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Surface modification of SiO₂ nanoparticle and its impact on the properties of PES-based hollow fiber membrane

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ABSTRACT

In this work, polyethersulfone (PES) hollow fiber membranes incorporated with modified silicon dioxide (SiO₂) nanoparticles were prepared and characterized for water treatment process. Prior to dope preparation, commercial SiO₂ nanoparticles were first modified using sodium dodecyl sulfate (SDS) solution to minimize their agglomeration in dope solution. The surface-modified nanoparticles were analysed by TEM, BET and zeta potential to determine the particle size, surface area and surface charge, respectively. The effect of modified SiO₂ loadings ranging from zero to 4 wt.% on the properties of PES-based membranes was examined with respect to thermal stability, hydrophilicity, mechanical strength, pure water flux and protein rejection. Results showed that the modified nanoparticles have reduced agglomeration and greater negative surface charge in comparison to the unmodified nanoparticles. SEM-EDX and FTIR analyses confirmed the presence of modified SiO₂ in the PES membrane matrix. It is also found that the thermal stability and hydrophilicity of composite

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membranes were improved upon the addition of modified SiO₂. The pure water flux and protein rejection of the composite membranes were significantly higher than the control PES membrane. At optimum nanoparticles loading (2 wt.%), the composite membrane demonstrated 87.23 L m⁻² h⁻¹ water flux and 93.6% protein rejection in comparison to 44.2 L m⁻² h⁻¹ and 80.8% shown by the control PES membrane. The results suggested that the modified SiO₂ nanoparticle is very potential to improve membrane water flux without compromising its rejection capacity.

Keywords: Polyethersulfone; SiO₂ nanoparticles; Modified SiO₂; Sodium dodecyl sulfate; Agglomeration

1 Introduction

Nowadays, membrane technology has become an incipient technology that has been widely used to treat contaminated water. Its role in providing clean water for human consumption has become more important and significant since the breakthrough of membrane technology in the 1960s.¹ Polyethersulfone (PES) is one of the polymeric materials that have been used in making asymmetric membranes for microfiltration,² ultrafiltration,³ and nanofiltration⁴ process. The PES membranes are commonly prepared by phase inversion method where a demixing process takes place in a water medium. In this process, the polymer solution is immersed in a non-solvent coagulation bath where precipitation occurs due to the exchange of solvent from the polymer solution and non-solvent from the coagulation bath.⁵ PES membrane is always desired owing to its high temperature and chemical resistance; flexibility in fabrication; wide pH tolerances and pore size range as well as lower in production costs compared to inorganic membrane materials.^{6,7} Nonetheless, PES has one major drawback of having low hydrophilic properties.⁸ This membrane is more susceptible to fouling problem during filtration and could lead to higher cost of operation, inefficient filtration processes and shorten lifespan.⁹

A variety of organic and inorganic additives has been used to modify the properties of the PES membrane, aiming to enhance its separation performance.⁸ Currently, there is a lot of works focusing

on incorporating inorganic nanoparticles into polymeric membranes to enhance membrane separation performance.⁷ The ratio of surface area to volume is much higher for nanoparticles compared to microparticles and the particle size is affected by quantum effects that lead to some physical changes.¹⁰ The incorporation of nanoparticles in the membrane materials tend to have synergistic effects in the processes of water and wastewater treatment such as fouling mitigation, improvement of water flux and permeate quality.¹¹ The nanoparticles that have been previously used include silver nitrate (AgNO_3), zirconium oxide (ZnO), silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), titanium dioxide (TiO_2), and magnesium oxide (MgO).⁷ Among these inorganic nanoparticles, silicon dioxide (SiO_2) shows huge potential to be used in membrane making owing to its hydrophilic properties and wide availability in particle sizes.¹¹ SiO_2 nanoparticles has a widespread resource as it can be easily found in the earth's crust. In terms of price, it is cheaper than Al_2O_3 and TiO_2 nanoparticles.¹² Other than being chemically and thermally stable, SiO_2 provides large surface area and fine suspendability in aqueous solution. It is also preferable in water treatment as it contains lower toxicity and environmentally inert.⁷

Like any other nanoparticles, SiO_2 nanoparticles tend to agglomerate when incorporated into the polymeric matrix. In view of this, the surface of nanoparticles must be chemically modified to minimize agglomeration. According to Kango et al.,¹³ the surface of inorganic particles can be modified either by surface absorption of small molecules, such as silane coupling agents or by grafting polymeric molecules onto the particles. For this study, SiO_2 nanoparticles will be modified using sodium dodecyl sulfate (SDS) surfactant. Studies have shown that SDS can be used to reduce the aggregation and provides stable colloidal distribution.¹⁴⁻¹⁶ Furthermore, SDS can increase the dispersibility of nanoparticles by forming micelles when they are in water.¹⁷

The studies regarding the incorporation of SiO_2 at various concentration in the flat sheet PES-based membrane is very common among researchers.^{3,18-20} It has been shown that the incorporation of SiO_2 in the membrane could potentially improve membrane hydrophilicity, fouling resistance, flux and rejection. Nonetheless, the effect of SDS-modified SiO_2 on the properties of hollow fiber PES membrane has yet to be reported. The main objective of this work is to study the effect of modified SiO_2 loadings on the properties of PES-based membranes that were fabricated in hollow fiber

configuration. The morphology of the membrane was analyzed using scanning electron microscope (SEM) while energy-dispersive X-ray spectroscopy (EDX) was used to detect the elemental composition of SiO₂-PES membranes. The functional group of SDS-modified SiO₂ was observed by Fourier transform infrared spectroscopy (FTIR). The contact angle and differential scanning calorimeter (DSC) analysis were conducted in order to determine the hydrophilicity and thermal stability of membrane, respectively. The mechanical properties were assessed by the tensile strength and elongation at break ratio. The performance of the membranes was evaluated based on pure water flux and protein rejection.

2 Experimental

2.1 Materials

Polyethersulfone (PES) as a polymer was purchased from Arkema Inc. (Philadelphia, USA). Polyvinylpyrrolidone (PVP, 40,000 g mol⁻¹) was used as pore former agents in the membrane. SiO₂ nanopowder, (average particle size of 10-20 nm) was used as inorganic additives. Sodium dodecyl sulfate (SDS) was used for surface pre-treatment of the SiO₂ nanoparticles while N,N-dimethylacetamide (DMAc) was used as solvent. Bovine serum albumin (BSA, 67,000 g mol⁻¹) was used for membrane rejection test. All of these chemicals were supplied by Sigma Aldrich (USA). Glycerol was purchased from J.T Baker (USA) and used for membrane post treatment.

2.2 Membrane preparation

2.2.1 Surface modification of SiO₂ nanoparticles

The SiO₂ nanoparticles were modified using SDS following the procedures described by Shen et al.¹⁸ SDS (CH₃(CH₂)₁₁OSO₃Na) is a surfactant that has an amphiphilic characteristic of polar head and non-polar tail that enable it to be self-association or micellization in solution. During micellization, the polar head will form the micelle-water-interface while the non-polar tail will form the micelle core.¹⁷ Thus, the SDS micelle will attach to the individual SiO₂ nanoparticle as illustrated in Fig. 1. In this modification process, 3.5 vol.% SDS solution was prepared by adding commercial SDS powder into 1000 mL of milli-Q water. The SDS solution was then stirred for a while until all the

powder was dissolved. After that, 5.0 g SiO₂ nanopowder was added to the SDS solution before the solution pH was adjusted to 4. The solution was vigorously stirred for 8 h followed by centrifugation and drying process to obtain the white powder of modified SiO₂-SDS nanoparticles.

(Figure 1 should be here)

2.2.2 Hollow fiber membrane fabrication

The control PES and PES-SiO₂ membranes were produced via phase inversion technique. The dope solutions were initially prepared by adding 18 wt.% of PES into pre-weighed DMAc solvent. Then, the solution was stirred using mechanical stirrer at 800 rpm until all the PES pellets were fully dissolved. After that, 6 wt.% of PVP and modified SiO₂ nanoparticles (ranging from 0 to 4 wt.%) were added to the solution to produce dope solutions with different SiO₂ concentrations.

Table 1 shows the compositions of the dope solutions. Prior to the spinning process, each dope solution was ultrasonic-vibrated for 30 min to eliminate any trapped air bubbles in the solution. The prepared dope solution was transferred into a dope reservoir before it was delivered into a spinneret by gear pump motor with pump delivery rate of 0.3 cm³ rev⁻¹. The bore fluid was set at 1.8 cm³ min⁻¹ and the dope extrusion rate (DER) at 3 cm³ min⁻¹. The ratio of dope flow rate to bore fluid flow rate was kept constant throughout the process. The diameter of the inner and outer spinneret was 0.55 mm and 1.25 mm, respectively. The bore fluid was deionized water while the external coagulant was tap water with temperatures of 18-20°C. The dope solution was pressurized from the tip of the spinneret to the coagulation bath with an air gap of 10 cm so as phase inversion process could take place to solidify polymeric liquid. The as-spun membrane was guided to a drum take-up unit before it was being cut and stored in a water container at room temperature for 24 h to get rid of any residual solvent.

(Table 1 should be here)

2.2.3 Membrane post-treatment

For the post-treatment, the fabricated hollow fibers were kept in a water container containing 10 vol.% of glycerol for 24 h. The main reason of post-treating membrane is to prevent hollow fiber structure from collapsing during air-drying. Later, the hollow fibers were dried in the air at room temperature for 3 days before subjecting to module preparation.

2.3 Membrane characterization

The particle size and shape of the SiO₂ and modified SiO₂-SDS nanoparticles was determined using transmission electron microscope (TEM, Hitachi HU-11B). The specific surface area of the SiO₂ and SDS-modified SiO₂ nanoparticles was calculated using the multiple-point Brunauer Emmett Teller (BET) method while the particle size distribution and zeta potential (ξ) was measured using Malvern Zetasizer Nano ZS, U.K. The presence of functional groups in the unmodified and modified SiO₂ nanoparticles was analyzed by Fourier transform infrared spectroscopy (FTIR, NICOLET 5700 FT-IR, Thermo Electron Corporation) recorded in the range of 500–4000 cm⁻¹. In order to get better visible spectra, dried potassium bromide (KBr) was mixed with the samples before the analysis was conducted. The morphologies of the control PES and PES-SiO₂ membranes were studied using a tabletop scanning electron microscope (SEM) (Hitachi, TM3000). Prior to analysis, the membrane samples were immersed in liquid nitrogen for few minutes before being fractured to obtain a clear view of the cross sectional samples. All membrane samples were subject to sputter coating process using platinum to avoid membrane surface charge during analysis. The elemental composition in membranes was detected using energy-dispersive X-ray spectroscopy (EDX) (Bruker, QUANTAX 70). The contact angle of the membrane was measured using a contact angle system (Dataphysics, OCA 15Pro) to determine the hydrophilicity of the membrane. Five measurements of contact angles were recorded at various locations on the membrane surface. The membrane surface roughness was characterized by atomic force microscope (AFM) (SPA-300HV, Seiko). The membrane sample was prepared by placing it on a 1 cm² square paper card using double-sided tape. The surface of the membrane was scanned in the size of 3 μm \times 3 μm and the mean surface roughness (Ra) of each sample was recorded. The thermal stability of the membranes was determined using differential scanning calorimeter (DSC822^o, Mettler Toledo). The effect of particle modifications toward glass

transition temperature (T_g) was observed at heating rate of $10^\circ\text{C min}^{-1}$ up to 300°C . The DSC signal was enhanced by heating the samples to 300°C at the same heating rate followed by cooling down to room temperature before re-heating to 300°C . The T_g of the sample was determined from the second run. The tensile test was conducted to measure the tensile strength and the percentage of elongation at break using a tensile tester (LRX2.5KN, LLYOD). The gauge speed was set at 10 mm min^{-1} and the gauge length of the membrane sample was fixed at 50 mm. Average of five samples was reported. The viscosity of each dope solution was measured using basic viscometer (EW-98965-40, Cole Parmer) and average of five readings was recorded.

2.4 Membrane performance

The permeation and rejection of each membrane was tested by filtration experiments. BSA solutions were used for the rejection experiments. The feed concentration was kept at 1.0 g L^{-1} . A UV/Vis spectrophotometer (DR5000, HACH) was used to measure the concentration of BSA in the feed and permeate samples at the wavelength of 280 nm. Before conducting the filtration experiments, the hollow fiber membrane modules consisted of 10 hollow fibers with an effective length of 20 cm were prepared by sealing both ends of fibers with epoxy resin. All experiments were conducted at the feed pressure of 1.0 bar. Prior to any measurement, the membranes were compacted with deionized water at 3.0 bar for 1h. After that, rejection of BSA solution was determined at 1.0 bar. The pure water flux, J_w and rejection, R (%) were defined as Equation (1) and (2), respectively.

$$J_w = \frac{V}{At} \quad (1)$$

where J_w is the water flux ($\text{Lm}^{-2} \text{ h}^{-1}$), V is the permeate volume (l), A is the membrane area (m^2) and t is the time (h).

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

where C_p is the concentration of permeate (mg L^{-1}) and C_f is the concentration of feed (mg L^{-1}).

3 Results and discussion

3.1 Study of SiO_2 and modified SiO_2 -SDS nanoparticles

The purpose of modifying nanoparticles is to get uniform nanoparticle dispersion and distribution in polymeric matrix. Fig. 2 represents the TEM images of SiO_2 nanoparticles before and after SDS modification. As can be seen from the images, the SDS-modified SiO_2 nanoparticles show less aggregation and better dispersion compared to the unmodified SiO_2 nanoparticles that are seriously aggregated with larger size. The unmodified SiO_2 nanoparticles are overlapped with each other and distinct particles are rather difficult to be observed. This is further supported by the particle size distribution of SiO_2 before and after surface modification shows in Figure 3. The average particle distribution size recorded for the unmodified SiO_2 is 484.0 nm while for modified SiO_2 -SDS nanoparticles, the size significantly decreased to 180.7 nm that might have been due to the less agglomeration between nanoparticles. These results confirm that the agglomeration of nanoparticles could be effectively reduced with SDS owing to the greater repulsion force between the SDS-modified nanoparticles. The specific surface area analysis revealed that the SDS-modified SiO_2 had lower BET surface area ($122.6 \text{ m}^2 \text{ g}^{-1}$) compared to the unmodified SiO_2 nanoparticles ($156.0 \text{ m}^2 \text{ g}^{-1}$). The decrease of BET surface area for the modified SiO_2 -SDS nanoparticles might due to the adsorption of SDS onto the inner surface of the nanoparticles and micropore.²¹ The surface modification process has also affected the surface charge properties of the nanoparticles. Fig 4 shows the zeta potential of the nanoparticles before and after modification. The zeta potential of unmodified SiO_2 colloids that was around -17.7 mV is attributed by the negatively charged hydroxyl and silanol groups of SiO_2 nanoparticles.¹² However, with the addition of surfactant, the magnitude of the negative zeta potential for SiO_2 -SDS colloids was increased to -29.3 mV. This can be explained by the fact that as SDS comes in contact with water, it tends to form SDS micelle in which anionic charge of dodecyl sulfate ions are adsorbed onto the SiO_2 nanoparticles and increase the negative surface charge of the nanoparticles.²²

(Figure 2 should be here)

(Figure 3 should be here)

(Figure 4 should be here)

3.2 FTIR analysis

The FTIR-ATR spectra of (a) SiO₂, (b) SDS and (c) SDS-modified SiO₂ nanoparticles are shown in Fig. 5. From curves (a) and (c), the peak at 797 cm⁻¹ is resulted from symmetrical stretching vibration of Si–O while the peaks at 1082, 1071, 973 and 951 cm⁻¹ are the asymmetric Si–O–Si stretching.^{3,21} The strength of the absorption band at 3463 cm⁻¹ which corresponding to stretch vibration of -OH and the bending vibration of H–O–H at 1626 cm⁻¹ is increased for the modified SiO₂ nanoparticles. These could indicate interactions between -OH groups and the modified SiO₂ nanoparticles.^{3,21} For the spectrum of SDS particles, the band at 1082 cm⁻¹ indicates the SO₃ stretching.²³ The primary peak at 1219 cm⁻¹ shows the S-O stretching absorption that is due to the sulfate group of SDS.²⁴ From curves (b) and (c), the peaks at 2920 and 2918 cm⁻¹ are due to stretching vibration of CH₃,²³ while the peaks at 2851 and 1468 cm⁻¹ represent CH₂ stretching band from SDS.²⁵ In comparison with the vibrational bands of pure SDS, the relative intensity of the asymmetric CH₃ and CH₂ stretching band for the SDS-modified SiO₂ nanoparticles became significantly weak after surface modification process. This show that anionic surfactant of SDS has been adsorbed onto SiO₂ nanoparticles by hydrophobic interaction between surfactant hydrocarbon chains and SiO₂ surfaces.²³ The detection of SDS functional groups in the surface-modified SiO₂ indicates the existence of surfactants on the surface of the SiO₂ and confirmed the successful modification of the nanoparticle surface.

(Figure 5 should be here)

3.3 Membrane morphology

The SEM cross-sections images of control PES and PES-SiO₂ membranes with different magnifications are shown in Fig. 6. It can be seen that the membranes prepared exhibited a typical asymmetric structure, with a dense top-layer supported by teardrop-like structure and a porous spongy

sub-layer. However, with the addition of SiO₂ in the dope solution, the PES-SiO₂ membranes demonstrated thicker top-layer with more porous sub-layer membranes compared to the control PES membrane. This is because, during membrane formation, the presence of SiO₂ tends to decrease the thermodynamic stability of the process, leading to faster liquid-liquid phase separation which forms more porous structures of membrane.²⁶ Similar observations were also reported in the work of Zhang et al.²⁷ At the highest SiO₂ concentration (4 wt.%), the structure of the membrane seemed to be much denser with less porous sub-layer formed. This is likely due to delayed demixing process of solvent and non-solvent when the dope solution contains significant amount of SiO₂.²⁸

During phase inversion process, the solution viscosity can affect the morphology of membranes. It will influence the multitransfer between solvent and non-solvent exchange during the process and produces membrane with varied structure.⁶ Table 1 shows the effect of SiO₂ concentration on the viscosity of dope solutions. The highest viscosity was found in the 4 wt.% SiO₂ dope with the value of 1,262 mPa S while the lowest was in the control solution with 683 mPa S. It can be seen that the increase of SiO₂ concentration in PES dope solution tended to increase the viscosity of the solution which produced denser membrane with fewer macro-voids. This is because the polymeric chains tend to form entanglements as the polymer concentration surpasses its critical value. That may change the polymer behaviour from fluid to solid state. The entangled network structure will create stronger fibers and prevent non-solvent intrusion. As a result, the formation of macro-voids is suppressed.²⁹

(Figure 6 should be here)

3.4 EDX analysis

The existence of the SiO₂ nanoparticles in PES-SiO₂ structure was studied by EDX and the results are shown in Fig. 7. EDX analysis confirmed the existence of SiO₂ in membrane matrix due to the presence of Si element peak. The higher the concentration of SiO₂ added into PES membrane, the greater the percentage of Si element detected. As a comparison, the control PES membrane showed almost negligible Si element while the quantity of SiO₂ in the composite membranes increased with increasing SiO₂ loading in the membrane. Furthermore, in order to investigate the dispersion quality

of SiO₂ nanoparticles, the EDX line mapping was performed on the active layer of the PES membrane incorporated with 2 wt.% SiO₂. The silica (Si) signal is used to show the distribution of silica in the membrane. The height of the green lines as shown in Fig. 8 reflects the relative 'counts' of Si across the active layer (shown in yellow line) of the membrane. From the results, it can be confirmed that SiO₂ nanoparticles are uniformly dispersed throughout the PES matrix.

(Figure 7 should be here)

(Figure 8 should be here)

3.5 Thermal stability of the membranes

The thermal stability of the membranes can be assessed by the glass transition temperature (T_g) in which the polymer is in a glassy state and above rubbery condition.³⁰ The T_g in membrane is affected by region of free volume and chain mobility existed between the nanoparticles and polymer molecules due to the attractive or repulsive interaction. The addition of SiO₂ in the PES matrix can increase the T_g value as the available free volume for segmental motion is reduced.³¹ Table 2 shows the DSC results for the membranes incorporated with different concentration of modified SiO₂. As can be seen, the SiO₂-modified membranes tend to have greater thermal resistance compared to the control membrane. This result is in agreement with Shariatmadar et al.³² in which they also found that the addition of SiO₂ nanoparticles in the PES matrix could increase the thermal resistance of the membranes. This is because the incorporation of SiO₂ nanoparticles could create stronger bonds between the mixture compounds and limiting the chain mobility.³⁰

3.6 Mechanical properties of membranes

The mechanical properties of PES-SiO₂ hollow fiber membranes were tested using a tensile tester and the results of tensile strength and break elongation ratio are shown in Table 2. The results show that the tensile strength and break elongation ratio of the PES-SiO₂ membrane is higher compared to the control PES membrane. The highest tensile strength and break elongation was observed in the membrane incorporated with 2 wt.% SiO₂. The values were recorded at 2.46 MPa and 10.27%,

respectively. As a comparison, the control membrane only showed 1.95 MPa tensile strength and 2.04% break elongation. However, with further increasing the concentration of SiO₂ from 2 to 4 wt.%, the tensile strength and break elongation is reduced to 2.19 MPa and 9.59%, respectively. The results show that although the addition of SiO₂ nanoparticles into the control PES membrane could increase membrane mechanical strength, it should be controlled at appropriate amount. Previous work has reported the importance of SiO₂ in improving the mechanical strength of the membrane made of cellulose acetate.³³ However, excessive use of SiO₂ could negatively affect the membrane mechanical properties mainly due to the particles aggregation in the polymeric matrix that reduces the membrane elasticity.

3.7 Hydrophilicity of membranes

The water contact angle measurement is one of the methods to determine the degree of membrane hydrophilicity.³⁴ Generally, the smaller the contact angle between the water and membrane surface, the higher the hydrophilicity of the membrane and the greater the water flux.³⁵ As shown in Table 2, the highest contact angle can be observed in the control PES membrane with the value of 77.9°. This value is generally found for the PES membrane reported in the literature. With the addition of 4 wt.% SiO₂ in the membrane, the value was decreased to 71.0°. The decrease in the membrane contact angle suggested the improvement in membrane hydrophilicity upon SiO₂ incorporation.

(Table 2 should be here)

3.8 Membrane performance

Fig. 9 shows three-dimensional AFM images of the membrane skin surfaces. The surface roughness of PES-SiO₂ membranes was higher compared to the control PES membrane. The mean roughness values, R_a of the membrane incorporated with zero, 1, 2, and 4 wt.% SiO₂ were reported to be 14.56, 19.98, 26.04 and 23.59 nm, respectively. The increase of surface roughness is directly proportional to the amount of SiO₂ added. Higher surface roughness is associated to the increase of membrane surface area which will contribute to higher water flux.³⁶ Based on Fig. 10, it can be seen that the pure water

flux and BSA rejection is higher in the PES-SiO₂ membrane in comparison to the control PES membrane. With increasing SiO₂ loading from zero to 2 wt.%, both water flux and BSA rejection were reported to increase from 44.2 L m⁻² h⁻¹ and 80.8% in the control membrane to 87.2 L m⁻² h⁻¹ and 93.6% in the composite membrane incorporated with 2 wt.% SiO₂. Further increase in SiO₂ concentration from 2 to 4 wt.%, however, decreased water flux and BSA rejection to 69.4 L m⁻² h⁻¹ and 89.5%, respectively. The significant decrease in water flux in the membrane is mainly due to its denser structure formed with low porosity.

(Figure 9 should be here)

(Figure 10 should be here)

Table 3 compares the performances of our in-house made membranes with other membranes reported in the literature. As can be seen, our membranes that were incorporated with SDS-modified SiO₂ showed better performance compared to the membrane incorporated with unmodified SiO₂ as reported by Arthanareeswaran et al.³³ Our best performing membrane (incorporated with 2 wt.% SiO₂) showed 80% and 11% higher water flux and rejection, respectively in comparison to the results reported in the work of Arthanareeswaran et al.³³ Higher water flux can be obtained by using modified nanoparticles as Yu et al.³ found that SiO₂ nanoparticles grafted with 5 wt.% N-Halamine could produce a membrane with water flux as high as 384.4 L m⁻² h⁻¹ at working pressure of 1 bar, in addition to better antifouling and antibacterial properties. The modification of SiO₂ nanoparticles using 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) and blended in PSF membrane achieved water flux of 190 L m⁻² h⁻¹ at 1 bar.²⁷ Shen et al.¹⁸ modified the SiO₂ nanoparticles using SDS solution in order to reduce its dispersion in PES matrices. As a result, the produced membranes displayed superior permeability (255.4 L m⁻² h⁻¹) and retention (97.8%) at 2 wt.% SiO₂. The lower water flux of our membranes could be due to different fabrication conditions and/or membrane configuration. For instance, a flat-sheet membrane is usually cast from a low viscosity of polymer solution of few hundred centipoises (cP) but for hollow fiber membrane, the minimum viscosity for polymer solution

is usually higher than flat sheet membrane making.³⁹ Hence, the structure of hollow fiber membrane formed is denser and has relatively lower flux than that of flat sheet membrane.

(Table 3 should be here)

4 Conclusion

The PES hollow fiber membranes incorporated with SDS-modified SiO₂ nanoparticles were successfully fabricated via phase inversion technique. Compared to the unmodified SiO₂, the SDS-modified SiO₂ shows reduction of agglomeration and BET surface area. The addition of modified SiO₂ in the dope solution increased the dope viscosity which affected the solvent and non-solvent exchange rate, leading to the changes in membrane morphology as evidenced from SEM images. Upon addition of SiO₂, thicker top-layer and porous sub-layer were formed. Further increase in SiO₂ concentration to 4 wt.% however produced a membrane with lower porosity and denser structure. EDX analysis showed the existence of SiO₂ nanoparticles in the PES membrane while FTIR analysis confirmed the functional group of the SDS-modified SiO₂. DSC analysis showed the SiO₂-modified PES membranes had better thermal stability than the control PES membrane. The mechanical properties of PES-SiO₂ membrane was improved as the tensile strength was higher than the control PES membrane. With respect to filtration performance, the pure water flux and BSA rejection of membrane were improved upon addition of SiO₂ nanoparticles. Experimental results showed that the incorporation of 2 wt.% SDS-modified SiO₂ is the best loading to produce PES-SiO₂ composite membrane with good balance of water flux and solute rejection.

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Nomenclature

A : membrane area (m^2)

C_p : concentration of permeate (mg L^{-1})

C_f : concentration of feed (mg L^{-1})

J_w : water flux ($\text{L m}^{-2} \text{h}^{-1}$)

R : rejection (%)

t : time (h)

V : permeate volume (l)

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