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Effect of PVP Addition in the Preparation of Polyethersulfone (PES)-$AgNO_3$ Antibacterial Membrane

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ABSTRACT

Association of antibacterial agent into polymer-based material is an interesting, recent extension in membrane technologies research area. Asymmetric polyethersulfone–silver nitrate (PES-$AgNO_3$) nanocomposite membranes were synthesized by wet phase inversion with polyvinylpyrrolidone (PVP) as additive. Three different molecular weights (MW) of PVP in the range of 10 K to 360 K were tested for their ability to stabilize and disperse silver in the polymer solution. Results showed that PVP 360 K plays a significant role in altering silver particle size with better dispersion compared to the membranes prepared without addition of PVP and with the addition of lower MW of PVP. Results agreed with the leaching detected by ICP-MS where silver loss during membrane fabrication for PES-Ag-P360 is only 0.4636 ppm (0.0093%). The antibacterial activity for the resultant membranes was tested using inhibition zone method. Results indicated that PES-$AgNO_3$ and PES-$AgNO_3$-PVP (loaded with only 0.5 wt% silver) were antibacterial to *Escherichia coli* and *Staphylococcus aureus*. The improvement of antibacterial properties of the prepared membranes could be primarily attributed to the PVP addition as well as the surface morphology and permeation properties.

Keywords: Polyethersulfone, polyvinylpyrrolidone, silver leaching, antibacterial

1.0 INTRODUCTION

Antibacterial compound is defined as a synthetic or natural compound that destroys bacteria or suppresses their growth or their ability to reproduce [1]. There are many antibacterial products commercially available for cleaning and hygienic purposes. In addition, invention on loading/incorporating antibacterial agent into our daily needs such as clothing, soap, containers for food-packaging and water filtration system is seriously under taken. Water treatment and effluents disinfection by using membrane technologies has been growing interest topic recently due to the environmental friendly factor as compared to the common disinfectant, chlorine. Therefore the combination of membrane technologies and the relevancy of antibacterial agent incorporation such as silver is an area that should be seriously looked into.

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Silver is a metal that has potential in technological application such as catalysis [2], sensing [3], environmental [4] and biomaterials due to its distinctive properties such as good conductivity, chemical stability, catalytic and antibacterial activity [4–5]. Therefore, extensive research were done on loading silver into polymer in order to produce composites for antibacterial application such as clothing, membrane for waste water treatment and food packaging. The fact that silver can be dispersed well in various polymer matrix have attracted broad scientific interest including optoelectronics, sensing and biomaterials [3,6–7] applications. Previous research for polymer-silver loading has been done on polyacrylonitrile (PAN)[8–9], polyurethane (PU) [10–11], polyimide (PI) [12], cellulose acetate (CA)[13–14] polysulfone (PSf) [15] and chitosan [16] embedded with silver for clothing, food-packaging and water treatment applications. Since polymer is known to be an excellent host material for metal, polyethersulfone (PES) which is widely used for microfiltration (MF), ultrafiltration (UF) and gas separation membranes, had been chosen in this study. Besides, PES is principally favorable due to its characteristics of wide temperature limits, wide pH tolerances, fairly good chlorine resistance and good chemical resistance to aliphatic hydrocarbons, alcohols and acids [17–19].

Poly(vinyl pyrrolidone)(PVP) is known as a water soluble polymer which had frequently been studied to see the effects as additive in membrane fabrication. It is also known as an agent for suppressing macropore formation in phase inversion membranes. In Rafizah and Ismail's work, PVP with MW 10, 000 had been used as a sizing agent to promote the adhesion between carbon molecular sieve (CMS) with polysulfone (PSf) [20]. Other studies by Ismail and Hassan deduced that addition of 1 wt% of PVP (MW 40,000) has increased membranes fluxes as well as decreased salt rejection [21]. The effects of adding PVP with higher MW (40 K and 360 K) also resulted in significant morphology change from sponge-like morphology to finger-like morphology in polyimide(PI)/NMP/water membrane system [22].

Loading metal into polymer matrices has few advantages including to protect the metal, at the same time trapped metals can be distribute evenly and finally made the fabrication easier. In addition, physical properties of metal can benefit the performance of polymer embedded metal. A successful preparation of metal embedded polymer is determined by the ability to produce particles with uniform distribution and long stability, given their tendency to rapidly agglomerate in polymer solution. For polymer-silver, most of the releasing products are in the forms of sheet, sponge and fiber. Several methods have been established for the preparation of various silver-polymer composite including chemical reduction [23], photolysis [24] and in-situ fabrication [11,17, 25]. The methods of preparation may lead to small differences in physical and chemical properties of the end product.

To the best of our knowledge, this paper describes an easy synthetic route to load silver nitrate into PES by using PVP as dispersant. The PES-$AgNO_3$ membranes were characterized by various techniques to prove that silver is successfully loaded to PES which then exhibit antibacterial activity against *Escherichia coli (E.coli)* and *Staphylococcus aureus (S.aureus)* in an inhibition zone test.

2.0 MATERIALS AND METHODS

2.1 Materials

PES was supplied by Solvay Advanced Material (USA) and N-Methyl-2-pyrrolidone (NMP) was purchased from Merck. PVP, with average MW of 10,000 (P10), 40,000 (P40) and 360,000 (P360) and silver nitrate, $AgNO_3$ (analytical reagent grade) were supplied by Fluka. For antibacterial test, microbiology agar was purchased from Merck. Chemicals were used as received.

2.2 Preparation of PES-silver Membrane

PES, $AgNO_3$ and NMP was used as the base polymer, as an additive as well as antibacterial agent and as the solvent respectively. PVP was also used as pore-former as well as dispersant which prevent particle aggregation and control the average particle size of silver in polymer solution [26–28]. To see the effects of PVP addition one solution was prepared without PVP (as control). Detailed membrane composition is listed in Table 1. PES was dried in an oven at 120°C overnight before dope preparation. An in situ approach has been applied in preparing PES-$AgNO_3$ membrane [16–17] where PVP and $AgNO_3$ were allowed to react in NMP with magnetic stirring for an hour (Solution A). First, silver nitrate was dissolved in NMP. Then, PVP was added slowly and the agitation continued for an hour. In other beaker, after PES completely dissolved in NMP (solution B), A was added into B. For all solution, PES weight percent concentration is 15% with $AgNO_3$ of 0.5%. The studied PVP/$AgNO_3$ ratio is constantly kept to ~1 due to the work done by Lee *et al.* to discover that PVP/$AgNO_3$=1 is the best to produce high dispersion and substantially small particle of silver [29]. The homogeneous solution of PES/$AgNO_3$/PVP was agitated continuously for at least 24 hours. Control solution was prepared by dissolving silver nitrate in PES/NMP solution.

Flat sheet membrane was prepared according to the dry/wet phase inversion technique, as described elsewhere [21, 30]. The solution was poured onto a clear, flat and smooth glass plate that was placed on the trolley. Stainless steel support casting knife was used to spread the solution to a uniform thickness. The glass plate with the membrane film was then immersed into a coagulation bath containing tap water. During this process, solvent exchange occurred and solidified the thin film to a complete membrane structure. To ensure all the solvent in the composite structure is removed, membrane was immersed in the coagulation bath for one day. As the final stage of membrane fabrication, membrane was left air-dried for 24 hours.

2.3 Characterization of PES-silver Membranes

Thermogravimetric analysis (TGA) using Mettler Toledo thermogravimetry analyzer (TGA TSO800GC1A) was performed to investigate the compatibility of PVP with PES. Membranes were prepared for thermal analysis as described elsewhere [20]. Heating were carried out from 50 to 750°C with a heating rate of 20°C/min. Attenuated Total Reflection Fourier transformed infrared (ATR-FTIR) was used to correlate the changes in chemical bonding before and after silver and PVP were added. The IR-spectra were recorded on Thermo Nicolet 5700 ATR-FTIR spectroscopy, which is supplied by Thermo Nicolet Corporation & Spectra Tech, USA. From the spectra, qualitative differences in the distribution of functional groups were investigated.

Morphological studies were done by recording SEM images using Ziess Supra 35 VP Field-Emission Scanning Electron Microscope, (FE-SEM). Silver content in membrane was evaluated by energy dispersive spectroscope (EDS) which is coupled with FE-SEM. For cross-section image, 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 [21, 31]. After gold sputtering, the samples were

Table 1 Composition of casting solutions

	PES-$AgNO_3$	PES-$AgNO_3$-P10	PES-$AgNO_3$-P40	PES-$AgNO_3$-P360
PES	15.09	15.02	15.00	15.03
NMP	84.51	84.18	84.01	84.23
PVP-K15	–	0.52	–	–
PVP-K30	–	–	0.51	–
PVP-K90	–	–	–	0.51
$AgNO_3$	0.50	0.53	0.51	0.50

Coagulation bath content : tap water
MW P 10 = 10,000, P 40 = 40,000, P 360 = 360,000

examined using FE-SEM coupled with EDS with potentials of 10.0 kV and magnifications ranging from 500 to 50,000x.

The membrane performance evaluation is done by measuring the pure water permeation where the permeation test was conducted by using a simple cross-flow permeation cell as described elsewhere [21]. Circular membrane discs were cut and mounted in a stainless steel cylindrical membrane test cell by a porous support and tightened by a rubber O-ring. Effective permeation area of each membrane was about 13.2 cm^2. Feed pressure was controlled at 1–6 bar while the permeate side was opened to the atmosphere. Experiments were carried out at ambient temperature (27°C). Membrane characterization of pure water permeation (PWP) for the PES membrane was calculated from the equation

$$PWP = \frac{Q}{A \times \Delta t}$$

Where Q is volume of the permeate (L), A is membrane surface area (m^2) and Δt is permeation time (hour).

The antibacterial activity of resultant membranes was tested by an inhibition zone method [19]. In this method, a nutrition agar culture medium (nutrient Agar, Merck) was melted and poured in a Petri dish and solidified. Two kinds of different bacteria including Gram-positive bacteria (*S.aureus*) and Gram-negative bacteria (*E.coli*) were used. For measurement of the antibacterial activity, membrane samples were punched to make disks (diameter = 24 mm), and were put onto the petri disk which have been inoculated with bacteria culture. The plates were visually examined for possible clear zones after incubation at 37°C for 24 h. The presence of any clear zone that formed around the membrane disk on the plate medium was recorded as an indication of inhibition against the bacteria species. Suspension cultures without any membranes were used as a control. In this study, the four silver nitrate-loading PES membranes were put on the agar surface and then incubated at 37°C for 1 day.

During fabrication, the loss of silver was assessed by measuring its concentration in the non-solvent immersion bath, determined with a Perkin Elmer Inductive Coupled Plasma Mass Spectrometry (ICP-MS), model ELAN 6000 with argon as gas carrier. Reagents used for ICP-MS analysis were ultrapure nitric acid and single-element plasma grade standards in 1–2 % nitric acid.

3.0 RESULTS AND DISCUSSION

By introducing PVP into PES-$AgNO_3$, silver ions, Ag^+ is expected to coordinate with N in PVP or O in PVP or PES, Eq 1, 2 and 3[27, 28]. The coordinate bond formed is responsible to the protection from agglomeration and also reduction in silver leaching during fabrication. The detailed chemical reactions can be expressed in Eq (1–3) [27, 28].

TGA curves shown in Figure 1 show the thermal decomposition of PES-$AgNO_3$ and PES-$AgNO_3$-PVP (PES-Ag-P10/40/360) occurred in a single step starting at 450, 408, 395 and 350 °C. The weight loss for PES-$AgNO_3$ membranes is in the order of PES-$AgNO_3$>PES-$AgNO_3$-P360>PES- $AgNO_3$-P40>PES-$AgNO_3$-P10 and the loss in percent are (59.3%), (58.9%), (58.7%) and (57.3%) respectively. Results show PES-$AgNO_3$ degrades latter than PES-$AgNO_3$-PVP by mean, has better thermal stability relatively compared to PES-$AgNO_3$-PVP. When $AgNO_3$ was added into the PES–PVP matrix, they chemically interact with the PVP molecules preferentially; as suggested in Eq. (1–3). However, the addition of only 0.5 wt% PVP of different molecular weight does not affect very much on the thermal stability, hence particularly PES-$AgNO_3$-P360 degrades at the lowest temperature, 350°C. Here it is to be noted that the thermal degradation pattern of PES-$AgNO_3$ and PES-$AgNO_3$-PVP (PES-$AgNO_3$-P10/40/360) membranes are quite similar.

In order to investigate the interaction of $AgNO_3$-PVP, PVP-PES and PES-$AgNO_3$, ATR-FTIR spectra of the top surface on membranes are measured and showed in Figure 2. It was found that all the IR spectrum showed no apparent difference in the range of 700-1600 cm^{-1}; only absorption peak arising at 1666 cm^{-1} which is attributed to amide carbonyl group from PVP [30, 32]. Absorption peaks at 1011and 1106 cm^{-1} which

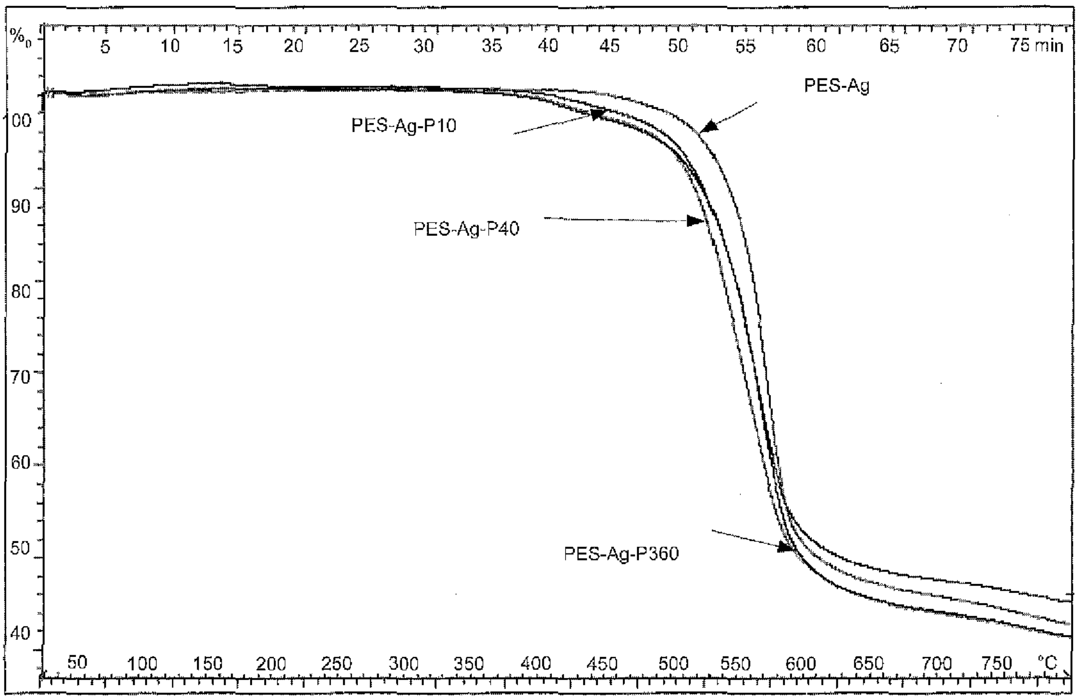


Figure 1 Thermo gram of (a) PES-$AgNO_3$ and (b) PES-$AgNO_3$P10, (c) PES-$AgNO_3$P40, (d) PES $AgNO_3$ P360 membranes

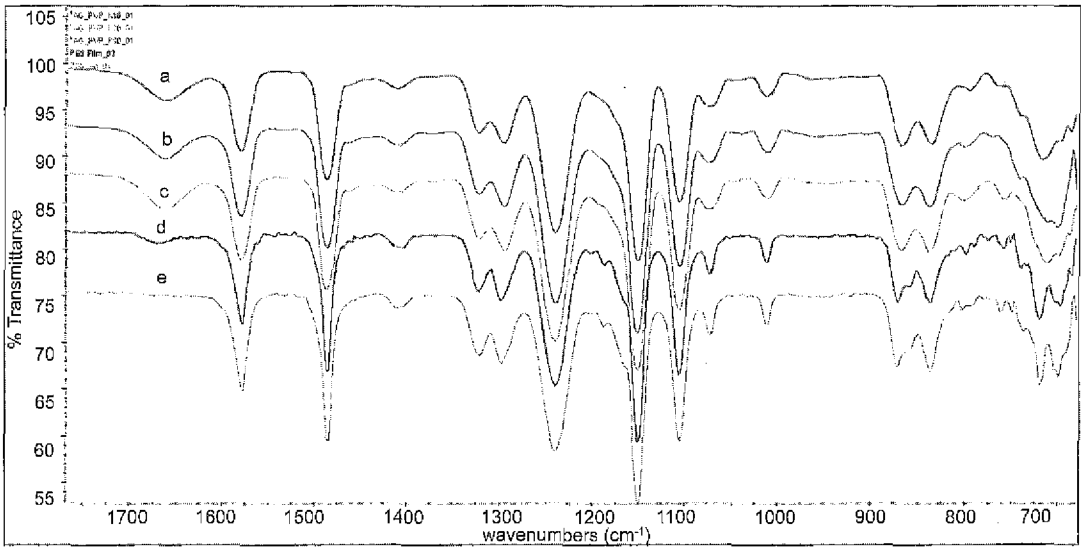


Figure 2 ATR-FTIR spectra of (a) PES-$AgNO_3$-P10, (b) PES-$AgNO_3$-P40, (c) PES-$AgNO_3$-P360, (d) PES, (e) PES-$AgNO_3$

originally (PES- $AgNO_3$) correspond to stretching mode of C-O bond has been weakened by the existence of C-N at the close region (1074 and 1019 cm^{-1}) similarly as studied by Wang *et al.* [27]. The other reason might be due to coordination of silver to N, which strengthened the steric effect and prevented coordination of silver to O [27] experienced that silver with size smaller than 50 nm can be produced when silver is coordinated with N or else larger particle will be formed if Ag is coordinated to O, as been discussed in the following subsection.

Loading PVP as well as silver in PES might induce specific changes in membrane morphology which in turn would affect the porosity, macrovoid formation and also permeability of membranes. For example, it has been reported that by adding PVP into PES [33], PSf [34] and PVC [35], membrane produced will have the properties of high porosity with well-interconnected pores and surface. It is possible to obtain silver in PES matrix but the amount of particles is always reduced from the amount considered during dope preparation due to silver leaching which occurred during fabrication [11, 15–17]. Therefore, the addition of PVP is to overcome this problem in order to produce membrane with better antibacterial property.

As shown in Figure 3, the membrane outer surfaces were recorded at 10,000 × magnifications while cross section images were analyzed at 25,000 × magnifications. The EDS spectra confirmed the presence of Ag component on membrane surface. It is clearly seen that silver distribution gets better after PVP addition. In addition, silver content analyzed by EDS techniques confirmed that silver content in membranes get higher. The presence of PVP having molecular weight of 40,000 and 360,000 in membrane formulation (PES-$AgNO_3$-P40 and PES-$AgNO_3$-P360) (Figure 3) had also tremendously alter the silver particle into smaller size, as listed in Table 2 with reduction 63–74 % relatively compared to PES-$AgNO_3$. The results agreed with Wang *et. al.*, which PVP can protect Ag from growing and agglomerating [27]. However, by adding PVP with molecular weight 10,000, as shown in Figure 3, silver particle size is similar to the silver from the control (PES-$AgNO_3$). This is due to PVP with smaller size (P10) may cover silver surface in general, reduce the protection from agglomeration and therefore produced large diameter of silver particle [11]. Nevertheless, for PVP with higher MW(P40 and P360), protection from agglomeration occurred that made the particles obtained smaller. Studies by Taurozzi also noted that silver which formed *in situ* in PSf matrix resulted in smaller particle size and more homogeneously distributed as compared to the one prepared *ex situ* [18]. Table 2 lists the silver particle size and the silver content of resultant membranes obtained from FE-SEM images and EDS spectra respectively.

The cross sectional morphology of all membranes shows finger-like structure, agreed to PSf/Ag obtained by Taurozzi *et al.* [18] in which silver were observed embedded within the polymer of the interpore walls and most nanoparticles were located along the pore surface. This result however differ from the one obtained by Chou *et al.* for cellulose acetate with silver loading hollow fiber [26] and Yu's work on PAN-based hollow fiber with silver nitrate loading [11] which produced sponge-like structure. The different morphology obtained might be ascribed to different polymer used.

Table 2 Analysis from FE-SEM micrographs

Membranes	Content	Ag particle size (nm)	Skin layer thickness (nm)
PES-$AgNO_3$	PES-$AgNO_3$	129.5	51.4
PES-$AgNO_3$-P10	PES-$AgNO_3$-PVP K15	295.6	34.6
PES-$AgNO_3$-P40	PES-$AgNO_3$-PVP K30	33.5	54.7
PES-$AgNO_3$-P360	PES-Ag-PVP K90	48.4	30.9

Left (outer surface) Right (cross section)

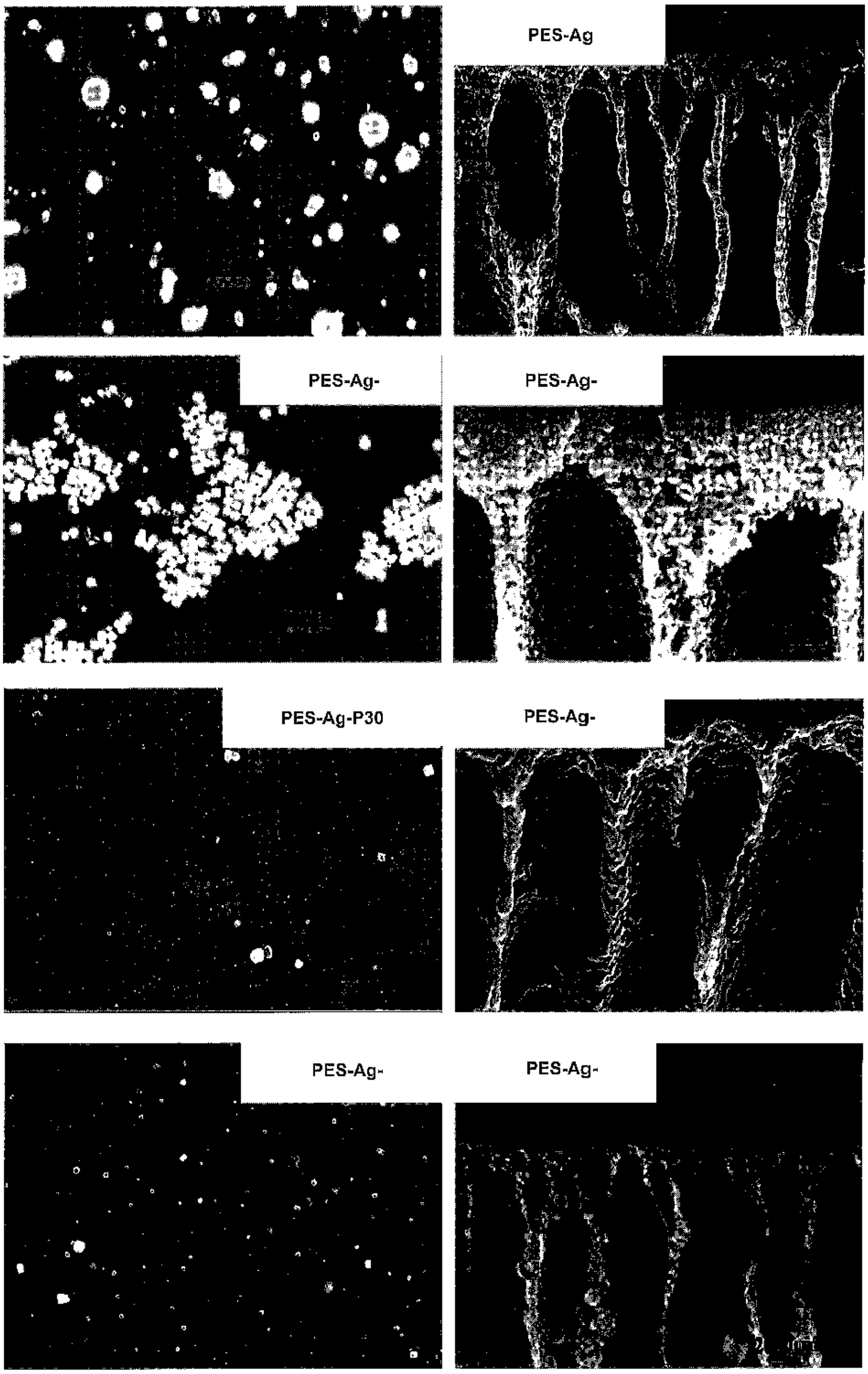
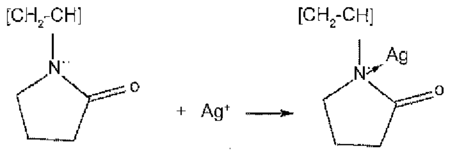


Figure 3 FE – SEM surface and cross section images of membranes



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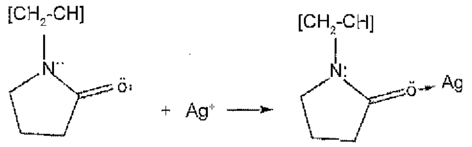

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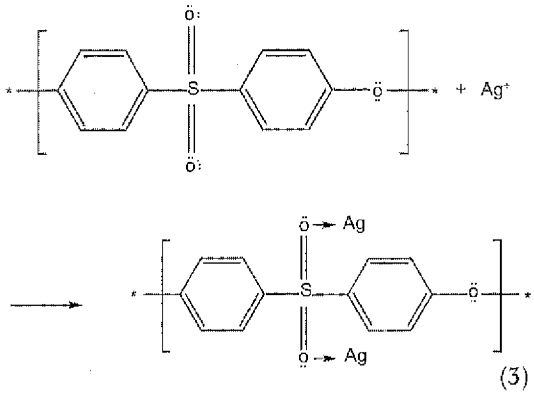


(3)

Membrane permeability tests were conducted to make sure flat sheets are strong enough to avoid collapse or bursting [11] for the pressure applied within 1–6 bars. Furthermore, the hydraulic permeability of pure water is an important index for the mass-transfer performance of PES-AgNO$_3$ antibacterial membrane. Figure 4 depicts the PWP results of PES-AgNO$_3$ membrane with and without addition of PVP. As can be seen, membrane permeability increased linearly with increasing operating pressure. It is because ultrafiltration (UF) membrane is one of the pressure-driven membrane processes. Results also revealed that PES-AgNO$_3$ exhibited the highest PWP followed by PES-AgNO$_3$-P360. Other than as dispersant, PVP is also known as a pore-forming agent; therefore, by adding PVP, membrane porosity could be affected, and thus explained for the low PWP exhibited by PES-AgNO$_3$-P360.

Elemental silver has been believed to exhibit antibacterial effect against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) [4,11,17,19,36]. A study done by Choi and co-workers revealed that silver nanoparticles and silver chloride colloids strongly inhibited microbial growth depending on their size and bioavailability

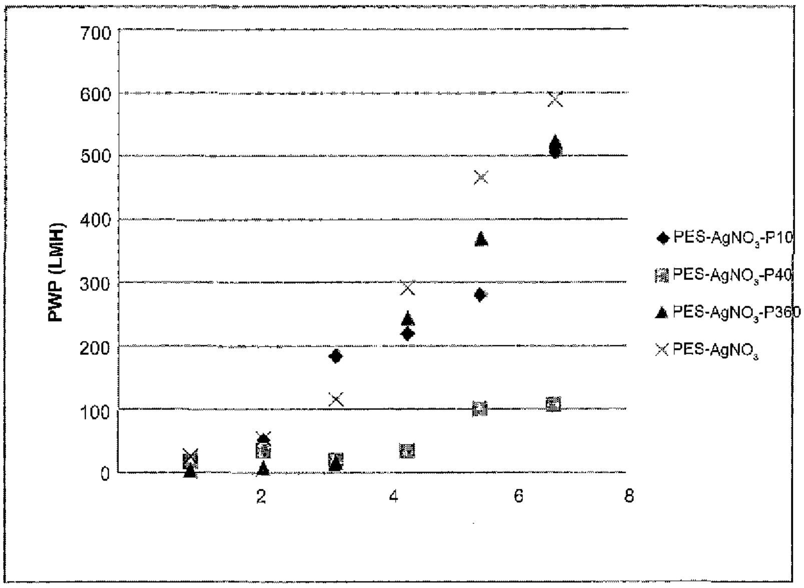


Figure 4 Pure water permeability (Lm^{-2}hr^{-1}) for PES-AgNO$_3$-P10, PES-AgNO$_3$-P40, PES-AgNO$_3$-P360 and PES-AgNO$_3$

[28]; while 100% inhibition against *E. coli* can be reached when concentration of silver ion (Ag^+) is as low as 4.2 μm. The principal antibacterial mechanism of silver was including inhibition of protein synthesis and the metabolic pathway in microbes as well as interference with nucleic acid and cell wall synthesis [37]. The antimicrobial activity of silver is dependent on the silver cation Ag^+, which binds strongly to electron-donating groups in polymer matrix containing sulfur, oxygen or nitrogen. Hence the silver based antimicrobial polymers have to release the Ag^+ to a pathogenic environment to be effective. Upon in contact with bacteria, silver will immediately inhibit the bacteria growth through the mechanism mentioned.

Previous studies have been done on incorporating silver, as an antibacterial agent into polymers for the application of waste-water treatment, clothing and food packaging. For example Ma and co-workers prepared chitosan, a known biopolymer which also exhibit antibacterial property [38–39] blended with nylon-6, chelated with silver ions, has resulted in an antibacterial biopolymer potentially for food-packing material [19]. Yu [11], Son [10], Chou [17] and Taurozzi [18] who incorporated silver into polymer matrix for waste water treatment reported silver leaching in the filtration but still exhibit antibacterial activity against *S. aureus* and *E. coli*.

Using the disk diffusion method, the bactericidal effects of PES-$AgNO_3$, PES-$AgNO_3$-P10, PES-$AgNO_3$-P40 and PES-$AgNO_3$-P360 were evaluated comparatively [19]. After 24 hours incubation at 37°C, the membranes showed antibacterial effect on Gram positive *S. aureus* and Gram-negative *E. coli*. The diameter of inhibition zone for the PES-$AgNO_3$-P10, PES-$AgNO_3$-P40 and PES-Ag-P360 is slightly larger than that for the PES-$AgNO_3$ (see Figure 5), obviously seen in *S. aureus* plates. PES-$AgNO_3$ membranes have been believed to function antimicrobially either as a release system for silver ions or as a contact-active material.

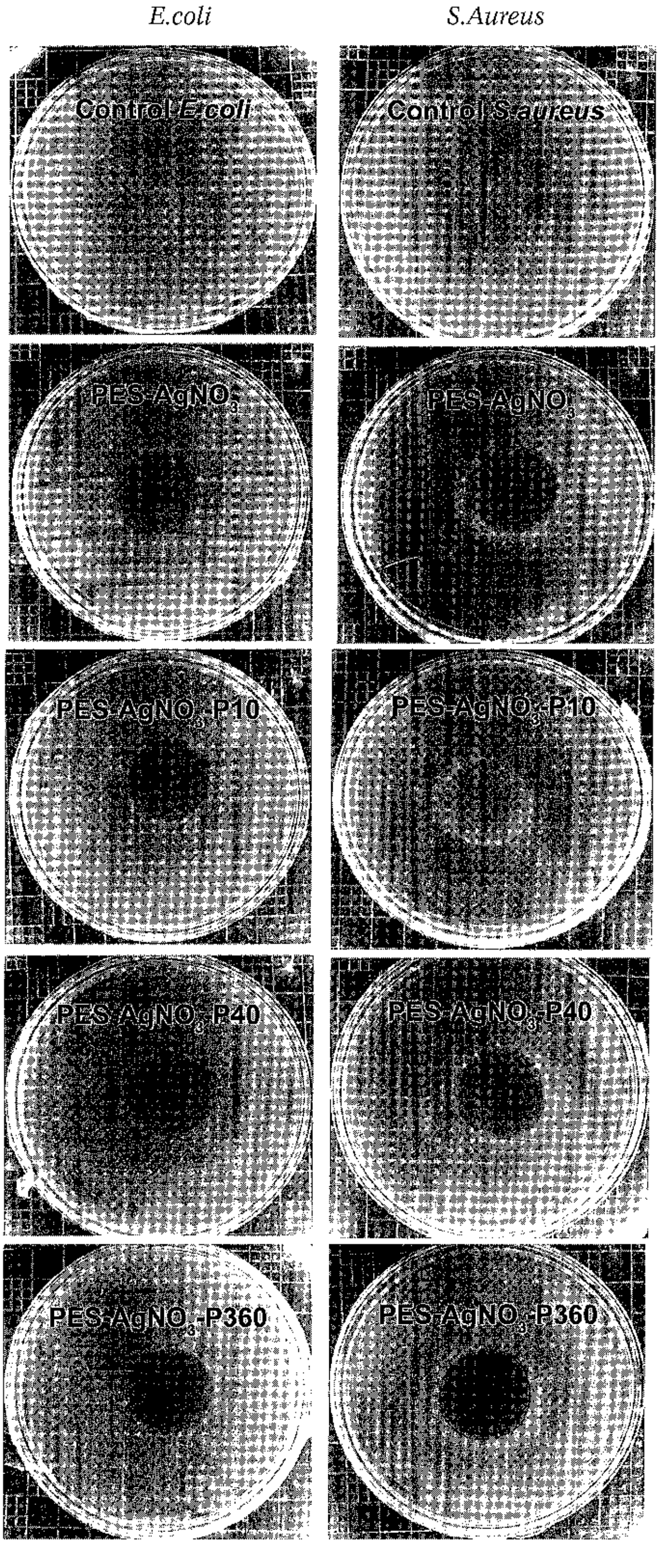
Even though silver has successfully been incorporated in membrane matrices as proven by FE-SEM and EDS, silver-leaching during fabrication still occurs. However by doping PVP into the formulation, silver-loss has been reduced. Table 3 shows satisfactory results obtained from the analysis of silver content in the coagulation bath during fabrication by ICP-MS. Silver leaching is may be due to non-attached silver particles on the membrane surface region which are more accessible to water (coagulation bath) [11]. Other factors that may contribute to leaching is membrane porosity as well as silver nanoparticle size, by mean if the particle's size is larger than its pore, it may easily be leached out during phase inversion process.

4.0 CONCLUSION

The effects of PVP in the preparation of PES-silver membrane have been investigated in this work. PVP-K90 (MW 360 K) has shown great contribution in reducing silver-loss during fabrication due to the attachment that bound the silver ion and prevent it from leaching during phase inversion. The use of PVP-K90 as additive has also altered the silver nanoparticles size, to improve the upon-contact with bacteria during antibacterial activity. By incorporating only 0.5 wt% of silver nitrate, the resultant membranes exhibited the antibacterial activity against *S. aureus* and *E. coli*. In summary, incorporation of silver into PES membrane matrix appears to be an attractive approach in the design of antibacterial membrane for waste water treatment.

Table 3 Silver loss during fabrication

Membranes	Silver loss (pm)	Silver loss (%)
PES-$AgNO_3$	17.3687	0.3474
PES-$AgNO_3$-P10	10.8623	0.2172
PES-$AgNO_3$-P40	1.6556	0.0331
PES-$AgNO_3$-P360	0.4636	0.0093



E.coli *S.Aureus*

Figure 5 Photographs of the antibacterial test result of the membranes against E. Coli (left) and S. aureus (right)

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