



# Preparation and characterization of polysulfone and modified poly isobutylene-alt-maleic anhydride blend NF membrane

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## ARTICLE INFO

### Article history:

Received 30 June 2011

Received in revised form 24 September 2011

Accepted 26 September 2011

Available online 1 November 2011

### Keywords:

PIAM

Polysulfone

Water flux

Salt rejection

Nanofiltration

## ABSTRACT

Recently nanofiltration (NF) is gaining more importance for water treatment. It is replacing the conventional method of water treatment due to advantages of NF membranes over RO system. In this work, we are discussing the preparation of NF membrane for desalination of sea water. We herein report the synthesis of polymer, by the reaction of p-amino benzoic acid (PABA) and poly isobutylene-alt-maleic anhydride (PIAM) and its blend membrane preparation with polysulfone (PSf). The new membranes were characterized by SEM images, surface wettability to investigate the hydrophilic nature of the membrane, water swelling, pure water flux, molecular weight cut-off and salt rejection of the membranes. The membranes showed nano size (<50 nm) pores in SEM image, and the contact angle data revealed that membrane surface is moderately hydrophilic. Membrane with 70:30 (PSf:modified PIAM) composition has shown good salt rejection of 96% at 200 kPa for 3500 ppm of NaCl solution with a pure water flux of  $38.36 \text{ Lm}^{-2} \text{ h}^{-1}$ .

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## 1. Introduction

Pure, safe, reliable and sustainable supply of fresh water is integral for existence of human society and vital for agriculture, industry, energy production, and domestic usage. In fourth century BC, people used to obtain fresh water from sea water by the process of evaporation [1]. As the time proceeded, scientific community exploited the potency of cellulose acetate membrane to reject NaCl from aqueous solution [2]. Nowadays researchers are utilizing polysulfone, modified polysulfone, polyethersulfone, aromatic polyamides and their composites with other surface modifiers for the preparation of filtration membranes [3–7].

The major drawback of the membrane industry is biofouling of the membrane. Fouling is the major issue which threatens most of the pressure driven membrane technique. In order to overcome this biofouling problem, one has to use chlorinated feed water. However most of the commercially available membranes are polyamide based membranes. If the feed water is chlorinated, then the chlorine will attack the nitrogen–hydrogen bonds which hold the polyamide polymers tougher. This will damage the membrane by creating holes and eventually the rejection efficiency decreases [1,8].

Because of these hurdles, search for more efficient membrane materials with appreciable salt rejection, better water flux and antifouling property is on the move and the quest for best NF membrane continues. So, polysulfone which doesn't have such nitrogen–hydrogen bonds is

the best choice for the preparation of chlorine resistant membranes. In order to have better flux, membrane should be hydrophilic in nature, so that it can take up water and transport it across the membrane. To increase the hydrophilicity of the membrane, researchers use many modifications such as functionalizing the polymer back bone [5,7,9], using different blend materials such as anhydride containing groups [10].

PIAM (poly isobutylene alt maleic anhydride) was being used as one of the components for the preparation of NF membranes. In our previous work [10], we have presented the utility of hydrolyzed PIAM as blend material for NF membrane preparation. Our present paper describes the usage of modified PIAM as hydrophilic surface modifier with PSf for the preparation of NF membrane. In this work, we have utilized the anhydride back bone of PIAM to construct pendant ion exchange groups by treating it with PABA (p-amino benzoic acid). The insertion of amino group of PABA into the anhydride back bone, allows free carboxylic acid group for the exchange of ions and also it increases the hydrophilicity of the membrane, which is very essential in NF membranes.

## 2. Experimental

### 2.1. Materials and method

Polysulfone (PSf) with  $M_w$  35,000 Da and PIAM with  $M_w$  6000 Da were obtained from Sigma-Aldrich Co, Germany. 1-Methyl-2-pyrrolidone (NMP) and dimethylsulfoxide (DMSO) solvents were procured from Merck India, Ltd. These materials were used without any further purification. PABA was obtained from Spectrochem India and was used after purification by recrystallizing it with water. To prepare

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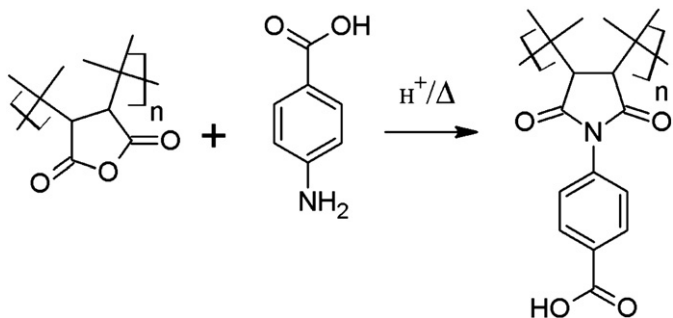


Fig. 1. Synthetic route for mPIAM.

modified PIAM (mPIAM), the ring oxygen of anhydride group was replaced by nitrogen, by treating with amine under acidic condition [11–13] (Fig. 1). 1 g of PIAM was dissolved in 10 mL of DMSO solvent and 1 g of PABA was added to it with catalytic amount of sulfuric acid. Further this mixture was heated at 100 °C for 10 h. Progress of reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, reaction mixture was poured into ice cold water and then the precipitated product was filtered and dried in hot air oven.

## 2.2. Characterization of modified polymer

The modified PIAM (mPIAM) was analyzed by FTIR and gel permeation chromatography (GPC) for the confirmation of modification and to find out the molecular weight of the new polymer. The FTIR was recorded using Thermo NICOLET AVATAR 330 FTIR system. In FTIR as shown in Fig. 2, it bears a broad –OH stretching at 3420 cm<sup>-1</sup> and carboxylic carbonyl stretching at 1709 cm<sup>-1</sup>. In stacked spectra

of PIAM and mPIAM, we can clearly observe that, the intensity of carbonyl peaks in mPIAM less as compared to PIAM. This confirms the insertion reaction for modification of PIAM.

The modified polymer was also tested for molecular weight using GPC. The GPC was recorded using poly styrene as standard and tetrahydrofuran as eluent. The weight average molecular weight  $M_w$  of the polymer was found to be 2200 Da, the number average molecular weight was 950 Da and polydispersity of 2.3 was observed. From these data, it can be concluded that during reaction, polymer chain might have broken and formed smaller molecule than that of the initial polymer.

## 2.3. Preparation of membranes

Using PSf and mPIAM the membranes of different composition (70:30, 80:20, 90:10) were prepared by phase inversion technique [14–17]. The required amount of PSf and mPIAM were dissolved in NMP. The solution was stirred for 24 h, after which the casting solution was casted over the glass plate using glass rod. The glass plate was dipped into a non-solvent (water) bath, and this allowed the membrane to separate from glass plate. Once the membrane was separated, it was washed with distilled water to remove any solvent occluded on the surface of the membrane. The clean membranes were soaked in distilled water for 24 h. The membranes were taken out of the water and dried at room temperature in a dust free area. Further these membranes were taken up for characterization.

## 2.4. Filtration performance

Filtration experiments were performed using dead end filtration cell (Fig. 3). The effective membrane area available for the filtration was 5 cm<sup>2</sup>. All the experiments were carried out at room temperature with constant stirring. Before taking membranes for testing all dry membranes were soaked in distilled water for at least 24 h.

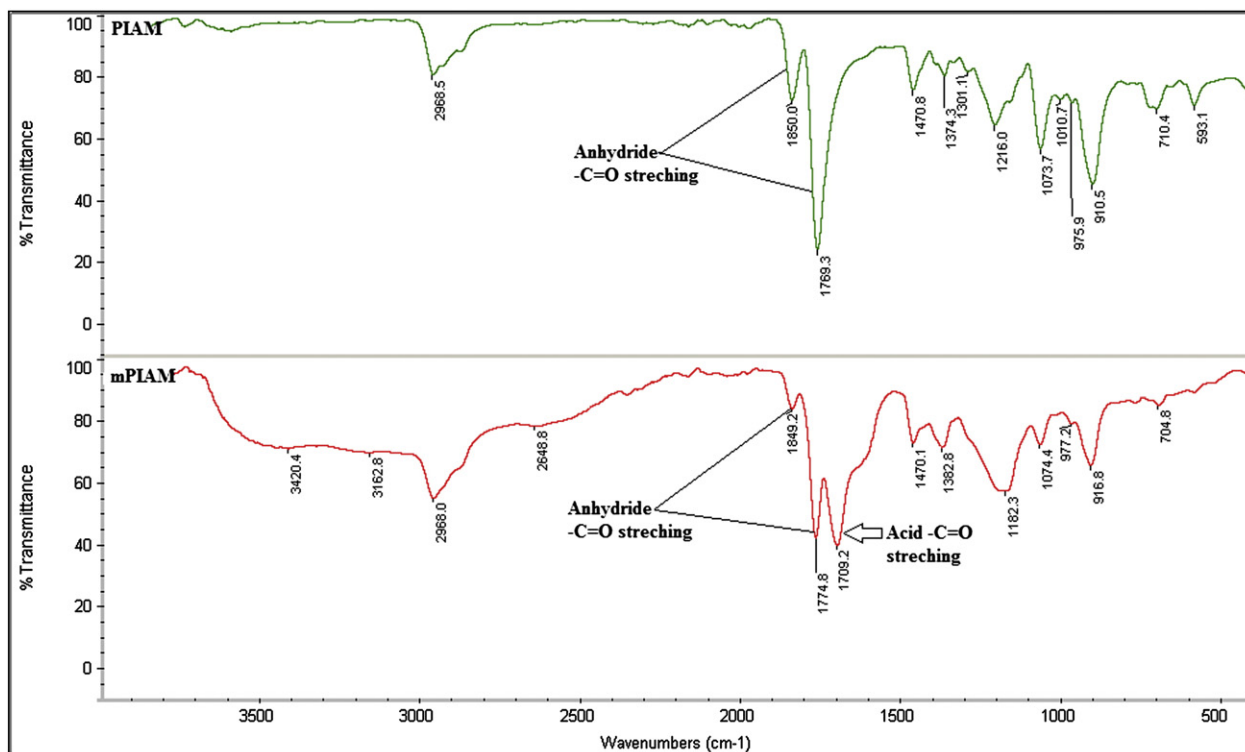


Fig. 2. Stacked FTIR spectrum of PIAM and mPIAM.

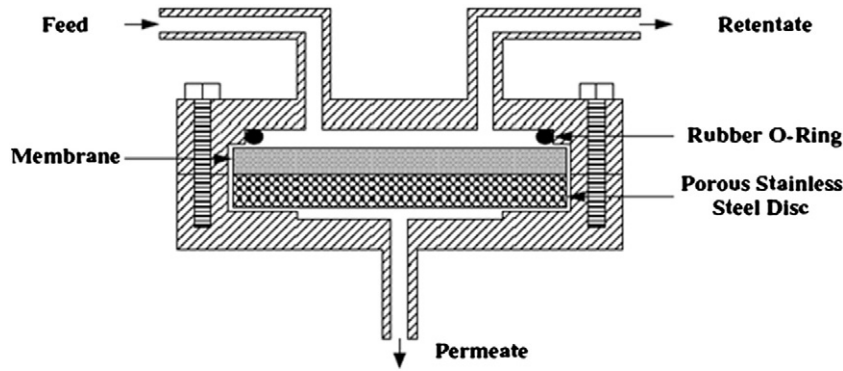


Fig. 3. Schematic diagram of permeation testing cell.

2.5. Membrane characterization

2.5.1. Pure water flux (PWF)

All the membranes were checked for pure water flux at different pressures [18]. Pure water flux was calculated using following formula,

$$J_w = \frac{Q}{\Delta t A}$$

where,  $J_w$  is pure water flux ( $L/m^2 h$ ), and  $Q$  is amount of water collected for  $\Delta t$  (h) time duration using a membrane of area  $A$  ( $m^2$ ).

2.5.2. Morphology of the membrane

The membranes were cut into small pieces and mounted onto a sample holder. Then the membrane surface was sputtered with thin film of gold using JEOL-1600 AUTO FINE COATER in order to give the electric conductivity to the membrane surface. The surface and cross sectional SEM images were taken using JEOL-6380LA Analytical SEM instrument. Scanning was performed with the potential of 20 kV in order to get the magnification of 50,000 $\times$ .

2.5.3. Wettability of the membrane

The wettability of the membrane was studied by measuring the contact angle of the membrane with water using FT-200 Dynamic contact angle analyzer [19,20]. The clean and flat membrane samples were placed on the sample bench and a drop of water was carefully deposited on to the membrane surface and left for 25 s to achieve equilibrium spread of the drop. Then the contact angle was measured.

The same procedure was repeated for 4 times for each sample and the average value was reported.

2.5.4. Water uptake of the membrane

The water uptake of the membrane is direct indicative of hydrophilicity of the membrane. In order to understand the water uptake property of the membrane, the dry membranes were cut into small pieces of about 1  $cm^2$  sizes and weight was noted. Then these pieces were immersed in water for 24 h. After 24 h membranes were taken out of the water, and the surface water was removed using blotting paper. Then the wet weight was noted. The percent water uptake was calculated using the formula,

$$\% \text{ water uptake} = \frac{W_w - W_d}{W_d} \times 100$$

where,  $W_w$  and  $W_d$  are the weight (g) of dry and wet membranes respectively. For each membrane five samples were tested and the average result was reported.

2.5.5. Molecular weight cut-off

The molecular weight cut-off of the membranes was found using polyethylene glycol (PEG) of different molecular weights. PEG with molecular weight 900 Da, 1000 Da, and 2000 Da were used for the study. The rejection experiment was carried out similar to that of water flux study. PEG of several molecular weights (900–2000 Da) at 50 ppm was filtered in a dead end cell and permeate concentration was estimated using spectrophotometer [21]. Throughout the experiment a constant pressure of 200 kPa was maintained. In brief, 4 mL of permeate sample solution was added to 1 mL of reagent A (5 % (w/v)  $BaCl_2$  in 1N HCl) and reagent B (1.27g  $I_2$  in 100 mL 2% KI (w/v) solution). This mixture was allowed to develop the color (light blue color) for 15 min at room temperature and absorption was measured using a spectrophotometer (Equip-Tronics Digital spectrophotometer Model No-EQ-820) at 535 nm against a blank reagent.

2.6. Salt rejection

The salt rejection performances of all membranes were checked using dead end flow stirred cell. 3500 ppm NaCl solution was used as the feed. All the membranes were checked against above said feed solution at different pressures (200 kPa, 400 kPa, 600 kPa and 800 kPa). The feed solution was filled into a dead end flow cell and pressurized as required using a nitrogen cylinder. Then permeate was collected for a known interval of time and the concentration of the solution was found out by conductivity measurement. Then the salt rejection was calculated using the formula,

$$\% \text{ salt rejection} = \left( 1 - \frac{C_p}{C_f} \right) \times 100$$

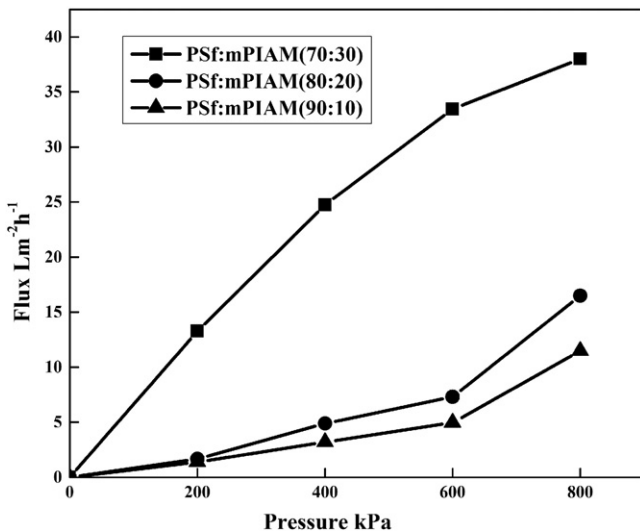


Fig. 4. Variation of PWF with pressure.

where,  $C_p$  and  $C_f$  are the concentrations (mM) of permeate and feed solutions, respectively.

The salt rejection study was conducted in triplicates for each membrane and the mean deviation of the result was taken, the variations between three results were negligible so the average result was reported.

### 2.7. Flux reduction

All pressure driven membrane process are bound to problem of flux reduction with time. In order to check the performance of prepared membranes, all the membranes were checked for flux reduction with time. After measuring the pure water flux, flux for 3500 ppm NaCl solution was measured ( $J_o$ ), then NaCl flux at different time intervals ( $J_t$ ) was measured. Further flux reduction was calculated using following formula [22].

$$FR(\%) = \frac{J_o \times J_t}{J_o} \times 100$$

## 3. Result and discussion

### 3.1. Pure water flux (PWF)

The pure water flux is an important characteristic of a nanofiltration membrane. The PWF is shown in Fig. 4. In this result it is clear that the membrane with 30% of mPIAM is having more PWF value than others. It is attributed to the fact that as the percentage of mPIAM increases, the hydrophilic nature of the membrane also increases due to the presence of more  $-COOH$  groups. This is also in agreement with the contact angle measurement. Hence membrane with 70:30 composition of PSf and mPIAM showing maximum of  $38.36 \text{ Lm}^{-2} \text{ h}^{-1}$  under a transmembrane pressure of 800 kPa, whereas, other two membranes showing  $16.5 \text{ Lm}^{-2} \text{ h}^{-1}$  and  $11.5 \text{ Lm}^{-2} \text{ h}^{-1}$  respectively and also pure water flux increases with increase in applied pressure which can be observed in Fig. 4. Further to investigate the effect of mPIAM concentration on hydrophilicity and water flux, the mPIAM content was increased to 40%. The casting solution became turbid and the same was not homogeneous mixture, due to this reason the prepared membrane will lose the mechanical stability. So we concluded that 30% of mPIAM is the optimum composition.

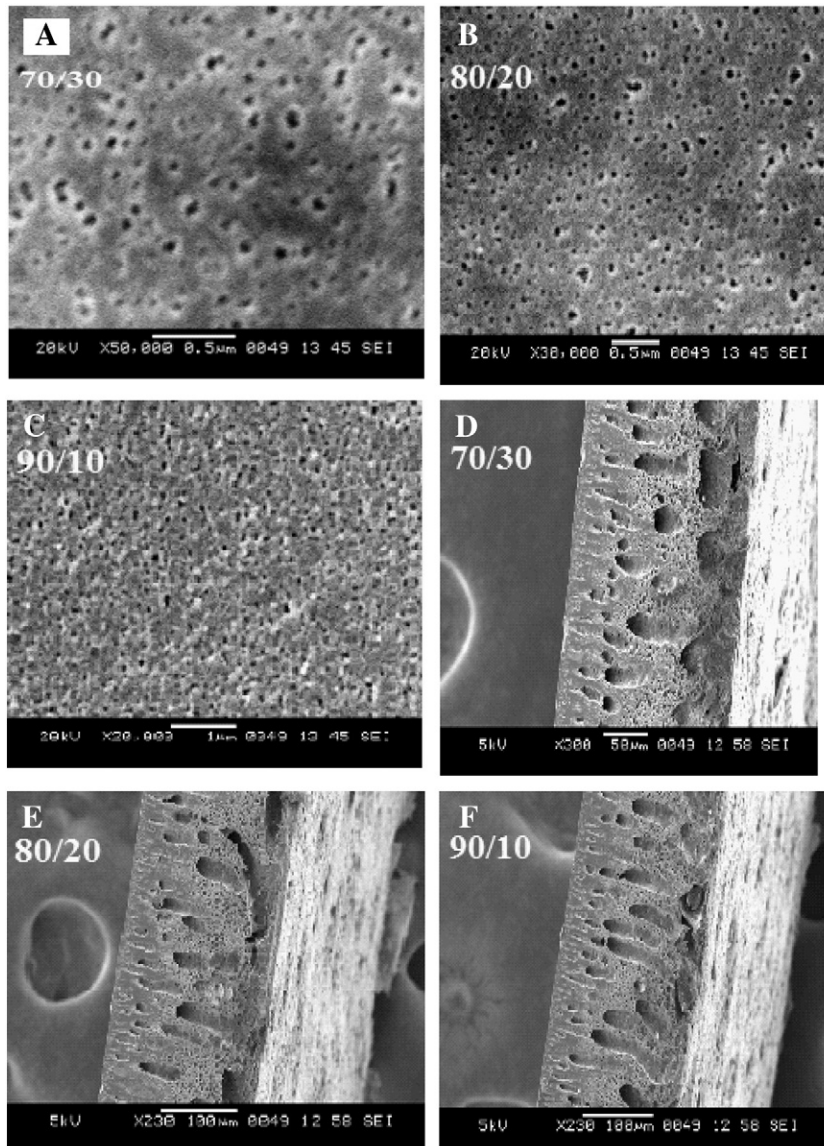


Fig. 5. Surface (A, B and C) and cross section (D, E and F) SEM images of membranes.

### 3.2. Morphology of the membrane

The membrane morphology was studied using SEM images obtained as described in Section 2.5.2. When we look at the surface images, it can be clearly observed that the membrane is having morphology with asymmetric pores and the pores are of nano size and the size is varying from 50 nm and below. The surface image of the membrane in Fig. 5 (A, B and C) shows uniform distribution of nano pores. The cross sectional image shows in Fig. 5 (D, E and F) that the membranes are having finger like projections with micro voids in them which will facilitate the flow of water through the membrane. As all the three membranes showed similar morphology with uniform distribution of the pores, the water permeability and selectivity are very much dependent on the percent composition of the mPIAM rather than on the pore distribution and morphology of the membranes. It has been observed that the water flux and salt rejection for the membrane with 30% mPIAM is comparatively more than that of other two membranes.

### 3.3. Wettability and water uptake of the membrane

In order to understand the surface hydrophilicity of the membranes, contact angle measurement was performed as described in Section 2.5.3. The observed contact angle results are presented in Fig. 6. From the contact angle measurement, it can be concluded that, as the percentage composition of mPIAM increases from 10 to 30, the contact decreases from 89.4 to 60.96 which clearly indicates that, increase in the mPIAM content increases the hydrophilic group in the composition, thereby, increases the surface hydrophilicity. The water uptake behavior of the membranes is presented in Fig. 6. It can be concluded that, highest water uptake observed was 79% and the minimum of 53.7%. Membrane with highest percentage of mPIAM showed maximum water uptake. This provides an evidence for the fact that the increase in carboxylic group in the membrane component increases the hydrophilic nature of the membrane. The obtained results followed same trend as reported by M. Padaki et al. [10] in which, it increased in PIAM concentration, the contact angle decreased and water uptake was increased.

### 3.4. Molecular weight cut-off

Molecular weight cut-off of a membrane gives an idea about the membrane pore size. Fig. 7 demonstrated the MWCO of the membranes wherein it can be observed that, all the membranes showed above 90% rejection to 1000 Da PEG solution and near 100% rejection for 2000 Da PEG solution. It was observed from these results that, all three membranes are showing almost same MWCO. So we can conclude that the membrane pores are of nano size [23]. This is also clear from the SEM images which manifest the presence of pores of less than 50 nm in size. As the pore distribution and MWCO of the membranes are similar so the permeability of the membrane is mainly dependent on the content of mPIAM.

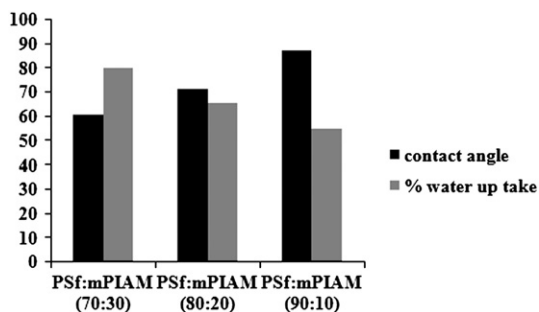


Fig. 6. Variation of contact angle and water uptake of the membranes with mPIAM percentage.

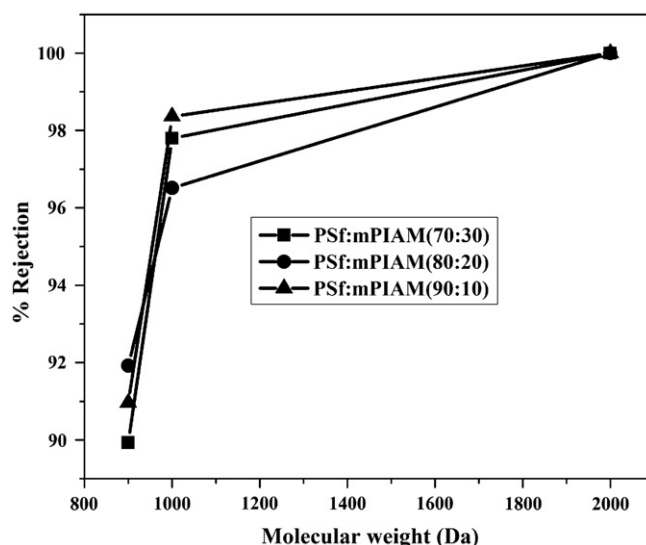


Fig. 7. MWCO of the membranes.

### 3.5. Salt rejection and flux decline study

Salt rejection was calculated as mentioned in Section 2.6. Fig. 8 shows the salt rejection behavior of all membranes. Here it can be observed that, salt rejection increases with mPIAM percentage in the membrane composition. The salt rejection for membrane (70:30-PSf:mPIAM) is 96.6% at a transmembrane pressure of 200 kPa. The rejections for other two membranes are 96.18 and 94.91 respectively. In nanofiltration membrane the rejection is achieved by two means, first by size exclusion and secondly by electrostatic repulsion. The size exclusion factor dominates for the rejection of uncharged solutes whereas the electrostatic repulsion is the deciding factor when it comes to charged solutes. Here for NaCl rejection one has to consider the electrostatic repulsion as major factor. The result shows rejection increases with mPIAM percentage. It directly indicates that, increase of  $-COOH$  group in membrane composition, will make it more and more negatively charged. As a result, the chloride ions will get repelled by the membrane surface. In order to maintain the electrical neutrality sodium ions are also gets rejected [24–26]. Also it has been observed that for (70:30-PSf:mPIAM) membrane the rejection trend almost remains same throughout the pressure gradient. For other two membranes the rejection decreases to 60% at 600 kPa and

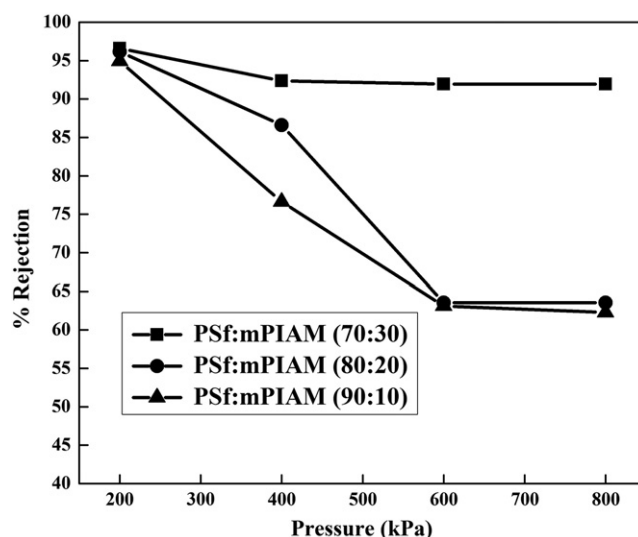


Fig. 8. Salt rejection of the membranes.

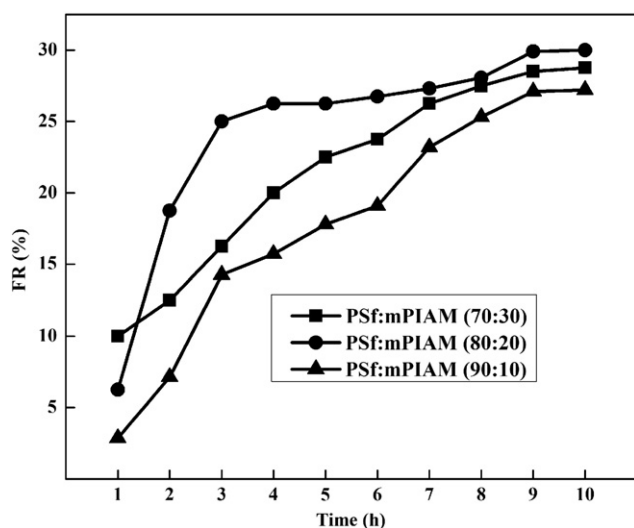


Fig. 9. Flux reduction with time for NaCl solution.

remains same thereafter. The NaCl rejection of these novel membranes was found to be more than or almost equal to that of the commercially available polyamide membranes as investigated by S. Bandini et al. and M. Sua et al. [27,28]. Also membranes were examined for flux decline by measuring the flux at various time intervals using same NaCl solution as described in Section 2.7. It has been observed from Fig. 9 that, the flux was decreased up to 9 h and then remains constant. In 10 h almost 29%, 30% and 27% flux decline was observed for membrane with 70:30, 80:20 and 90:10 (PSf:mPIAM) membranes respectively.

#### 4. Conclusion

New modified poly isobutylene-alt-maleic anhydride was successively synthesized by the reaction between PIAM and PABA. PSf and mPIAM blend membranes were prepared by phase inversion method and studied for their performance for hydrophilicity, water flux and NaCl rejection at various pressures. It was observed that, membrane with highest mPIAM composition had shown maximum hydrophilicity, pure water flux and salt rejection. The maximum salt rejection of 96.6% and water flux of  $38.36 \text{ Lm}^{-2} \text{ h}^{-1}$  were witnessed for (70:30) membrane. These results were explained by the hydrophilic nature of mPIAM and also by the fact that it imparts negative charge to the membrane surface. The NaCl rejection was explained on the basis of charge exclusion.

#### Acknowledgments

AMI thank the Department of Atomic Energy, Board for Research in Nuclear Sciences, Government of India for the “Young Scientist” award and the financial support.

#### References

- [1] R.F. Service, Desalination freshens up, *Science* 313 (2006) 1088–1090.
- [2] C.E. Reid, E.J. Breton, Water and ion flow across cellulosic membranes, *J. Appl. Polym. Sci.* 1 (1959) 133–143.
- [3] H. Wanga, L.L.X. Zhanga, S. Zhanga, Polyamide thin-film composite membranes prepared from a novel triamine 3,5-diamino-N-(4-aminophenyl)-benzamide monomer and m-phenylenediamine, *J. Membr. Sci.* 353 (2010) 78–84.
- [4] K. Bousso, C. Vandecasteele, B.V.D. Bruggen, Study of the characteristics and the performance of self-made nanoporous polyethersulfone membranes, *Polymer* 47 (2006) 3464–3476.
- [5] L. Wu, T. Xu, W. Yang, Fundamental studies of a new series of anion exchange membranes: membranes prepared through chloroacetylation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) followed by quaternary amination, *J. Membr. Sci.* 286 (2006) 185–192.
- [6] J.D.L. Roux, D.R. Paul, J. Kampa, R.J. Lagow, Modification of asymmetric polysulfone membranes by mild surface fluorination. Part I. Transport properties, *J. Membr. Sci.* 94 (1994) 121–141.
- [7] B.V.D. Bruggen, Comparison of redox initiated graft polymerisation and sulfonation for hydrophilisation of polyethersulfone nanofiltration membranes, *Eur. Polym. J.* 45 (2009) 1873–1882.
- [8] P.R. Buch, D.J. Mohan, A.V.R. Reddy, Preparation, characterization and chlorine stability of aromatic-cycloaliphatic polyamide thin film composite membranes, *J. Membr. Sci.* 309 (2008) 36–44.
- [9] W.R. Bowen, T.A. Doneva, H.B. Yin, Polysulfone-sulfonated poly (ether ether) ketone blend membranes: systematic synthesis and characterization, *J. Membr. Sci.* 181 (2001) 253–263.
- [10] M. Padaki, A.M. Isloor, G. Belavadi, K.N. Prabhu, Preparation, characterization and performance study of poly(isobutylene-alt-maleic anhydride) [PIAM] and polysulfone [PSf] composite membranes before and after alkali treatment, *Ind. Eng. Chem. Res.* 50 (2011) 6528–6534.
- [11] C. Ego, D. Marsitzky, S. Becker, J. Zhang, A.C. Grimsdale, K.M. Ilen, J.D. MacKenzie, C. Silva, R.H. Friend, Attaching perylene dyes to polyfluorene: three simple, efficient methods for facile color tuning of light-emitting polymers, *J. Am. Chem. Soc.* 125 (2003) 437–443.
- [12] H.S. Panah, A. Khosravi, K. Gharanjig, M. Khorassani, M.K. Zadeh, F.A. Taromi, Synthesis and characterization of new fluorescent polymerizable dyes based on naphthalimide, *Iran. Polym. J.* 19 (2010) 491–500.
- [13] P.H. Grayshan, A.M. Kadhim, A.T. Peters, Heterocyclic derivatives of naphthalene-1,8-dicarboxylic anhydride. Part III. (I) Benzo [k,l] thioxanthene-3,4-dicarboximides, *J. Heterocycl. Chem.* 11 (1974) 33–38.
- [14] J.F. Blanco, J. Sublet, Q.T. Nguayena, P. Schaezel, Formation and morphology studies of different polysulfones-based membranes made by wet phase inversion process, *J. Membr. Sci.* 283 (2006) 27–37.
- [15] M. Bodzek, J. Bohdziewicz, Porous polycarbonate phase-inversion membranes, *J. Membr. Sci.* 60 (1991) 25–40.
- [16] K.E. Kinzer, D.R. Lloyd, M.S. Gay, J.P. Wightman, B.C. Johnson, J.E. McGrath, Phase inversion sulfonated polysulfone membranes, *J. Membr. Sci.* 22 (1985) 1–29.
- [17] A.J. McHugh, D.C. Miller, The dynamics of diffusion and gel growth during nonsolvent-induced phase inversion of polyethersulfone, *J. Membr. Sci.* 105 (1995) 121–136.
- [18] E. Saljoughi, M. Sadrzadeh, T. Mohammadi, Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membranes, *J. Membr. Sci.* 326 (2009) 627–634.
- [19] E. Jeong, T.S. Bae, S.M. Yun, S.W. Woo, Y.S. Lee, Surface characteristics of low-density polyethylene films modified by oxyfluorination-assisted graft polymerization, *Colloids Surf. A* 373 (2011) 36–41.
- [20] A. Akthakul, R.F. Salinaro, A.M. Mayes, Antifouling polymer membranes with subnanometer size selectivity, *Macromolecules* 37 (2004) 7663–7668.
- [21] A.D. Sabde, M.K. Trivedi, V. Ramachandran, M.S. Hanra, B.M. Misra, Casting and characterization of cellulose acetate butyrate based UF membranes, *Desalination* 114 (1997) 223–232.
- [22] D. Rana, Y. Kim, T. Matsuura, H.A. Arafat, Development of antifouling thin-film-composite membranes for seawater desalination, *J. Membr. Sci.* 367 (2010) 110–118.
- [23] A. Idris, N.M. Zain, M.Y. Noordin, Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives, *Desalination* 207 (2007) 324–339.
- [24] A. Seidel, J.J. Waypa, M. Elimelech, Role of charge (Donnan) exclusion in removal of arsenic from water by a negatively charged porous nanofiltration membrane, *Environ. Eng. Sci.* 18 (2001) 105–113.
- [25] A.E. Childress, M. Elimelech, Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics, *Environ. Sci. Technol.* 34 (2000) 3710–3716.
- [26] S. Mafé, P. Ramírez, J. Pellicer, Activity coefficients and Donnan coion exclusion in charged membranes with weak-acid fixed charge groups, *J. Membr. Sci.* 138 (1998) 269–277.
- [27] M. Sua, D. Wanga, X. Wanga, M. Andob, T. Shintanic, Rejection of ions by NF membranes for binary electrolyte solutions of NaCl, NaNO<sub>3</sub>, CaCl<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub>, *Desalination* 191 (2006) 303–308.
- [28] S. Bandini, J. Drei, D. Vezzani, The role of pH and concentration on the ion rejection in polyamide nanofiltration membranes, *J. Membr. Sci.* 264 (2005) 65–74.