

Polystyrene derivative-blended nanocomposite membranes for pervaporation dehydration of hydrazine

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Abstract—Hydrazine is an inorganic chemical that has found use in various applications, such as fuel for jets, rockets, missiles and space shuttles. In the present study, polystyrene (PS) based membranes were developed and explored for hydrazine dehydration by pervaporation process. In addition to the separation performance, the physiochemical and morphological characteristics of the membranes were assessed and correlated to the findings. Investigation of the effects of structural and operating parameters revealed that increase in the membrane thickness enhanced selectivity and separation index (PSI) to 18.79 and 61, respectively. In addition, raising feed temperature from 36 °C to 56 °C caused increments in membrane flux, selectivity and PSI. However, increasing feed flow rate only improved water flux. Membranes exhibited reasonable flux and separation performance for the wide range of studied feed compositions. Two modification methods were employed to tailor the characteristics of PS membranes. Blending PS with acrylonitrile butadiene styrene (ABS) led to 27% improvement in total flux while selectivity and PSI reached to as high as 14.3 and 104.6, respectively. Also, nanocomposite membranes containing 2 wt% TiO₂ exhibited total flux of 30.9 (g/m²·h) and PSI of 175.9.

Keywords: Hydrazine Hydrate, Pervaporation, Polystyrene, Nanocomposite Membrane, Polymer Blend

INTRODUCTION

Advances in science, research and technology have led to the emergence of new chemicals that are more environmentally friendly, have higher energy content as well as requiring less resources and production costs [1]. Hydrazine is an inorganic chemical that has been put into use for various applications such as fuel for jets, rockets, missiles and space shuttles [2]. Other applications of hydrazine include corrosion inhibition, heat stabilization, oxygen scavenging and as reducing agent in the metal industry. Aside from its widespread applications in the energy sector, hydrazine and its derivatives have found diverse applications in organic synthesis for agricultural and pharmaceutical industries as well as in thin film transistors for displays.

Hydrazine, owing to its featured characteristics, is regarded as one of the rivals of hydrocarbons. For instance, volatility and flammability of hydrazine are less than conventional fuels. In comparison, hydrazine also degrades in a relatively faster pace. Upon combustion, hydrazine generates large amounts of energy as heat and the reaction products are water and nitrogen. This is in contrast to carbon dioxide as combustion product of hydrocarbons, which is one of the main culprits of global warming. These features have intro-

duced hydrazine as an environmentally friendly chemical.

The prevailing reactions for the production of hydrazine involve formation of hydrazine hydrate requiring a dedicated dehydration process afterwards for water removal to generate anhydrous hydrazine [3]. Conventional distillation plants can only achieve 71.5% hydrazine solution because of the formation of azeotropic mixture, which makes further purification impossible in such a system. In addition, hydrazine is very prone to explosion in the presence of oxygen at elevated temperatures, imposing extra risks to the use of distillation process for this purpose.

Membrane separation processes since their emergence have found widespread acceptance for a variety of applications, including gas and vapor separation [4-6], desalination [7-11], water and wastewater treatment [12-14] among others. As one of the attractive processes, pervaporation (PV) enables separation of liquid mixtures based on their different transport rates. The transport in PV is governed by the solution-diffusion mechanism in which the liquid feed mixture comes into close contact with the membrane surface, followed by the preferential absorption of component into the membrane matrix in the form of vapor. The sorbed molecules diffuse at different rates according to their size across the membrane thickness, relying on the chemical potential gradient as the prevailing driving force, resulting in the separation of components at the other end of the membrane [15-17].

Hydrazine dehydration by PV has been proposed as an alternative to distillation and favorable in terms of energy saving, simple

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and efficient operation and with low risks. Most importantly, unlike distillation, PV has no limitations in dealing with azeotropic mixtures and can be used for dehydration of aqueous organic mixtures, as well as for purification of aqueous solutions consisting of heat-sensitive and low volatile compounds [18-20].

A few studies have been devoted to the PV dehydration of hydrazine [21-29]. Ravindra et al. [21] prepared ethylcellulose based PV membranes for dehydration of hydrazine and monomethylethylhydrazine (MMH). They reported that due to the low sorption and poor interaction with water, the membranes showed the least desorption resistance towards water. Moreover, higher sorption of hydrazine and MMH did not result in preferential separation in spite of lower membrane resistance. Their findings suggested that desorption resistance and diffusivity were predominant factors compared to corresponding solubilities. Satyanarayana and Bhattacharya [22] explored the performance of several hydrophilic and hydrophobic polymers, including PERVAP® as a commercial membrane as well as polystyrene, acrylonitrile butadiene styrene (ABS) and modified ethyl cellulose as laboratory made membranes for dehydration of hydrazine hydrate. Except PERVAP®, the rest of the membranes exhibited better performance compared to the distillation process. Their results suggested higher separation efficiency for apolar membranes than polar ones. They also highlighted the effective role of diffusion than sorption in the transport of species. Mandal et al. [23] prepared membranes based on ethyl cellulose (EC) and ABS for dehydration of a commercial grade hydrazine hydrate. Their findings revealed that addition of ABS into EC and increase in its portion in the blend membrane reduced the amorphous characteristics of the membranes with subsequent reduction in flux. This was attributed to the increased hydrophobicity of the membranes contributed by the presence of ABS in the membrane matrix. However, pervaporation separation index (PSI) values improved, which was in conjunction with the significant reduction in membrane free volume upon addition of ABS. Sridhar et al. used cross-linking method for improving the performance of chitosan membrane for pervaporative separation of dimethylethylhydrazine (DMH) [24]. They reported that the cross-linked chitosan membrane effectively enriched the aqueous azeotrope of the propellant (20 wt%) to purity beyond 90%. They also demonstrated that an increase in feed concentration or membrane thickness led to a drop in membrane flux and selectivity due to the strengthened bond between water and DMH and higher transport resistance, respectively. Similarly, increase in permeate pressure negatively affected membrane performance due to reducing the required driving force.

Besides the experimental studies, Hoda et al. [25] performed mathematical modeling and a simulation study on the pervaporative separation of hydrazine/water mixtures using hollow fiber membrane modules. Their findings indicated the formation of an azeotrope at water concentration of 17.5 and 28.42 wt% at the membrane lumen and shell sides, respectively, which was in contrast to the azeotropic water concentration of 28.5 wt% in distillation. This study also suggested the use of a better selective membrane or a hybrid process for this application.

An important point to consider is the high alkalinity of hydrazine as a powerful hydrolyzing and reducing agent, which limits the choice of eligible candidates as polymer material for membrane

fabrication. Polystyrene (PS) is one of the engineering polymers with good thermal stability and chemical resistance [30]. However, the problems associated to PS are brittleness and hydrophobicity in majority of its grades. A surprising aspect of PS is that despite its widespread applications in variety of commodity products over the years, its potential as membrane material has been rarely explored. Based on our comprehensive literature survey, limited studies were found on the development of PS membranes focusing on gas separation and water treatment applications and none on PV [31-34].

The main aim of the present study was to explore the potential of PS based membranes for hydrazine dehydration through PV process. In addition, the effects of various important parameters including membrane thickness, feed temperature, flow rate and composition on the separation performance were investigated. Another aspect of the study was to improve the characteristics and separation performance of PS membranes, and accordingly two strategies were used to accomplish this objective. First, ABS was blended with PS and its contribution to the membrane properties and performance were evaluated at selected compositions. Second was through incorporation of TiO₂ nanoparticles and preparation of nanocomposite membranes. The effect of nanoparticles and variation in their concentration within the membrane matrix were investigated. To the best of our knowledge, this is the first systematic study on the fabrication of PS membranes and exploring the potential of derived membranes in the PV process, particularly for hydrazine dehydration. In addition, no prior reports could be found on the performance of PS/ABS blend and PS/TiO₂ nanocomposite membranes for such a process and application explored in the course of this study.

EXPERIMENTAL

1. Materials

Hydrazine hydrate in the form of concentrated water-based solution was purchased from Arkema Co. (France) and was further diluted with water for preparation of feed samples with desired compositions. Acrylonitrile-butadiene-styrene (ABS) (grade: 600 PW) including 60% rubber with density of 0.99 g/cm³ was purchased from Ghaed Basir Petrochemical Company (GBPC), Iran. Polystyrene (PS) (grade: GPPS 1160), including less than 500 ppm additional styrene monomer with density of 1.04 g/cm³ and MFI

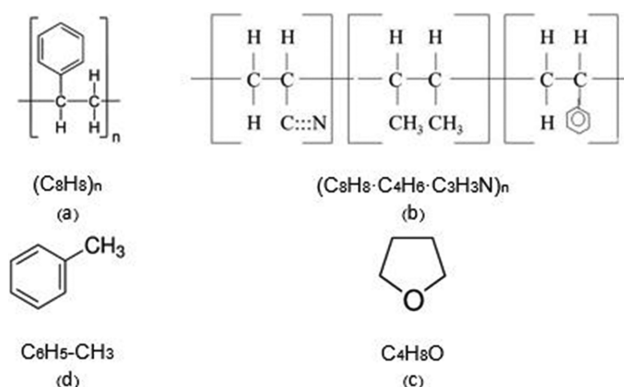


Fig. 1. The chemical structure and formula of polymers and solvents: (a) PS (b) ABS (c) THF (d) Toluene.

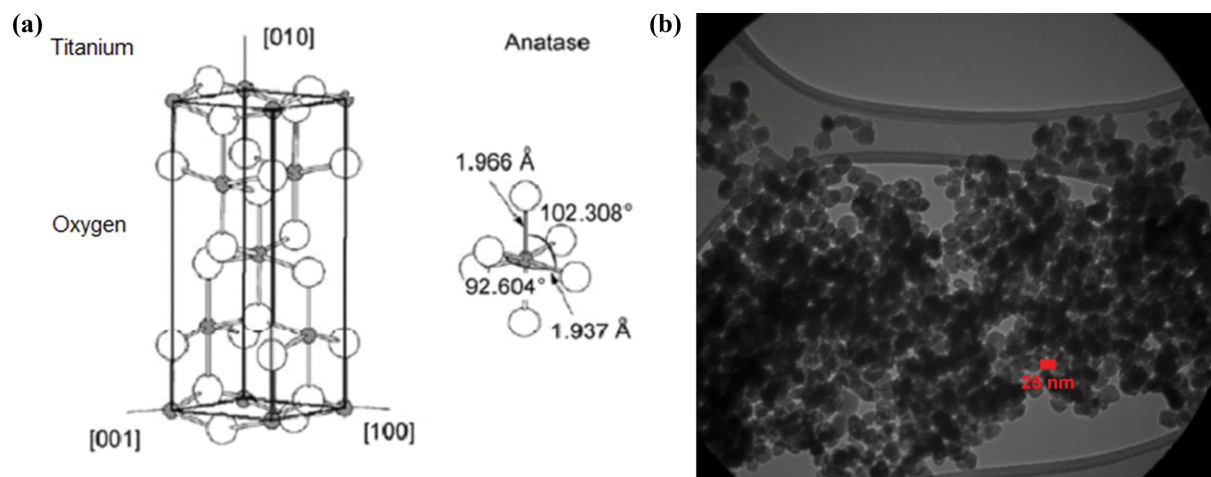


Fig. 2. (a) 3D anatase structure and (b) TEM image of TiO_2 nanoparticles (Source: <http://www.us-nano.com>).

of 2.5 g/10 min, was obtained from Tabriz Petrochemical Company (TPC), Iran. Tetrahydrofuran (THF) (CAS No. 109-99-9) was purchased from Merck (Germany) and used as the solvent for the preparation of dope solutions from PS and its derivative nanocomposites. Toluene (CAS No. 108-88-3) also from Merck was used as the solvent for preparation of dope solutions from PS/ABS blends. The chemical structure of polymers and solvents is shown in Fig. 1. TiO_2 nanoparticles with tetrahedron molecular structure (anatase) and particle size range of 10-25 nm were obtained from US Research Nanomaterials Co. and used for the preparation of nanocomposite membranes (Fig. 2).

2. Preparation of Neat Membranes

Dense symmetric membranes were fabricated by solution casting followed by solvent evaporation. Prior to the preparation of dope solutions, both PS and ABS polymers were dried in a vacuum oven at 50 °C for 12 hours. PS was dissolved in THF by stirring for about 4 hours, while ABS was dissolved in toluene by stirring for about 24 hours at room temperature. The concentration of polymer in both solutions was 5 wt%. After homogeneous solutions were obtained, they passed through a filter mesh to remove any residual dust and undissolved solids and then allowed for degassing. The solutions were poured into a petri-dish and then placed in a vacuum oven at room temperature and 0.2-0.4 bar for solvent evaporation. After about 3 to 4 days, nascent films were peeled off by pouring small amount of deionized water into the dish. To ensure residual solvent removal, membranes were then put in a vacuum oven at 50 °C for 12 hours and then stored in desiccator until use. Membranes were prepared in the thickness range of 25-80 μm measured by micrometer (accuracy $\pm 1 \mu\text{m}$).

3. Preparation of Blend Membranes

To prepare PS/ABS blended membranes, first ABS powders were dissolved in toluene. Then PS granules were gradually added to the solution at PS/ABS composition of 15/85 wt%, 10/90 wt% and 5/95 wt%, respectively. Stirring was continued until complete dissolution and mixing of the ingredients. Similar to the neat membranes, the total polymer concentration of all solutions was controlled at 5 wt%. The casting and drying were conducted similar to the procedure used in the preparation of neat membranes. The aver-

age thickness of membranes was $50 \pm 1 \mu\text{m}$.

4. Preparation of Nanocomposite Membranes

To prepare nanocomposite membranes, TiO_2 nanoparticles were first dispersed in THF and rigorously stirred for 4 hours. The suspensions were then placed in an ultrasonic bath for 15 minutes to break down any agglomerations, followed by gradual addition of PS granules in four parts while stirring. The total solid content including polymer and nanoparticle in the dopes was controlled at 15 wt% in order to have enough viscosity to prevent sedimentation of nanoparticles. The ratio of TiO_2 nanoparticle to polymer was controlled in a range of 0.1-5 wt%. After complete homogeneity, dope solutions were degassed followed by casting and solvent removal. The average thickness of membranes was $50 \pm 1 \mu\text{m}$.

5. Performance Analysis

Membrane flux and separation factor were evaluated using a lab-scale PV set-up schematically shown in Fig. 3. The membranes were cut in the size of $\sim 4 \times 6 \text{ cm}$, mounted in the cell and sealed using aluminum tapes. A centrifugal pump was used to transfer feed (at 1 bar) to the cell and the flow rate was regulated in the range of 0.5-5 L/min with a needle valve. The feed could either permeate through the membrane in cross-flow mode or exit as a retentate stream. To maintain a constant feed concentration, the retentate stream always returned to the feed tank and circulated within the system. The permeate stream was condensed in a cold trap tube submerged in a liquid nitrogen tank at temperature of about -150 °C. The permeate side pressure was maintained at 0.05 mmHg using a strong vacuum pump to maintain the desired driving force.

The permeate stream composition was determined using an iodometry titration method as reported elsewhere [35], in which the appearance of elementary iodine indicates the end point. In this method, hydrazine first reacts with periodate according to Eq. (1) and results in the formation of iodate.



Next, according to Eq. (2) iodate is transformed into iodine in acidic condition in the presence of I^- :



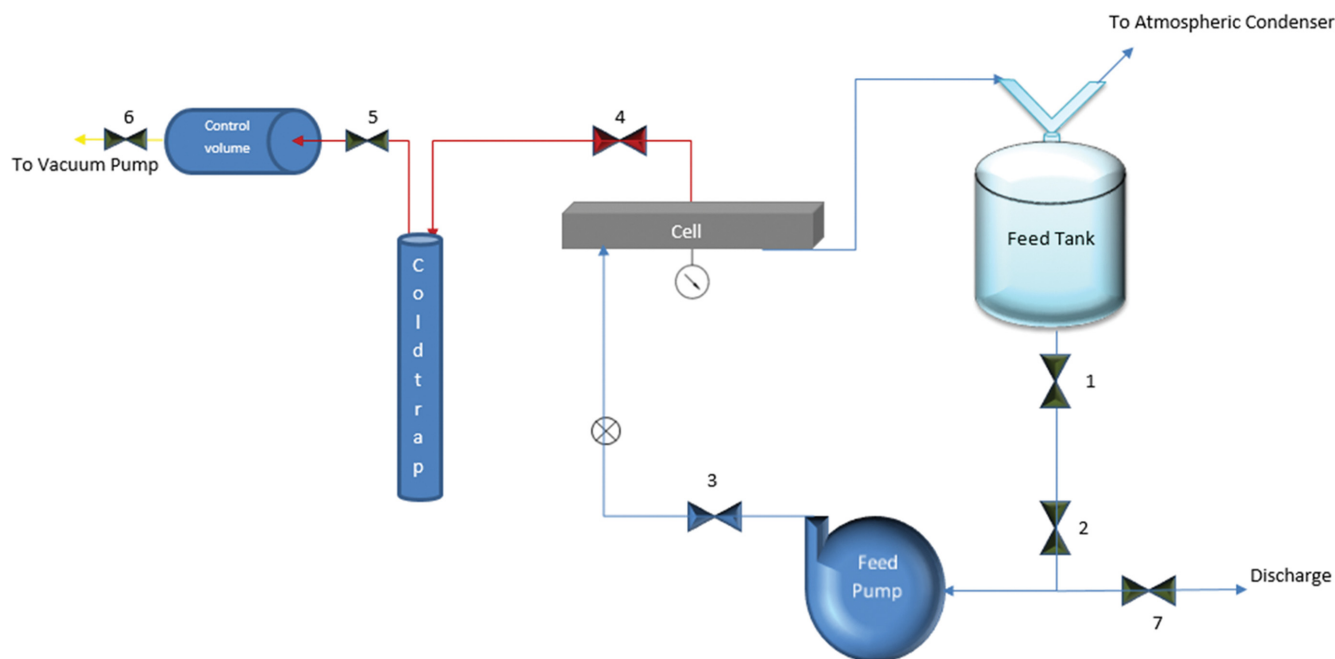


Fig. 3. A schematic representation of the lab-scale PV set-up.

In the last step, the amount of iodine is measured by titration using thiosulfate according to the following equation:



The concentration of hydrazine for each sample was calculated considering the stoichiometry involved in the reactions as follows:

$$\begin{aligned} \% \text{N}_2\text{H}_4 &= V \text{ ml S}_2\text{O}_3 \cdot M \text{ mole/1,000 ml} \cdot \\ &1 \text{ mole I}_2/2 \text{ mole S}_2\text{O}_3 \cdot 1 \text{ mole IO}_3/3 \text{ mole I}_2 \cdot \\ &1 \text{ mole N}_2\text{H}_4/2 \text{ mole IO}_3 \cdot 32 \text{ g N}_2\text{H}_4/1 \text{ mole N}_2\text{H}_4 \cdot \\ &1/M \text{ N}_2\text{H}_4 (\text{solution}) \cdot 100 \end{aligned} \quad (4)$$

It must be highlighted that hydrazine is a very hygroscopic substance that absorbs carbon dioxide; thus, attention must be paid to carrying out the analysis right after sample collection to prevent errors in the results.

Performance of the membranes was analyzed in terms of permeation flux and composition. The permeation flux ($\text{g}/\text{m}^2 \cdot \text{h}$) was calculated gravimetrically using Eq. (5) as follows:

$$j = \frac{m}{A \cdot t} \quad (5)$$

in which m is the weight of collected liquid permeate (g), A is the effective membrane area (m^2), and t is the time period (h) for permeate collection. The partial permeation flux was calculated based on the total flux and permeate composition.

Since membranes were produced at different thicknesses, the flux was normalized based on the membrane thickness of $50 \mu\text{m}$ and denoted as J using Eq. (6) as follows:

$$J = \frac{j \cdot l}{50} \quad (6)$$

where l is the membrane thickness. Such normalization is accord-

ing to the Fickian behavior during mass transport through the membrane.

Selectivity defined by the separation factor (α) and PSI was evaluated using Eqs. (7) and (8), respectively.

$$\alpha = \frac{y/(1-y)}{x/(1-x)} \quad (7)$$

$$\text{PSI} = J(\alpha - 1) \quad (8)$$

where y and x stand for the water mass fractions in the permeate and feed, respectively.

6. Characterization

The morphology of the fabricated membranes was analyzed using SEM SERON AIS-2100. Small samples were fractured in liquid nitrogen and sputter-coated by gold to improve conductivity. Thermomechanical properties of membranes were evaluated by thermal scanning in extended state using DMA242C (Netzsch) equipment. The exerted frequency and rate of temperature increase were 1 Hz and 2°C , respectively. Data analysis was accomplished using the built-in Proteus module.

Contact angle of membranes was evaluated by sessile drop method using a Jikan-CAG-10 goniometer. Deionized water droplets were placed on five different spots at the membrane surface to ensure the reported values represent the overall membrane surface characteristics.

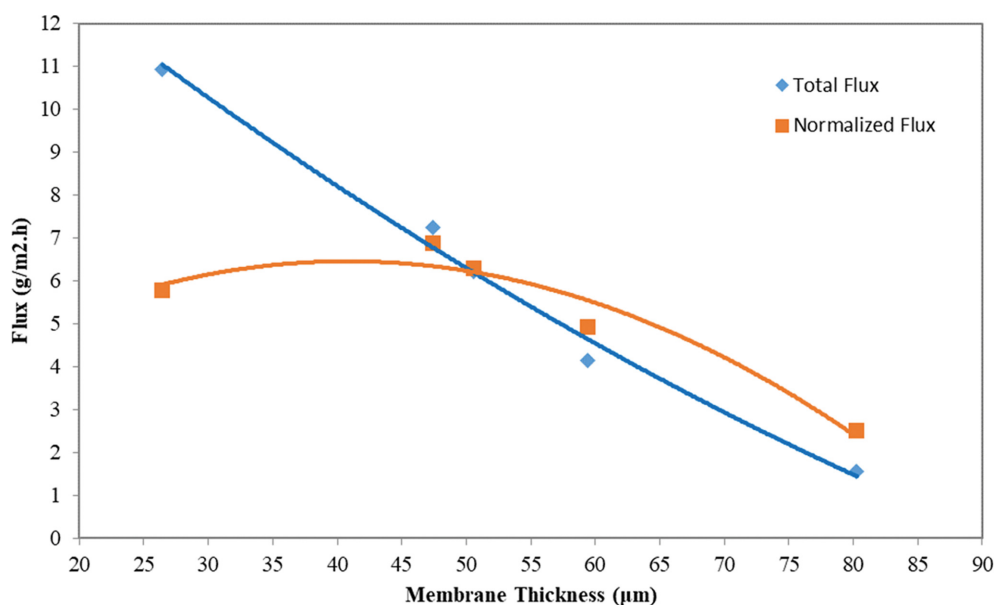
The thermogravimetry (TG) analysis was carried out using a Shimadzu TGA-50H instrument. Each sample in a mass of about 2 grams was uploaded into the TG platinum pan and heated at the rate of $10^\circ\text{C min}^{-1}$ by purging nitrogen at flow rate of 25 mL/min . Experiments were carried out in the range of room temperature to 600°C .

Fourier transform infrared (FTIR) spectroscopy of membranes

Table 1. The effect of PS membrane thickness on the flux, selectivity and PSI*

Membrane thickness (μm)	Total flux ($\text{g}/\text{m}^2\cdot\text{h}$)	Normalized flux based on $50\text{ }\mu\text{m}$ ($\text{g}/\text{m}^2\cdot\text{h}$)	Hydrazine in permeate (wt%)	Selectivity (α)	PSI
26.5	10.93	5.78	9.09	5.49	49.10
47.5	7.24	6.87	5.49	9.45	61.21
50.6	6.22	6.29	4.85	10.77	60.80
59.4	4.15	4.93	3.82	13.83	53.23
80.3	1.56	2.50	2.84	18.79	27.75

*Testing conditions: Feed composition (Hydrazine/Water): 35.45/64.55 wt%, T: $40\text{ }^\circ\text{C}$, Feed flow rate: 3 L/min, Downstream P: 0.5 mmHg.

**Fig. 4.** The trend of changes in total flux and normalized flux as the function of PS membrane thickness.

was conducted using a Tensor 27 spectrometer (Bruker, USA) in the range of $400\text{--}3,500\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

1. The Effect of Thickness on the Performance of PS Membranes

It is always desirable to make membranes as thin as possible due to the minimized resistance provided to the transport of species. However, reducing the membrane thickness also increases the risk of defect formation. At the same time, tolerance toward the trans-membrane pressure as well as handling is deteriorated. In the PV process, feed solution often causes swelling of membrane materials. On the other hand, the swelling condition on membrane permeate side is less severe [36]. The uneven swollen conditions of PV membrane result in significantly changed normalized flux, PSI, and selectivity. Thus, gaining true understanding about the effect of membrane thickness on the performance characteristics of PV membranes is crucial. This was investigated in the present study on the PS membrane using an experimental approach and by preparation of membranes of different thicknesses ranging from $26.5\text{--}80.3\text{ }\mu\text{m}$.

The results shown in Table 1 indicate that the total permeation

flux was reduced upon increase in the membrane thickness. Specifically, while the total permeation flux for a membrane with a thickness of $26.5\text{ }\mu\text{m}$ was $10.93\text{ g}/\text{m}^2\cdot\text{h}$, it dropped by about 86% to $1.56\text{ g}/\text{m}^2\cdot\text{h}$ as the thickness increased to $80.3\text{ }\mu\text{m}$. According to a general practice relying on the assumption of the presence of a reciprocal relationship between membrane flux and membrane thickness [37,38], the normalized flux was calculated based on $50\text{ }\mu\text{m}$ and the values are plotted along with the total flux data in Fig. 4.

It is evident from Fig. 4 that total flux decreased almost linearly upon increase in membrane thickness. The declining trend of changes based on normalized flux was quite similar to the total flux, except for the membrane possessing the least thickness, which could be attributed to the effect of boundary conditions close to the surface of the thin film. Further insight was obtained by plotting the partial and normalized flux of individual components versus membrane thickness (Fig. 5(a)) and reciprocal membrane thickness (Fig. 5(b)), respectively.

Results shown in Fig. 5(a) indicate that the increase in membrane thickness was effective in reducing the partial flux and partial normalized flux in the case of both water and hydrazine. However, it was interesting to realize that the increase in membrane thickness reduced hydrazine flux by 96% compared to 85% in the case of water. Similarly, considering normalized flux values,

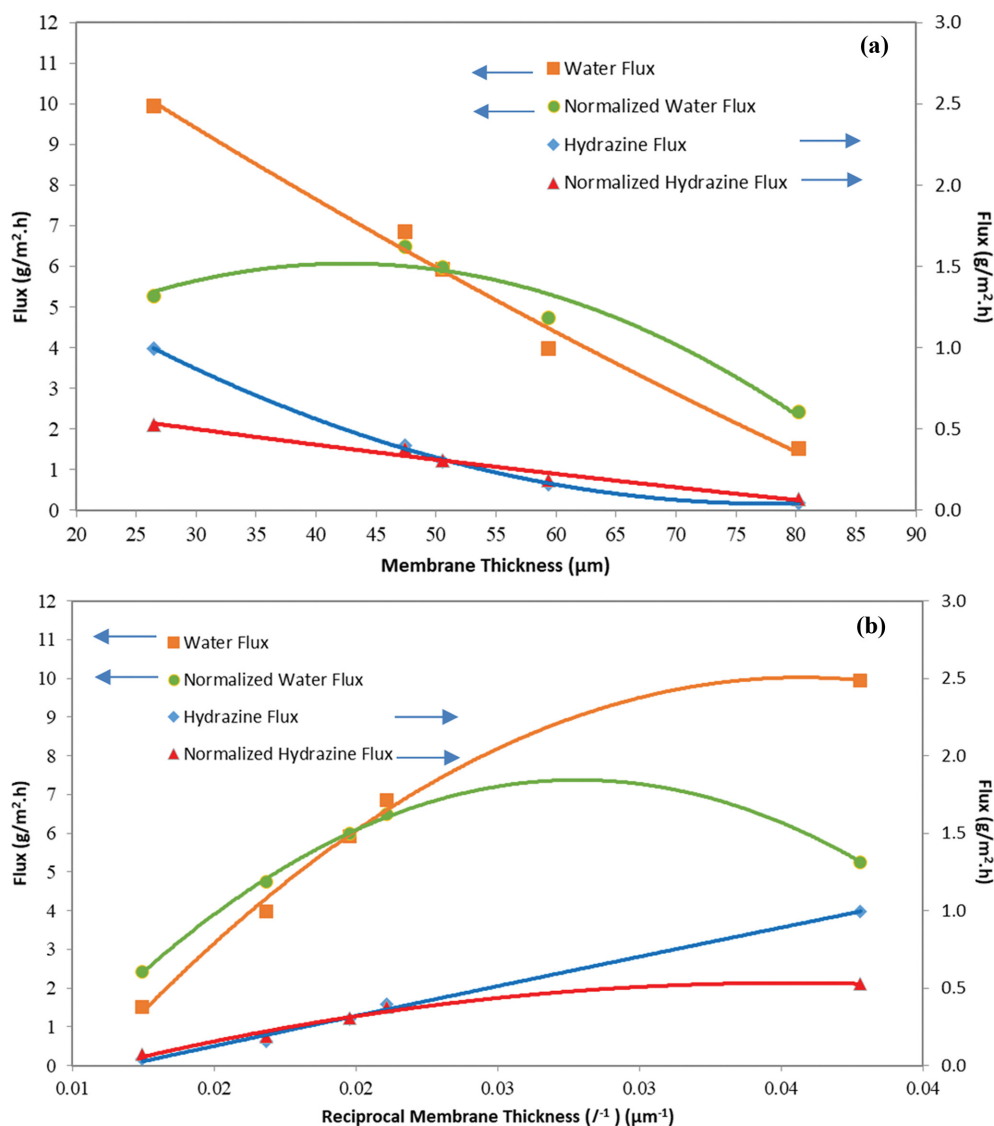


Fig. 5. The trend of changes in partial and normalized fluxes of water and hydrazine versus (a) PS membrane thickness (b) reciprocal membrane thickness.

increase in membrane thickness reduced normalized hydrazine flux by 87% compared to 54% in the case of water. The above findings clearly indicate that membrane thickness affected the flux of both components differently with direct consequence on the separation performance. Thus, the less reduction of water flux compared to that of hydrazine in thicker membranes corroborates the important role of thickness in design and fabrication of membranes with desirable separation performance.

Another interesting finding was that according to the plots in Fig. 5(b), the trend of variation in flux strongly differed depending on the fast and slow permeating species. It could be seen that upon reduction in reciprocal membrane thickness (i.e., increase in membrane thickness) both water flux and normalized water flux reduced polynomially in faster pace, whereas the reduction in hydrazine flux and normalized hydrazine flux followed an almost linear trend in a slower pace. This might suggest that it would be misleading to make any prediction, by either interpolation or extrapo-

lation, about the partial flux of permeating species based on assumption of inverse relationship between flux and thickness.

According to Fig. 6, variation in membrane thickness also affected selectivity and PSI of membranes. PSI values were calculated based on both total flux and normalized flux and according to the plots shown in Fig. 6, water/hydrazine selectivity of membranes improved from 5.49 to 18.79 upon increase in membrane thickness from 26.5 to 80.3 μm , respectively. The results are well in accordance with the observed trends of changes in partial flux of components across the membranes. It was also noted that overall performance of membranes (PSI) improved upon increase in membrane thickness only up to the range of 47.5–50.6 μm . PSI for the membrane with thickness of 26.5 μm was 25.99 and increased to about 61 by increase in membrane thickness to 47.5–50.6 μm . However, PSI reduced upon further increase in the membrane thickness to 80.3 μm , indicating the presence of an optimum thickness that should be taken into consideration in design and fabrica-

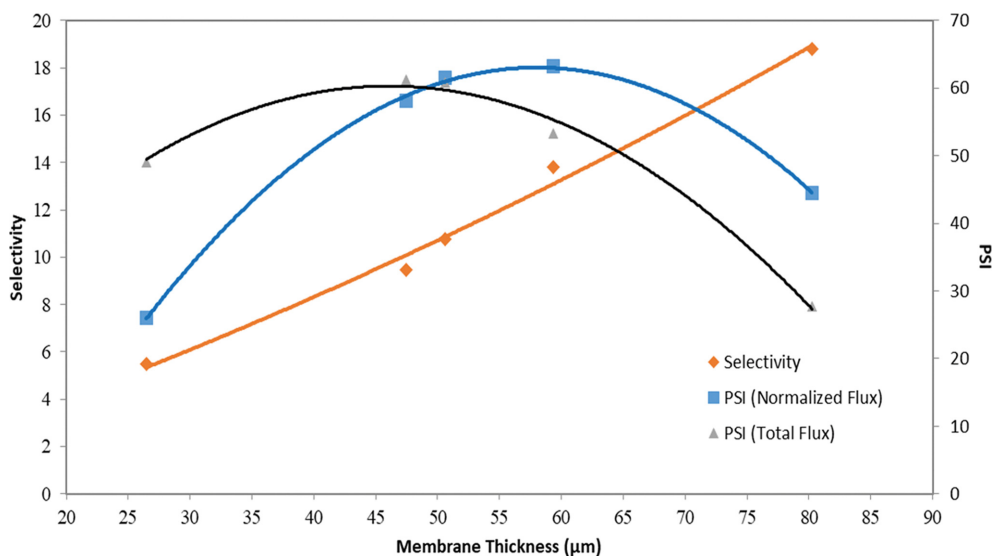


Fig. 6. The effect of variation in PS membrane thickness on selectivity and PSI calculated based on total and normalized fluxes.

tion of efficient membranes. Based on the above findings, the rest of the experiments in this study were conducted on the membranes fabricated at thickness of 50 μm .

2. The Effect of Feed Temperature on the Performance of PS Membranes

Temperature, which is an important factor in the thermodynamic and kinetics of membrane processes, is often used as a viable tool in PV for tuning membrane productivity. In PV, the energy required for the evaporation is supplied by the latent heat of liquid; thus the feed temperature needs to be maintained at the designed level by external heating to ensure process reliability. To gain a better understanding of the correlation between feed temperature and separation performance, the effect of feed temperature in the range of 36–56 $^{\circ}\text{C}$ on the membrane performance was investigated and the results are shown in Fig. 7. It can be seen that an increase in feed temperature led to considerable improvement in total flux of membranes. According to the data in Fig. 7(a), the total flux at feed temperature of 36 $^{\circ}\text{C}$ was 6.38 $\text{g}/\text{m}^2\cdot\text{h}$ and increased by about 68% to 10.75 $\text{g}/\text{m}^2\cdot\text{h}$ at 56 $^{\circ}\text{C}$. Considering the data obtained for feed temperatures of 40 $^{\circ}\text{C}$ and 50 $^{\circ}\text{C}$ indicates that improvement in total flux followed a linear trend in the range of investigation.

Plotting partial flux data for individual components revealed that the major contribution to the observed improved total flux was made by increase in water flux, whereas the contribution by hydrazine flux was minor. With reference to the data, increase in feed temperature from 36 $^{\circ}\text{C}$ to 56 $^{\circ}\text{C}$ improved water flux by 71% to 10.26 $\text{g}/\text{m}^2\cdot\text{h}$, but hydrazine flux only improved by 29% to 0.49 $\text{g}/\text{m}^2\cdot\text{h}$. This corresponds to a higher sensitivity of membrane toward water than hydrazine molecules.

The effect of change in the feed temperature on the separation performance was also evaluated and the results are plotted in Fig. 7(b). Findings revealed that similar to the trends in flux, increase in feed temperature led to considerable increase in membrane selectivity as well as PSI. According to data in Fig. 7(b), water/hydrazine selectivity at feed temperature of 36 $^{\circ}\text{C}$ was 8.79 and increased by about 32% to 11.82 upon increase of temperature to 50 $^{\circ}\text{C}$.

However, the effect of temperature on selectivity was useful up to 50 $^{\circ}\text{C}$ and no considerable change in selectivity was noted beyond that. Also, a high increase was observed in membrane PSI from 49.70 to 113.96 (129%) at 56 $^{\circ}\text{C}$, indicating the strong dependency of PSI on feed temperature.

The effect of feed temperature on the process can be explained by considering its role in the driving force as well as membrane microstructure. Essentially, increase in temperature improves the vapor pressure of the permeating components and this increases the driving force for vapor transport. At the same time, the segmental thermal mobility of polymer chains increases at a higher temperature, which promotes faster formation of transient free volumes as well as extension in the size of free volumes that facilitate diffusion of vapor molecules. Permeation, sorption and diffusion are all activated processes and the temperature effect on these parameters can be described by the Arrhenius relationship. Considering the improved selectivity of the membranes, increase in size of free volumes has been to the extent that the transient volumes still hindered the permeation of hydrazine molecules due to its larger size while facilitating the transport of water molecules and in fact promoting diffusivity selectivity. The sorption may also contribute to process since generally the degree of crystallization is reduced at higher temperatures, which creates more sorption and diffusion sites in membrane structure.

3. The Effect of Feed Flow Rate on the Performance of PS Membranes

Feed flow rate in membrane based separation is important, especially since it directly governs the productivity of process. Therefore, it is always desirable to operate at maximum flow rate while maintaining the efficiency. In this regard, the effect of feed flow rate was investigated in the case of hydrazine dehydration to identify the optimum values. The results are shown in Fig. 8. According to the data in Fig. 8(a), increase in feed flow rate did not affect membrane total flux and the values remained almost unchanged on average in the range of 7.2 $\text{g}/\text{m}^2\cdot\text{h}$. However, the increase in feed flow rate from 1 to 3 L/min improved partial water flux from 5.86

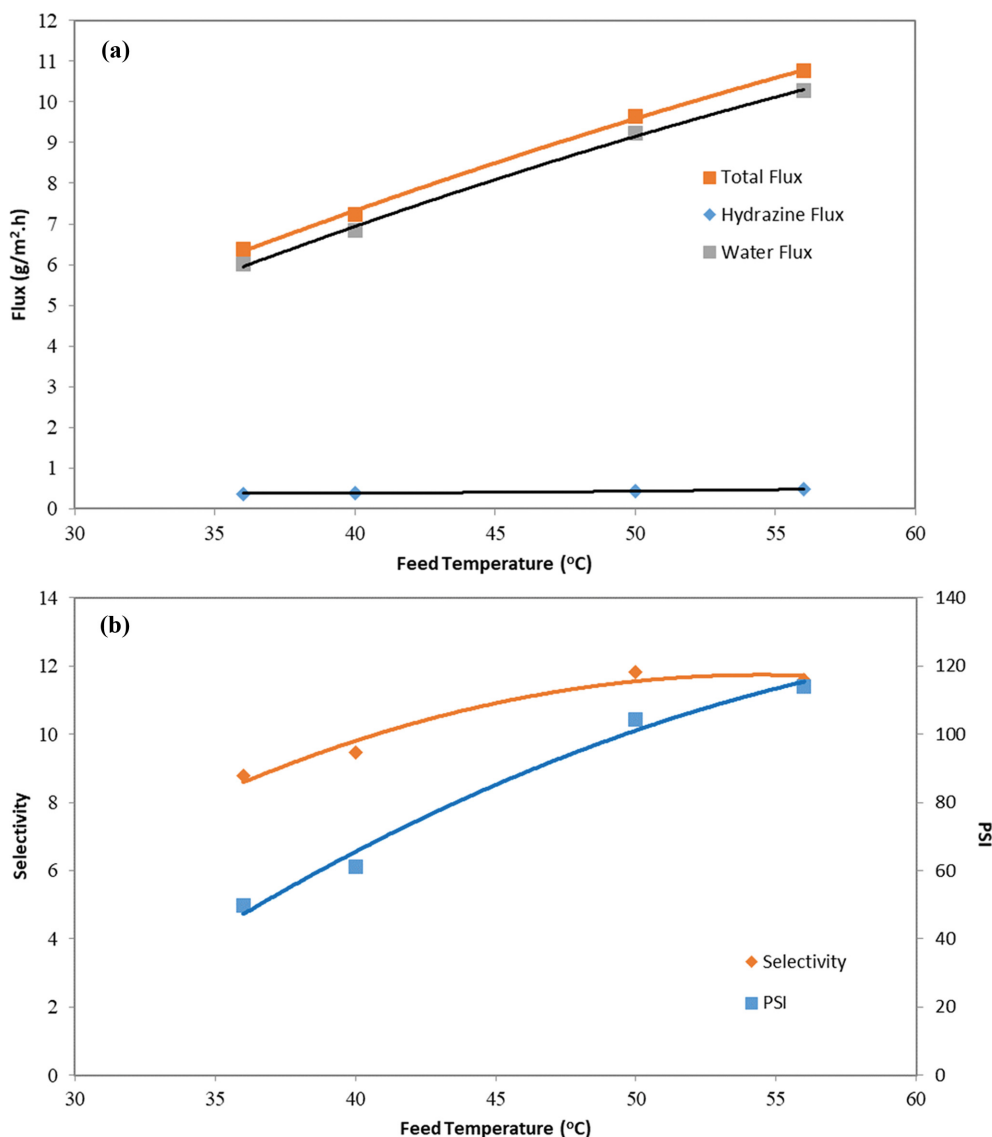


Fig. 7. The effect of feed temperature on the performance of PS membranes (a) total and partial flux of the components (b) membrane selectivity and PSI (Testing conditions: Feed composition (Hydrazine/Water): 35.45/64.55 wt%, Membrane thickness: 47.5 μm , Feed flow rate: 3 L/min, Downstream P: 0.5 mmHg).

$\text{g}/\text{m}^2\cdot\text{h}$ by about 20% to $6.83 \text{ g}/\text{m}^2\cdot\text{h}$. In contrast hydrazine partial flux declined by about 75% from $1.60 \text{ g}/\text{m}^2\cdot\text{h}$ to $0.40 \text{ g}/\text{m}^2\cdot\text{h}$.

The effect of changes in the feed flow rate on the separation performance was also evaluated and results are plotted in Fig. 8(b). Data revealed that in accordance with the trends seen in partial flux, membrane selectivity and PSI values improved significantly. According to Fig. 8(b), water/hydrazine selectivity at feed flow rate of 1 L/min was 1.95 and increased by 3.8 fold to 9.45 upon increase of feed flow rate to 3 L/min. Membrane PSI values followed a similar trend, yet higher intensity of improvement and experienced 7.8 fold increase in the studied range.

The effect of feed flow rate on the process performance can be explained by concentration polarization. Increasing flow rate led to the increased turbulence and mixing of feed components flowing over the membrane surface. Particularly, concentration polarization as the result of much faster permeation rate of water at the close

vicinity of surface boundary of the membrane was minimized due to higher turbulence and replenishment of concentration changes. This enabled continuous exposure of water molecules to the membrane surface based on the bulk composition and facilitating their sorption to the membrane while retarding transport of hydrazine across the membrane. As a result, the overall flux remained unchanged due to the compensated increased water flux by equivalent reduction in hydrazine flux. Overall, the increase in feed flow rate was found effective in boosting membrane selectivity and PSI while maintaining total flux.

4. The Effect of Feed Composition on the Performance of PS Membranes

Based on the above findings, membranes were investigated to evaluate their response with regards to the changes in feed composition. The results of variation in hydrazine concentration in the range of 34.45–82.02 wt% on the process performance are provided

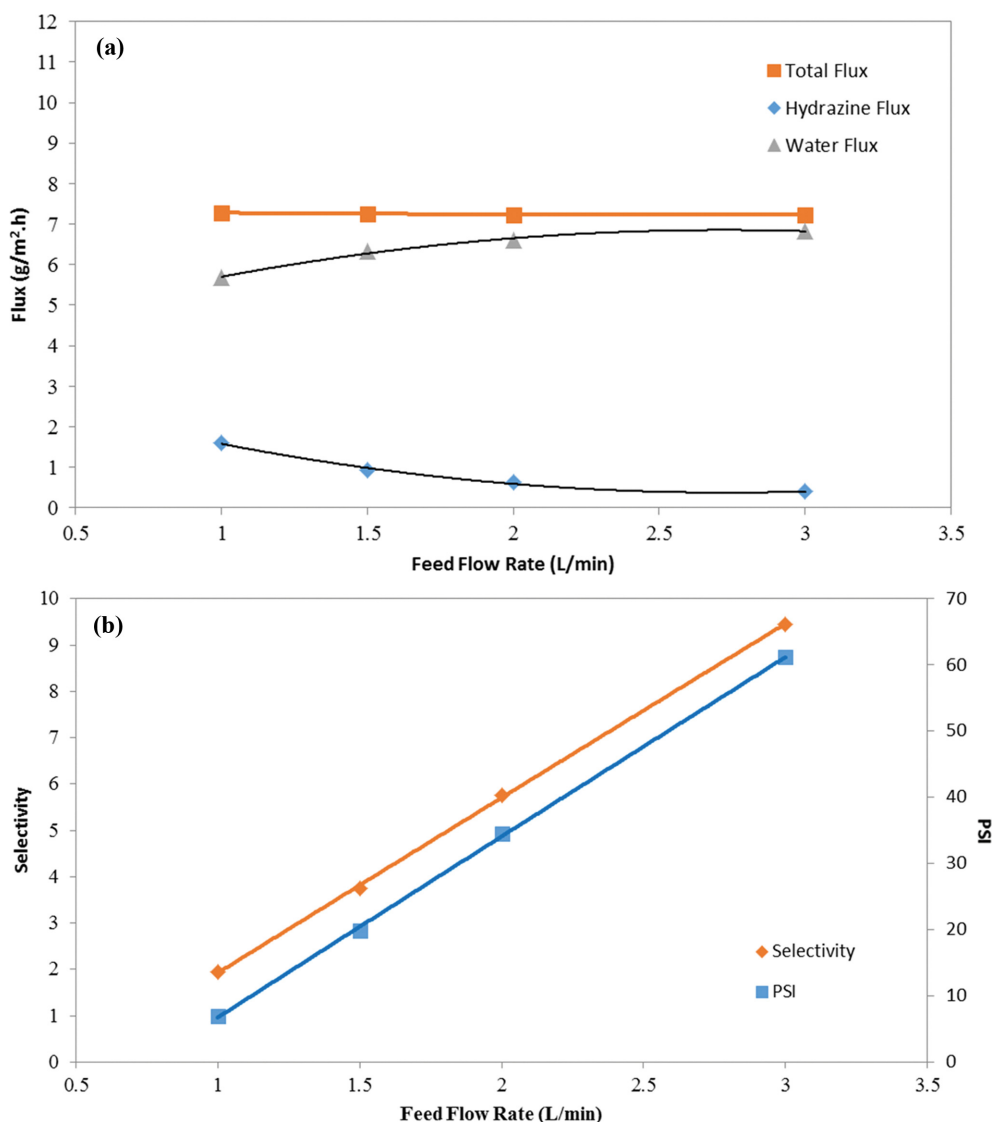


Fig. 8. The effect of feed flow rate on the performance of PS membranes (a) total and partial flux of the components, (b) Selectivity and PSI. (Testing conditions: Feed composition (Hydrazine/Water): 35.45/64.55 wt%, Membrane thickness: 47.5 μm , Downstream P: 0.5 mmHg, T: 40 $^{\circ}\text{C}$).

in Fig. 9.

According to data in Fig. 9(a), increase in hydrazine concentration slightly improved total membrane flux. The overall improvement in range of investigated feed composition was about 4%. However, increase in hydrazine concentration from 34.45 to 82.02 wt% led to significant decline in partial water flux from 5.92 $\text{g}/\text{m}^2\cdot\text{h}$ by about 54% to 2.70 $\text{g}/\text{m}^2\cdot\text{h}$. In an opposite trend, hydrazine partial flux was improved by about 11.5 fold and reached to 3.77 $\text{g}/\text{m}^2\cdot\text{h}$. As shown in Fig. 9(b), both membrane selectivity and PSI declined considerably. Data indicated that in the investigated range, membrane selectivity for water/hydrazine reduced by about 70% from 10.77 to 3.27 and similarly, PSI decreased by 76% from 60.80 to 14.68. Sunitha et al. reported the selectivity of about 10 for the feed containing 41% hydrazine in water for the membrane derived from Pebax, though the operating conditions were different from the present study [29]. It could be concluded that despite

the wide range of investigated feed composition, membranes still exhibited satisfactory performance. This indicates durability of the developed membranes and their potential for the wide range of feed composition of water/hydrazine mixtures as well as reliability upon unwanted fluctuation in feed composition. Findings may also suggest that process efficiency is highly dependent on the feed composition, and best performance can be obtained using the feeds containing minimum hydrazine concentration. Sunitha et al. reported the selectivity of about 10 for the feed containing 41% hydrazine in water.

The effect of feed composition on the process can be explained from a few aspects. First, the increased total flux can be attributed mainly to the enhanced interaction of the membrane with its hydrophilic nature and increased number of hydrazine molecules. This creates opportunity for the sorption of more hydrazine molecules into membranes matrix that can even surpass the reduced

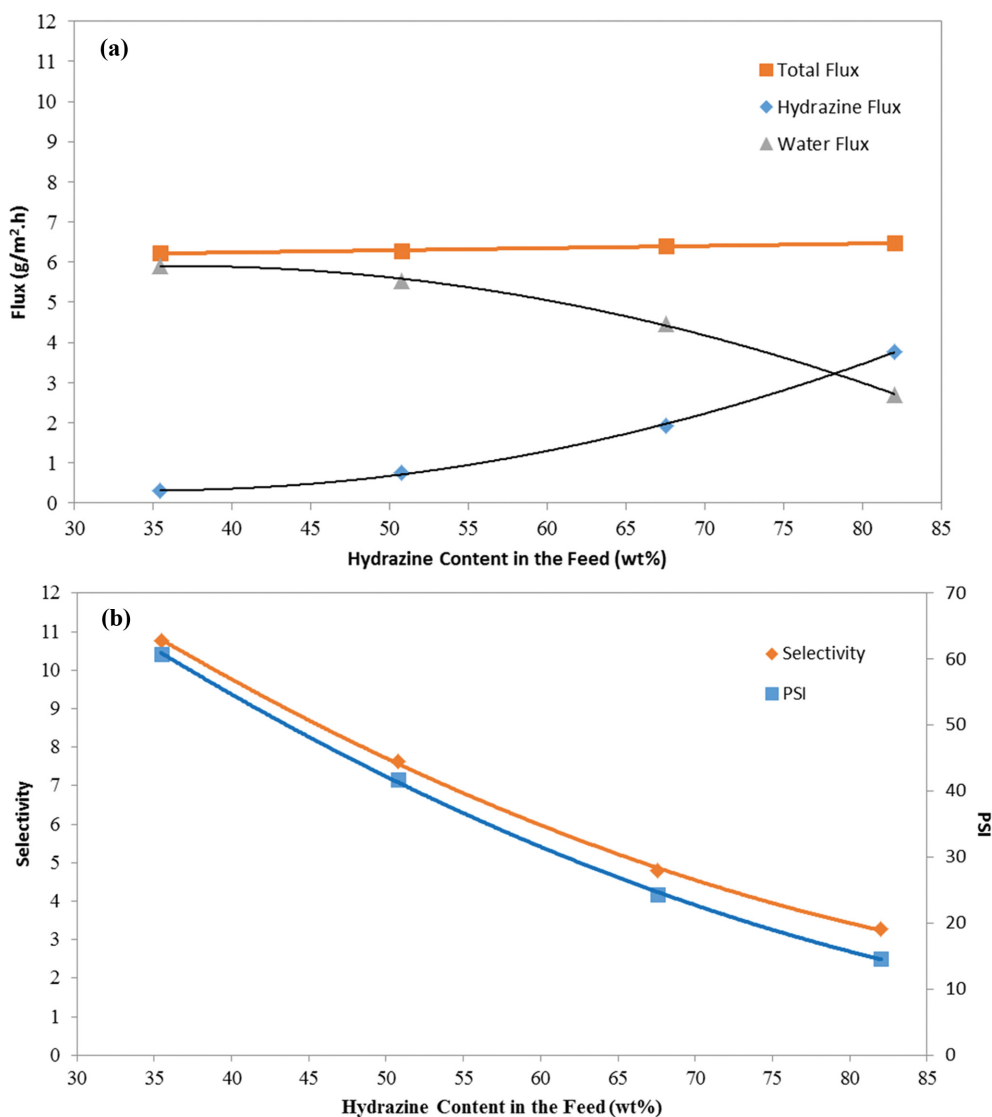


Fig. 9. The effect of feed composition on the performance of PS membranes (a) total and partial flux of the components, (b) Selectivity and PSI (Testing conditions: Membrane thickness: 50.6 μm , Feed flow rate: 3 L/min, Downstream P: 0.5 mmHg, T: 40 $^{\circ}\text{C}$).

sorption of water molecules. On the other hand, hydrazine molecules are larger than water molecules and the caused swelling promotes accelerated co-diffusion of water molecules to some extent. Overall, these competing effects led to the slight increase in membrane total flux. It could also be noticed that partial hydrazine flux surpassed partial water flux when the concentration of hydrazine in the feed exceeded 78%. It must also be noted that water and hydrazine are highly polar components and this caused the formation of strong hydrogen bonding between their molecules. Mixtures prepared from water and hydrazine are azeotropic at hydrazine concentrations of 71.5 wt%, which results in membrane swelling.

5. Analysis of the Characteristics and Performance of Blend Membranes

One of the viable options for improving the performance characteristics of membranes is through combining the synergistic properties of individual polymer via polymer blending. This approach was investigated in the present study by exploring the incorpora-

tion of ABS as a high performance polymer into PS matrix and exploring the characteristics of the resultant membranes.

The results of performance analysis of the membranes are pro-

Table 2. The effect of blending ratio on the membrane flux, selectivity and PSI*

PS/ABS (wt%)	Total flux ($\text{g}/\text{m}^2\cdot\text{h}$)	Hydrazine in permeate (wt%)	Selectivity (α)	PSI ($\text{g}/\text{m}^2\cdot\text{h}$)
100/0	6.22	4.85	10.77	60.80
15/85	7.87	3.7	14.29	104.62
10/90	7.94	3.84	13.75	101.26
5/95	8.01	4.05	13.01	96.21
0/100	8.22	4.21	12.50	94.49

*Testing conditions: Feed composition (Hydrazine/Water): 35.45/64.55 wt%, T: 40 $^{\circ}\text{C}$, Feed flow rate: 3 L/min, Downstream P: 0.5 mmHg, Average membrane thickness: 50 μm .

Table 3. Contact angle values of the membranes investigated in this study

Membrane	PS	Blend PS/ABS (wt%)					Nanocomposite TiO ₂ (wt%)				
		100/0	15/85	10/90	5/95	0/100	0.1	0.5	1	2	5
Contact angle (°)	78.9	78.9	78.4	78.4	78.3	78.3	78.2	77.3	75.6	74.5	72.1

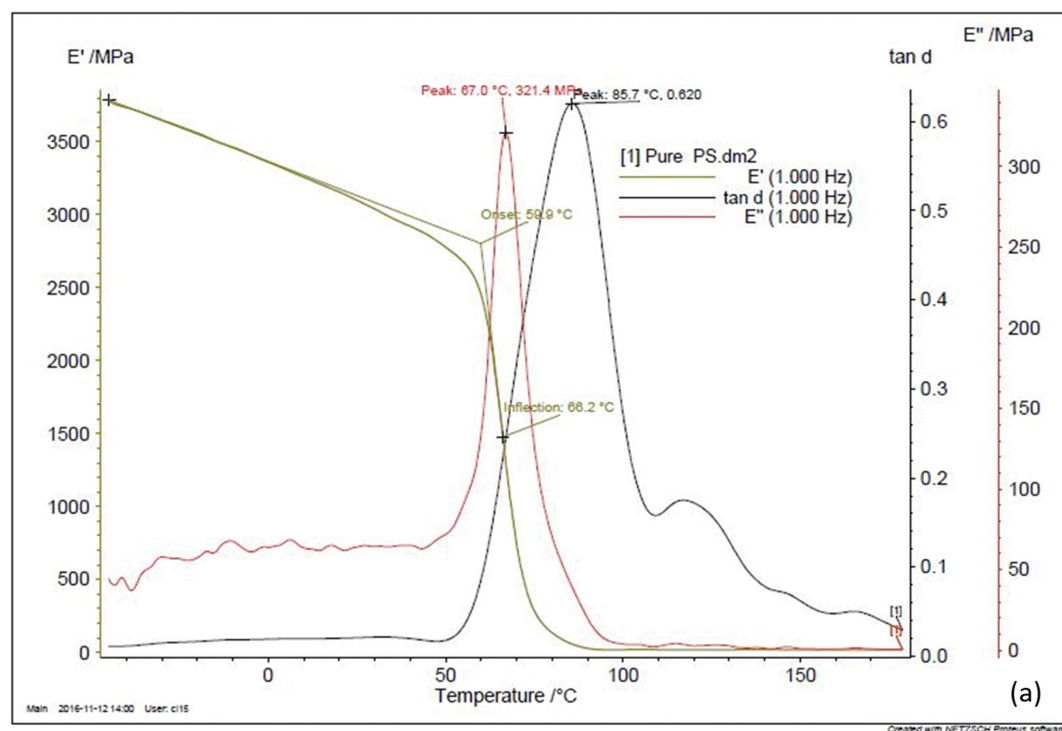
vided in Table 2. The superior characteristics of ABS and its contributing role in blend membranes can be realized from the data. Essentially, the total flux of blend membranes fell within the total flux values of neat PS and ABS membranes. It is evident that the incorporation of ABS into PS matrix led to improvement in total flux in blend membranes. While the flux in neat PS membrane was 6.22 g/m²·h, the blend membrane comprised of 85 wt% ABS exhibited flux of 7.87 g/m²·h, which is about 27% higher. Further increase in ABS concentration in the blends to 90 and 95 wt% was also effective in flux improvement to 7.94 and 8.01 g/m²·h, respectively. This can be well related to the change in the hydrophilicity of the membranes. According to the data provided in Table 3, addition of ABS with its high hydrophilicity led to considerable increase in the hydrophilicity of the neat PS membranes, which in fact facilitated the transport of water across the membrane.

It was noted that blending was also effective in improving the selectivity and PSI of membranes. The selectivity of blend membrane comprising 85 wt% ABS improved considerably (33%) with respect to the neat PS membrane and reached 14.29. The selectivity of other two blend membranes comprising 90 and 95 wt% ABS reduced, though they were still higher than those of neat PS and ABS membranes. Similar trend was observed in the case of PSI of blend membranes. The blend membrane comprising PS/ABS (15/

85 wt%) exhibited the maximum PSI among all other blend and the neat membranes by the value of 104.62.

The above findings can be interpreted based on the prior reports, that sorption selectivity of PS and ABS membranes toward water for water/hydrazine system is less than unity, mainly because of the apolar and poor hydrophilic characteristics of both polymers [22]. Since the water contact angles of both PS and ABS are similar, (78.9° and 78.3°, respectively), they differ slightly from their contact angle with respect to hydrazine hydrate. Thus, the hydrazine hydrate contact angles of PS and ABS are 73.7° and 69.5°, respectively. On this basis, the diffusivity selectivity should play the key role in governing the total transport characteristics of a membrane. Based on the results, it is speculated that the presence of ABS has transformed the internal microstructure of the membranes in a way that the diffusion of water molecules is facilitated through the newly formed free volumes at the interspace of PS and ABS chains. However, in contrast to the free volume in the neat PS, the size of free volumes in the blend membranes has been more restrictive toward the diffusion of hydrazine molecules, and this overall has led to the higher selectivity and PSI of blend membranes. This was confirmed by investigating the thermomechanical properties of the membranes.

Small scale local motions of polymer chains play an important

**Fig. 10. Viscoelastic behavior of (a) PS, (b) PS/ABS blend (15/85 wt%) (c) ABS membrane samples.**

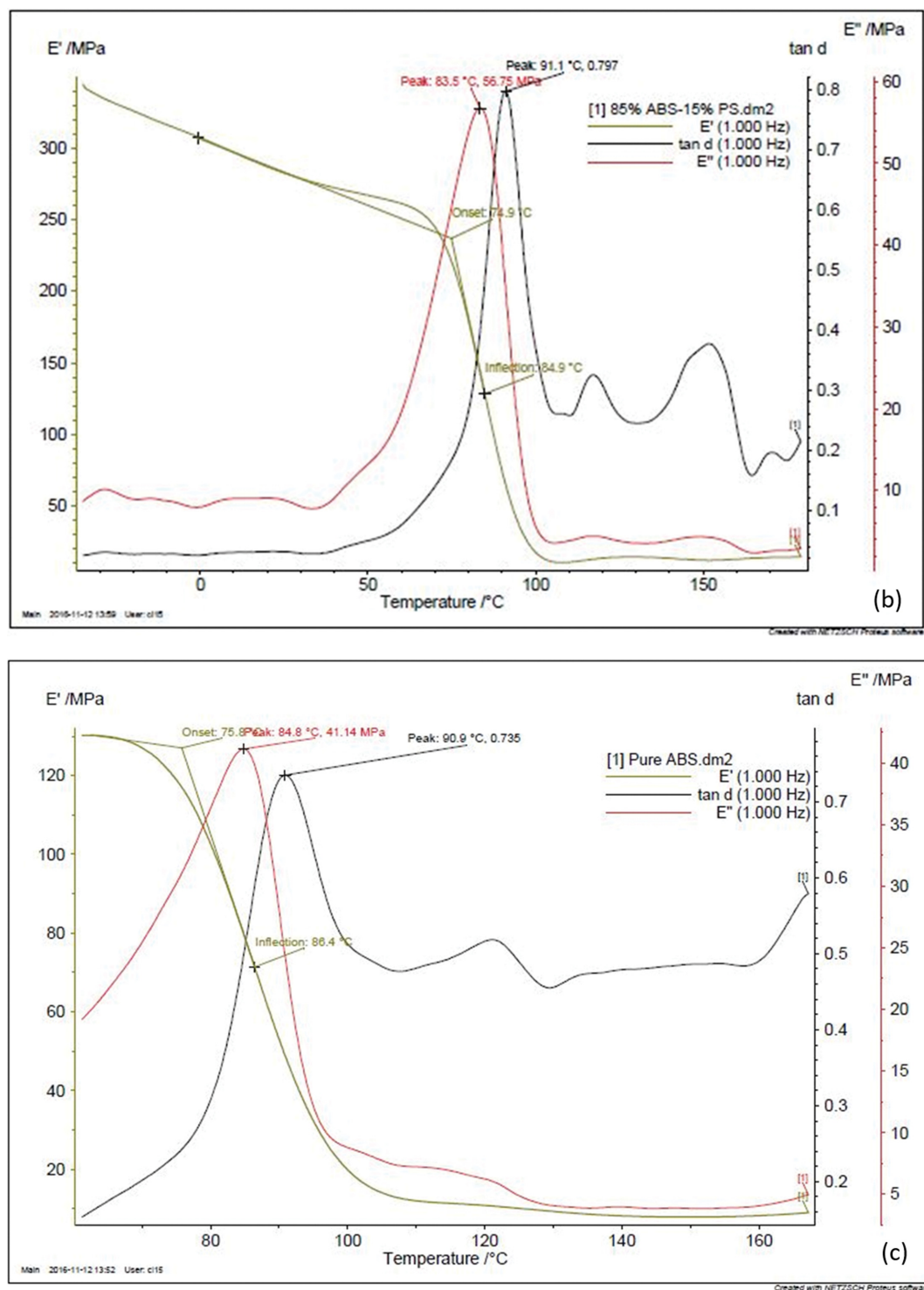


Fig. 10. Continued.

role in governing the diffusion of molecules across the membrane and consequently the overall permeability [39]. Particularly, this applied to the transport through dense layers where the transient free volumes are present and depending on the scale of molecular motions determines the diffusion rate. The results of DMA analysis for pure PS and ABS as well as the blend PS/ABS membranes are shown in Fig. 10. Based on consideration of peak tan delta as

the measure of glass transition temperature (T_g), it was found that T_g for pure PS and pure ABS membranes was 85 °C and 91 °C, respectively. However, T_g for the blend membrane appeared at 90 °C, between both pure membranes, which is somehow an indication of the miscibility. Note that investigation on the miscibility studies of PS and ABS indicates that although some reports indicate immiscibility of these polymers, other findings revealed that

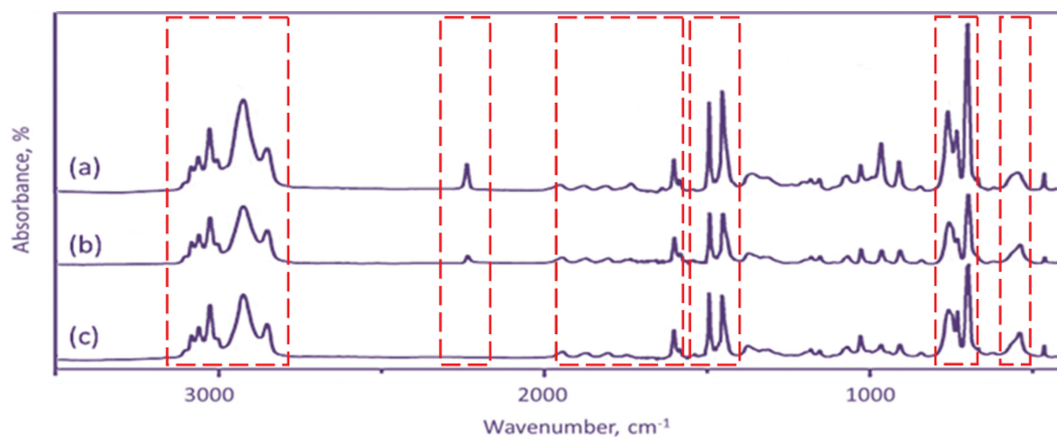


Fig. 11. The FTIR spectra of (a) PS, (b) PS/ABS (15/85 wt%) blend, and (c) ABS membranes.

extended mixing of the polymers has resulted in miscibility [40–42].

Fig. 11 shows the FTIR spectra of the neat PS and ABS as well as the PS/ABS (15/85 wt%) the representative blend membrane. The indicative peaks are very similar and not much difference can be seen in between. The characteristic peaks at 698, 752, 1,495, 1,599 and $3,018\text{ cm}^{-1}$ are related to the C-H bond stretching of the aromatic rings in PS. The peaks between $1,660$ and $1,950\text{ cm}^{-1}$ correspond to the C=C bond stretching in the aromatic rings, whereas those at $2,848$ and $2,922\text{ cm}^{-1}$ are associated with the C-H bond stretching of CH_2 groups. On the other hand, the indicative peak of acrylonitrile in CN group of ABS appeared at about $2,240\text{ cm}^{-1}$. In the case of blend, this peak is correspondent with the composition and is increased by increase in ABS concentration.

Further analysis of the blends by TGA revealed no significant change in the stability of the membranes and all the samples exhibited a similar trend (Fig. 12). However, slight shifts could be noted in the onset of degradation in the case of blend membranes. Accordingly, the degradation starting point of the blend membrane occurred at slightly lower temperature and further shifted upon increase

of ABS composition in the blend. The results are in good agreement with prior reports [43].

6. Analysis of the Characteristics and Performance of Nanocomposite Membranes

Another approach investigated in the present study for tailoring the performance characteristics of the PS membranes was through benefitting from the presence of nanoparticles inside the membrane matrix by formation of nanocomposite membranes [44]. TiO_2 nanoparticles were selected for this purpose with the hypothesis that their highly hydrophilic nature could contribute to the preferential and facilitated transport of water molecules through the membranes [45–47]. Accordingly, the characteristics and performance of nanocomposite membranes containing 0.1 to 5 wt% TiO_2 were examined. Fig. 13 shows the surface morphology for the neat PS and nanocomposite membrane containing 1 wt% TiO_2 . It is evident that the surface of both membranes was smooth with no detectable defects. In contrast to the neat PS membrane, partial presence of TiO_2 nanoparticles could be identified at the top surface of nanocomposite membranes.

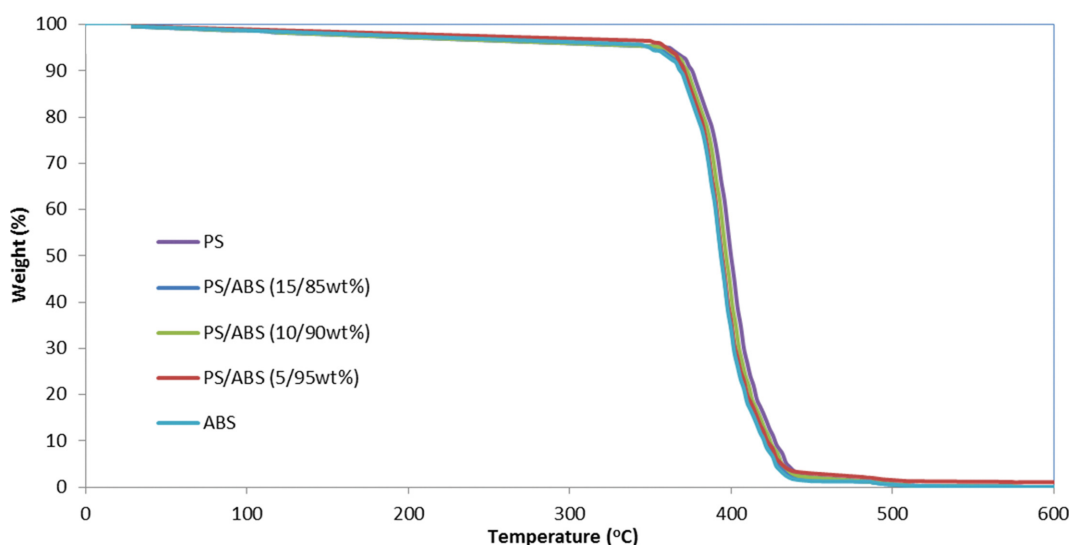


Fig. 12. TGA results of PS, ABS and blend PS/ABS membranes.

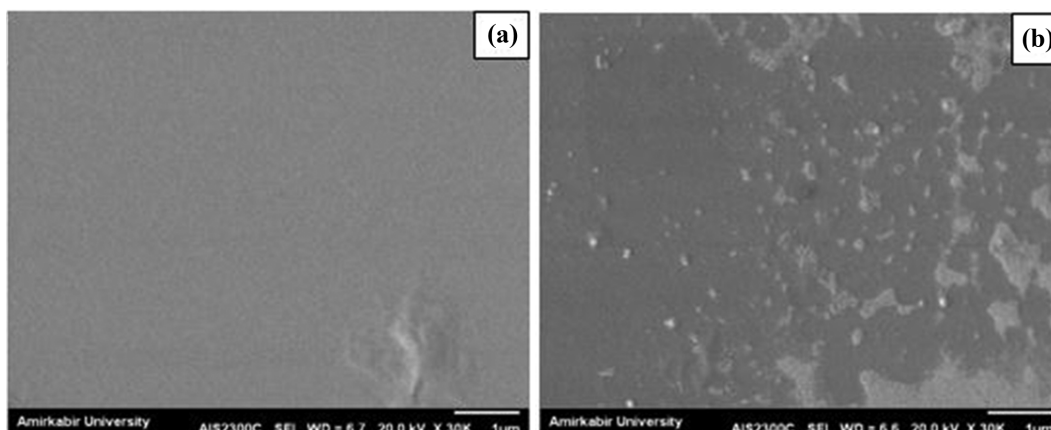


Fig. 13. SEM images showing top surface of (a) neat PS and (b) nanocomposite PS+1 wt% TiO_2 membranes (Magnification: 30 K).

Also Fig. 14 shows cross-sectional morphology of neat PS and nanocomposite membranes containing 1, 2 and 5 wt% TiO_2 nanoparticles. A general point to note is the uniform morphology of all the membranes across their thickness, indicating successful formation of the dense structure. However, upon addition of nanoparticles, the microstructure of membranes slightly changed partly due to the dispersion of nanoparticles as well as due to partial agglomerations specifically visible in the nanocomposite membranes containing 5 wt% TiO_2 which resulted in formation of tiny voids at

different spots.

Fig. 15 shows the thermogravimetric analysis results of the membranes. It is evident that all of the membranes were stable well above the intended operating temperatures and the membranes followed a similar trend in weight loss. All samples gradually lost their weight up to about 345°C , after which the rapid weight loss initiated due to the release of the atoms present in the structure of the polymer matrix. In addition, the residual of the nanocomposite membranes possessed higher weight corresponding to the load-

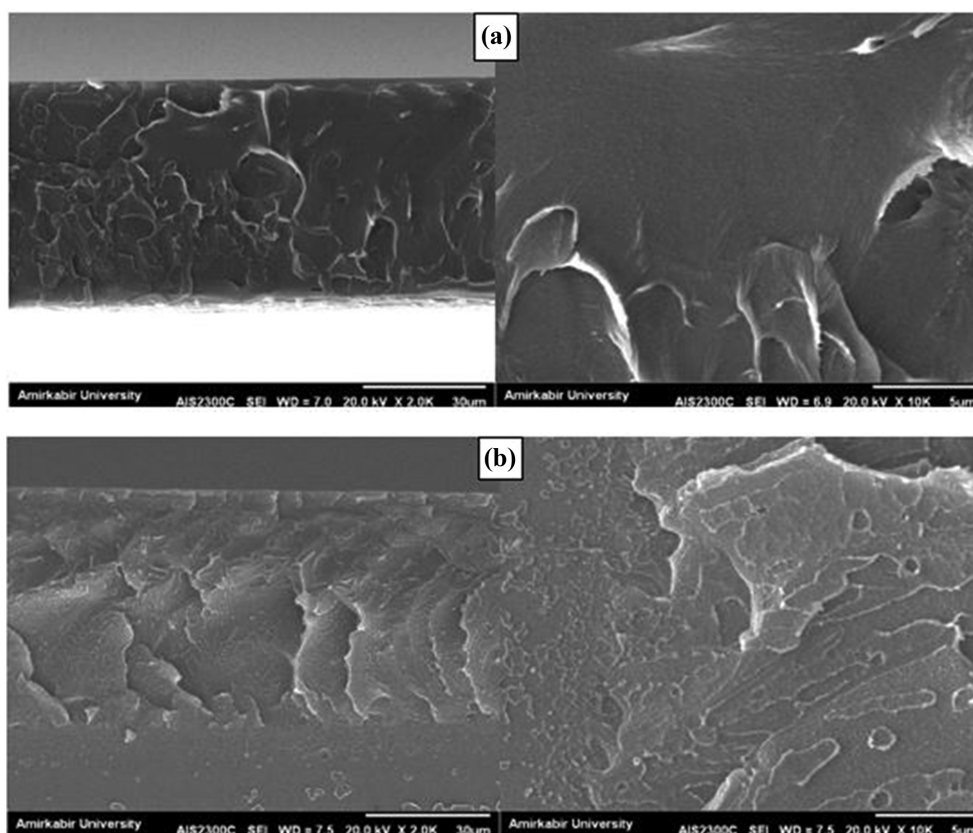


Fig. 14. The cross-sectional morphology of (a) neat PS membrane, (b) nanocomposite PS+1 wt% TiO_2 membrane; (c) nanocomposite PS+2 wt% TiO_2 membranes; (d) nanocomposite PS+5 wt% TiO_2 membranes at two different magnifications (left 2 K; right 10 K).

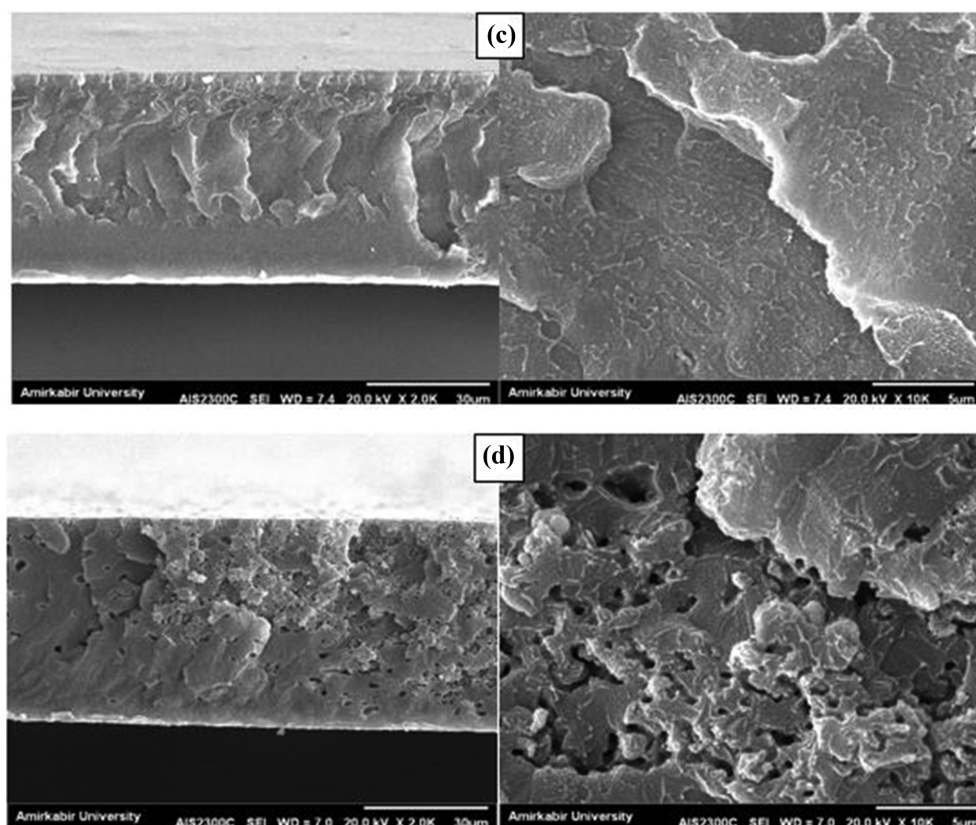


Fig. 14. Continued.

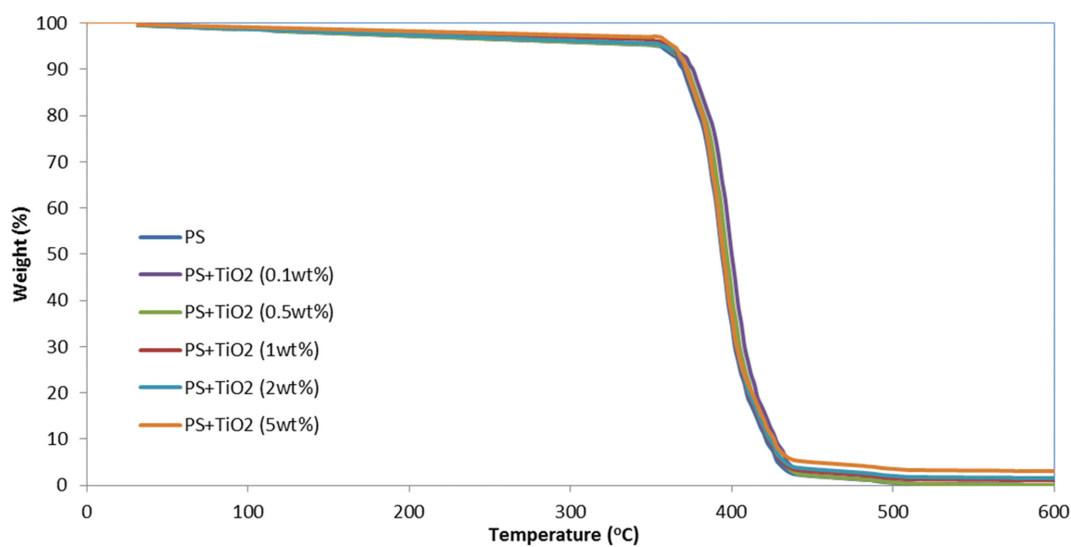


Fig. 15. TGA results of the neat and nanocomposite PS membranes.

ing of the TiO_2 nanoparticles inside compared to the neat PS sample. Thus, membranes containing higher loadings of TiO_2 had higher residual weight at the end of the process since TiO_2 could not be degraded in the tested temperature. A similar trend has been reported elsewhere [48].

The results of the performance evaluation of the membranes are provided in Table 4. All the nanocomposite membranes exhib-

ited improved total flux. Even the addition of small amount of 0.1 wt% TiO_2 improved the water flux of the membranes from $6.22 \text{ g/m}^2 \cdot \text{h}$ in the case of neat PS by 34% to $8.34 \text{ g/m}^2 \cdot \text{h}$. It was interesting that TiO_2 nanoparticles showed their strong contribution in the range of 0.5, 1 and 2 wt% by significant increase in total water flux by 2.5, 3.6 and 4 fold, respectively. Thus, the highest total flux belonged to the nanocomposite membrane containing

Table 4. The effect of TiO₂ concentration on the flux, selectivity and PSI of nanocomposite membranes*

TiO ₂ content (wt%)	Total flux (g/m ² ·h)	Hydrazine in permeate (wt%)	Selectivity (α)	PSI (g/m ² ·h)
0 (Neat PS)	6.22	4.85	10.77	60.80
0.1	8.34	4.9	10.66	80.55
0.5	21.55	5.82	8.89	169.97
1	28.52	7.22	7.06	172.75
2	30.93	7.59	6.69	175.88
5	19.37	5.34	9.74	169.20

*Testing conditions: Feed composition (Hydrazine/Water): 35.45/64.55 wt%, T: 40 °C, Feed flow rate: 3 L/min, Downstream P: 0.5 mmHg, Average membrane thickness: 50 μ m.

2 wt% TiO₂. The results are in good agreement with the improvement noted in the contact angle of the membranes (Table 3). In fact, the hydrophilicity of the membranes increased upon the presence of TiO₂ nanoparticles, which could facilitate transport of water molecules due to their high affinity. Note that surface hydrophilicity is attributed not only to the presence of functional groups lying on the membrane surface, but is also associated with the surface roughness of the membranes caused due to the presence of nanoparticles.

The total flux of nanocomposite membranes suddenly declined upon further addition of TiO₂ nanoparticles to 5 wt%. Although this value was still high compared to the neat PS membrane, the results could indicate occurrence of undesirable changes within the microstructure of the membrane. This could be due to the formation of blocked pathways within the membrane thickness caused by the agglomeration of large number of nanoparticles, which could prevent easy transport of molecules through non-permeable inorganic sites.

Despite the attractive feature of TiO₂ in enhancing total flux, the selectivity of the majority of the nanocomposite membranes was less than that of the neat PS membrane. The selectivity of membranes reached its minimum in the case of nanocomposite membrane containing 2 wt% TiO₂. On the other hand, all nanocomposite membranes offered improved PSI compared to the neat PS membrane with the value as high as 175.88 in the case of nanocomposite membrane containing 2 wt% TiO₂.

CONCLUSIONS

Membranes were successfully developed from PS and explored in terms of their potential for PV dehydration of hydrazine hydrate aqueous mixtures. The effect of prominent parameters on the characteristics and performance of the membranes was investigated. It was found that the properties of membranes were strongly dependent on their thickness. Increase in membrane thickness from 26.5 μ m to 80.3 μ m led to significant drop in total flux from 10.93 g/m²·h to 1.56 g/m²·h, respectively. Similar effects were observed in terms of partial flux of components. In contrast, selectivity and PSI of membranes increased to 18.79 and 61, respectively. Variation of feed temperature from 36 °C to 56 °C improved water flux

by 71% to 10.26 g/m²·h, but hydrazine flux only improved by 29% to 0.49 g/m²·h. Also, selectivity and PSI of membranes improved to 11.60 and 113.96 for the investigated range of feed temperature. While increase in feed flow rate from 1 to 3 L/min improved partial water flux from 5.86 g/m²·h by about 20% to 6.83 g/m²·h, hydrazine partial flux declined by about 75% from 1.60 g/m²·h to 0.40 g/m²·h. Also, membrane selectivity and PSI increased by 3.8 and 7.8 fold. Attempts for gaining more insight on the potential applications of the developed membranes revealed that membranes provided reasonable flux and separation performance for the wide ranges of feed compositions. Although all the experiments and findings were for the feed containing 34.45 wt% hydrazine, despite increase in hydrazine concentration to 82 wt% total flux remained unchanged, but selectivity and PSI of declined to 3.27 and 14.68, respectively. Strategies of blending and the use of nanoparticles were adopted as possible means for tailoring of PS membranes. Incorporation of 85 wt% ABS into PS matrix improved the total flux of membranes by 27%. Also, membrane selectivity and PSI reached the highest values of 14.29 and 104.62, respectively. On the other hand, addition of TiO₂ nanoparticles was effective up to certain extent. The highest performance was obtained in the membrane comprising 2 wt% TiO₂ by exhibiting total flux of 30.93 (g/m²·h) and PSI of 175.88.

REFERENCES

1. S. S. Hosseini and S. Najari, in *Nanostructured polymer membranes, volume 2: Applications*, P. M. Visakh and N. Olga Eds., Wiley-Scrivener, Beverly, Massachusetts (2016).
2. W. C. Schumb, *J. Chem. Educ.*, **28**, 10 (1951).
3. E. W. Schmidt, *Hydrazine and its derivatives: Preparation, properties, applications*, John Wiley & Sons, New York (2001).
4. J. A. Dehkordi, S. S. Hosseini, P. K. Kundu and N. R. Tan, *Chemical Product and Process Modeling*, **11**, 11 (2016).
5. M. Zhang, L. Deng, D. Xiang, B. Cao, S. S. Hosseini and P. Li, *Processes*, **7**, 51 (2019).
6. S. S. Hosseini, J. A. Dehkordi and P. K. Kundu, *Korean J. Chem. Eng.*, **33**, 3085 (2016).
7. J.-A.-D. Sharabati, S. Guclu, S. Erkoc-Ilter, D. Y. Koseoglu-Imer, S. Unal, Y. Z. Menciloglu, I. Ozturk and I. Koyuncu, *Sep. Purif. Technol.*, **212**, 438 (2019).
8. S. S. Hosseini, M. A.-R. Jalili Palandi and N. Mokarinezhad, *Polym. Adv. Technol.*, **31**, 2209 (2020).
9. Y. Xue, C. Lau, B. Cao and P. Li, *J. Membr. Sci.*, **575**, 135 (2019).
10. M. A. A. Shahmirzadi, S. S. Hosseini and N. R. Tan, *Korean J. Chem. Eng.*, **33**, 3529 (2016).
11. Y. Xue, J. Huang, C. H. Lau, B. Cao and P. Li, *Nat. Commun.*, **11**, 1461 (2020).
12. G. M. Urper-Bayram, B. Sayinli, R. Sengur-Tasdemir, T. Turken, E. Pekgenc, O. Gunes, E. Ates-Genceli, V. V. Tarabara and I. Koyuncu, *J. Appl. Polym. Sci.*, **136**, 48205 (2019).
13. A. Vedadghavami, F. Minooei and S. S. Hosseini, *Iranian J. Chem. Chem. Eng. (IJCCCE)*, **37**, 1 (2018).
14. S. S. Hosseini, H. Khodadadi and B. Bakhshi, *Korean J. Chem. Eng.*, Accepted, In Press (2021).
15. D. Unlu, *Korean J. Chem. Eng.*, **37**, 698 (2020).

16. P. Peng, B. Shi and Y. Lan, *Sep. Sci. Technol.*, **46**, 234 (2010).
17. F. Qasim, J. S. Shin and S. J. Park, *Korean J. Chem. Eng.*, **35**, 1185 (2018).
18. D. Unlu, *Macromol. Res.*, **27**, 998 (2019).
19. M. Tamaddondar, H. Pahlavanzadeh, S. Saeid Hosseini, G. Ruan and N. R. Tan, *J. Membr. Sci.*, **472**, 91 (2014).
20. S. S. Hosseini, H. Pahlavanzadeh and M. Tamadondar, *Ir. Chem. Eng. J.*, **13**, 76 (2014).
21. R. Ravindra, S. Sridhar, A. Khan and A. Rao, *Polymer*, **41**, 2795 (2000).
22. S. Satyanarayana and P. Bhattacharya, *J. Membr. Sci.*, **238**, 103 (2004).
23. M. K. Mandal, S. Dutta and P. Bhattacharya, *Chem. Eng. J.*, **138**, 10 (2008).
24. S. Sridhar, G. Susheela, G. J. Reddy and A. A. Khan, *Polym. Int.*, **50**, 1156 (2001).
25. N. Hoda, S. V. Suggala and P. K. Bhattacharya, *Comput. Chem. Eng.*, **30**, 202 (2005).
26. S. Sridhar, T. Srinivasan, U. Virendra, A. Khan and P. D. Group, *Chem. Eng. J.*, **94**, 51 (2003).
27. R. Ravindra, S. Sridhar and A. Khan, *J. Polym. Sci. Part B: Polym. Phys.*, **37**, 1969 (1999).
28. S. Sridhar, R. Ravindra and A. Khan, *Ind. Eng. Chem. Res.*, **39**, 2485 (2000).
29. K. Sunitha, P. Nikhitha, S. Satyanarayana and S. Sridhar, *Sep. Sci. Technol.*, **46**, 2418 (2011).
30. A. J. Pasztor, B. G. Landes and P. J. Karjala, *Thermochim. Acta*, **177**, 187 (1991).
31. Y. Bussi, S. Golan, C. G. Dosoretz and M. S. Eisen, *Desalination*, **431**, 35 (2018).
32. G.-L. Zhuang, H.-H. Tseng and M.-Y. Wey, *Chem. Eng. Res. Des.*, **111**, 204 (2016).
33. Y. Li, H. Pu, J. Cheng, J. Du, H. Pan and Z. Chang, *J. Appl. Polym. Sci.*, **135**, 45917 (2018).
34. Y. Tang, Z. Liu and K. Zhao, *J. Appl. Polym. Sci.*, **136**, 47262 (2019).
35. Y. Gawargious and A. Besada, *Talanta*, **22**, 757 (1975).
36. B. Liang, Q. Li, B. Cao and P. Li, *Desalination*, **433**, 132 (2018).
37. D. A. Devi, B. Smitha, S. Sridhar and T. M. Aminabhavi, *Sep. Purif. Technol.*, **51**, 104 (2006).
38. P. Srinivasa Rao, B. Smitha, S. Sridhar and A. Krishnaiah, *Sep. Purif. Technol.*, **48**, 244 (2006).
39. K. J. Lee, J. Y. Jho, Y. S. Kang, J. Won, Y. Dai, G. P. Robertson and M. D. Guiver, *J. Membr. Sci.*, **223**, 1 (2003).
40. P. A. Tarantili, A. N. Mitsakaki and M. A. Petoussi, *Polym. Degrad. Stab.*, **95**, 405 (2010).
41. L. B. Brennan, D. H. Isaac and J. C. Arnold, *J. Appl. Polym. Sci.*, **86**, 572 (2002).
42. H. Keskkula, D. R. Paul, K. M. McCreedy and D. E. Henton, *Polymer*, **28**, 2063 (1987).
43. M. Y. Chan, P. L. Teh and C. K. Yeoh, *J. Eng. Sci.*, **15**, 63 (2019).
44. R. Jalili Palandi and S. S. Hosseini, *Ir. Chem. Eng. J.*, **15**, 86 (2016).
45. S. S. Hosseini, S. Fakharian Torbati, M. A. Alaei Shahmirzadi and T. Tavangar, *Polym. Adv. Technol.*, **29**, 2619 (2018).
46. A. Khodakarami, S. S. Hosseini and E. Nxumalo, *Polym. Eng. Sci.*, **60**, 1795 (2020).
47. H. R. Shahriari and S. S. Hosseini, *Chem. Eng. Process. - Process Intensification*, **147**, 107766 (2020).
48. A. H. Farha, A. F. Al Naim and S. A. Mansour, *Polymers*, **12**, 1935 (2020).