer is the key challenge. Further in the search of better HIXM, series of blend systems based on poly(vinyl chloride) (PVC)/polystyrenesulfonic acid (PSSA) [8,9], polysulfone (PSF)/polystyrenesulfonic acid (PSSA) and polycarbonate/PSSA [10], polyethylene/sulphonated poly(1,4-phenylene sulfide) [11], polyvinylidene fluoride/polyaniline [12] have been studied to optimize the electrochemical properties and mechanical strength of HIXM. All these membranes showed high ionic conductivities and distinct phase morphologies at a high loading (>50 %) of ion-exchange resin in the blend. Hosseini and co-workers also followed solution casting methods for preparation of HIXM from the blend of polymer binder such as polycarbonate/styrene-butadiene-rubber and PVC/styrene-butadiene-rubber, and strong cation-exchange resin particles [13,14]. However, in the membrane formation they either incorporated carbon nanotube into casting solution or deposited nanosilver by plasma treatment on the membrane surface. At optimum concentration of nanoparticle the resultant heterogeneous nanocomposite membranes exhibited increased electrical conductivity and relatively uniform surfaces. However, the use of nanoparticles further added the cost of membrane. Addition of surfactant to certain concentration in casting solution helped in getting uniform dispersion of resin particles into polymer binder during membrane formation [15]. Another important approach in optimization of membranes properties is to use suitable particle size of resins and to add optimum content of ion-exchange resin to binder polymer for preparation of HIXM [9]. Using PVC as a binder, and resin particles of -300+400 mesh, it is possible to incorporate 60% resin to get flexible membranes whereas the use of resin particle of -100+200 mesh, only allows 40% resin incorporation to PVC binder and more than that resulted in brittle membrane. Thus, to obtain membranes with better properties, selection of proper binder, resin particle size, additives loading and surface treatment are the important aspects.

Poly(vinyl alcohol) (PVA) is a versatile water-soluble and biodegradable/biocompatible polymer possessing a very good film forming, binding and crosslinking ability along with surface active properties [16,17]. The present paper explores the HIXMs preparation using PVA as a binder with uniformly dispersed ion-exchange resin particles. The preparation route of these membranes eliminates the use of the hazardous carcinogenic chemicals/solvents like sulfuric acid, chlorosulfonic acid, chloromethylether, triethylamine, tetrahydrofuran (THF) etc. Thus, an eco-friendly route for the preparation of HIXM has been selected. Moreover, the HIXM preparation adopted in this study avoided the multiple steps such as film formation, crosslinking, sulfonation, quarternization, etc., which are required in IPN and homogeneous membrane preparation; advantageously, this technique can be used/ translated for the preparation of membrane in continuous form at pilot/ large scale. Moreover, the use of PVA as a binder for HIXM has several advantages like low cost, uniform morphology, and high electrical conductivity. Electrochemical and physicochemical properties of HIXMs based on the PVA binder has been compared with standard HIXMs based on the PVC binder at varying concentration of ion-exchange resin particles.

2. Experimental

2.1. Materials

Commercial strong cation- (Indion 225) and anion- (Indion FFIP) exchange resin (CXR and AXR) with ion-exchange capacity (IEC) of 4.2 and 3.4 meq/g respectively were procured from Ion Exchange (India) Ltd. PVA of molecular weight 14000 and degree of hydrolysis 98-99%, and solvent THF were obtained from SD Fine Chemicals, India. PVC (PVC 67 GEF092), flexible lamination film grade of K value 67 was supplied by IPCL, India. Polyamide woven fabric of thickness 120 μm (Nylon 101) was brought from Indu Corporates India. Silver Nitrate, AR grade, was supplied by Ranbaxy Fine Chemicals Ltd., India.

2.2. HIXM preparation

2.2.1. Preparation of HIXM based on PVA and PVC binder

First both the CXR and AXR were kept in oven at 60 °C for 24 hours to remove any moisture from resin, followed by grinding in a ball-mill and sieving to the desired mesh size. The average particle size and particle size distribution of the resultant CXR and AXR powders were studied with the help of particle size analyzer (Mastersizer 2000 Malvern, UK) employing water as a dispersing agent. For membranes preparation, finely powdered CXR and AXR of desired particle size were dispersed separately in the PVA solution (PVA: water is 1:10 w/v) in different weight ratios (30-70%), wherein PVA solution contained a cross-linker maleic acid (MA) (30-60 wt.% with respect to PVA). Membranes were prepared in the form of flat sheet by solution casting technique followed by drying at room temperature (35 °C) for about 24 h and crosslinking. Crosslink time and temperature was varied from 15-90 minutes and 90-140 °C respectively. Optimized HCXM and HAXM containing 30% MA were cross-linked at 140 °C for 30 and 60 minutes respectively [18]. Similar methodology was also followed for the preparation of HIXMs based on PVC binder, where finely powdered CXR and AXR of desired particle size were separately dispersed in the varying ratios in the PVC solution (PVC:THF is 1:10 w/v). HIXMs were made using a spray/dip coating technique followed by drying at 35 °C for 30 minutes; and resulting heterogeneous cation and anion-exchange membranes (HCXM and HAXM) were equilibrated in 1N NaOH and 1N HCl solution respectively. Finally, both types of membranes were conditioned and equilibrated in NaCl solution.

2.2.2. Preparation of composite HCXM and HAXM

Polyamide cloth of different thickness, % open area, thread diameter, mesh count have been selected initially for the preparation of the reinforced HIXMs. By evaluating the capacity and resistance of the membranes the final selection of cloth has been made. A laboratory scale casting machine (Figure 1) was used for fabricating reinforced HIXMs. Both PVC and PVA based reinforced membranes having 60:40 resin: binder ratio (of resins particle size of –300+400 mesh) have been prepared by dip coating technique. PVC based membranes were dried at about 35 °C for 24 h and then equilibrated in NaCl solution. PVA based membranes were cross-linked at specific temperature and time, and then equilibrated in NaCl solution.

2.3. Membrane characterization

Swelling study was performed to find the dimensional stability and also to optimize the crosslink conditions of membranes. Membrane samples of 2.5×2.5 cm² (average thickness ≈150-200 μm) were dipped in de-ionized water for 7 days. The % swelling (by area) was determined as previously described in [18]. While the water content was determined by determining moist and dry weight of resin/HIEM according to (eq. 1). Ion-exchange capacity of ion-exchange resins (IXR) and membranes were evaluated after the activation of ion-exchange site of resin/membrane by alternatively equilibrating in 1N HCl and 1N NaOH solution respectively to convert CXR/HCXM from Na^+ to H^+ and AXR/HAXM from Cl^- to OH^- form. This cycle is repeated at least three times. Finally, washed CXR/HCXM and AXR/HAXM in the form of H^+ and Cl^- respectively transferred to NaCl and NaOH solution, and kept for 24 hr. The H^+ and Cl^- liberated is estimated by titration with standard solution of NaOH and $AgNO_3$ and IEC is determined according to eq. (2).

For measurement of surface electrical resistance of the membranes, a Perspex cell consisted of two half cells separated by a circular membrane sample (K^+ or Cl^- form) (active area=1.228 cm²) assembled in series for

solution flow (0.1 N KCl) were used with a resistance bridge to quantify the surface electrical resistance of HIXMs in K^+ or Cl^- form. Measurement of cell resistance was conducted with and without membrane. The difference of the surface electrical resistance provided the membranes resistance, which was multiplied by the active area of membrane to get surface electrical resistance (ohm.cm^2) according to eq. (3)

Heterogeneous cation or anion membranes in K^+ or Cl^- form respectively was clamped between two Perspex half-cells fitted with saturated calomel electrodes (Ag/AgCl) and stirring arrangements. The two halves of the cell were separated by membrane (active area 5.3 cm^2) and filled with 0.2 N and 0.1 N KCl solutions respectively at both side of membrane. The potential of the cell generated due to difference in chemical potential was determined with microvolt meter (Advanced Engineers, India). The transport number was evaluated from the practically measured potential and the theoretical chemical potential according to eq. (4). Experimental detail of water content, IEC, surface electrical resistance and transport number evaluation of the membranes followed in this study is described in [8,9,19].

$$Water\ content\ (M,\ \%) = \frac{W_R}{W} \times 100 \qquad (1)$$

$$IEC\ (meq/g) = \frac{V_t N V_e}{W_{rd}(100-M)} \times 100 \qquad (2)$$

$$Surface\ electrical\ resistance\ (ohm\ cm^2) = \frac{V}{I} \times A \qquad (3)$$

$$Membrane\ potential\ (E_m) = (2t_m-1)\frac{RT}{F}\ln\frac{a_2}{a_1} \qquad (4)$$

where W_R and W is weight of resin/membrane after air and heat drying respectively. V_t and V_e is the titrate volume required (burette reading) and volume of aliquot taken for equilibrium of resin/membrane. N is the normality of NaOH or AgNO$_3$ solution. While E_m is the membrane potential (volt), t_m is the transport number of membrane, a_1 and a_2 are the electrolytes activity, F is the Faraday constant (96,500 coulombs/mole), and R and T are the universal gas constant (8.31 Jules/mole/Kevin) and temperature (in kelvin) respectively; and V, I and A are the voltage applied (volt), observed current (A) and active area of membrane (cm^2) respectively.

Thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) (Mettler Toledo instrument, with star^e software) were respectively used to find thermal behavior and transition temperature i.e. T_g of HIXMs under N$_2$ environment at heating rate of 10 °C/min. For morphological evaluation, HIXM samples were sputter coated using gold and scanning electron microscope (SEM, Leo Microscope) images were recorded at 11-20 kV accelerating voltage.

2.5. Membrane desalination performance evaluation

Electrodialysis stack containing 5 cell pairs of membranes was constructed using HCXM and HAXM membranes each having an active area of 80 cm^2. Desalination of brackish (total dissolved solid 500-7500 ppm) water was carried out in single pass mode with a series-cum-parallel flow pattern. Electrical potential of 1-2 volt/cell pair was applied between the anode and cathode electrodes connected to AC-DC rectifier. Flow rates of the treated solution maintained at 0.5-5 l/h. The ratio of concentrate to dilute flow rate in the ED stack was kept at 1:3. A solution of sodium sulphate (0.1M) was continuously fed in the anode and cathode chambers to retain the overall stack conductivity. Current and voltage were recorded during desalination. Samples of the dilute and concentrate streams were collected at different time intervals to measure the conductivity (using the conductivity meters) and concentration of chloride ions (by titration). The HCl/NaCl liberated was determined by titration using standard aqueous solution of NaOH/AgNO$_3$ employing phenolphthalein/potassium chromate indicator respectively.

3. Result and discussion

Grinding and sieving of ion-exchange resins to desire particle size is required for the optimization of electrochemical and mechanical properties of HIXMs. From the previous study, it has been established that resins with particle size of –300+400 BSS mesh (39 µm) give flexible homogeneous membranes and resins particle size greater than –300+400 BSS mesh produce brittle membranes with lesser ion-exchange capacity [9]. Particle size distribution of IXR obtained in the present study (mesh size of –300+400 BSS) by grinding and sieving is shown in supporting information (Figure S1). Estimated average particles size of 90% CXR and AXR were 17 µm and 39 µm respectively.
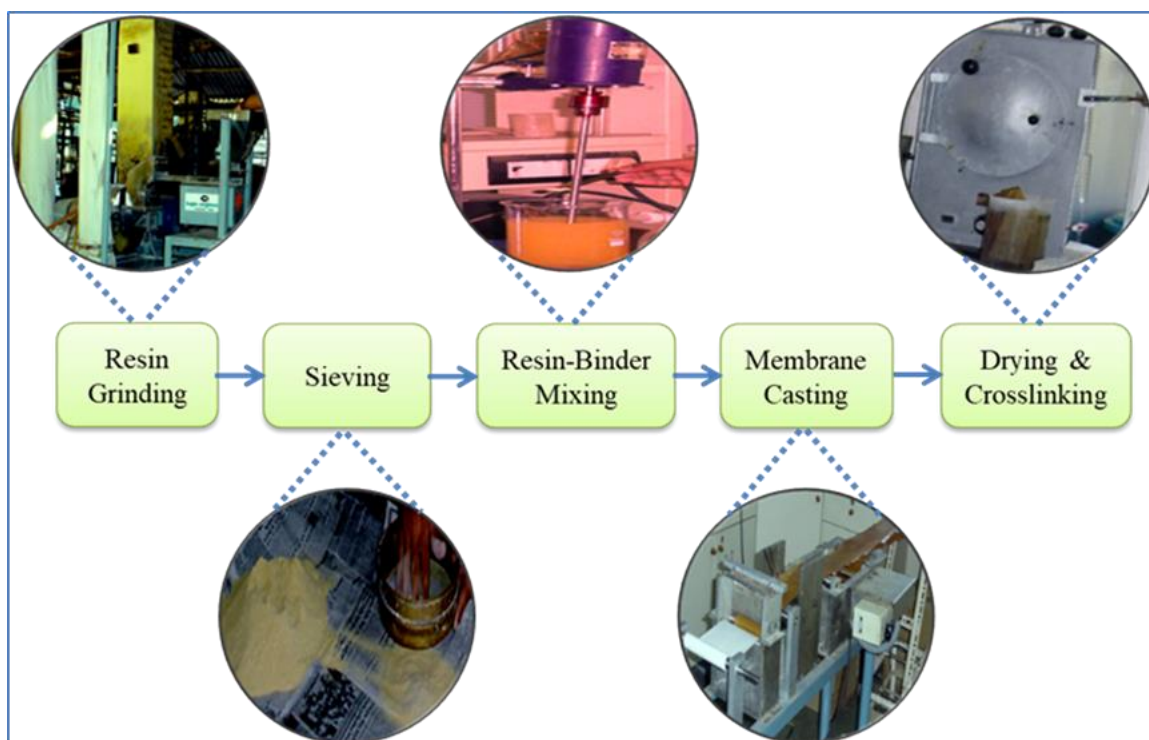

Fig. 1. Schematic of reinforced composite HIXMs preparation.

Heterogeneous ion-exchange membranes produced using PVC as a binder do not require crosslinking as PVC is not soluble in the aqueous medium. In the case of HIXM prepared using PVA binder it is inevitable to crosslink PVA matrix further to prevent excessive swelling of membranes during desalination application by ED process. Membrane swelling has no direct relation with the desalination performance of the membranes. It is necessary to take care of the swelling properties of the membranes from viewpoint of dimensional stability of the membrane. Each ED stack has a definite length and width and membrane dimension should match with the ED stack design. If the membranes mounted in the ED stack swell excessively during its performance, the membranes will be deformed, there will be formation of wrinkles in the membrane surface and two consecutive membranes may collide with each other resulting a restriction of fluid flow in the feed or permeate channel. As a result, cell resistance will increase and desalting performance of the ED stack will be inferior. Hence, it is necessary to optimize the membrane swelling within a restricted limit by controlling the crosslink density of the binder network (in case it has water affinity like PVA).

Figure 2 shows the % area swelling (in water) of cross-linked HCXMs and HAXMs. A longer crosslink time and a higher temperature favored reduction in % swelling. Both the HCXMs and HAXMs exhibited a minimum swelling of 15% (100% gel) at curative dose of 60% and cure time 30 minutes at 140 ℃. No further decrease in swelling is observed for heating HIXM beyond 30 minutes. However, 30% MA dose resulted in some flexible membranes with about 10% higher swelling. This is due to low crosslink density of PVA matrix. Further from the previous study on the crosslinking of PVA with MA showed that MA dose greater than 30% induces brittleness in

PVA matrix without much beneficial effect of thermal and swelling properties. The effect of crosslink time on the IEC of both HCXMs and HAXMs prepared using a PVA binder (at 30% MA and crosslinking temperature of 140 ℃) is shown in the Figure S2 (Supporting information). Diminishing effect in ion-exchange capacity was observed for a longer crosslink time. For every 30 ℃ rise in temperature, 15% reduction in IEC observed. This is attributed due to loss of labile ionic charges of IXR for longer duration heat treatment. Heating of HCXM and HAXM beyond 30 and 60 minutes respectively at 140 ℃, resulted in brittle membranes. Therefore, 30% MA as crosslinker dose, curing temperature of 140 ℃ and cure time of 30 and 60 minutes were optimized for HCXM and HAXM respectively.

Figure 3 shows cation- and anion-exchange capacities of HIXMs at varying resin: binder ratios. IEC of the membranes enhanced linearly as the proportion of IXR increased. This is due to the rise in charged groups (-SO_3H for HCXM and -NR_4Cl for HAXM) per unit weight of membranes with increasing resin loading. Interestingly, PVA based HCXMs showed higher IEC compared to PVC based HCXM for corresponding all the resin content studied here. Higher IEC of HCXM based on PVA is attributed to contribution of additional –OH and –COOH charged groups from PVA and MA respectively. However, PVA based HAXMs possessed slightly lesser IEC value than PVC based HAXM at the same resin loading. The diminishing effect could be due to the reduction of effective anionic charged groups in the membranes because of the interactions among quaternary ammonium chloride groups (-NH_4Cl) of the AXR and residual carboxylic acid groups (-COOH) of MA (i.e. acid-base type interactions). However, values of IEC for the both type of HAXM based on PVA and PVC are quiet comparable and suitable for practical application.
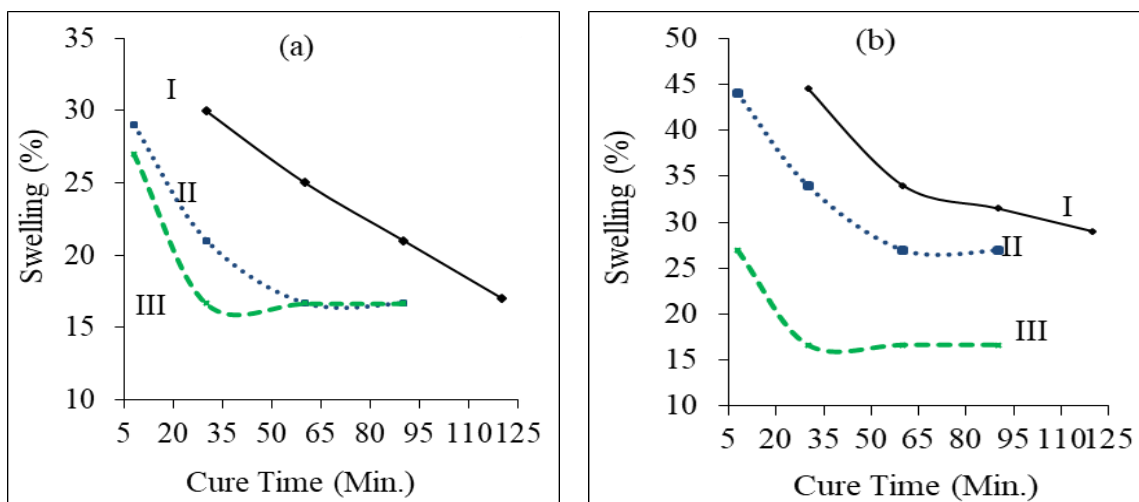

Fig. 2. Cure time versus % swelling (by area) for (a) HCXM, and (b) HAXM. (Resin: Binder (PVA) ratio: 60:40; Curing conditions: I: 90 ℃, 30% MA; II: 140 ℃, 30% MA; III: 140 ℃, 60% MA).
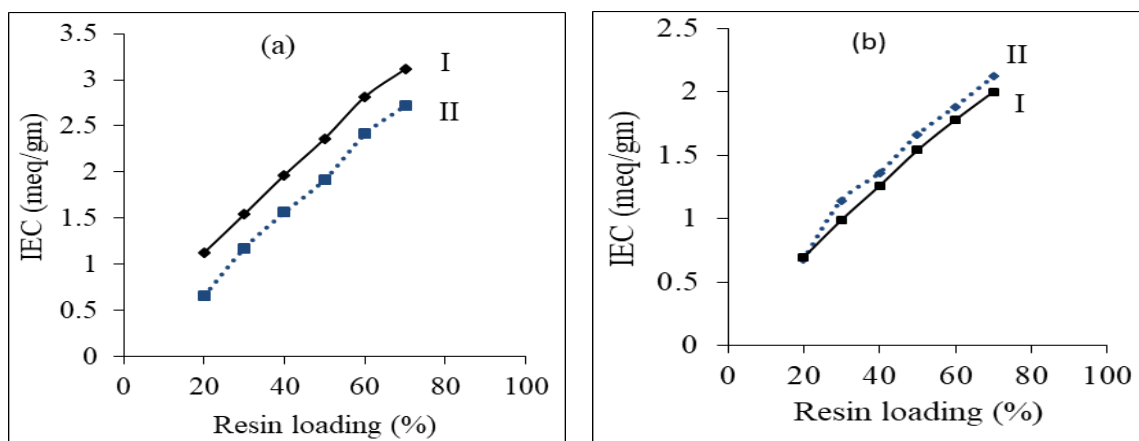

Fig. 3. Resin loading (%) versus IEC for (a) HCXMs, and (b) HAXM based on I: PVA and II: PVC binder.

Apart from swelling properties, surface electrical resistance and transport number of the membranes depended upon water content and IEC. The % water content of HIXM (based on different binders PVA and PVC) is plotted as function of % resin loading is presented in Figure 4. Increment in % resin content in PVA and PVC matrix was expected to enhance the water content because of strong solvation property of the $-SO_3H$ and $-NR_4Cl$ groups. The behavior of PVC based cation- and anion-exchange membranes followed the expected trend. PVC is absolutely hydrophobic; hence replacement of PVC by relatively more hydrophilic IXR enhanced water content of the membranes. However, a reverse trend was observed for PVA based HIXMs. For such membranes, water content lessened with resin loading. PVA absorbs more water due to presence of enormous number of hydroxyl group compare to cross-linked sulfonated/aminated PS resin. Hence, in the blend (membrane), replacement of PVA by ion-exchange resins results in diminution in water content. Apart from crosslinking of PVA, drop in water content is also as a result of physicochemical interaction among -OH and, -COOH groups of PVA and MA respectively, and $^{-}SO_3^{-}H^{+}$ or $^{-}NH_4^{+}Cl^{-}$ charged groups of IXR, which led to the lowering of hydrogen bonding sites for water molecules. Higher water content of PVA based HIXM further displayed lower surface electrical resistance.

Apart from the swelling (dimensional stability), IEC and % water content, the surface electrical resistance (R_m) of HIXM play a key function in the desalination performance of the membranes in ED operation. HIXMs should possess optimum IEC and a very low R_m. As anticipated, for PVC based HIXMs of comparable thickness (about 200 μm) the value of R_m dropped with increase in % resin loading (Figure 5). Initially, there was a sharp fall in resistance up to 40% resin loading, beyond which the fall becomes marginal. Hence, 40% resin loading is a threshold value, where the non-conducting membrane converts to electrically conducting medium. However, PVA membranes behave in different way. The resistance values showed that even with very low resin content (~20%) the membranes became electrically conducting. This is true for both HCXM and HAXM. HCXM and HAXM based on PVA showed surface electrical resistance of 4 Ω cm² and 6.1Ω cm² respectively which was even lower than of HCXM prepared using carbon nanotube and silver nanoparticles reported in [13,14], and some commercial heterogeneous ion-exchange membranes shown in Table 1. Water affinity of PVA resulted in the penetration of electrolyte solution through the interstices of the membrane and made it electrically conducting. In general, because of inherent nature of PVA, membranes exhibited much lesser resistance than the PVC based membranes at all the resin loadings.

Transport numbers of HIXMs based on two different binders is displayed in Figure 6. Transport number is the fraction of the total current carried by a given ionic group (i.e. cation or anion) in an ion-exchange membrane. Hence, increase in % resin content results in improvement in the transport number because of the enhancement of the selective sites. In spite of higher water content of PVA based HCXMs the transport number is comparable to that of PVC based HCXM. Meanwhile the HAXM based on PVA showed lower transport number than PVC based HAXM, this is further due to their lower IEC of PVA based HAXM.

Thermal stability of heterogeneous membranes depended upon the type of binder, and relative proportion of binder and resin. The TGA/DSC curves for IXR and binders are shown in supporting information Figure S3. Overall

thermal stability order in the temperature range of 300-600 °C for the binders and resins obtained from the TGA was CXR > AXR≈PVC >PVA. Ion-exchange resins (IXR) are made up of cross-linked PS (cross-linked by 8% divinyl benzene) hence showed higher thermal stability than those of PVC and PVA. In addition $^{-}NH_4^{+}Cl^{-}$ is thermally more labile than $^{-}SO_3^{-}H^{+}$ hence heat stability of CXR > AXR. TGA curves for HIXMs having PVA and PVC as binders are shown in the Figure 7. TGA curves revealed three degradation steps in HIXMs, which are related to moisture removal, desulfonation, and thermo-oxidation of the IXR/polymer binder [22,23]. In the first stage, temperature up to 150 °C the observed change in weight (up to 10-15%) is due to desolvation of absorbed water molecules, which exists in a bound sate via intramolecular hydrogen bonds formation with the polymer binders and/or the $-SO_3H$, groups. The second weight loss (between 150 and 300 °C) relates to the removal of labile charged groups. In the third stage of degradation (at temperatures >300-400 °C), the membranes were further degraded, which is due to the breakdown of the backbone of polymer chain. Thermal stability and residual weight of membranes increased with increase in resin loading. In case of PVA based HCXM, TGA showed only similar weight loss pattern irrespective of resin content, this indicates the presence of intermolecular attraction forces between PVA and CXR particles. However, degradation pattern of PVA and PVC based HAXMs is found to be anomalous, this may be due to inherent nature of AXR that show almost comparable degradation pattern to that of PVC and PVA binders (Supporting information Figure S3). Further, PVA based HIXMs displayed more weight loss in temperature range of 25-150 °C compare to PVC based HIXMs. This clearly indicates the higher capacity of PVA based HIXM of holding bound water that has subsequently reflected in higher water content and lower surface electrical resistance of membranes.

Table 1
Surface electrical resistance of some commercial heterogeneous cation- and anion-exchange membranes [20,21].

| HCXM/ Company	SER (Ω cm²)	HAXM/ Company	SER (Ω cm²)
CR67-HME /Ionics Inc., USA	9	MK-40 /JSC Shchekinoazot, Russia	9-11
MC-3470 Ionac / Sybron Chemicals, USA)	25	MC-7500 Ionac /Sybron Chemicals, USA	30
MC IONSEP /Hangzhou Iontech Environmental Technology, China	6-10	MC IONSEP /Hangzhou Iontech Environmental Technology, China	8-10
Composite HCXM (PVA Based) (PVA:Resin /40:60)	5-6 (This work)	Composite HAXM (PVA: Resin/40:60)	5-6 (This work)
HCAM (PVA:Resin /40:60)	4 (This work)	HAXM (PVA:Resin /40:60)	6 (This work)

SER: Surface electrical resistance
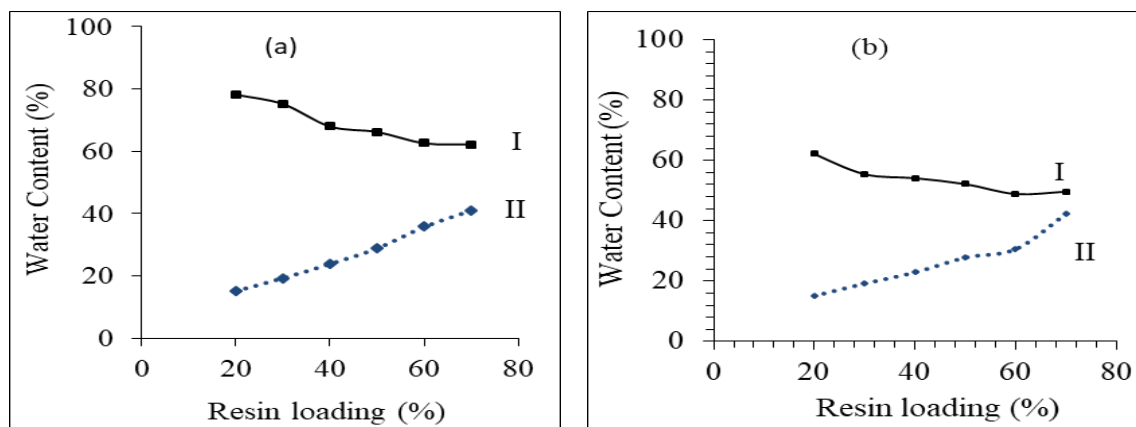
Fig. 4. Resin loading (%) versus % water content for (a) HCXM, and (b) HAXM, based on I: PVA, and II: PVC binder.
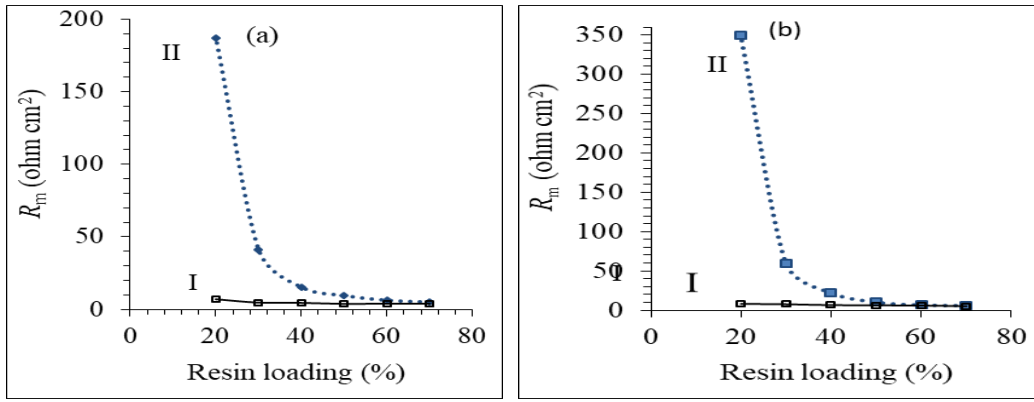
Fig. 5. Resin loading versus R_m for (a) HCXM, and (b) HAXM, based on I: PVA and II: PVC binder.
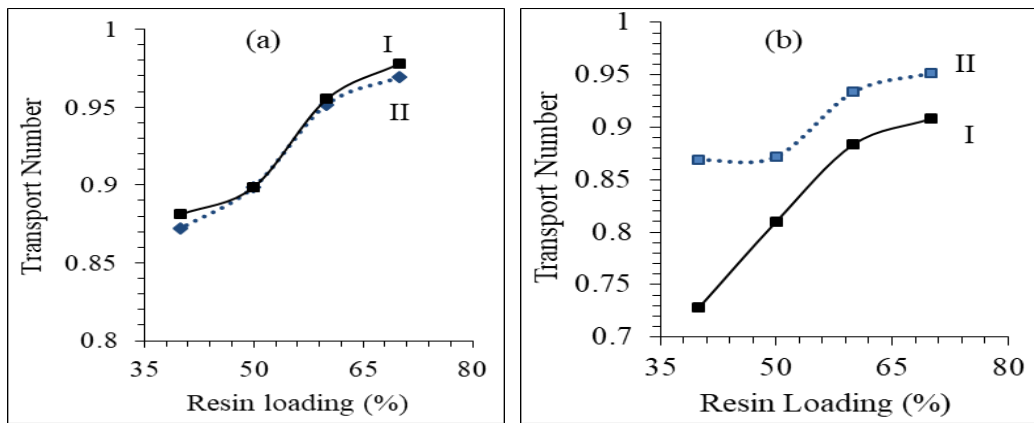

Fig. 6. Variation of transport of number with resin loading for (a) HCXM, and (b) HAXM, based on I: PVA, and II: PVC binder.
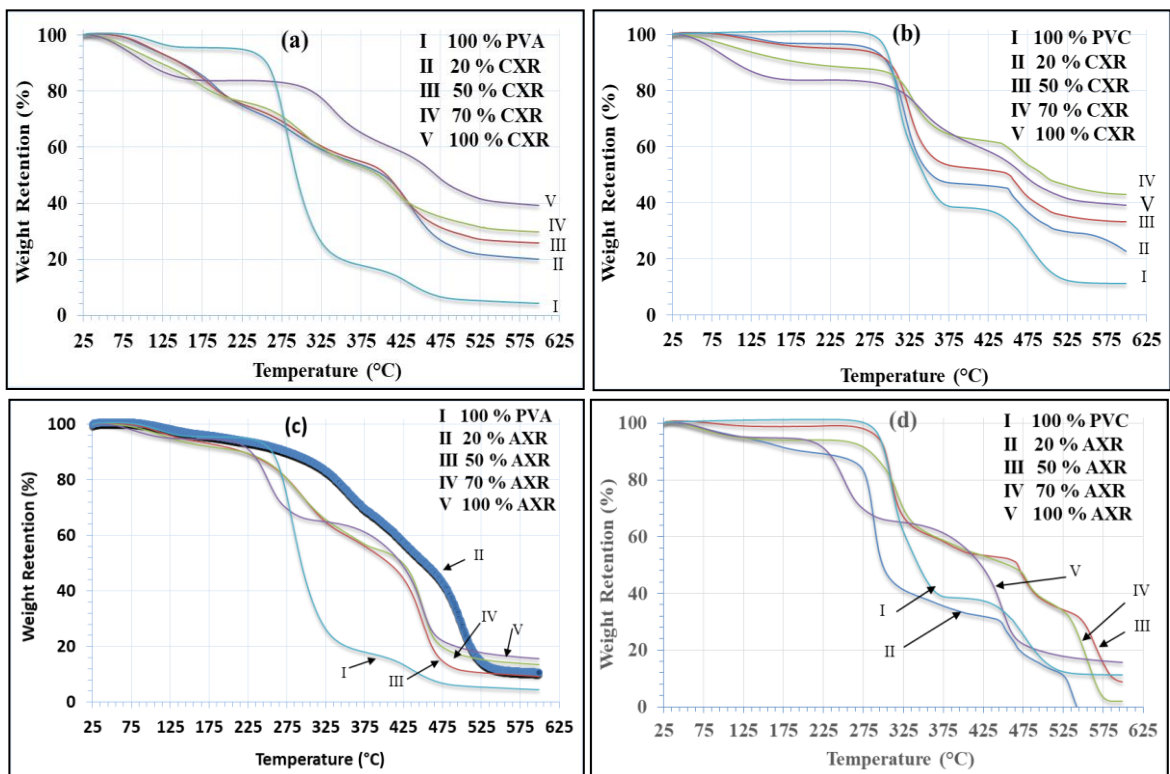

Fig. 7. TGA curve for HCXMs based on (a) PVA, and (b) PVC binder and for HAXM based on (c) PVA and (d) PVC binder.
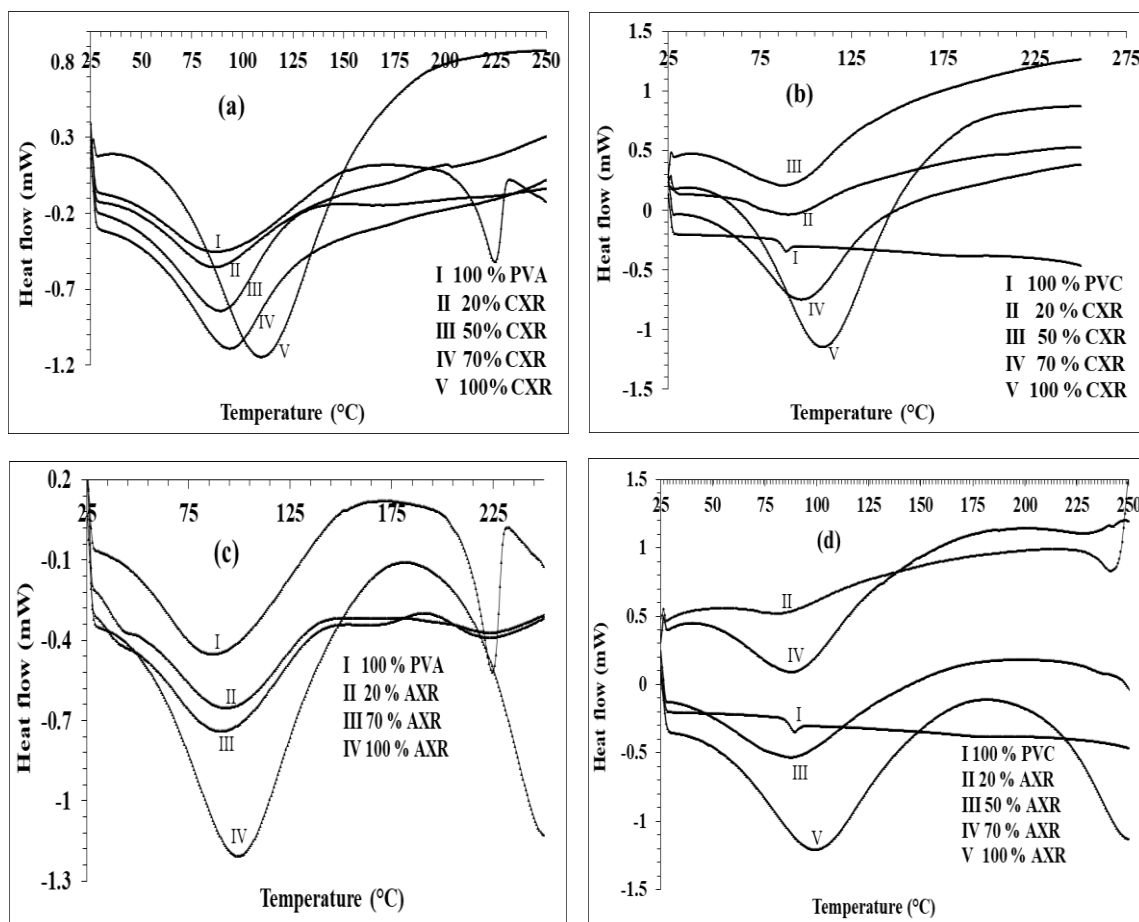
Fig. 8. DSC curves for HCXMs based on (a) PVA, and (b) PVC binder, and for HAXM based on (c) PVA, and (d) PVC binder.

The glass transition temperatures (T_g) of the HIXMs of different composition have been studied by DSC analysis. Measurement of T_g is common method to determine the relative miscibility of the blend [24]. Here, in this study the measured T_g of CXR, AXR, PVC, and PVA was in the order of 109.8 > 98.9 > 86 > 80.4 respectively. The DSC curves for the HIXMs based on PVA and PVC binders at varying resin content are shown in Figure 8. It is seen from figures that heterogeneous blend membranes exhibited higher T_g as compared to that of pure PVA or PVC binder. All the membranes showed single T_g peak irrespective of resin to binder content in the blend, indicating their compatibility. As the resin content in the membranes increased the glass transition temperature peak shifts towards the higher temperature. HIXMs based on PVA binder showed positive deviance in T_g from linear additivity according to Fox eq. (5) [24], which often interpreted as a presence of strong interpolymer interactions in heterogeneous membranes. However, HIXM based on PVC binder showed negative deviation in T_g from linear mixing that shows relatively weak specific interaction between IXR and PVC.

$$1/T_{gHIXM} = w_{IER}/T_{gIER} + w_{binder}/T_{gBINDER} \qquad (5)$$

Figure 9 shows comparative cross-sectional phase morphology of HIXM prepared using resin: binder ratio of 60:40. Evidently, PVA based membranes displayed more homogeneous structure compared to PVC based membranes. In PVC based HIXM phase distribution of resin particles and binder are clearly visible. Again, as confirmed by DSC analysis, PVA and the ion-exchange resins (either cationic or anionic) forms miscible blend because of their affinity for polar solvent like water as well as presence of strong hydrogen type bonding. In the blend of PVC and IXR, resin and binder only holds together by very weak van der Waals forces and forms distinct phase boundary between continuous and dispersed phase.

It is known to us that ion-exchange membranes have a polymeric matrix to which ionizable groups are covalently bonded. When such membranes are immersed in the water, the ionizable groups dissociate resulting a net charge in the matrix, which is balanced by the charge of the counter-ion released.

These counter-ions are basically responsible for carrying the ion flux through the membranes. Hence, these counter-ions should have a reasonably high mobility within the membrane matrix. This is only possible if the ionizable groups are evenly i.e. homogeneously distributed in the membrane matrix. Morphological (Figure 9) as well as thermal analysis (Figure 8) reveal better homogeneity for the PVA based membranes. Hence, the distribution of ion clusters for such membranes will be more uniform than the membranes with PVC binder. Comparatively better distribution of ion clusters for the PVA based membranes results in facile hopping of the counter-ions through the membrane matrix under application of electric field resulting in better conductivity. Whereas for PVC based membranes the distribution of ion clusters are comparatively more heterogeneous (Figure 9 c and d). As the hopping sites of the counter-ions are randomly distributed for PVC based membranes, hence the counter-ions have to travel a comparatively longer pathway resulting in lesser conductivity for such membranes.

The polyamide cloth selected for the composite HIXM preparation possessed 37 % open area with a mesh opening of 130 micron. The properties of the composite HIXMs based on the different binders are presented in Table 2.

Table 2
Properties of the composite HIXMs.

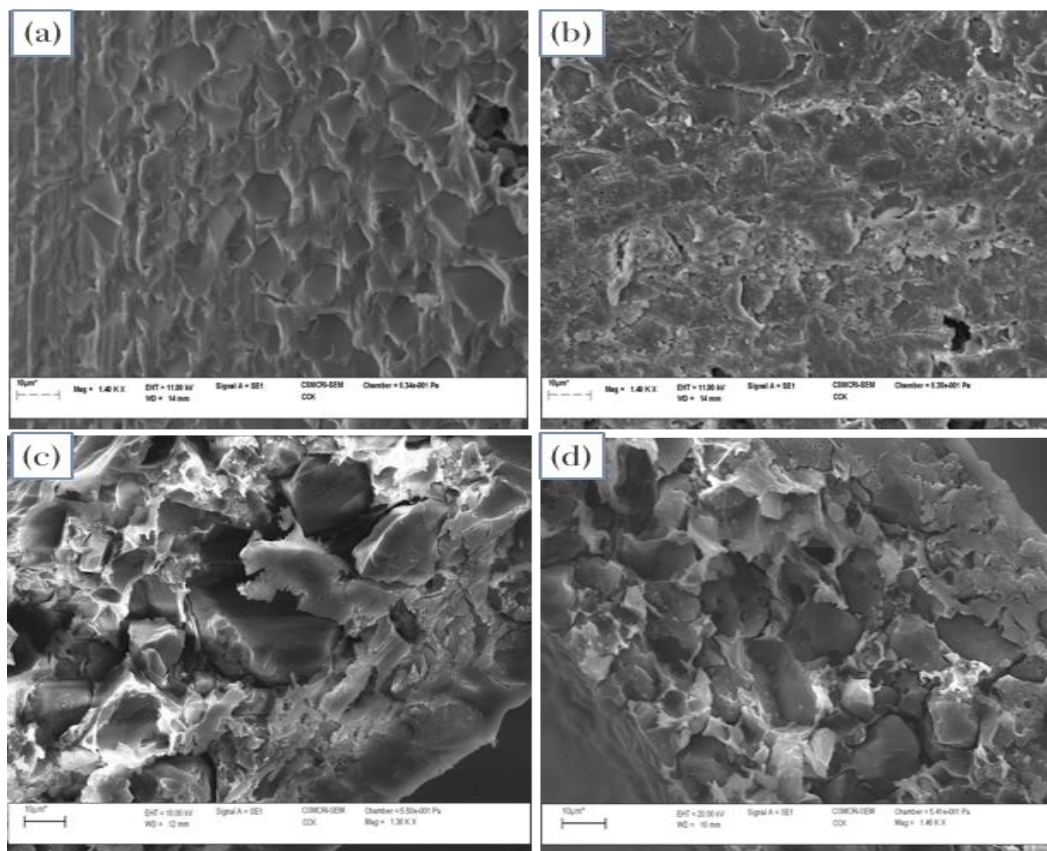| Properties	HCXM		HAXM	
	PVC Based	PVA Based	PVC Based	PVA Based
Water content (%)	22.05	42.38	23.12	38.15
IEC (meq/g)	1.18	1.23	1.13	0.95
R_m (Ohm·cm^2)	10-12	5-6	15-16	5-6

Fig. 9. SEM of PVA based (a) HCXM and (b) HAXM, and PVC based (c) HCXM and (d) HAXM.(Resin: binder is 60:40).

The membranes have also been tested for their acid and alkali resistance. PVC based membranes were resistant to both the acid and alkali, while the PVA based membranes were resistant to 3N acid and 4N alkali solution up to 1 month.

The desalting capacity of both PVC and PVA based membranes have been tested in ED stack by using brackish water (1000 to 5000 ppm NaCl solution) as a feed, and applied potential varied from 1.25 to 2 Volt/cell pair at different flow rates, the selected data are presented in Table 3 for comparative study.

The desalting performance of an electrodialysis stack depends on several factors like feed solution concentration (ion concentration in the feed water), flow rate, current density, geometry of the ED stack and membrane properties. Out of all these factors, membrane properties like transport number and surface electrical resistance are playing pivotal role in stack performance. Counter-ion transport constitutes the major electrical ion movement in an ED process and the fraction of the current carried by the counter-ions in the membrane is the membrane transport no. It is observed from Figure 6(a) that at 60% resin loading both the PVC and PVA based cation-exchange membranes are exhibiting almost equivalent transport no. However, for anion-exchange membranes PVA based membranes are showing slightly lesser transport no. than PVC based membranes (Figure 6(b)). This indicates that in case of PVA based anion-exchange membrane co-ions are also influencing the current transport. This is happening because of the high water affinity of PVA compare to PVC, which results in diffusion of water along with the electrolyte (NaCl) through the membranes. Such water diffusion may also take place in case of PVA based cation-exchange membranes, however it is not predominantly affecting the transport no. because in such membrane the –OH and -COOH groups may also take part in ion transport in addition to $-SO_3H$ group and this joint contribution takes a predominant role in the counter ion transport than the co-ion transport through diffused water. It is observed from Table 2 that both PVA based HCXM and HAEM are having much lower surface electrical resistance than PVC based heterogeneous cation- and anion-exchange membranes. The membrane surface electrical resistance basically depends upon the presence of active functional groups in the membrane, which is basically the ion-exchange capacity of the membranes. It is seen from Table 2 that among the HCXM, the PVA based membranes have higher ion-exchange capacity than the PVC

based membranes at the same resin loading. This may be due to the additional contribution of –OH and –COOH groups of PVA and maleic acid in counter-ion transport. For HAXM, the PVA based membranes have lesser IEC than the PVC based membranes which may be due to the interaction of quaternary ammonium chloride group with the residual –COOH group of maleic acid.

As for both PVC and PVA based membranes the resin loading is same i.e. 60%, hence active functional groups are expected to be equal for both the cases. But because of higher water affinity the interstices in the PVA based membranes are expected to be filled with feed NaCl solution that is contributing in the reduction of membrane resistance. Moreover because of the comparatively more heterogeneous phase morphology of the PVC based membranes (Figure 9), it is also possible that all the functional groups are not equally exposed in ion transport. Because of the overall lower resistance of the ED stack containing the PVA based cation- and anion-exchange membranes, the current and hence the current density in the stack becomes higher than the ED stack comprising PVC based cation- and anion-exchange membranes which is evident from Table 3. Results in Table 3 also reveals that co-ion transport due to slight lower transport no. PVA based anion-exchange membrane has negligible effect on salt reduction. As a result, the % reduction in salt concentration is higher for PVA based HIXM than PVC based HIXM.

At any given value of applied potential, increase in flow rate results in rise of current ($V=IR$). This is owing to the fact that enhancement in flow rate results in increase of linear velocity that lowers overall resistance of stack. Similarly, reduction in salt concentration in the product stream is observed with increase in flow rate at any applied potential. This is attributed to lowering of the residence time of the feed solution in the stack, which led to more concentrated treated stream at a higher flow rate. Further, current efficiency increased with increase in linear velocity of feed solution i.e. flow rate. The current efficiency indicates how effectively ions get transported through ionic membranes at applied current i.e. ratio of the amount of ions removed to the total current supplied to ED stack. The current efficiency is directly proportional to concentration of treated stream and flow rate, and inversely proportional to the stack current. ED stack equipped with PVA based HIXMs exhibited higher current, salt rejection and current efficiency compared to that was observed when ED stack packed using PVC based HIXMs.

4. Conclusions

Heterogeneous membranes were successfully prepared by hand casting and laboratory casting machine using strong cation- and anion-exchange resins powder and PVA binder by eco-friendly method. Physico- and electrochemical characteristics of the ion-exchange membranes depend on the ion-exchange resins loading and types of binder used. HIXM prepared using PVA binder showed very low surface electrical resistance and homogeneous morphology compared to HIXM based on PVC binder. ED stack packed with PVA based HIXMs displayed higher current, salt rejection and current efficiency in brackish water desalination.

Table 3
Desalination performance of HIXM

Membrane type	Flow rate (l/h)	Current (mA)	TDS of water (ppm)	Reduction (%)	CE (%)	Energy (Kwh/Kg)
PVA-HIXM	0.75	364	564	85.5	61.8	1.455
	1.44	465	1375	64.7	70.4	1.279
	2.34	535	1870	52.06	79.9	1.126
PVC-HIXM	0.536	270	736	78.9	49.3	1.825
	1.33	400	1560	55.4	57.9	1.553
	2.01	470	1904	45.5	61.2	1.47

No. of cell pairs: 5; Applied potential 10V; Membrane area 80 cm^2; Initial total dissolved solid (TDS) ≈3796 ppm; Parallel flow arrangement.

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