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Effect of Polymer Ratio and Heat Treatment on Inhouse Membrane of Polyethersulfone

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ABSTRACT

The membrane technology has gaining more attention due to their crucial use in different fields such as water purification, sugars recovery. A small modification in the membrane morphology has significant impact on membrane performance. The impact of heat treatment on PES membranes was investigated in this study. Two flat sheet membranes were prepared from casting solution having 15 % and 18 % Polyethersulfone (PES) by phase inversion method. The fabricated membranes were then heated for 20 min at 100 ^{o}C. Initially, the performance of membranes was evaluated by measuring their water flux as well as salt rejection. The membranes were further characterized to investigate their morphology by measuring their roughness and porosity. The results revealed that the heat treatment has significant influence on the membrane structure, the PES 15 % membrane roughness improved from 41.9 to 36.1 nm after heat treatment, also PES 18 % membrane roughness improved from 16.5 to 18.6 nm after treating thermally. The water flux of PES 15 % and 18 % dropped from 148 to 33 and from 25 to 13 respectively which proved that the membranes shrank due to heat treatment. In addition, salt rejection results supported water flux results. Thus, heat treatment showed an important effect on membrane morphology and can enhance the membrane performance.

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1. INTRODUCTION

Membranes play a significant function in various application such as desalination [1], food industries [2], water purification [3]. The membranes that having a good resistant and desirable selectivity are necessity for the industrial sector, an efficient separation process is highly demanded in order to acquire high purity products [4]. The selectivity of membrane is dependent on the membranes pore size. The membrane pores is very important in determining the efficiency of purification [5]. A small modification in the structure of membrane has a severe influence on membrane presentation. Heat treatment is considered as one of the post formation treatments commonly applied to membranes to modify the membrane pores [6]. A number of studies have been recorded to explore the effects of heat treatment and polymer concentration on the membrane performance which will be listed as follow: Gholami et al. [7] studied the impact of hot air on the PES membrane at different temperature (120, 150, and 180 ^{o}C) for different time (5, 15, 30, and 45 min), the best performance result was at 150 ^{o}C for 5 min, also it can be observed that membrane pores shrank because of heat treatment, the solution rejection increased whereas water flux dropped, a significant decrease of water flux was noticed as temperature increased. Rahimpour et al. [8] investigated the impact of hot water and air

treatment on the PVDF and PES membranes structure and their performance, to achieve that, both membranes exposed to hot air at 100, 120, 150 and 180 ^{o}C for 20 min, then the best temperature was varied at different period of time (5, 20, and 60 min), while for hot water, the membranes immersed in hot water bath at 55, 75, and 95 ^{o}C for 20 min, then the best temperature was varied for different period of time for 5, 20, and 60 min. Both membranes exhibited an improvement of protein rejection after heat treatment by water and air. The optimum conditions were 95 ^{o}C in water and 100 ^{o}C in air for 20 min. Su et al. [9] managed to fabricate Cellulose acetate (CA) NF hollow fiber membranes for forward osmosis (FO) by two step of heat therapy at 60 ^{o}C for 60 min, and then at 95 ^{o}C for 20 min. the findings showed major shrank of pore size from 0.63 to 0.30 nm. Rohani et al. [10] studied the impact of heat treatment as well as other parameters to fabricate NF membrane from polyaniline (PANI), where the heat treatment performed in the oven at 150 ^{o}C for 3h, the influence of heat treatment was obvious where the electrical conductivity of the HCl doped PANI membranes drops from around 4 S cm^{-1} to 0 S cm^{-1} and the membrane surface become smoother after heat treatment. Sun et al. [11] improved the NF performance and stability of chitosan/PAA composite membranes during long time of NF by heat treatment and crosslinking. The salt rejection improved significantly when the membrane heated up to 150 ^{o}C for 60 min. furthermore, the membrane stability enhanced more after heat treatment. Gholap et al. [12] grafted N-tertiary butyl acrylamide on PVA molecular chains to increase the membrane properties, however, the solution flux of the membrane dropped only after heat treatment due to crystallinity inducement. The crystallinity of polymers is a main stuff in responsible the permeability of the polymer and mechanical stability. Both crystallinity and glass transition temperature are regulated by the chain interactions, chain flexibility as well as molecular weight of the polymer [13]. Several studies showed that high crystallinity reduced the membrane water flux [14-16]. Fujioka et al. [17] used hot water for heat therapy to develop the rejection and antifouling properties of a polyamide reverse osmosis (RO) membrane. The water flux dropped from 4.1 to 2.8 L/m^2.bar due to heat treatment of PA membrane at 70 ^{o}C, however, conductivity rejection improved from 95.5 to 97.0 %. Shintani et al. [18] accompanied a research to investigate the effects of heat treatment on chlorine rejection using RO membrane. From 40 to 120 ^{o}C for 3 min, the membrane was heated and hence the salt rejection and water flux were measured. The outcomes showed a remarkable impact of temperature on salt rejection as temperature increased, while water flux dropped as temperature reached to the maximum value.

Thus, this study aimed to examine the impact of heat treatment on PES membrane at various polymer concentrations at 15, and 18 % membranes in order to produce NF membrane. The heat treatment conditions were chosen at 100 C for 20 min. Furthermore, the fabricated membranes undergo to series of analysis such as water flux, Di-valent salt rejection, porosity, and AFM.

2. RESEARCH METHOD

2.1. Materials

Table 1. Materials used for membrane fabrication

Material name	Manufacturer	Function
Polyethersulfone (PES) granule	Goodfellow	Membrane based polymer
N-Methyl-2-Pyrrolidone (NMP)	Fluka, Germany	Solvent
Distilled water	Available in the lab	Non-solvent.

2.2. Membrane Preparation

The two membranes at 15, and 18 % were fabricated through wet phase inversion technique, which widely and commonly used due to its simplicity [19]. Initially, PES polymer was dried in the oven at 60 ^{o}C for 72 h to eliminate moisture. Each cast solution was heated and stirred at 60 ^{o}C for 8 h until homogenous solution was obtained. In order to prevent pinholes and highlights in the membranes, the cast solutions were left for 24h prior to casting to release bubbles [20]. Next, suitable amount of the dope solution was poured on the glass sheet and casted by knife set at 200 μm at atmosphere temperature. Finally, the fabricated membranes were left for 30 s for solvent evaporation before immersed in water bath for 2 h for solvent exchange purposes [21]. To ensure complete solvent exchange, the coagulation water bath was changed. The synthesized membranes were deposited in distilled water at ambient temperature prior to use.

2.3. Heat Treatment Procedures

Based on our previous work [22], all fabricated membrane were left to dry for 24 h at room temperature (± 25 ^{o}C). Then, they were positioned in the oven and heated up with the air circulation at 100 ^{o}C for 20 min.

2.4. Membrane Performance Evaluation

2.4.1. Membrane Performance

In order to estimate the performance of the fabricated membranes, the dead end cell filtration (Sterlitech HP4750, Sterlitech Corporation, USA) was utilized to assess the pure water flux of the fabricated membranes at operating pressure 4 bar. The water flux value was calculated from equation (1):

$$J_w = \frac{V}{A.t} \quad (1)$$

Where "J_w is the water flux ($L.m^{-2}.h^{-1}$), V is the permeate volume (L), A is the effective membrane area (0.00146 m^2), and t is the filtration time (h)".

Furthermore, salt rejection was estimated using 20 mM Na_2SO_4. Using the same apparatus, the experiments were conducted at 4 bar and the rejection percentage was calculated from equation 2.

$$R = \frac{Cf-Cp}{Cf} X\ 100 \quad (2)$$

Where "R is rejection value, C_f and C_p are the feed and permeate concentrations".

2.4.2. Porosity Measurement

The porosity of these membranes was determined by their capacity of water absorption, and calculated using the expression below [23]:

$$\text{Porosity } (\varepsilon) = \frac{W1-w2}{V.\rho} \text{x}100 \quad (3)$$

Where "W_1 and W_2 are the mass of membrane in the dry and wet states (mg), ρ_{water} is the density of water at room temperature (ml/mg) and V is the volume of the membrane in the wet state (ml)". After wiping away excess water with filter papers and drying the membranes in a vacuum oven at 60^oC for 6 hours before weighing it, the porosity (ε) of the membranes was measured.

2.4.3. Atomic Force Microscopy (AFM) analysis

Surface morphology of the changed PES membranes with different polymer concentration was quantitatively measured by AFM (model Scanning Probe Microscope, NTEGRA Prima, NT- MDT, Russia). Small strip of membranes was positioned on the sample holder and the samples were measured in tapping mode and scanning area is 10 µm x 10 µm.

3. RESULTS AND ANALYSIS

3.1. Membrane Performance Before Heat Treatment

The membrane performance measured through its pure water flux (PWF) profile at different PES ratios in the dope solution during its synthesis is presented in Figure 1. The filtration was conducted at 4 bars with stirring speed at 300 rpm. The outcomes clearly displayed that the water flux diminished as the PES content in the dope solution increased. The PWF has decreased from 148 to 25 L/m^2.h as PES ratio increased from 15 % to 18 %. This was possibly due to the increase in solid PES content in the dope solution that has improved the solution's viscosity and affected the mass transfer of NMP solvent from the dope solution during the membrane formation. High polymer concentration solutions were believed could adjust the mass transfer process between solvents and non-solvents during polymer coagulation when the dope polymer solution was in communicates with the coagulant (water). The polymer ratio in the membrane matrix has wide and sigfnificant effect on the membrane structure as well as rejection. It influences the mass transfer among the non-solvent and solvent through phase inversion. A higher polymer load in the membrane decreases the solvent volume fraction, causing the binodal curve to shift towards the polymer/solvent axis [24], and requiring less non-solvent to accomplish phase separation. Furthermore, the effect of polymer ratios on viscosity will disturb the kinetics of solvent/non-solvent exchange. A larger polymer concentration could lead to the creation of a thicker skin layer, which would impair separation performance as well as the traditional trade-offs between rejection and flux [25]. Water flux is mainly affected by the membrane pore size which are formed based on the polymer concentration in the dope solution; greater polymer concentration causes the membrane pores to become smaller and results in a lower water flux [26].

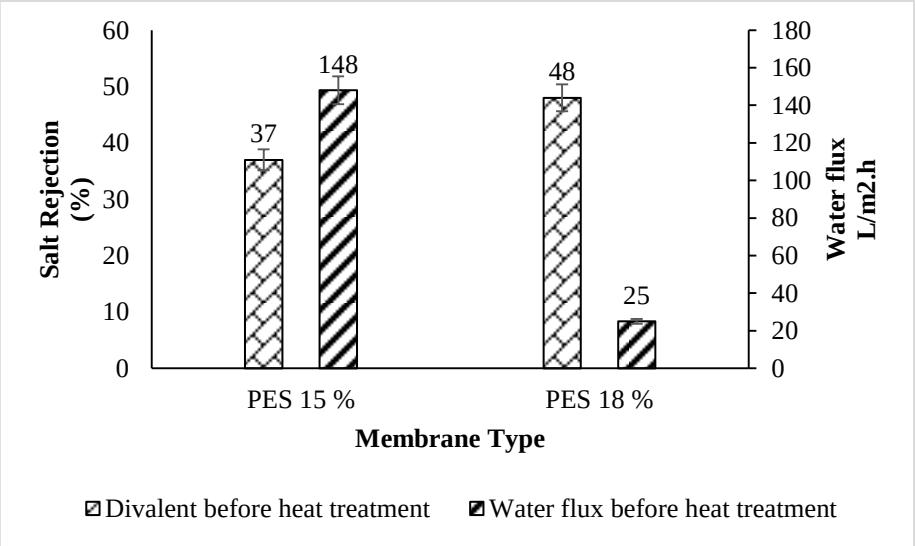

Figure 1. Water flux and salt rejection results of PES membranes before and after heat treatment

Figure 1 also presented the divalent salt rejection together with the water flux of pure membranes at different PES ratios. It was found that the divalent salt rejection increased significantly as the PES content improved in the doped solution. Initially, PES 15 % membrane has 37 % divalent salt rejection. After the PES content in the membrane was amplified from 15 % to 18 %, the salt rejection further amplified from 37 % to 48 %. This rise in rejection could be due to the reduction in the membrane pores and porosity, which results are presented in the next figure (Figure 2). Opposite trend was observed in the water flux where the water flux found to reduce as the PES content increased, maybe also due to the reduction in the membrane pores and porosity (refer to Figure 1), thus resulting in the reduce in water flux and improve in salt rejection. The membrane performance for both the rejection and the water flux are conceptually related to the membrane pores where smaller pores could lead to higher rejection and lower flux [27]. Furthermore, the polymer content in the dope solution is also responsible for the membrane top layer formation. At the point when the casting solution touches the non-solvent in the coagulation bath, the solvent comes out slowly from the casting solution to the coagulation bath and resulting in high concentrated polymer molecules to be aggregated at the top layer [28]. Lower polymer content causes a strong interaction among the polymer and non-solvent, thus forms a thin top layer of the membrane. Sofia et al. (2010) conducted a research to compare the effects of PES polymeric content at 13 %, 15 % and 17 % on the membrane morphology, the findings showed that PES 17 % membrane has the densest top skin layer compared to other fabricated membranes, and the use of PES polymer at 17 % increased the dope solution viscosity which led to formation of smaller membranes pores [27].

In general, salt rejection is an important parameter to estimate the membrane separation performance. The divalent salt rejection presented in Figure 1 confirmed that NF range was not achieved in the membranes based on the comparison of their divalent salt rejection values of the commercial NF membrane. The divalent salt rejection for commercial NF membranes usually range between 55 % to 99 %, and the big difference in the range is based on the manufacturer, pore size and top layer's material of the membranes [29, 30], while the PES synthesized membranes possessed salt rejection at 37 to 48 % only.

3.2. Membrane performance after heat treatment

3.2.1. Salt Rejection

The divalent salt rejection consistent with water flux results as presented in Figure 2. The salt rejection of PES 15 % membrane increased from 37 % to 50 % after heat treatment, same trend can be notice for PES 18 % membrane. The salt rejection of PES 18 % membrane raised from 48 to 77 % after post treatment. These results showed better performance when heat treatment applied to fabricate NF membrane. The membrane performance changed because the membrane structure shrank due to heat treatment which was evidenced by water flux reduction [31].

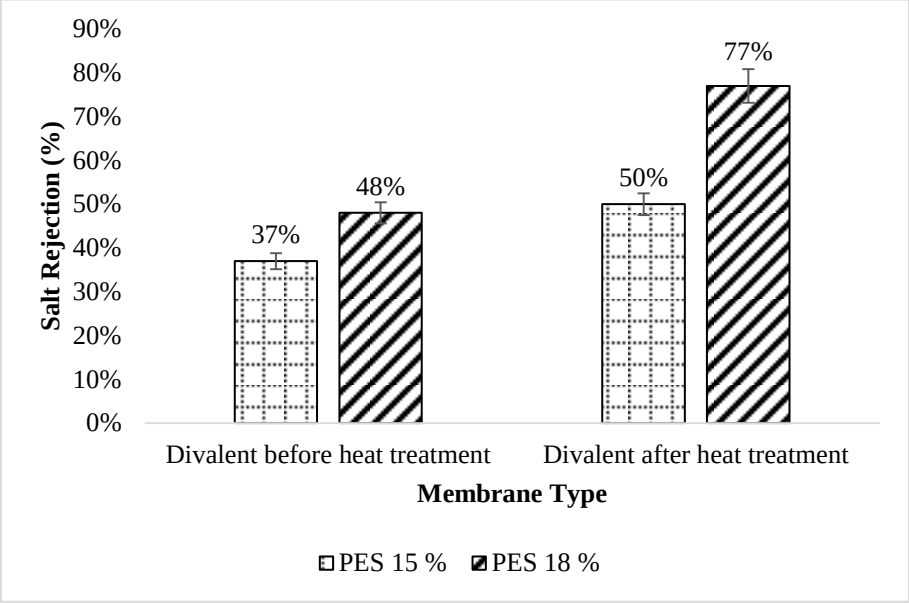

Figure 2. Salt rejection of PES membranes before and after heat treatment.

3.3. Porosity

The stimulus of heat treatment on membrane porosity was studied, the outcomes are given in Table 2. The membrane porosity was decreased by applying heat treatment on the membranes. The porosity of the PES membranes was found to have decreased somewhat after heat treatment. The increased fibre diameter following thermal treatment was the main driver of the decrease in membrane porosity. In theory, heat treatment of membranes reduces porosity, lowering the membrane's permeate flux. This is consistent with the PES membranes' pure water flux measurements. Although the porosity decreased after thermal treatment, the porosity was still significantly higher than those of high PES ratio in the dope solution [32].

Table 2. Membrane porosity of PES membranes.

Membrane Type	Porosity before heat treatment (%)	Porosity after heat treatment (%)
PES 15 %	65	53
PES 18 %	48	41

3.4. Atomic Force Microscopy (AFM) analysis

In order to investigate the impact of heat treatment on the surface morphology and roughness of the membrane, membrane samples were subjected to AFM analysis. AFM analysis of the membranes was categorized at a scan size of 10 µm × 10 µm. Table 3 displays the membrane roughness with/without heating. While there was no obvious modify in the hollow-fiber dimension, Gholami et al. [7] discovered that the hollow fibre membranes shrank following heat treatment, resulting in a decrease in flow and an increase in solution rejection. The surface roughness of flat-sheet PES membranes changed following microwave irradiation, as demonstrated by surface roughness changes [33].

The investigation of the surface morphology of membranes can support clarify the separation processes in these membranes are the qualities of pore structure (pore size, pore diameter, and pore size distribution) and to hinder mine their filtration properties [34].

Table 3. Roughness results of PES membranes with/without thermal treatment.

Membrane Type	Roughness before heat treatment	Roughness after heat treatment
PES 18 %	18.571 nm	16.545 nm
PES 15 %	41.991 nm	36.005 nm

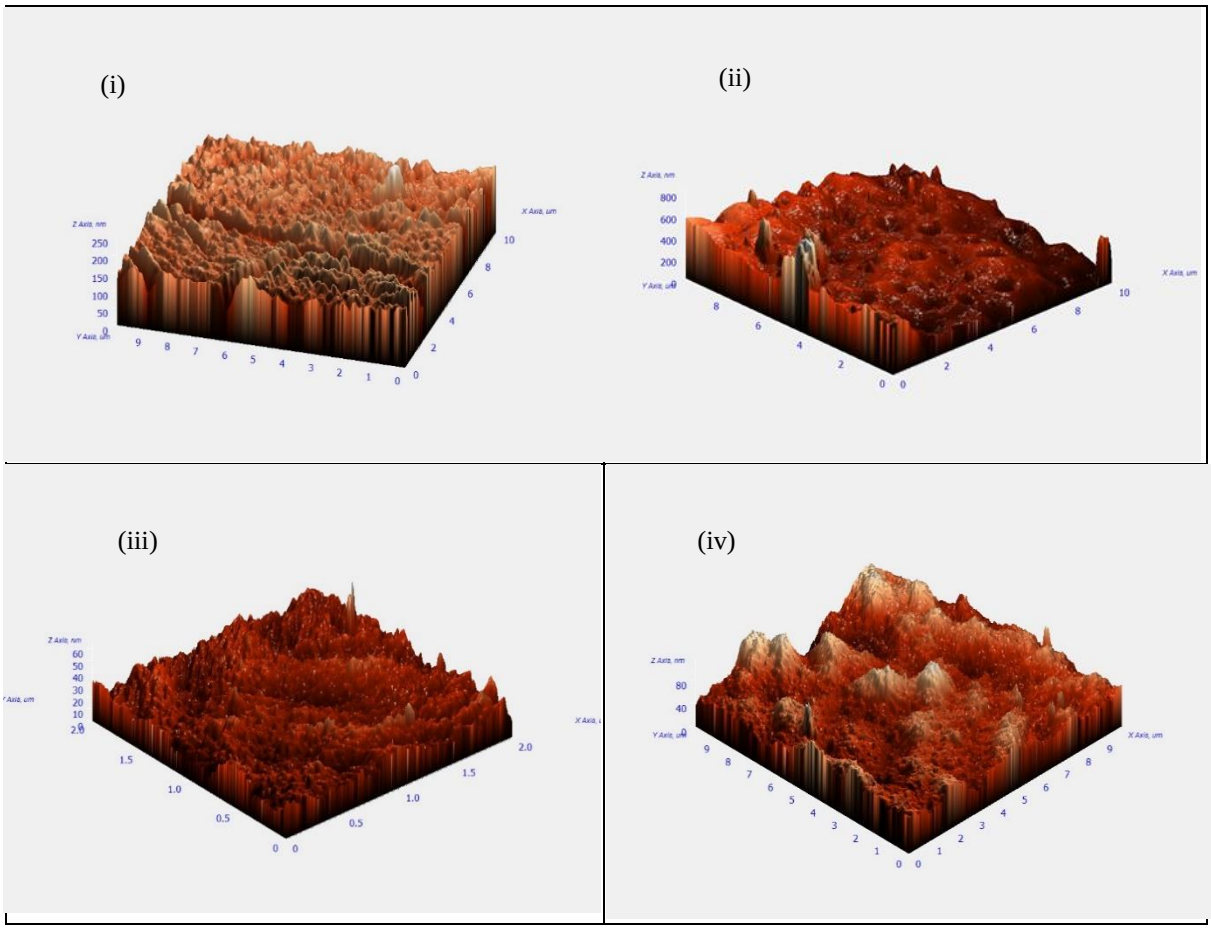

Figure 3. AFM images of (i) PES 15 % before heat treatment, (ii) PES 15 % after heat treatment, (iii) PES 18 % before heat treatment, (iv) PES 18 % after heat treatment.

4. CONCLUSION

In conclusion, PES membranes at 15 % and 18 % were successfully fabricated through phase inversion technique. The classifications of the membranes with/without heat treatment were examined. The key conclusions are listed as explains as follow:

• The water flux of both fabricated membranes decreased after subjecting to heat treatment.

• Heat treatment has important influence on both membrane properties where the salt rejection has increased positively to show membranes at NF level.

• applying the heat treatment on PES membranes enhanced the membrane roughness

• Treatment the membranes by hot air affected the membrane porosity, both membranes showed decreasing in their porosity.

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