

Polyethersulfone (PES) ultrafiltration (UF) membranes loaded with silver nitrate for bacteria removal

H. Basri^{1,2}, A.F. Ismail^{1,3*} and M. Aziz^{1,4}

¹Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia

²Science and Mathematics Department, Faculty of Science, Art and Heritage
Universiti Tun Hussein Onn Malaysia

³Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia

⁴Chemistry Department, Faculty of Science, Universiti Teknologi Malaysia

(Received October 15, 2009, Accepted July 19, 2010)

Abstract. PES UF membranes containing silver were prepared to impart antibacterial properties for waste water treatment. Asymmetric membranes for antibacterial application were prepared from polyethersulfone (PES) and silver nitrate (AgNO_3) (PES/ AgNO_3 =15/2 by weight) solution in N-Methyl-2-pyrrolidone (NMP) via simple wet phase inversion technique. These membranes were characterized by polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) of different molecular weights (1000 ppm in water) at room temperature and on operating pressure of 5 bars. It was observed that the water flux of PES- AgNO_3 membrane is slightly lower than virgin PES but still increased linearly with the increment of pressure applied. The morphology of the resulting membranes was examined using Field-Emission Scanning Electron Microscope (FESEM) coupled with Energy Dispersive Spectroscopy (EDS). Elemental analysis using EDS proved that silver is successfully loaded on the membrane surfaces. Due to the success of loading silver on membrane surfaces, antibacterial activities were evaluated via agar diffusion method against *Escherichia coli* (*E.coli*) and *Staphylococcus aureus* (*S.aureus*) culture. By incorporating 2 wt% of silver nitrate, PES- AgNO_3 showed significant inhibition ring on both *E.coli* and *S.aureus*. Filtration of *E.coli* solution (OD 0.31) showed satisfactory rejection data with ~100% inhibition growth after 24 hours incubation at 37°C. Resultant membranes also exhibit better tensile strength (compared to virgin PES) up to 71% may be due to the suggested interactions. The residual silver during fabrication was measured using ICP-MS and result showed that the residual silver content of PES- AgNO_3 membrane was only ~1% of the original silver added in the polymer solution. These studies have shown that PES- AgNO_3 UF membranes are potential in improving the filtration in water treatment.

Keywords: polyethersulfone; silver nitrate; ultrafiltration; antibacterial.

1. Introduction

Microfiltration (MF) and ultrafiltration (UF) have been known from the earliest 1920 as efficient processes to remove contaminants, significantly for bacteria, virus, yeasts and fungi, and also organic molecules (Mulder 1991, Nandi *et al.* 2010) in the level/size ranging from 0.01 to 10 μm . MF and UF asymmetric membranes usually have a finely porous surface layer or skin supported on a much more open microporous substrates. The finely porous surface layer performs the separation while the microporous substrate offers good mechanical strength (Jung *et al.* 2004, Baker 2004, Carreon *et*

* Corresponding author, Professor, E-mail: afauzi@utm.my

al. 2010). A common technique for the preparation of polymer membranes with asymmetric structure is the phase inversion process. During the process, a thin layer of the polymer is dissolved in an appropriate solvent, cast on a suitable support and immersed in coagulation bath (Mulder 1991). However, the classical procedure is not versatile enough to produce all the desirable membrane structure and properties. Modifications of the basic procedure are usually needed, including the addition of suitable additive to the casting solution or the coagulation bath.

In order to obtain membranes with special properties, additional additives can be dissolved in the casting solution. It has been well known that the membrane morphology can be controlled by the addition of a small amount of additive (Ismail *et al.* 2007). For an example, in Ismail's work, the larger amount PVP K30 (MW40,000) was added, the thinner top layer membrane is formed; whilst membrane pore size and macrovoids has also been affected. Polyvinyl pyrrolidone (PVP) in PES as studied by Marchese *et al.* acts preventing to some extent pore blockage due to its hydrophilic action (Marchese *et al.* 2003). It was also reported by Idris *et al.* that polyethylene glycol (PEG) can be used very well as polymeric additive, to increase the polymer dope viscosity and enhance the pore interconnectivity when added in appropriate amounts (Idris *et al.* 2007).

Recently, metal particles dispersed in polymer matrix have attracted broad scientific interest because of potential application including optoelectronics, optical devices (Chatterjee *et al.* 2008) and antibacterial agent in food-packaging materials (Ma *et al.* 2008) and clothing (Yao *et al.* 2008). Silver as an element with effective antimicrobial properties and low toxicity toward mammalian cells with in ionic form, is highly bactericidal, with no reported resistance but have a beneficial effect in decreasing wound surface inflammation is a metal of growing interest (Atiyeh *et al.* 2007). Silver nitrate, AgNO_3 is the standard and most popular silver salt solution, which at 0.5 mg/L of Ag^+ , inhibited the growth of *E.coli* by 100% (Choi *et al.* 2008).

Polyethersulfone (PES) based membrane had been extensively investigated for its application as microfiltration (MF) and ultrafiltration (UF) membrane materials during the past four decades, due to good thermal stability (glass transition temperature $\sim 225^\circ\text{C}$), moderate chemical resistance (resist against many alkalis, exhibit excellent biology and blood compatibility), excellent process ability and convenience in controlling the porosity and morphology (Barth *et al.* 2000, Ismail *et al.* 2007, Deng *et al.* 2008, Johnson 2003). PES is also approved for use with food, water and medical applications (Rahimpour *et al.* 2008).

To further extend the knowledge of developing PES asymmetric membrane, the current paper aims to study the effect of AgNO_3 addition in the membrane. Hence, the membranes' performance in terms of pure water flux and antibacterial activity was also investigated. To the best of our knowledge, this paper is the first to report rejection in *E.coli* suspension filtration.

2. Experimental

2.1 Membrane fabrication

Polyethersulfone ultrafiltration membranes were made using the wet phase-inversion process. All chemicals used in this work were analytical grade materials and they were used without purification. First, silver nitrate (AgNO_3 , Fluka) was dissolved in 1-Methyl-2-pyrrolidone (NMP, 99.5%; Merck) in one container with magnetic stirring. Polyethersulfone (PES, RADEL A-300, MW \sim 15,000 Da; Amoco Chemicals), after drying at 120°C overnight was also dissolved in NMP in separate container.

Only after both AgNO₃ and PES were dissolved completely, then the two solutions were mixed and agitated using mechanical stirrer at 200 rpm to reach homogeneity. The homogeneous solution was agitated continuously for at least 24 hours. PES alone was prepared for control.

Visual observation indicated that the color of dope solution become darker (yellow to chrome) after AgNO₃ addition. The final solution was composed of 15% PES, 2% AgNO₃ and 83% NMP by weight while the control solution only composed of 15% PES and 85% NMP. The solution was deposited on a smooth glass plate and stainless steel support casting knife was used to spread the solution to a uniform thickness. The glass plate with the membrane film was quickly transferred to a water bath at room temperature for the remainder of the phase-inversion process. For this study, sample of coagulation bath was taken and analyzed for silver residue. Membranes were immersed in water bath for 24 hours, for the further removal of solvent followed by air-dried at 24°C, room temperature (Kusworo *et al.* 2008).

2.2 Membrane characterization

2.2.1 ATR-FTIR and thermal analysis

The interaction between AgNO₃ and PES was investigated using attenuated total reflection fourier transform infrared (ATR-FTIR)(Thermo Nicolet Instrument Corporation, Madison, WI). Membranes were dried 24 hours at 60°C before being analyzed. Five spots from the top and bottom of membrane surfaces were scanned at a rate of 16 scans per second to investigate the functional groups formed before and after silver nitrate addition. Omnic Software was used to control spectral acquisition and to process the acquired data. PES-AgNO₃ and PES spectra were subtracted digitally in order to study the functional groups associated to silver nitrate on the membrane surface.

Thermal analysis was also carried out to study the compatibility between polymer (PES) and additive added (silver nitrate). In addition, information on the effects of silver nitrate addition to the thermal property of polymer can also be obtained. The TGA was carried out by Mettler Toledo thermogravimetric analyzer (TGA TSO800GC1A). Membrane sample of ~4 mg was dried at 60°C for 24 hours before scanned from 50 to 750°C with a heating rate of 20°C/min. DSC measurement was carried out using Mettler Toledo differential scanning calorimeter in DSC/TGA mode at the same heating rate under nitrogen atmosphere.

2.2.2 Morphological studies and silver residue

The particle size, distribution as well as morphological and membrane thickness were analyzed using Ziess Supra 35 VP field-emission scanning electron microscope, (FESEM) coupled with energy dispersive spectroscopy (EDS). For cross-section images, the membrane samples were dried and then fractured cryogenically in liquid nitrogen before mounting on sample stubs. The samples were then sputtered with a thin layer of gold using a sputtering apparatus; scanned with magnification ranging from 500 to 50,000x with potentials of 10.0 kV.

During fabrication, silver leaching was evaluated using inductive coupled plasma mass spectrometer (ICP-MS), Perkin Elmer; model ELAN 6000 with argon as gas carrier. The analytical range of solution extends from the ppt (parts per trillion) to the ppm (parts per million) regions. The sample of water bath (coagulation and immersion) were quickly been tested by ICP-MS in order to measure the silver content leached. Results will somehow correspond to the amount of silver left in membrane.

2.2.3 Pure water permeation test and UF identification (MWCO)

Membrane permeability was determined from distilled water flux measurement using a cross-flow

cell over a pressure range of 1-6 bars as described elsewhere (Ismail *et al.* 2007). The experiments were carried out at ambient temperature (27°C) and pure water permeation (PWP) for the PES membrane was calculated from the equation, $PWP = \frac{Q}{A \cdot \Delta t}$ (volume of the permeate, L) divided by A (membrane surface area, m^2), P (pressure, bar) and Δt (permeation time, h).

The membranes were tested for ultrafiltration (UF) using aqueous solution containing non-ionic macromolecules *i.e.*, polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) of average MW from 8000 to 360,000. In this test, pure water permeation flux (PWP) was first measured at temperature of 27°C, $P=5$ bar for about 1 hour (Khayet *et al.* 2003). The solute retention tests were then performed with PEG and PVP of increasing molecular weight. Permeate will only be taken after feed aqueous solutions were circulated through the feed permeation cell for about 1 hours. The feed temperature was 27°C, the solute concentration was 1000 ppm and the feed pressure was 5 bars. The system was thoroughly flushed with distilled water after each run. The solute concentration of the feed and permeate solutions were measured by the total organic carbon (TOC) analyzer, TOC-V_{CSH}, Shimadzu. An exponential plot of rejection versus molecular weight (KDa) will be drawn to get the molecular weight which is 90% rejected by membranes (Mulder 1991).

2.2.4 Contact angle and mechanical strength studies

Hydrophobicity/hydrophilicity of membranes was determined by sessile drop contact angle measurement (Suk *et al.* 2002, Liu *et al.* 2008) on a Contact Angle goniometer (Krüss Gambult, Germany). Measurement is done within 10 s after the water drop in order to reduce evaporation effect. The reported values are the average of at least five different measurements.

The effect of silver nitrate addition into PES membrane was also investigated in terms of mechanical strength. The tensile strength was measured using mechanical testing system, MTS (LRX 5kN, Lloyd Instruments, Fareham hants, UK) with rate 5 $mmmin^{-1}$ (Mohd. Norddin *et al.* 2008). Membranes were cut into strips with 5 cm long and 1 cm wide, the thickness of each strip was measured by vernier calipers. The two ends of each strip were wrapped with adhesive tape before it was clipped between the retaining clips of the testing machine. All specimens were drawn at ambient temperature. The tensile rate was 5 mm/min. At least three sample measurements were performed and the results were quoted as average values.

2.2.5 Antibacterial properties of membrane

The initial antibacterial property of resultant membrane was investigated by an agar diffusion method (Ma *et al.* 2008). *S.aureus* and *E.coli* were inoculated on agar prepared on petri dish. Membrane circular disks were put on the *S.aureus* and *E.coli* culture and were incubated in 37°C for 24 hours. The presence of any clear zone that formed around the film disk indicates that membrane is active antibacterial. The culture without membrane is used as control.

To assess further effectiveness on the antibacterial property of the resultant membranes, 3 mL of stationary phase *E.coli* was serially diluted from a stock of 10^9 CFU/mL to get the optical density at $\lambda=600$ nm (OD_{600}) 0.3-1, measured by Buck Scientific 100 Vis spectrophotometer in Minimal Davis (MD) medium. Diluted *E.coli* solution was filtered onto sterile PES and PES-AgNO₃ membranes using a vacuum filtration cell (Zodrow *et al.* 2009). Before the filtration, all the glasswares and membranes were autoclaved at 121°C for 15 min. The OD_{600} value was taken before and after filtration, calculated for early indication of *E.coli* rejection. Membranes after filtration were then placed on Luria-Bertani (LB) plates (with the top side touching the culture) and incubated at 37°C overnight. The total number of viable cells after filtration was observed on the next day to compare

the growth inhibition by both membranes.

3. Results and discussion

Silver nitrate was loaded into PES polymer solution in order to add the antibacterial property of the membrane. This study will reveal the influence of AgNO_3 addition into membrane formulation in terms of thermal, morphological, permeability and antibacterial properties.

3.1 ATR-FTIR and thermal analysis

The ATR-FTIR spectra identified functional groups of organic materials depositing on the membrane surface. Physically, PES membrane is white in colour. Silver nitrate is white crystals but after loaded in the membrane, the white PES film became grayish on the top surface. Both top and bottom side of the membrane was scanned for at least five spots to differentiate the fingerprints spectra (if any). Since this technique is exclusively useful on samples with covalent bond, Fig. 1 presented the identical FTIR spectra of PES and PES- AgNO_3 .

Subtraction of spectra will be informative to gather small differences in membrane surface after filtration (Mimi Sakinah *et al.* 2007) or after additive addition (Slistan-Grijalva *et al.* 2008). In Fig. 1 FTIR spectrum of PES- AgNO_3 , PES and subtraction of both suggests that Ag(I) may have interacted with oxygen from the sulphonic group in PES backbone indicated by : significant shift peak at 1155 cm^{-1} (c) due to S=O stretchings within aromatic ring and significant peak at 750 cm^{-1} (c) due to stretching of aromatic ring. These could be due to the formation of complex between silver ion, Ag(I) with the oxygen atom from PES; the stretching adsorption of S=O shifted to some degree. The existence of nitrate, NO_3^- group originally from AgNO_3 can still be detected in spectra (c) as peaks at wavenumbers 1540 and 830 cm^{-1} .

Previous studies discussed on the coordination of cyano nitrogen from PAN (Wang *et al.* 2005) and PVP (Su *et al.* 2002, Slistan-Grijalva *et al.* 2008), proposing a mechanism of Ag(I) interacting to N from PAN and PVP. The cyano nitrogen from PAN and PVP can donate its lone-pair electron to coordinate with Ag^+ ion and form a δ -bond. Other findings obtained by Han *et al.* showed that

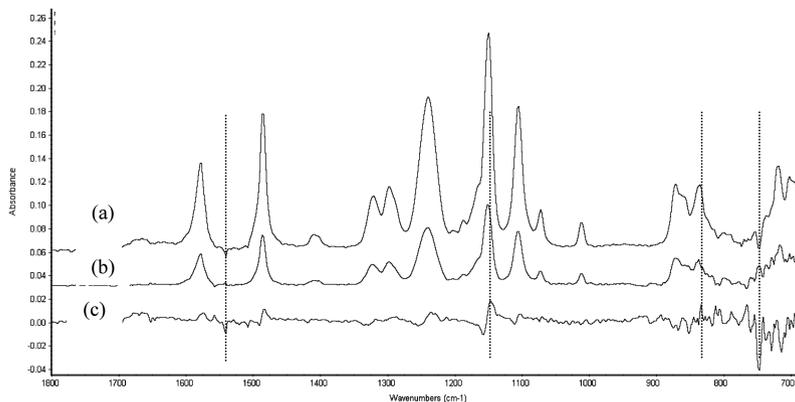


Fig. 1 ATR-FTIR spectra of (a) PES, (b) PES- AgNO_3 and (c) Subtraction of PES- AgNO_3 and PES

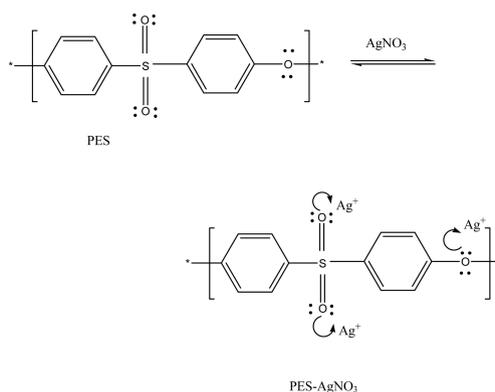


Fig. 2 The scheme of interactions between PES as polymer and AgNO₃ as additive

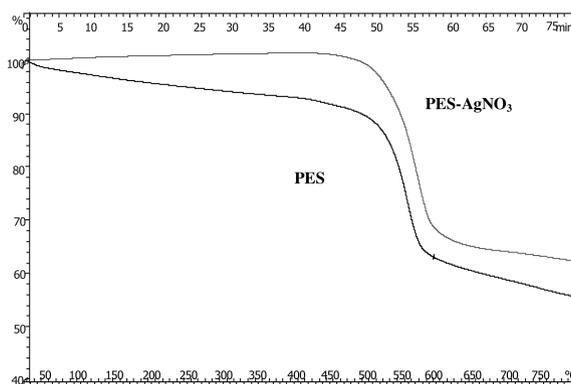


Fig. 3 Thermo gram of PES and PES-AgNO₃ membranes. Result showed the thermal stability of PES membrane improved after loaded with AgNO₃

silver ion (Ag(I)) possessed possible bonding sites with oxygen contributed from 4-(4-pyridylthiomethyl)benzoic acid (Han *et al.* 2005). We suggest that PES may interact with Ag⁺ due to the lone-pair electron of the oxygen atom attached to the sulfur atom in PES backbone structure. The scheme of interactions between PES and Ag(I) of AgNO₃ in this work is suggested in Fig. 2.

Fig. 3 showed the results of thermal stability tests from Mettler Toledo thermogravimetric analyzer (TGA TSO800GC1A), which is expressed as sample mass loss (%) and temperature (50–750°C). Both PES and PES-AgNO₃ membranes loose weight as temperature increases, occurred in a single step correspond to the compatibility of AgNO₃ to PES. Significantly, PES-AgNO₃ showed its thermal stability when it decomposes only after the temperature reached 500°C, in contrast PES start to degrade as early as 50°C. DSC curves of both membranes are shown in Fig. 4. Fig. 4 showed that the glass transition temperature, T_g of PES-AgNO₃ is slightly higher than PES alone. This is in accord with the result of TGA which showed that PES-AgNO₃ is more thermally stable. According to Arthaneswaran *et al.* a higher T_g indicates that membrane possesses more free volume fraction which may contribute to better performance in permeability (Arthaneswaran *et al.* 2004). Results overall indicate that the thermal stability of PES is slightly modified by the presence of AgNO₃.

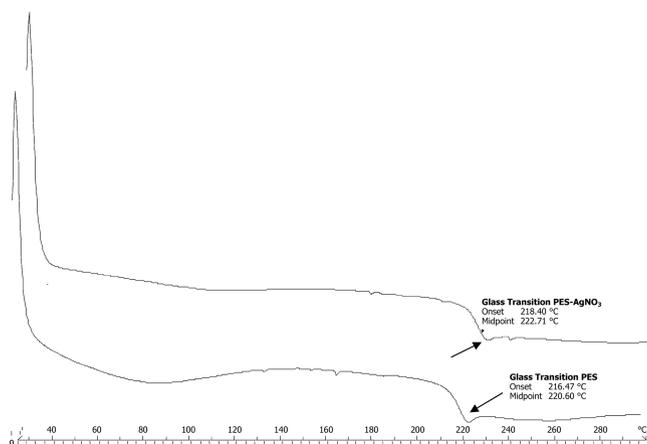


Fig. 4 DSC thermograms of PES and PES-AgNO₃ membranes

3.2 Morphology studies and silver residue for PES-AgNO₃ membranes

It has been found that a broad variety morphologically different polymeric membrane can be prepared by changing the parameters such as composition and concentrations of polymer solvent and additive (Khayet *et al.* 2002). The determination of morphological characterizations is playing an important role in evaluating the performance of the membranes. The cross-sectional morphology of membranes has been used to ascertain the type and structure of pores and subsequently helpful in identifying the roles of membrane casting solution composition and casting conditions on the mechanism of formation of pores (Malaisamy *et al.* 2002).

Fig. 5 presents the cross sectional images of both membranes that show very similar morphologies with the asymmetry part for both are apparent. Generally, we can say that the loading of silver nitrate to PES membrane did not visibly alter the membrane structure, Fig. 5 (a) and (b), in agreement to the results obtained by Zodrow *et al.* (2009). The surface image of PES-AgNO₃, Fig. 5(d) showed white particles distributed almost evenly on the surface. By EDS, Fig. 5(c) the white particles were analyzed and confirmed that the white particles were indeed silver with size 180.85 ± 3.18 nm.

Silver leaching in PES-AgNO₃ fabrication was assessed by using ICP-MS method. By loading 2% (by weight) of silver nitrate, leaching was found to be 213.3 ± 0.5 ppm ($\sim 1.07\%$ from amount loaded) in the coagulation bath and 86.6 ± 3.1 ppm ($\sim 0.43\%$) in the immersion bath. From the value leached, we estimated the amount of silver nitrate left in the membranes for antibacterial activity $\sim 98.5\%$ (~ 1.97 wt%). The amount is promising to exhibit antibacterial activity as Chou *et al.* (2005) reported that the amount of silver in the silver-loading cellulose acetate (CA) hollow fibre reduced by $\sim 35\%$ during spinning but still antibacterial active (Chou *et al.* 2005). According to Chou *et al.* (2005) and Yu *et al.* (2003) silver ion which is not trapped in the polymer network especially on the surface can easily leach out due to the superficial position of AgNO₃ particles which are easily accessible into the water (Chou *et al.* 2005, Yu *et al.* 2003).

3.3 Pure water permeability (PWP) and UF identification of PES and PES-AgNO₃ membranes

Membranes incorporated with 2.0% (by weight) silver nitrate (PES-AgNO₃) had similar permeability

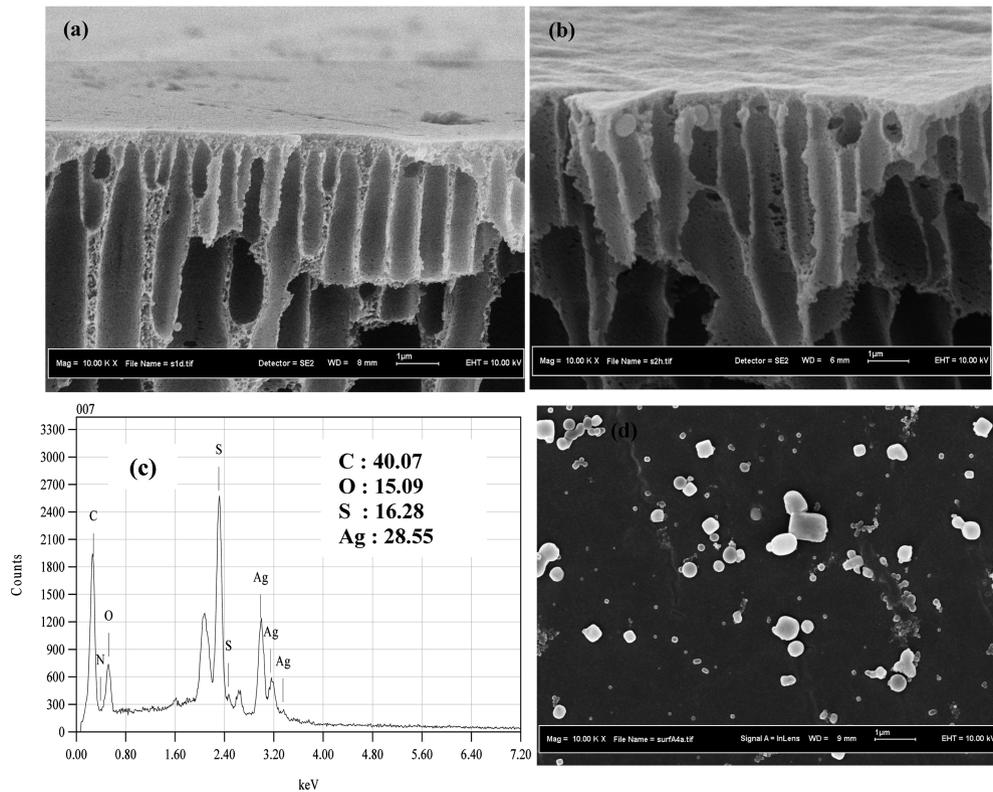


Fig. 5 (a) Cross-section image of PES, (b) Cross-section image of PES -AgNO₃, (c) Surface image of PES -AgNO₃, (d) EDX spectra of PES -AgNO₃(c). The addition of AgNO₃ did not change the morphology of PES membrane as evidenced in the cross sectional image of both membranes (a) and (b)

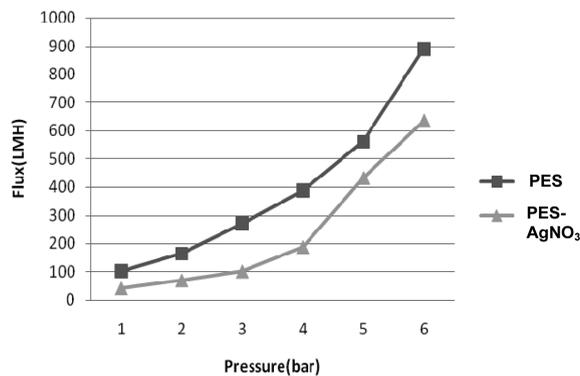


Fig. 6 Pure water permeability ($Lm^{-2}hr^{-1}$) for PES and PES-AgNO₃ membranes against pressure (bar)

and morphology (discussed in 3.2). Based on Fig. 6, which depicts the results from the permeation measurements, membrane fluxes were increased as the feed pressure is gradually increased. Result also shows that PES-AgNO₃ membranes are strong enough to avoid collapse structure up to the pressure of 6 bar. However, from the result, compared to virgin PES membranes, silver particles

Table 1 Results of the UF experiments of PES and PES-AgNO₃ asymmetric membranes

Membrane	Solute rejection (%)				Average pore size (KDa)
	Solute molecular weight				
	8000	10,000	40,000	360,000	
PES	46.04	54.68	69.73	92.45	272
PES-AgNO ₃	61.2	76.2	85.5	98.2	107

loaded in PES have affected the PWP. This is contradicting to the point that higher thermal property means larger pore volume with better permeability. The reason for slight decrement is the silver particle loaded may agglomerate as a result of larger attraction energy than repulsion energy between the particles (Lin *et al.* 2008), thus blocked the pores and reduced the PWP. Similar result obtained by Idris, (Idris *et al.* 2007) when PEG 200 is added in the PES casting solution, the size of microvoids reduced and very thin skin layer were formed. In her work, the reduction in the macrovoid size in PES-PEG 200 membranes contributes to high flux resistance and thus explained for the low flux exhibited.

The size of microbial cells can vary from as small as 0.1-0.2 μm in diameter to those more than 50 μm in diameter. For an example, the dimension of an average rod-shape bacterium, *E.coli* are about $1 \times 3 \mu\text{m}$ (Madigan *et al.* 2000). Therefore, to remove bacteria via membrane processes, one must have smaller pore size than bacterium so that they can be removed by size exclusion mechanism (Madaeni 1999). UF identification experiment was done to PES and PES-AgNO₃ and the results were summarized in Table 1. The molecular weight cut-off of the membranes was calculated based on 90% solute separation (Khayet *et al.* 2003). It can be seen from Fig. 5 that PWP is lower for PES-AgNO₃ membrane. This is in agreement with the results obtained from the UF experiment; pore size of PES-AgNO₃ is 61% smaller. Hence, it can be anticipated that the PES membrane pore size decreased after AgNO₃ loading. The pore size of both membranes obtained from the MWCO experiment is in UF range (Mulder 1991).

3.4 Contact angle and mechanical strength of PES membranes

Hydrophobicity and hydrophilicity of membrane surfaces are characterized by the static contact angle made between a water droplet and the surface. A surface is hydrophilic when the value is less than 90° and hydrophobic when the value is greater than 90°. Hydrophilic membranes decrease the resistance of water permeating through membrane and may increase fluxes. The contact angle for PES membrane is 78.5 ± 0.7 . When loaded with AgNO₃ the contact angle for PES-AgNO₃ become 120.6 ± 3.7 , due to the surface that is covered with silver particles; as evidenced in FESEM surface image, (Fig. 5) which somehow reduced the hydrophilicity.

Playing a role as a selective barrier to filtrate bacteria from water-flow required adequate mechanical strength. The addition of silver into polymers for example PAN by Yu *et al.* (2003) and CA by Chou *et al.* (2005) decreased the mechanical strength of original polymer limited to ~10%. However, Ma *et al.* revealed that chitosan-nylon-6 blended membranes containing silver ion exhibit better tensile strength which maybe attributed to the inter-molecule interaction which is more intense between chitosan and silver ion (Ma *et al.* 2008). The same results were obtained in this study where PES-AgNO₃ showed better mechanical strength, Fig. 7, maybe ascribed to the interaction of Ag and PES, as suggested in the mechanism in Fig. 2. This is in agreement with

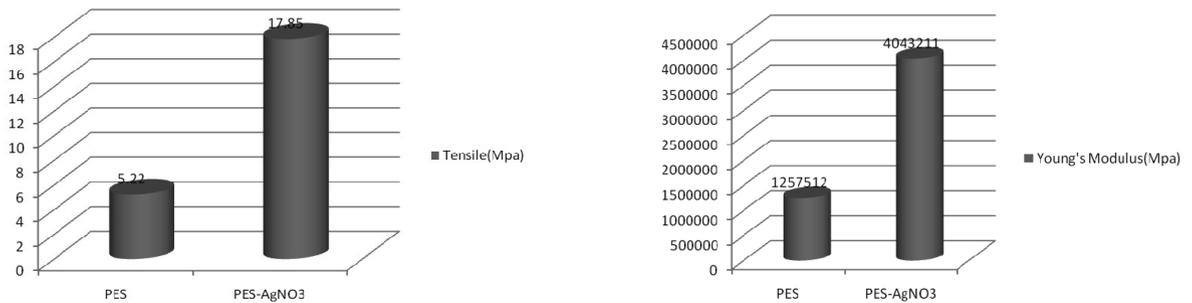


Fig. 7 Mechanical properties of PES and PES-AgNO₃ membranes. Comparison showed mechanical properties of PES membrane improved after loaded with AgNO₃

studies by Yiu *et al.* (2004) which relate hydrophilicity of polymers with surface roughness and mechanical properties. According to Yiu, hydrophobic surface exhibits better mechanical strength for the reason that the penetration of water to hydrophilic polymer surfaces can cause a softening to polymer and therefore reduced the frictional forces between polymer chains (Yiu *et al.* 2004).

3.5 Antibacterial properties of membrane

Initial antibacterial properties have been tested using disk diffusion method (Ma *et al.* 2008, Yu *et*

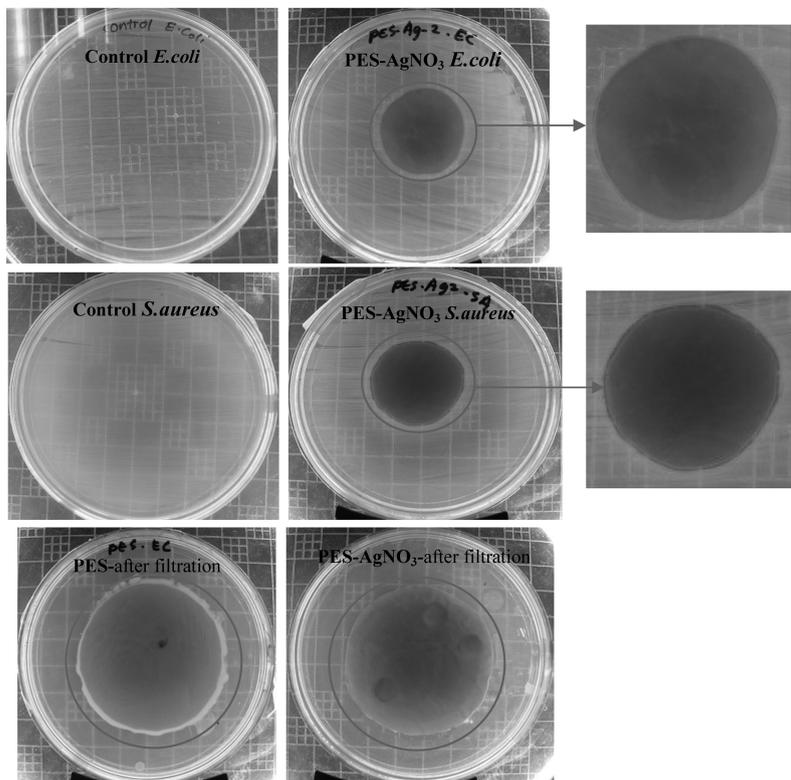


Fig. 8 Photographs of an antibacterial test result of the membranes against *E. coli* and *S. aureus*

Table 2 Separation of *E.coli* solution of OD₆₀₀=0.31

Membrane	OD ₆₀₀ of <i>E.coli</i> solution		% R
	Before (feed)	After (permeate)	
PES	0.31	0.30	4.84
PES-AgNO ₃	0.31	0.21	31.94

al. 2003). Results show satisfactory inhibition zone as shown in Fig. 8. After 24 hours incubation at 37°C, PES-AgNO₃ showed antibacterial effect on both gram positive, *S.aureus* and gram negative, *E.coli*. However, the diameter expansion of inhibition zone is clearly seen only at *S.aureus* culture, Fig. 8. We decided to do further testing on filtrating *E.coli* suspension (Zodrow *et al.* 2009) with OD₆₀₀ 0.3-1.0 using vacuum flask pump. After filtration, membranes used were quickly placed on LB plates and incubated for 37°C overnight to investigate whether bacteria growth will continue or not on the plates. Significant result was obtained where plate with PES membrane still allows bacteria growth; in contrast plate with PES-AgNO₃ membrane inhibit bacteria growth almost 100% as evidenced in photo images in Fig. 8. As an additional data, the OD₆₀₀ for *E.coli* suspension is evaluated before and after filtration to give some idea of bacteria rejection by membranes. Table 2 lists the rejection values solely based on the OD₆₀₀ on the feed and permeate of *E.coli* suspension. Rejection then is calculated based on

$$\%R = 1 - \frac{OD_p}{OD_f} \times 100\%$$

4. Conclusions

Within the limits of the present study, the following conclusions can be drawn

1. Silver nitrate can be loaded into polyethersulfone membrane with leaching in the range of ~1% from the original amount loaded, approved by EDS technique.
2. The loading of silver nitrate results in the improved thermal and mechanical property of PES membrane suggested that there is an interaction between PES and AgNO₃.
3. The addition of 2 wt% of silver nitrate, proven by EDS analysis made PES-AgNO₃ antibacterially active to *S.aureus* and *E.coli*, as indicated in the agar diffusion method as well as the filtration test which proved the inhibition grow of *E.coli*.
4. Future work should be established on improving the silver leaching during fabrication as well as to derive the mechanism of bacteria-killing during filtration.

Acknowledgments

The authors would like to thank Minister of Science, Technology & Innovation (MOSTI) for funding this project, Universiti Teknologi Malaysia (UTM) and Universiti Tun Hussein Onn Malaysia (UTHM) for the generous financial support. Authors also thank Ms Nadirah Ismail and Dr. Zaharah Ibrahim, for permission and technical assistance for antibacterial analysis of membranes.

References

- Arthaneswaran, G., Thanikaivelan, P., Srinivasan, K., Mohan, D. and Rajendran, M. (2004), "Synthesis, characterization and thermal studies on cellulose acetate membranes with additive", *Eur. Polym. J.*, **40**, 2153-2159.
- Atiyeh, S.B., Costagliola, M., Hayek, S.N. and Dibo, S.A. (2007), "Effect of silver on burn wound infection control and healing; review of the literature", *Burns*, **33**, 139-148.
- Baker, R.W. (2004) *Membrane technology and application.*, 2nd Edition, John Wiley & Sons.
- Barth, C., Goncalves, M.C., Pires, A.T.N., Roeder, J. and Wolf, B.A. (2000), "Asymmetric polysulfone and polyethersulfone membranes: effects of thermodynamic conditions during formation on their performance", *J. Membrane Sci.*, **169**(2), 287-299.
- Carreon, J., Saucedo, I., Navarro, R., Maldonado, M. and Guibal, E. (2010), "Mercury recovery from aqueous solutions by polymer-enhanced ultrafiltration using a sulfate derivative of chitosan", *Membrane Water Treatment*, **1**(4).
- Chatterjee, U., Jewrajka, S.K. and Guha, S. (2008), "Dispersion of functionalized silver nanoparticles in polymer matrices : stability, characterization and physical properties", *Polym. Composites*, **30**(6), 827-834.
- Choi, O., Deng, K.K., Kim, N.J., Ross, Jr. L. and Surampalli, R.Y. (2008), "The inhibitory effects of silver nanoparticles, silver ions and silver chloride colloids on microbial growth", *Water Res.*, **42**(12), 3066-3074.
- Chou, W.L., Yu, D.G. and Yang, M.C. (2005), "The preparation and characterization of silver-loading cellulose acetate hollow fiber membrane for water treatment", *Polym. Advan. Technol.*, **16**, 600-607.
- Deng, B., Li, J., Hou, Z., Yao, S., Shi, L., Liang, G., and Sheng, K. (2008), "Microfiltration membranes prepared from polyethersulfone powder grafted with acrylic acid by simultaneous irradiation and their pH dependence", *Radiat. Phys. Chem.*, **77**, 898-906.
- Han, L., Wang, R., Yuan, D., Wu, B., Lou, B. and Hong, M. (2005), "Hierarchical assembly of a novel luminescent silver coordination framework with 4-(4-pyridylthiomethyl) benzoic acid", *J. Mol. Struct.*, **737**, 55-59.
- Idris, A., Zain, N.M. and Noordin, M.Y. (2007), "Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives", *Desalination*, **207**, 324-339.
- Ismail, A.F. and Hassan, A.R. (2007), "Effect of additive contents on the performances and structural properties of asymmetric polyethersulfone (PES) nanofiltration membranes", *Sep. Purif. Technol.*, **55**, 98-109.
- Johnson, J., (2003), *A Novel Polyethersulphone microporous membrane*, Feature Article *Membrane Technology*, 5-10.
- Jung, B., Yoon, J. K., Kim, B. and Rhee, H.W. (2004), "Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes", *J. Membrane Sci.*, **243**, 45-57.
- Khayet, M., Feng, C.Y. and Matsuura, T. (2003), "Morphological study of fluorinated asymmetric polyetherimide ultrafiltration membranes by surface modifying macromolecules", *J. Membrane Sci.*, **213**, 159-180.
- Khayet, M., Feng, C.Y., Khulbe, K.C. and Matsuura, T. (2002), "Study on the effect of a non-solvent additive on the morphology and performance of ultrafiltration hollow-fiber membrane", *Desalination*, **148**, 321-327.
- Kusworo, T.D., Ismail, A.F., Mustafa, A. and Matsuura, T. (2008), "Dependence of membrane morphology and performance on preparation conditions : The shear rate effect in membrane casting", *Sep. Purif. Technol.*, **61**, 249-257.
- Lin, H.W., Hwu, W.H. and Ger, M.D. (2008), "The dispersion of silver nanoparticles with physical dispersal procedures", *J. Mater. Process. Technol.*, **206**(1-3), 56-61.
- Liu, S.X., Kim, J.T. and Kim, S. (2008), "Effect of polymer surface modification on polymer-protein interaction via hydrophilic polymer grafting", *J. Food Sci.* **73**(3), 143-150.
- Ma, Y., Zhou, T. and Zhao, C. (2008), "Preparation of chitosan-nylon-6 blended membranes containing silver ions as antibacterial materials", *Carbohydr. Res.*, **343**(2), 230-237.
- Madaeni, S.S. (1999), "The application of membrane technology for water disinfection, Review paper", *Water Res.*, **33**, 301-308
- Madigan, M.T., Martinko, J.M. and Parker, J. (2000), *Brock biology of microorganisms-Chapter 3 : Overview of cell structure and the significance of smallness*, 9th edition, Prentice-Hall, Upper Saddle River, NJ, 58-59.
- Malaisamy, R., Mohan, D.R. and Rajendran, M. (2002), "Polyurethane and sulfonated polysulfone blend

- ultrafiltration membranes (I. Preparation and Characterization Studies)", *J. Colloid Interf. Sci.*, **254**, 129-140.
- Marchese, J., Ponce, M., Ochoa, N.A., Prádanos, P., Palacio, L. and Hernández, A. (2003), "Fouling behaviour of polyethersulfone UF membranes made with different PVP", *J. Membrane Sci.*, **211**, 1-11.
- Mimi Sakinah, A.M., Ismail, A.F., Rosli Md Illias and Osman Hassan (2007), "Fouling characteristics and autopsy of a PES ultrafiltration membrane in cyclodextrins separation", *Desalination*, **207**, 227-242.
- Mohd Norddin, M.N.A., Ismail, A.F., Rana, D., Matsuura, T., Mustafa, A. and Tabe-Mohammadi, A. (2008), "Characterization and performance of proton exchange membranes for direct methanol fuel cell: Blending of sulfonated poly(ether ether ketone) with charged surface modifying macromolecule", *J. Membrane Sci.*, **323**, 404-413.
- Mulder, M. (1991), *Basic principles of membrane technology*, Kluwer Academic Publisher, The Netherlands.
- Nandi, B.K., Das, B., Uppaluri, R. and Purkait, M.K. (2010), "Preparation and characterization of inexpensive submicron range inorganic microfiltration membranes", *Membrane Water Treatment*, **1**(2), 121-137.
- Rahimpour, A., Madaeni, S.S. and Mehdi-pour Ataei, S. (2008), "Synthesis of a novel poly(amide-imide)(PAI) and preparation and characterization of PAI blended polyethersulfone (PES) membranes", *J. Membrane Sci.*, **311**, 349-359.
- Slistan Grijalva, A., Herrera Urbina, R., Rivas Silva, J.F., Avalos Borja, M., Castillon Barraza, F.F. and Posada-Amarillas, A. (2008), "Synthesis of silver nanoparticles in a polyvinylpyrrolidone (PVP) paste and their optical properties in a film and in ethylene glycol", *Mater. Res. Bull.*, **43**, 90-96.
- Su, C., Kuraoka, K. and Yazawa, T. (2002), "Increasing the stability of silver(I) ions in inorganic-organic hybrid membranes for C₂H₄/C₂H₆ separation by using weakly self-coordinating anions of the silver salts", *J. Mater. Sci. Lett.*, **21**, 525-527.
- Suk, D.C., Chowdhury, G. and Matsuura, T. (2002), "Study in the kinetics of surface migration of surface modifying macromolecules in membrane preparation", *Macromolecules*, **35**, 3017-3021.
- Wang, Y., Yang, Q., Shan, G., Wang, C., Du, J., Wang, S., Li, Y., Chen, X., Jing, X. and Wei, Y. (2005), "Preparation of silver nanoparticles dispersed in polyacrylonitrile nanofiber film spun by electrospinning", *Mat. Lett.*, **59**, 3046-3049.
- Yao, C., Li, X., Neoh, K. G., Shib, Z. and Kang, E.T. (2008), "Surface modification and antibacterial activity of electrospun polyurethane fibrous membranes with quaternary ammonium moieties", *J. Membrane Sci.*, **320**, 259-267.
- Yiu, C.K.Y., King, N.M., Pashley, D.H., Suh, B.I., Carvalho, R.M., Carrilho, M.R.O. and Tay, F.R. (2004), "Effect of resin hydrophilicity and water storage on resin strength", *Biomaterials*, **25**, 5789-5796.
- Yu, D.G., Teng, M.Y., Chou, W.L. and Yang, M.C. (2003), "Characterization and inhibitory effect of antibacterial PAN-based hollow fiber loaded with silver nitrate", *J. Membrane Sci.*, **225**, 115-123.
- Zodrow, K., Brunet, L., Mahendra, S., Li, D., Zhang, A., Li, Q. and Alvarez, P.J.J. (2009), "Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal", *Water Res.*, **43**, 715-723.