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# Development of Novel Thin Film Composite Reverse Osmosis Membranes for Desalination

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**Abstract.** Microporous Polyetherimide (PEI) membranes were prepared by wet phase inversion at different temperatures. The thin film composites (TFC) of polyamide on microporous PEI were prepared using meta-Phenylenediamine (MPD) and 1,3,5-Benzenetricarbonyl chloride (BTC). The ATR FTIR characterization showed the formation of polyamide (PA) on microporous PEI membrane, whereas scanning electron microscopy (SEM) revealed that a thin film of polyamide is formed on microporous PEI. The cross-sectional SEM of PEI prepared at 60 °C, showed finger like morphology and sparingly distributed balloon like morphology for PEI synthesized at 80 °C. The performance of PEI membranes and PA TFCs were ascertained by studying permeation of water and rejection of sodium chloride by reverse osmosis. The polyamide TFC with hydrophobic PEI support structures exhibited permeation of 28 to 50 l<sub>m</sub>-2h-1, with 98 – 95 % 2000 ppm NaCl rejection at 60 bar pressure.

## INTRODUCTION

Water treatment and desalination of sea or brackish water using membranes has become one of the most important 'un-conventional' growing sources of drinking water in many parts of the world and plays an important role in solving freshwater scarcity in the world [1]. Asymmetric membranes are used for the removal of salt impurities by Reverse Osmosis (RO). The wet phase inversion is one of the phase inversion method which is widely used to get asymmetric membranes. The thin film composite (TFC) membrane typically consists of a thick, porous, nonselective support layer and top coated by an ultrathin selective barrier layer. To sustain high pressure and to make TFC as an efficient and sustainable membrane during desalination, the pore size of microfiltration support membrane must be controlled [2]. If the pore size on microfilter is between 10-100 nm, then rejection of 3.5% NaCl by TFC would be greater than 90%. On the contrary, if the pore size is greater than 450 nm, then it may damage the ultra-thin membrane coating and making the membrane unsuitable for desalination [3].

Polyimides are group of polymers that are applicable for membrane formation due to their excellent film forming and mechanical properties. They possessed good thermal and moderate chemical resistance. Though these polyimides are used for contractor applications, there are no research studies reported on how to make use of it as support membrane for the production of thin film composite by interfacial polymerization [4-6]. In our research article we have made efforts to produce relatively denser sponge like PEI. Then this spongy PEI was top coated with polyamide to get TFC. The morphology and desalination capabilities of this PA/PEI TFCs are studied by Reverse Osmosis (RO).

## MATERIALS AND METHODS

### Materials

All the chemicals used in this work are enlisted in Table 1 and used as received. The high tensile and shear strength HOLLYTEX® is FDA approved non-woven spun bonded polyethylene terephthalate sheet. This HOLLYTEX sheet has been used as basic support for the preparation of asymmetric microporous PEI. MilliQ water was supplied from a Millipore water system with a resistivity of 18.2 MΩ.cm.

TABLE 1. Description of materials and their source

Material description	CAS number	Source
Polyetherimide (PEI) melt flow index 9g/10m (337 °C/6.6kg) density 1.27 g/ml	61128-46-9	
N-Methyl pyrrolidinone (NMP) anhydrous 99.5%	872-50-4	Sigma-Aldrich St Louis, Ohio, USA
m-Phenylenediamine (MPD) flakes >99%	108-45-2	
Benzene Tricarbonyl Chloride (BTC) 98%	4422-95-1	
Isopropyl alcohol (IPA) 99.5%	67-63-0	
Sodium lauryl sulfate (SLS)	151-21-3	
Sodium chloride (NaCl) > 9.5%	7647-14-5	
Hexane fraction from Petroleum specified	110-54-3	Fischer Scientific, Loughborough UK
Polyethylene terephthalate (PET) HOLLYTEX® 3265		Kavon filter products Farmingdale NJ USA

### Preparation of PEI support membrane

A known quantity of PEI, 22 and 25% by weight, was suspended in NMP for 72 h till it is completely dissolved. The polymer solution was degassed under vacuum. Using a doctor blade, 40 micrometer thick polymer solution was spread on non-woven polyethylene terephthalate (PET) at room temperature. After spreading, it was dipped in hot water bath at 60 and 80°C. The resulting membranes were allowed to cool on its own in the water bath. After 24 h, 22PEI/PET/60, 22PEI/PET/80, 25PEI/PET/60 and 25PEI/PET/80 membranes were washed with water and used for testing and interfacial polymerization. In the labels, the number 22 and 25 are weight percent of PEI, 60 and 80 are temperature at which membranes are developed.

### Preparation of thin film composite of PA on PEI

The TFC of polyamide on microporous PEI were prepared by interfacial polymerization. A 2% aqueous solution of MPD containing 10 % by volume Isopropyl alcohol (IPA) and 0.27% by weight sodium lauryl sulfate (SLS) was prepared by constant stirring at laboratory temperature [7]. The PEI/PET membranes were covered with MPD solution for 2 minutes and drained. Then this membrane was covered with organic solution of BTC in hexane (0.1% w/v) for 10 seconds, drained and cured at 60°C for 2 h [8, 9]. A shining thin film of PA was formed on the surface of PEI/PET. Then formed PA/22PEI/PET/60, PA/22PEI/PET/80, PA/25PEI/PET/60 and PA/25PEI/PET/80 TFC membranes were washed and stored in water.

### Characterization of membrane by ATR FTIR

Attenuated Total Reflectance-Fourier Transform (ATR-FTIR) spectra of the polyamide-polyetherimide thin films were obtained on a Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer. Each sample was scanned for 64 times with resolution of 4 cm<sup>-1</sup> and averaged to obtain the spectrum. All the spectra were scanned within the range 4000-400cm<sup>-1</sup>. Replicate measurements were made with five samples to minimize the effects of heterogeneity and ensure reproducibility. The final spectrum was obtained by averaging the five replicates. Each sample was placed on the ATR crystal with the anvil well above the sample. The anvil was then lowered straight down onto sample; a good reproducibility was achieved with this process.

## Characterization of Morphology by SEM

The scanning electron microscopy (SEM) images of surface and cryo-fractured PEI membranes and PA/PEI TFCs were recorded using Hitachi S5500 with the accelerating voltage of 5 kV to examine the cross section and surface morphology.

## Performance evaluation of Membranes

Filtration experiments were performed using closed loop RO unit. A high-pressure Hydra cell pump that can produce pressure up to 100 bar is used to pump feed into continuous flow cell (CF Cell) [10]. The Hydra cell was connected to CF through bypass valve and flow meter. The restricting needle valves connected to concentrate outlet and bypass valve in the feed stream was used to pressurize the feed to attain a desired pressure and constant flow rate in the CF Cell. Membrane coupons of effective surface area 0.0042 m<sup>2</sup> were used in CF cell. The concentrate permeate from CF cell and liquid from bypass are again sent back to feed tank to have same concentration. To have a stable membrane, pure water was pressurized through the TFC membrane for known time and used. Pure water permeation through the membranes was conducted at different pressure for all the membranes using Millipore water. The salt rejection experiment was conducted by taking 0.2% (2000 ppm) sodium chloride in milliQ water at a pH of 7.0. The flux of water through the membrane was measured by collecting the permeate for known time at constant pressure and reported as liters of water pass through square meter of membrane in one hour (l m<sup>-2</sup>h<sup>-1</sup>). The salt rejection was calculated by measuring the concentration of feed and permeates as shown below.

$$Rejection (\%R) = \left(1 - \frac{C_p}{C_f}\right) \quad (1)$$

Where C<sub>p</sub> and C<sub>f</sub> are concentration of permeate and feed respectively. The concentration would be direct measure of conductance of respective solutions under the laboratory conditions. The RO experiments were conducted in quartet and average values were reported.

## RESULTS AND DISCUSSIONS

### ATR FTIR

The representative spectra of PEI/PET, PA/22PEI/PET/60 and PA/25PEI/PET/60 are shown in Fig. 1. The functional groups present in the cross-linked polyamide layer are slightly different from polyimide support layer. The amide functional group of polyamides will be generally shown as amide I and amide II peaks. For PA in PA/PEI a broad peak centered around 1660 cm<sup>-1</sup> due to amide I band was found in figure 1. This is mainly due to C=O stretching, C-N and C-C-N stretching vibrations. The complex inters and intramolecular environments surrounding the carbonyl groups in polyamide-polyimide makes the amide I range considerably broader [11]. In Fig. 1, amide II band showed up at 1541 cm<sup>-1</sup> involved contributions due to in-plane N-H stretching, C-N and C-C stretching. The absorption band at 1778 cm<sup>-1</sup>, 1722 cm<sup>-1</sup> indicates the existence of imide group in PEI. In the structure of PEI, there are for CH<sub>3</sub> groups and it showed up as sp<sup>3</sup> bending at 1380 cm<sup>-1</sup> [12, 13]. The spectra of all the membranes clearly indicated the presence of polyamide and polyimide in the PA/PEI TFCs.

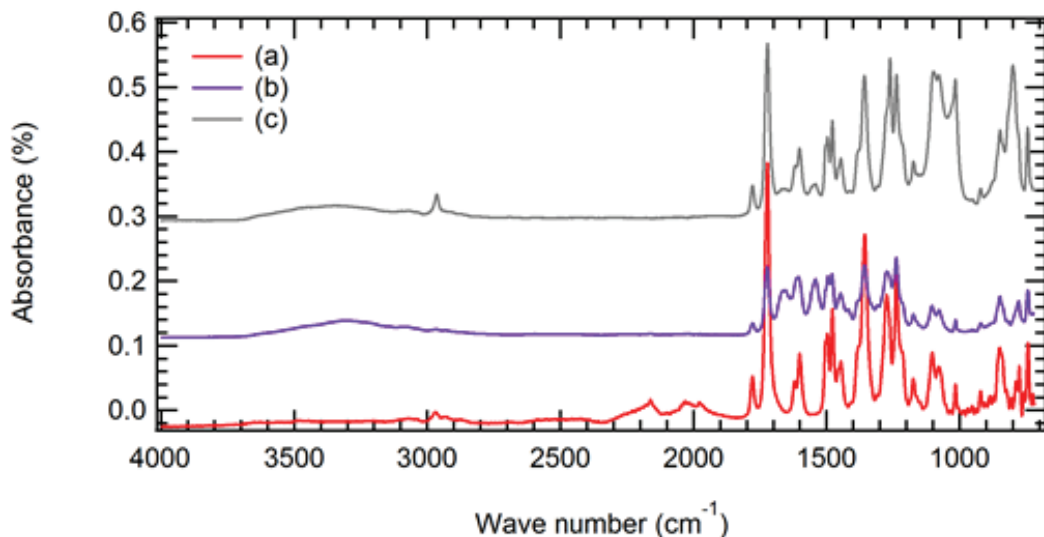


FIGURE 1. ATR FTIR spectra of (a) 22PEI/PET/60 (b) PA/22PEI/PET/60 and (c) PA/25PEI/PET/60

### Scanning Electron Microscopy

The morphology of membrane depends on rate of phase inversion. But, the rate of phase inversion is governed by thermodynamic stability of polymer solution and the rate of exchange of solvent and coagulant. The polymer solution of 22 and 25 % weight of PEI in NMP are immersed into coagulation bath maintained at 60 and 80 °C for wet phase inversion. Evaporation of solvent from the surface of polymer solution results in polymer rich region and becomes thin but dense top layer of the membrane. The layer underneath this will contain polymer lean layer with solvent-nonsolvent solution. Now liquid-liquid demixing happens in the polymer solution and this results in formation and propagation of pores in the matrix. During demixing, the delay in the process leads to the formation of spongy like morphology. Whereas instantaneous demixing facilitate the formation of finger like structure in membrane [14-17].

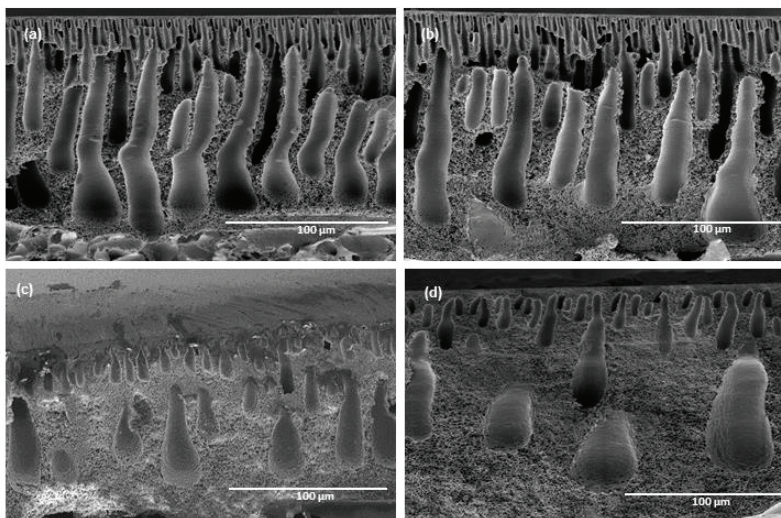


FIGURE 2. Cross-sectional SEM images for membranes obtained at (a)60 °C (b) 80 °C for 22 % PEI and (c) 60 °C (d) 80 °C for 25% PEI



The cryo-fractured cross-sectional SEM image of the 22 and 25% PEI are given in Fig. 2 (a) - (d). Generally, instantaneous demixing of PEI-NMP in water at laboratory temperature resulted in narrow finger like macro voids in PEI system [6].

In our polymer membranes, cross sectional SEM of 22% PEI [Figure 2 (a) & (b)] shows balloon like pores. And 25% PEI presented in Fig. 2 (c) & (d), exhibited sparingly distributed bulkier balloon like pores with spongier matrix. During the preparation of PEI membranes, it is possible that, higher temperature of coagulation bath may facilitate the mixing of solvent with nonsolvent and keeps them as solution for relatively longer time before demixing. As a result, there may be delay in demixing and this may facilitate the formation of sponge like structure in 25% PEI obtained at 80°C. In addition, the change in concentration from 22 to 25 % PEI results in increase in viscosity of the polymer solution. Increase in viscosity, delays solvent – nonsolvent exchange and leads to spongier like substructure for 25% PEI by suppressing the formation of macro voids [6,18]. The SEM image in Fig. 2 (d) for 25% PEI membranes obtained at 80°C reveals that this membrane is densest than the corresponding membranes produced at lower temperature and lower concentration.

A representative surface morphology of polyamide made by interfacial polymerization on the microporous 25% PEI support is presented (PA/25PEI/PET/80) in Fig. 3 (a) & (b). Closer view of Fig. 3 (a) was found to exhibit dense spongy structure of PEI and on which a nanoscale PA is coated as top barrier surface. The surface morphology of PA shown in Fig. 3 (b) seems to be dense and rough. A similar surface morphology was reported elsewhere for PA homolog [9].

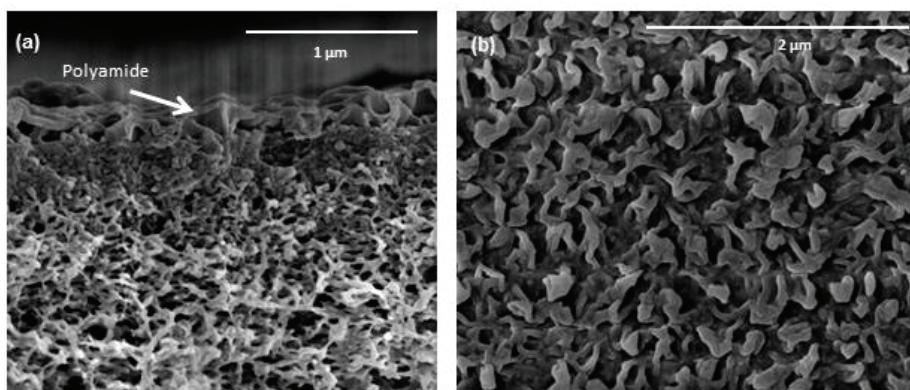


FIGURE 3. SEM images of (a) Cross-sectional and (b) Surface of polyamide film in PA/25PEI/PET/80

### Performance evaluation of microporous PEI/PET and PA/PEI/PET TFC membrane

The pure water permeation (PWP) through 22PEI/PET/60, 22PEI/PET/80, 25PEI/PET/60 and 25PEI/PET/80 at 5 bar pressure is shown in Fig. 4. From the figure, it was noticed that 22PEI/PET/60 membrane has highest flux for water and 25PEI/PET/80 is with lowest flux value. The reason for this could be due to the change in temperature and concentration during the synthesis of membranes. As the temperature changes from 60 to 80°C during the synthesis of both 22 and 25 % PEI membranes, there is slight decrease in PWP. However, increase in concentration of PEI from 22 to 25% showed substantial decrease in PWP. Increase in concentration of PEI from 22 to 25%, increases the viscosity of the solution, in which results in decreasing the possibility of macropores formation. The decrease in macropores results in spongy like structure [19]. This spongy like structure of the polymer matrix results in increase in tortuosity for the flow of water in the polymer system and thus, causing a substantial decrease in PWP for 25%PEI membranes. At the same time, increase in concentration could also result in very dense and cohesive top layer during coagulation of polymer solution. The combined effect of concentration and temperature results in denser top layer and spongier body for 25% PEI developed at 80 °C and this phenomenon is observed in morphological studies. Thus, 25PEI/PET/80 shows lowest PWP value.

The performance of PEI membranes was assessed using 2000 ppm NaCl solution and the results of flux as a function of pressure are given in Fig. 5. When the feed is changed from pure water to saltwater of 2000 ppm NaCl, the permeation decreased for all PEI membranes. Again, pattern of permeation followed by these membranes are same as that we noticed for permeation of pure water. But all membranes showed a very negligible salt rejection (0-2% not shown in figure), indicating that, pores in these membranes are big enough to allow ions permeated through it [6, 18].

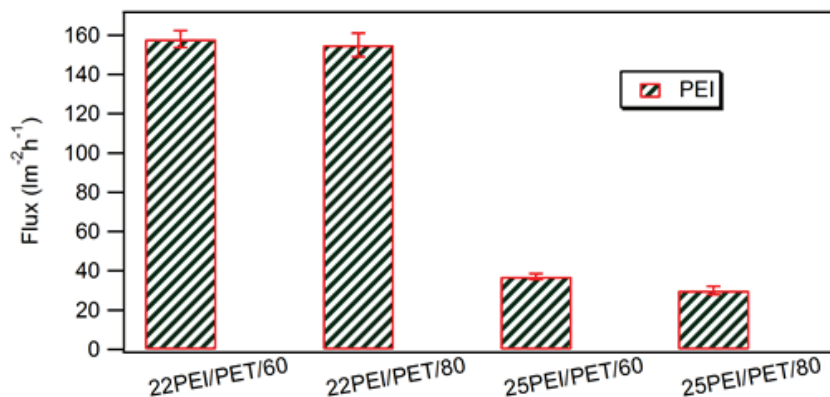


FIGURE 4. Pure water permeation for PEI membranes at 5 bar pressure

The evaluation of PA TFCs was ascertained using 2000 ppm NaCl and the permeation data is presented in Fig. 6. The membrane PA/22PEI/PET/60, exhibited maximum permeation of 50  $\text{lm}^{-2}\text{h}^{-1}$  at 60 bar pressure whereas PA/25PEI/PET/80 showed least permeation of 28  $\text{lm}^{-2}\text{h}^{-1}$  at the same pressure. This range of pressure is usually applied in large scale treatment processes [20]. In these TFC membranes there is an extra barrier film in the form of crosslinked aromatic polyamide TFC on the top of PEI membrane. This PA TFC film prevents the permeation of salts through the membrane and helps in removing salts from saline water. The filtration test using all the membranes indicated that, all the four membranes showed different degree of permeation with slight variation in salt rejection.

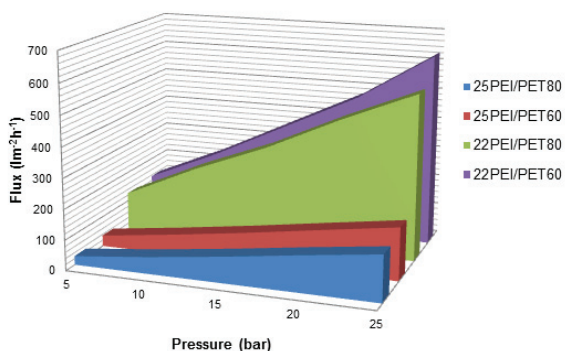


FIGURE 5. Change in flux at different pressure for PEI membranes

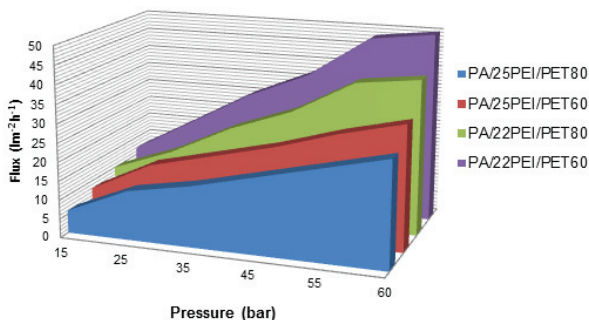


FIGURE 6. Measured flux as a function of pressure for PA/PEI TFCs

The other two membranes showed intermediate values with comparable rejection. In all these TFCs the top PA is the selective and rejection layer, the pore size and surface characteristics of this layer should be a limiting factor for the permeation and rejection. However, the PA on all the support systems are prepared under identical conditions. So, there should not be any change in surface and pore structures. As a result, the permeation and rejection exhibited by this selective layer should be same. The rejection of salts by all the TFCs is between 95 – 98 %, but permeation results shown in Fig. 7 follows a trend which is similar to the trend observed in earliest filtration tests with PEI membranes. The observed trend is, permeation of water in PA/22PEI/PET/60 < PA/22PEI/PET/80 < PA/25PEI/PET/60 < PA/25PEI/PET/80. Though in all the TFCs, PA surface is almost same, the variation in flux supports the fact that, the body of polymeric membrane becomes more and more dense from PA/22PEI/PET/60 > PA/22PEI/PET/80 > PA/25PEI/PET/60 > PA/25PEI/PET/80. This trend was observed in morphological and in permeation studies. The combined effect of surface characteristics of PA and denser PEI affects the permeation.

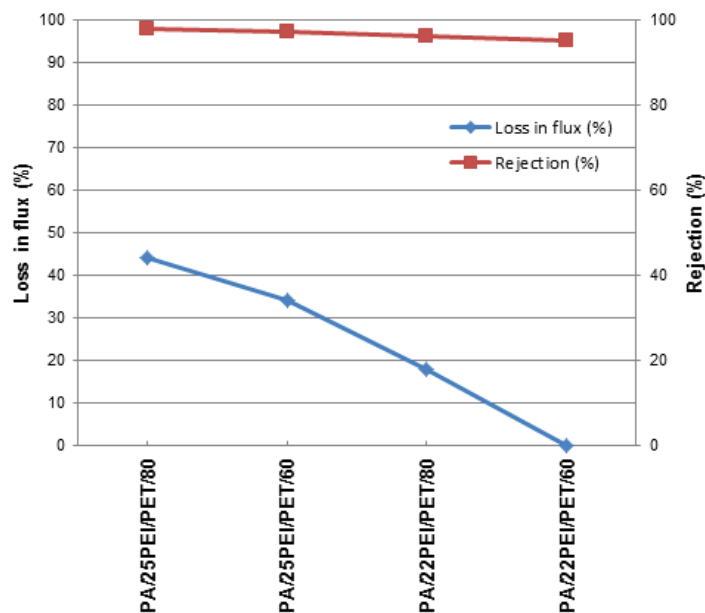


FIGURE 7. Rejection of salts by TFCs and loss of flux with respect to highly permeable PA/22PEI/PET/60 membrane

## CONCLUSIONS

The different membranes of 22 and 25 weight percent PEI in NMP were prepared using water as non-solvent by wet phase inversion at 60 and 80°C. Our investigations have revealed that higher temperature and higher concentration of PEI in NMP produces sponge like structure in the membrane. The polyamide on 22% PEI support showed better permeation of water with 95% rejection, whereas PA on 25% exhibited 98% rejection at the cost of 44% of flux. Further modification of these membranes is needed to enhance the permeation and improve the salt rejection credentials of these membranes.

## ACKNOWLEDGMENT

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