

EFFECT OF HEAT TREATMENT ON THE PERFORMANCE AND STRUCTURAL DETAILS OF POLYETHERSULFONE ULTRAFILTRATION MEMBRANES

ANI IDRIS¹ & NORASHIKIN MAT ZAIN²

Abstract. In this paper, the effect of heat treatment on polyethersulfone membranes is presented. Generally, a small change in membrane structure has a drastic effect on membrane performance. Ultrafiltration (UF) flat sheet membranes were prepared from casting solutions containing 20 wt% polyethersulfone (PES), 65 wt% N,N-dimethylformamide (DMF), and 15 wt% polyethylene glycol 200 (PEG 200) by phase inversion method. The membranes were then heated in air at various temperatures ranging from 50 to 150°C. The membrane performance was initially evaluated in terms of pure water permeation and solute separation using PEG 35000 Daltons solution. Next, the molecular weight cut off (MWCO) of PES UF membranes were then determined by further UF experiments using 1000 ppm polyethylene glycol (PEG) solution of various molecular weights ranging from 1000 to 35 000 Dalton. Mean pore size (μ_p) and standard deviation (σ_p) of the membranes were determined from solute transport data. It is observed that solute separation using PEG 35000 Daltons increased while flux decreased as the heating temperature increases. The MWCO and pore size of the membranes decreased with increased heating temperatures. Surface and cross section of PES UF membranes were characterized before and after heating using Scanning Electron Microscope (SEM). Atomic Force Microscopy (AFM) analysis revealed significant changes were observed in the surface of PES UF membrane with increased heating temperatures. The performance of the membrane was not only affected by heat treatment but also the heating temperatures.

Keywords: Ultrafiltration, polyethersulfone, heating, temperature, polyethylene glycol

Abstrak. Kertas kerja ini mengkaji kesan rawatan haba pada membran polietersulfon. Secara amnya, perubahan kecil pada struktur membran akan memberi kesan kepada prestasi membran. Membran ultrapenurasan (UF) disediakan dari larutan dop yang mengandungi 20 wt% polietersulfon (PES), 65 wt% N,N-dimetilformamida (DMF), dan 15 wt% polietilena glikol 200 (PEG 200) dengan kaedah fasa balikan. Membran ini kemudiannya dipanaskan dalam udara pada julat suhu 50°C hingga 150°C. Prestasi membran diukur dalam sebutan permeat air tulin dan pemisahan bahan larut menggunakan pada mulanya larutan PEG 35000 Daltons. Seterusnya, had berat molekul (MWCO) membran PES ditentukan dengan uji kaji UF selanjutnya menggunakan 1000 ppm larutan polietilena glikol (PEG) yang terdiri dari berbagai berat molekul dari 1000 hingga 35 000 Dalton. Saiz rongga purata (μ_p) dan sisihan piawai membran (σ_p) ditentukan dari data pemindahan bahan larut. Keputusan menunjukkan pemisahan bahan larut PEG 35000 Daltons meningkat manakala fluks menurun apabila suhu rawatan meningkat. MWCO dan saiz rongga membran menurun apabila suhu rawatan meningkat. Permukaan dan keratan rentas membran PES UF selepas dan sebelum dipanaskan dicirikan menggunakan Mikroskop Imbasan Elektron (SEM).

^{1&2} Department of Bioprocess Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

Analisis menggunakan Mikroskop Daya Atomic (AFM) menunjukkan perubahan yang ketara pada permukaan membran UF PES apabila suhu meningkat. Prestasi membran bukan sahaja dipengaruhi oleh rawatan haba tetapi juga oleh suhu pemanasan.

Kata kunci: Ultrapenurasan, polietersulfon, pemanasan, suhu, polietilena glikol

1.0 INTRODUCTION

Membranes with good resistant and selectivity are necessary where efficient separation process is very important for the industrial sector to obtain high purity products. Selectivity is dependent on the pore size of the membranes. The pore sizes of the membrane play a crucial role in determining the efficiency of filtration [1]. Some efforts have been carried out in attempting to enhance the selectivity of the membrane. For thin film composite preparation, curing temperature is important in imparting stability to the membranes. Percent salt rejection increased as curing temperature increased. When curing temperature is increased, two processes take place simultaneously, the pore size decreased and densification of the thin film increased, which then lead to further densification of active layer and reduced flux [2].

For asymmetric membranes, heating has been one of the methods applied to adjust pore size of the membranes [3]. Heating can be performed by two methods; heating in the air and heating in water. As reported by previous researchers, heating/drying temperatures affected the asymmetric membrane selectivity and flux [4]. Some researchers suggested that adjustment of pore size of the membranes would be possible by heat treatment [3]. They have studied the effect of heat treatment with air circulation on PES hollow fiber membranes containing PVP 10000 Dalton as additive. The results indicated that solute separation increased while the pure water flux decreased with heating temperature. SEM analysis showed that there was a significant change in the surface of the membranes after heating.

The following study by Kiyono *et al.* [5] on heterogenous polysulphone hollow fiber membranes with cation exchange functioning revealed that heat treatment increased the membranes transport number from 0.65 to 0.92 and increased their selectivities. Various heat treatment duration times were used ranging from 2 to 10 minutes. SEM analysis indicated that the heat treatment caused structure shrinkages and the spaces between the resin particles and the pore wall were reduced.

Other researchers reported that surface roughness of PES hemodialysis membranes was also affected by heating treatment [6]. The membranes were treated by heating in the air and heating in water at different heating temperatures. The roughness of outer and inner surface of the membranes was compared with the membrane that has not been heated and they found that the roughness parameter on the inner surface of hollow fiber membranes changed after heating. They also studied the effect of heat treatment on molecular weight cut off, pure water flux, and pore size distribution of the membranes.

Chloromethylated poly(phthalazinone ether sulfone ketone) (CMPPEK) nanofiltration membranes were treated by heating in an oven at 80°C for 10 and 15 minutes and boiled in water at 100°C for 10 minutes [7]. They reported that CMPPEK membranes treated by heat in an oven gave the highest rejection of MgCl₂ compared to boiling in water. Although the membranes had high rejection of MgCl, the rejection of NaCl was still over 22%. Other work was done by heating the cellulose acetate membranes in a hot water bath at different temperatures [8]. As shrinkage temperature increased, NaCl separation increased. Other researchers studied on the effect of heating at 60°C on transport parameter across cellophane membranes and found that there are possible chemical and transport modifications in the cellophane membrane due to heating treatment [9].

Besides Gholami's work [3] mentioned earlier on the effect of heat treatment on PES/PVP hollow fiber membranes, no work has been done regarding the effect of heat treatment on PES/PEG membranes. This present work attempts to investigate the effect of heating on the performance of PES UF flat sheet membranes prepared from casting solutions containing 20 wt% PES polymer, 15 wt% PEG 200 as additive, and 65 wt% N, N-dimethylformamide. The boiling temperatures for PEG 200 is 250°C, thus the heat treatment was carried out at 50, 100, and 150°C, so as not to incur any losses of additive caused by evaporation.

2.0 EXPERIMENTAL

2.1 Materials

Polyethersulfone (PES) supplied by BASF was used as polymer in the preparation of membrane casting solution. N, N-dimethylformamide (DMF) purchased from Labscan Asia Co. Ltd. was used as solvent. Polyethylene glycol 200 (PEG 200) supplied by Merck was used as additive. Polyethylene glycols of different molecular weights ranging from 1000 to 35 000 Dalton with molecular weight of 1000, 3000, 6000, 10 000, and 35 000 Daltons purchased from Fluka were used as solutes. Feed solutions were prepared using distilled water. Other chemicals used were sodium iodide (KI) purchased from SureChe Products Ltd., barium chloride (BaCl₂) obtained from Labguard, iodine (I₂) purchased from Emory, and hydrochloric acid (HCl) from Merck.

2.2 Preparation of Dope Solution

Polyethersulfone was dried in an oven with air circulation at 80°C for 24 hours to remove any moisture present. Dope solution was prepared by dissolving 20 wt% of polyethersulfone in 65 wt% of N, N-dimethylformamide with constant stirring for several hours. When the polymer was completely dissolved, 15 wt% of PEG 200 was subsequently added, and the solution temperature was maintained at 80°C with

continuous stirring for five hours until the additive was completely dissolved and homogeneous. The resultant polymer solution was filled in a glass bottle. The air bubbles in the resultant polymer solution were removed using ultrasonification process.

2.3 Membrane Casting

The dope solution was poured onto a clean glass plate at room temperature and it was manually casted on a glass plate using casting knife with a gap thickness of 200 μm . The glass plate with the casted film was immediately immersed in the distilled water at room temperature after casting. After few minutes of initiating the phase inversion, a thin polymeric membrane film was separated out from the glass. The membrane was kept in distilled water until membrane evaluation. All flat sheet membranes were visually inspected for defects and good areas were chosen for membranes evaluation.

2.4 Heat Treatment

Before heating, polyethersulfone ultrafiltration flat sheet membranes were dried for 24 hours at room temperature. The membrane samples were cut into pieces and placed on clean glass plates. They were then placed in an oven and heated with air circulation at various temperatures of 50°C, 100°C, and 150°C for 5 minutes. Finally, they were taken out and cooled down at room temperature before tested.

2.5 Membrane Performance Evaluation

2.5.1 Ultrafiltration Experiments

Membrane sample with an area of $2.0 \times 10^{-3} \text{ m}^2$ was placed in a cross flow test cell with the active skin layer facing the incoming feed. Initially, experiments were run using distilled water and then, separation experiments were conducted using aqueous solution of 1000 ppm [10, 11] polyethylene glycol of 35 000 Daltons at 3 bar. This process was followed by MWCO experiments using various molecular weights PEG ranging from 1000 to 35 000 Daltons as solute. The permeate was collected and its volume was measured to evaluate the membrane performance. System was thoroughly flushed with distilled water between runs of different molecular weight solutes of polyethylene glycol.

The concentration of feed and permeate solutions were determined using the analytical method given by Sabde *et al.* [12]. This analytical method involved addition of 1 ml of 5% BaCl_2 in 1 N HCL and 1 ml of solution prepared from a mixture 2% KI (w/v). The colour developed was then analysed using a UV-spectrophotometer at 535 nm against a reagent blank to measure the concentration of permeates. PES

ultrafiltration membranes were characterized in terms of pure water permeation (PWP), rejection rates (R), and flux (J). Pure water permeation (PWP) is given by:

$$\text{PWP} = \frac{Q}{A \times \Delta T} \quad (1)$$

where Q is the volume of the pure water permeate (l), A is the membrane surface area (m^2), and ΔT is the permeation time (hour). The solute rejection of the membrane was calculated using the following expression:

$$R (\%) = 1 - \left(\frac{C_p}{C_f} \right) \times 100 \quad (2)$$

where C_p is the solute concentration in permeate stream and C_f is the solute concentration in feed stream. The flux of the membrane, J , is obtained as follows:

$$J = \frac{V}{A \cdot \Delta T} \quad (3)$$

where V is the volume of permeate (l), A is the membrane surface area (m^2), and ΔT is the permeation time (hour).

2.5.2 Membrane Characterization by Solute Transport Data

The pore size of the PES ultrafiltration membranes were calculated using solute separation data as described by Singth *et al.* [13]. The Stokes radius of PEG, a (cm) was calculated from the molecular weight, M , using the following equation:

$$a = 16.73 \times 10^{-10} M^{0.557} \quad (4)$$

The solute separation was plotted versus solute diameter. Solute diameter is given by:

$$d_s = 2a \quad (5)$$

The solute separation curve was drawn to determine mean pore size (μ_p) and standard deviation (σ_p) of the membranes. The data of solute separation versus solute diameter was plotted on a log-normal graph paper. The mean pore size was calculated as d_s when $R = 50\%$ on the linear regression line. The standard deviation was calculated from the ratio of d_s at $R = 84.13\%$ and 50% . Moreover, molecular weight cut off (MWCO) can be measured from the regression line at $R = 90\%$.

2.6 Scanning Electron Microscopy (SEM) Observation

The cross sections and surface morphologies of PES UF membranes were obtained via high voltage scanning electron microscope after coating with gold. Samples of

membranes were frozen in liquid nitrogen to obtain clean break [14]. The samples were placed on a studs. The samples were then sputter coated with gold before being viewed with the SEM (Philip SEM Model XL-40) with 10 000 times magnification.

2.7 Atomic Force Microscopy (AFM) Analysis

The surface morphology (2D and 3D topographic images) and roughness analysis of mean roughness (R_a), the root mean square of Z data (R_z) and the mean difference in the height between the five highest peaks, and the five lowest valleys (R_v) for PES UF membranes with PEG of different molecular weights as additives in scan area of $2\ \mu\text{m} \times 2\ \mu\text{m}$ were characterized using Atomic Force Microscope model Shimadzu SPM-9500J2 at AMREC, SIRIM Berhad.

3.0 RESULTS AND DISCUSSION

3.1 Solute Separation, Flux, and Pure Water Permeation (PWP)

The performance of solute separation and flux after heating at different temperatures are presented in Figure 1. It is observed that solute separation of the membrane increased when heating temperature is increased from 50 to 150°C. PES UF membrane showed the highest solute separation of 97.6% at 150°C heating temperature. Performance of flux decreased with increased heating temperature.

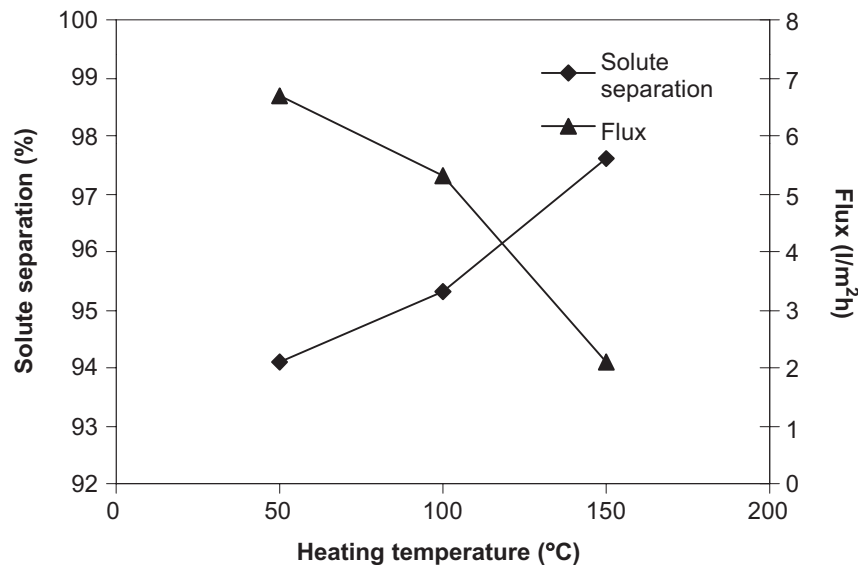


Figure 1 Performance of solute separation and flux using PEG 35kDa as solute after heating at different temperatures

The heat treatment may have caused a reduction in pore size and the densification of the thin layer thus resulting in increased solute separation but lower flux.

The effect of heat treatment is clearly observed upon comparison of PES ultrafiltration membranes heated at 50, 100 and 150°C and the untreated PES ultrafiltration membrane for pure water permeation as shown in Table 1. PES ultrafiltration membrane without heating exhibits $14.0 \text{ lm}^{-2}\text{h}^{-1}$ pure water permeation. As heating temperature increased from 50 to 150°C, pure water permeation decreased drastically from 12.5 to $4.70 \text{ lm}^{-2}\text{h}^{-1}$.

Table 1 Pure water permeation at different heating temperatures

Heating temperature (°C)	Without heating	50	100	150
PWP, $\text{lm}^{-2}\text{h}^{-1}$	14.0	12.5	6.50	4.70

3.2 Molecular Weight Cut Off (MWCO) Profiles

Further studies were carried out using PES UF membrane containing PEG 200 as additive. The membrane samples were heated at 50, 100, and 150°C respectively. Figure 2 shows the MWCO profiles for PES UF membranes without heating and after heating at different temperatures. Ultrafiltration experiments were carried out

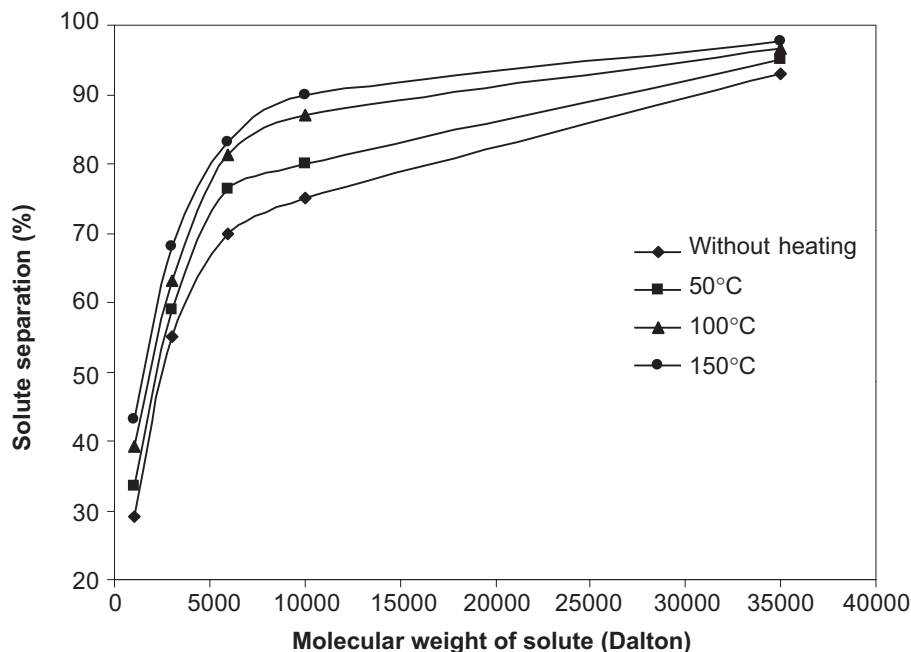


Figure 2 Molecular weight cut off profiles of PES UF with membranes with PEG 200 as additive heated at different temperatures

using PEG with molecular weight ranged from 1000 to 35 000 Dalton. It is observed that PES UF membranes perform diffuse profiles. The profiles clearly demonstrated that MWCO of PES UF membranes decreased with heating temperature from 50 to 150°C. This revealed that heating affects the pore size of the PES UF membranes.

3.3 Membrane Characterization by Solute Transport Data

The effect of heating on PES UF membrane was further analysed in detail using solute transport data. Log normal plots of solute separation versus solute diameter for the membranes without and after heating at different temperatures are presented in Figure 3. Regression line was drawn with high correlation coefficient ($r^2 \geq 0.92$). The Stokes diameter, d_s , for the membranes is calculated using Equation (5). The value of mean pore size (μ_p), standard deviation (σ_p), and molecular weight cut off (MWCO) of the membranes were calculated from solute separation curves and the results are given in Table 2.

As shown in Table 2, the membranes have pore size in the UF range. The results show that as heating temperature increased, the mean pore sizes decreased from 2.63 to 1.62 nm. MWCO for PES ultrafiltration membrane without heating is around 26 000 Dalton. For PES ultrafiltration membranes treated at 50, 100, and 150°C, the molecular weight cut off were measured to be around 20 000, 16 000, and 14 000

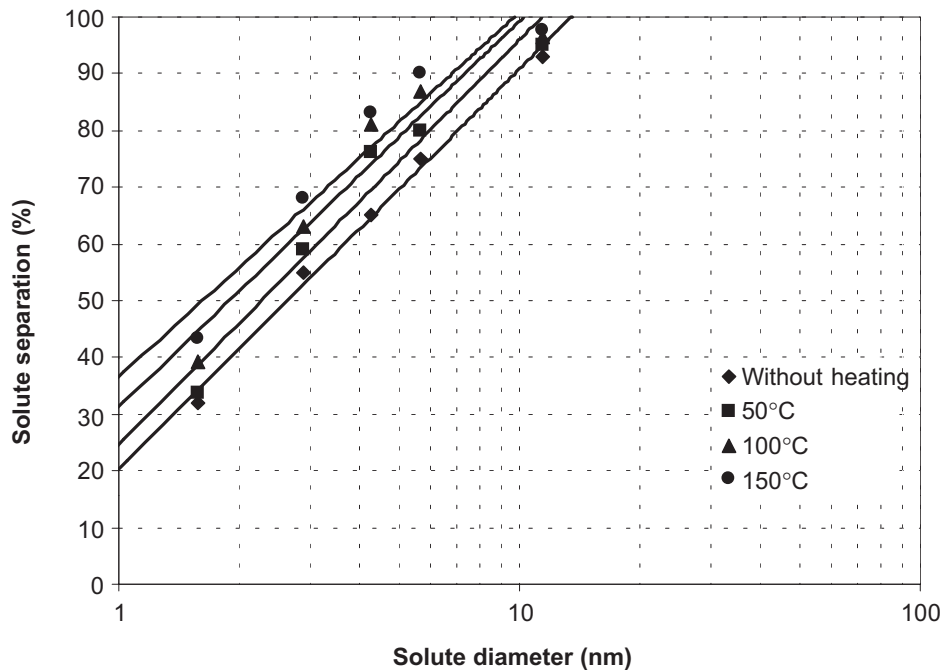


Figure 3 Solute separation curves for PES ultrafiltration membranes after heating at different temperatures

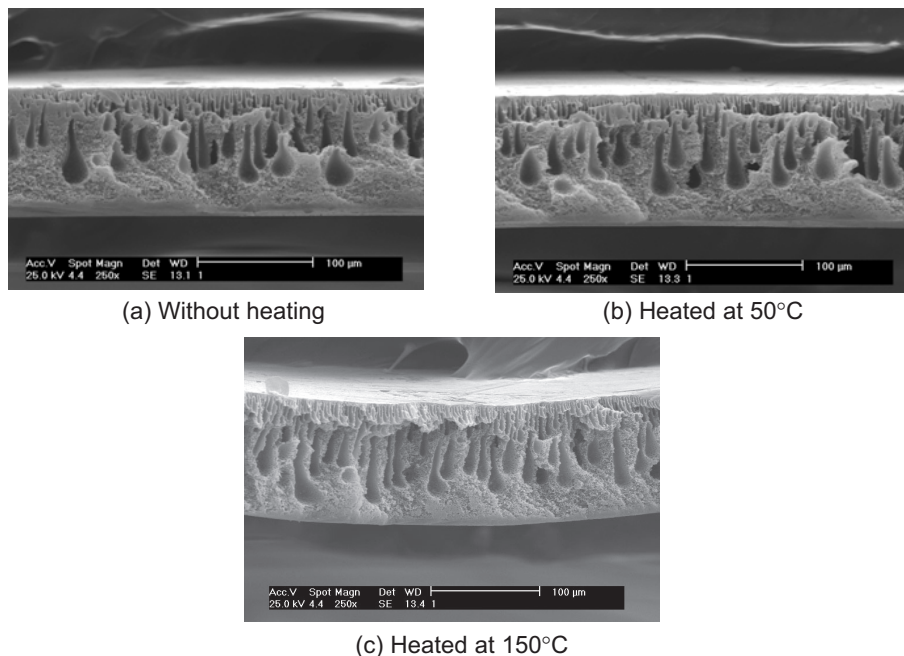
Table 2 Mean pore size, standard deviation, and molecular weight cut off of PES ultrafiltration membranes with different additives calculated from the solute separation curves

Heating temperature (°C)	Molecular weight cut off (kDa)	Mean pore size, μ_p (nm)	Standard deviation, σ_p
Without heating	26	2.63	3.05
50	20	2.27	3.00
100	16	1.89	3.17
150	14	1.62	3.40

Dalton respectively. MWCO acts as a guidance for pore size of membranes where large MWCO implies large pore size of the membrane [15]. Experimental results showed that as heating temperature increased, MWCO gradually decreased. The solute transport data analysis revealed that the pore size of the membrane decreased with an increase in heating temperature, thus explaining for the improved separation performance of the UF membranes.

3.4 Effect of Heating on Membrane Morphology

It is important to investigate whether any morphological changes occurred after heating treatment. The SEM images of cross-sectional PES UF membranes before and after

**Figure 4** SEM photograph of cross section of PES membranes without and after heating for five minutes

heating at different temperatures are presented in Figure 4. There seemed to be a reduction in the pore and macrovoids sizes though not too distinct for membrane heated at 50°C, as shown in Figure 4(b) compared to membrane without heating. The difference is very much visible for the membranes heated at 150°C as shown in Figure 4(c), where the macrovoids for the membranes heated at 150°C seem to be narrower and smaller compared to those without heating and heated at 50°C. The results seem to be in line with previous work on mixed matrix macroporous hollow fiber membrane where heating implies a reduction in porosity due to heat treatment [5]. The results are also in line with work done by Barzin *et al.* [6], where the finger like structure of PES hollow fiber membrane becomes narrower after heated at 150°C compared to membrane without heating.

Further analysis was performed by investigating the surface of the membrane changes after heating at different temperatures. Figure 5 shows the SEM images of membrane surfaces at 10 000x magnification. It is clearly observed that the surface of the membrane changed with different heating temperatures. Previous work by researchers [3] indicated that the membrane surface of PES hollow fiber membrane containing PVP 10000 as additive becomes rougher with increased heating temperature from 180 to 210°C.

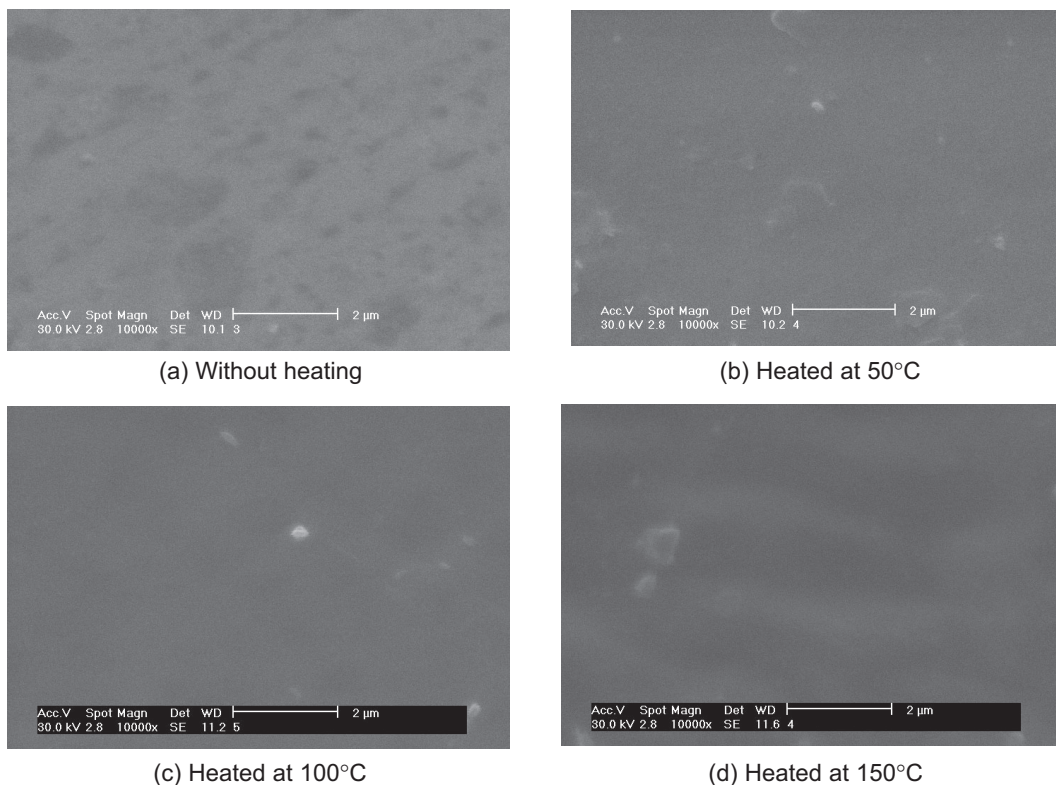


Figure 5 SEM images of the surface of PES membranes without and after heating for five minutes

In order to prove that the surface morphology and roughness of the membrane were affected by the heat treatment, Atomic Force Microscopy (AFM) analysis was carried out on the membrane samples. AFM analysis of the membranes was characterized at a scan size of $2\ \mu\text{m} \times 2\ \mu\text{m}$. Figure 6 shows the 2D and 3D AFM images of PES UF membrane without heating. The topographic images showed that the nodules are merged.

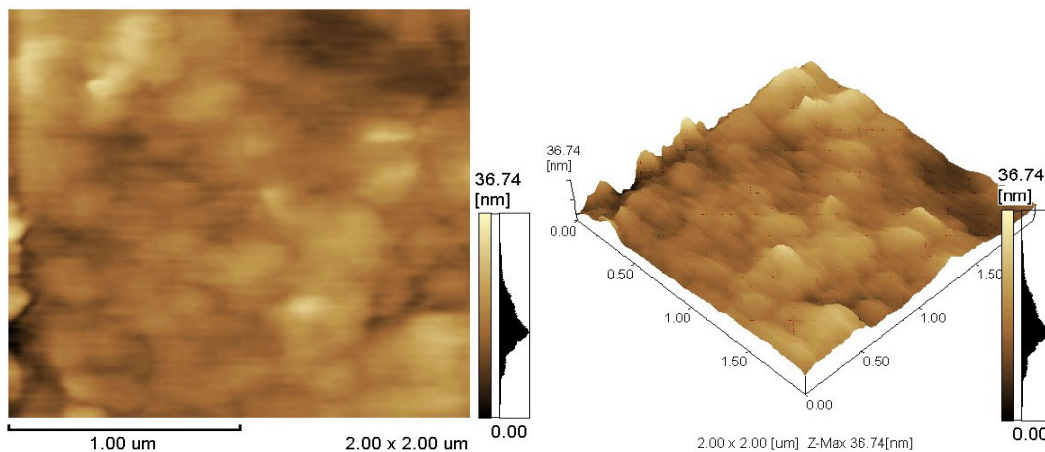


Figure 6 AFM images of PES UF membrane without heating

Figure 7 shows the AFM topographic images for PES UF membranes after heating at different temperatures. Visual differences are observed for the membrane which was heated at 50°C where the nodules are seen not to merge compared to the membrane without heating. The modules of membrane heated at 100°C shown in Figure 6(b) do not merge and are in rows. Figure 6(c) shows the topographic image of the membrane which was treated at 150°C where the nodules are not merged, in rows, and well defined.

The results for roughness parameter, R_a , R_q , and R_z characterised by AFM for PES UF without heating and after heating at 50 , 100 , and 150°C for five minutes are presented in Table 3.

The results revealed that the mean roughness, R_a , for PES UF membrane without heating is 3.288 . When the membrane shrinks, the surface of the membrane becomes rougher and this is indicated by the increase in the roughness parameter, R_a . The mean roughness increased up to 5.137 and 9.409 for 100°C and 150°C respectively. The surface roughness increased due to the degradation of the surface at high temperatures.

The results seems to be in line with work done by other researchers where they reported that the inside surface of PES hollow fiber membranes containing PVP

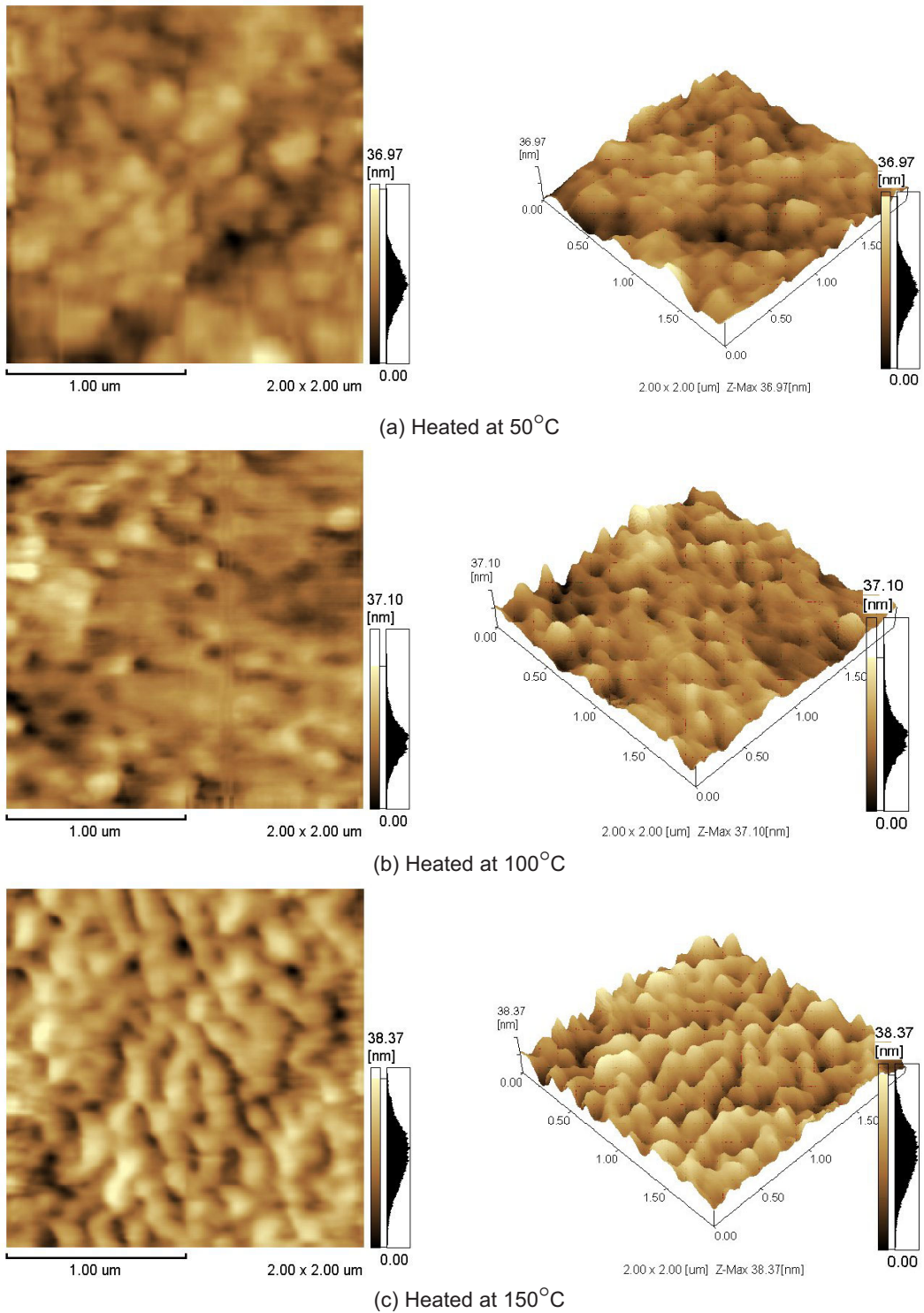


Figure 7 AFM images of PES UF membranes after heating for five minutes

Table 3 Roughness parameters for PES UF membranes heated at different temperatures

Heating temperature (°C)	R_a	R_q	R_z
Without heating	3.288	4.225	33.787
50	3.740	4.752	37.557
100	5.137	6.351	39.855
150	9.409	12.738	112.343

with 10 000 molecular weight as additive looked smooth before heating. There is no change of the surface until heat treatment reached 180°C, where the surface becomes rougher [3]. The membrane flux decreased tremendously when heating temperature increased from 50 to 180°C. Newton *et al.* [16] studied the effect of heat treatment on polyacrylonitrile (PAN) membranes and reported that as heat temperature increased, the roughness parameter increased, attesting that high heat supply has caused the degradation of the microroughness of surface. The chemical evolution of the layer is probably accompanied by release of gaseous product which increases the microroughness of the film.

Flux is dependent on the porosity of the membrane. In this study, heat treatment reduces the porosity of the membranes presented by SEM observation. Using the solute transport data calculation, it was found that increased temperature in the heat treatment reduces the pore size of the membranes as the membranes shrank after heating. This explains for the decrease in flux rates and increase in solute separation for the membrane with heat treatment.

4.0 CONCLUSIONS

PES UF flat sheet membranes have been prepared and pre-treated by heat treatment to enhance the membrane performance. Experimental results revealed that heat treatment decreased pure water permeation as well as flux rates and increased solute separation. The MWCO and mean pore sizes of PES UF flat sheet membranes decreased by heating. The analysis of solute transport data allows fine structural details to be proposed and explained the performance of PES UF membrane. The calculated results indicated that the pore size reduces as the heating temperature increased. SEM observation showed that the surface of the membrane changed and there was reduction in porosity after heat treatment. AFM analysis revealed that the morphology of the membrane surface changed by heating and the roughness parameter increased.

ACKNOWLEDGEMENTS

The financial support from the Ministry of Science, Technology and Environment through the IRPA funding vote no. 74170 is gratefully acknowledged.

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