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EFFECT OF DIFFERENT SOLVENT IN THE PREPARATION OF POLYETHERSULFONE(PES)-AG POLYMER COMPOSITE

HATIJAH BASRI[1], AHMAD FAUZI ISMAIL[2*] & MADZLAN AZIZ[3]

Abstract. Organic-inorganic composite materials have attracted great attention because of their potential to combine the features of organic materials with those of inorganic materials. Particularly organic-metal composite such as polymer-silver are promising functional materials in areas ranging from electronic and optical devices to biosensing, antimicrobial agents and catalysis. In general, there are two synthetic approaches of silver-polymer nanostructures : in situ and ex situ methods. In this study silver-polyethersulfone (PES) was prepared in situ. The morphology of the samples which has undergone permeation measurement was characterized by Field Emission-Scanning Electron Microscopy (FE-SEM)/Energy Dispersive X-Ray Analysis (EDX). The differences in their structure arises from using different solvents N-Methyl-2-pyrrolidone (NMP) which was labeled A16 and *N*,*N*-dimethylformamide (DMF) which was labeled B16. Fingerlike structure was observed for B16 while mixed finger-like and spongy structure with voids was observed for A16. Pure water permeability measurement proved that B16 can permeate five times better than A16. However, rejection by membranes only differs by 7.3%. Hence, the performance of composite can be explained in terms of the observed surface and cross section micrographs, which in turn is correlated with the permeation measurement.

Keywords: Composite; polyethersulfone; silver; finger; like structure-permeation

Abstrak. Bahan komposit organik-inorganik telah menarik perhatian para penyelidik disebabkan potensi untuk menggabungkan ciri-ciri bahan inorganik dalam bahan organik. Secara khususnya, komposit organik-inorganik misalnya polimer-perak adalah bahan yang berpotensi dalam pelbagai bidang seperti alat optik dan elektronik, bio-pengesan, agen antimikrob dan pemangkinan. Secara amnya, terdapat dua cara penyediaan struktur-nano polimer-perak sintetik, iaitu kaedah *in situ* dan *ex situ*. Dalam kajian ini, polyethersulfone (PES)-perak disediakan secara *in situ*. Morfologi bagi sampel membran yang telah melalui ujian pemeresapan dicirikan dengan menggunakan kaedah Mikroskopi Imbasan Elektron Pemancaran Medan (FE-SEM) /Analisis Penyerakan Tenaga Sinar-X (EDX). Perbezaan struktur membran yang dihasilkan adalah berpunca daripada penggunaan pelarut yang berbeza iaitu *N-Methyl-2-pyrrolidone* (NMP) yang dilabel sebagai A16 dan *N,N-dimethylformamide* (DMF) yang dilabel sebagai B16. Struktur seakan jejari telah dikesan bagi A16 dan campuran jejari dan struktur mampung sepan berongga dikesan bagi B16. Pengukuran

[1] Centre for Science Studies, Universiti Tun Hussein Onn, Malaysia
Email: hatijah@uthm.edu.my
[2] Advanced Composite Technology Research Center, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia
[3] Chemistry Department, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia
Email: madzlan@utm.my
* Corresponding author: Email: afauzi@utm.my

penelapan air menunjukkan prestasi B16 lima kali ganda lebih baik berbanding A16. Walau bagaimanapun, penolakan larutan garam bagi kedua-dua membran hanya berbeza sebanyak 7.3%. Oleh itu, kebolehan komposit dapat dijelaskan melalui struktur morfologi permukaan dan keratan rentas membran yang mempengaruhi keputusan pengukuran pemeresapan.

Kata kunci: Komposit; polyethersulfone; perak; struktur seakan jejari; pemeresapan

1.0 INTRODUCTION

More and more polymer-metal composite materials have been made in recent years. Among them, metal with their safety, heat-stability and long-lasting activity properties were used most frequently [1]. Silver and its compound have long been known to have strong inhibitory effects on bacteria [2]. Some forms of silver have been demonstrated to be effective against burn, severe chronic and central venous catheter infections [3]. Most of silver releasing products are in the forms of sheet, sponge and fiber. Modified polyacrylonitrile (PAN) [4, 5], polyurethane (PU) [6, 7], polyimide (PI) [8], cellulose acetate (CA) [9, 10] polysulfone (PSf) [11] and chitosan [12] had been developed, for clothing, food-packaging and water treatment applications.

Polyethersulfone (PES) is a polymer material which is widely used for the preparation of microfiltration (MF), ultrafiltration (UF) and gas separation membranes. Besides, they are principally to the favorable characteristics of wide temperature limits, wide pH tolerances, fairly good chlorine resistance, easy to fabricate membranes in a wide variety of configurations and modules, wide range of pore sizes available for UF and MF applications ranging from 10 Å to 0.2 μm and good chemical resistance to aliphatic hydrocarbons, alcohols and acids [13 – 15].

Porous polymer composites can be prepared using a number of metal particle incorporation strategies. These strategies based on whether the metal particles and composites are pre-formed or synthesized in situ during the formation of the polymer composite. In situ synthesis of metal particles on the pore surface of existing composites [16 – 17, 5] has the advantages of improved reproducibility of composite preparation. In contrast, incorporation of metal particles during composite formation [18 – 19] is appealing because it should allow the design of composite structures with improved mechanical and separation properties in term of permeability and rejection along with embedded metal particle.

To further extend the knowledge of developing PES-$AgNO_3$ asymmetric composite, the current paper aims to study the effect of different solvent used in the composite formulation in the morphology structure and permeability. Hence, the composites' performance in terms of pure water flux and salt rejection was also investigated. To the best of our knowledge, study of incorporating silver into PES composite formulation is the first attempt for waste water treatment.

2.0 MATERIAL AND METHODS

2.1 Materials

Polyether sulfone (PES) was supplied by Solvay Advanced Material (USA), *N*,*N*-dimethylformamide (99.8% anhydrous) by BDH, N-Methyl-2-pyrrolidone (NMP) and sodium chloride (NaCl) was purchased from Merck. Silver nitrate, $AgNO_3$ (analytical reagent grade) was supplied by Fluka.

2.2 Preparation of PES-silver Composite

PES was used as the base polymer, $AgNO_3$ was used as an additive and NMP/DMF was used as the solvent. The polymers were dried in an oven at 120 °C overnight before dope preparation. In situ approach has been applied in preparing PES-silver composite [9 – 10]. In order to prepare the homogeneous polymer solution, PES and $AgNO_3$ were dissolved in NMP/DMF solvent with PES and $AgNO_3$ concentrations were 16 and 1 wt% respectively. The homogeneous solution was agitated continuously for at least 24 hours. Composition of the polymer solutions were as listed in Table 1.

Table 1 Composition of polymer solutions

Polymer wt%	Solvent wt%	$AgNO_3$ wt%	Coagulation bath	Code
PES, 16	NMP	1.0	Tap water	A16-1
PES, 16	DMF	1.0	Tap water	B16-1

2.3 Flat-sheet Casting

Flat sheet composite was prepared according to the dry/wet phase inversion technique, as described elsewhere [20 – 21]. 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 composite film was then immersed into a coagulation bath. In this study tap water is used in the coagulation bath. During this process, solvent exchange occurred and solidified the composite film to a complete composite structure. To ensure all the solvent in the composite structure is removed, composite was left in the bath for one day. As the final stage, composite was left air-dried for 24 hours.

2.4 Measurement and Characterization

The composite 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 [20]. Schematic diagram is drawn in Figure

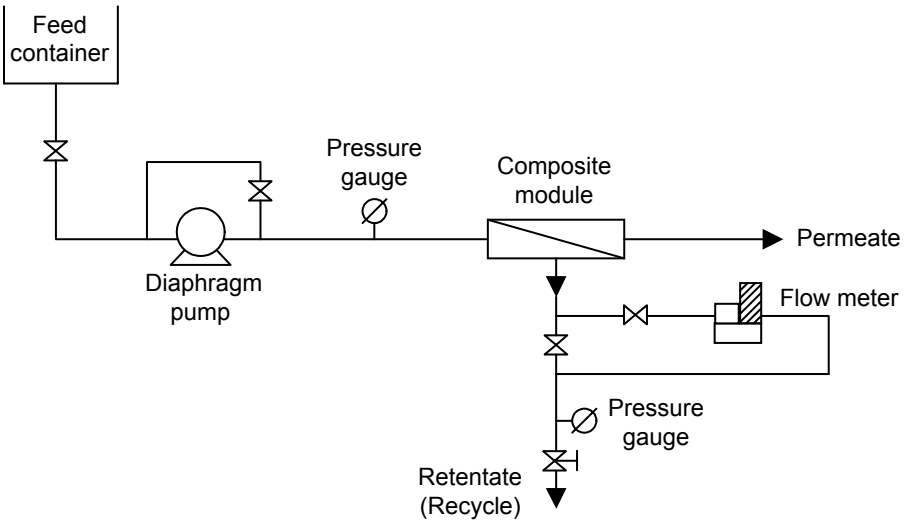

Figure 1 Schematic diagram of laboratory-scale permeation test system

1. Circular composite discs were cut and mounted in a stainless steel cylindrical composite test cell by a porous support and tightened by a rubber O-ring. Effective permeation area of each composite was about 13.2 cm^2. Prior to testing, the pure water permeability was measured to ensure that the composite used were stable. 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). Composite characterization of pure water permeability (PWP) for the PES$AgNO_3$ composite was calculated from the equation

$$\text{PWP} = \frac{Q}{A \times \Delta t} \tag{1}$$

where Q is volume of the permeate in liter (L), A is composite surface area (m^2) and Δt is permeation time (hour). For salt rejection test, sodium chloride (NaCl) solution with concentration 500 ppm is used as feed and rejection was calculated using the equation [22]:

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

where C_p is solute concentration in the permeate phase and C_f is solute concentration in the feed solution.

A Ziess Supra 35 VP Field-Emission Scanning Electron Microscope, (FE-SEM) coupled with energy dispersive X-ray (EDX) was used to study the composite morphology and to evaluate the silver content in composite. The surface and cross-sections of composites morphology of PES composites were observed. For cross-

section image, the composite samples were dried and then fractured cryogenically in liquid nitrogen before mounting on sample stubs. The samples were sputtered with a thin layer of gold using a sputtering apparatus [20 – 21]. After gold sputtering, the samples were examined using Ziess Supra 35 VP FE-SEM coupled with EDX with potentials of 10.0 kV and magnifications ranging from 500 to 50,000×. EDX analysis was done to evaluate the Ag content in composite.

3.0 RESULTS AND DISCUSSION

Visual observation indicated that flat sheet with DMF as solvent (B16-1) was reddish in colour. Flat sheet with NMP as solvent (A16-1) was grayish on the bottom side, similar to the result obtained by Deng *et al.,* in which work, silver was incorporated in polyimide (PI) [8]. Furthermore, B16-1 was more brittle than A16-1. FE-SEM analysis was carried out to reveal the presence and morphology of silver particle while EDX technique was used to confirm the silver incorporation. Figure 2 shows the SEM images of the surface (a & b) at magnification 5000× and cross section (c &

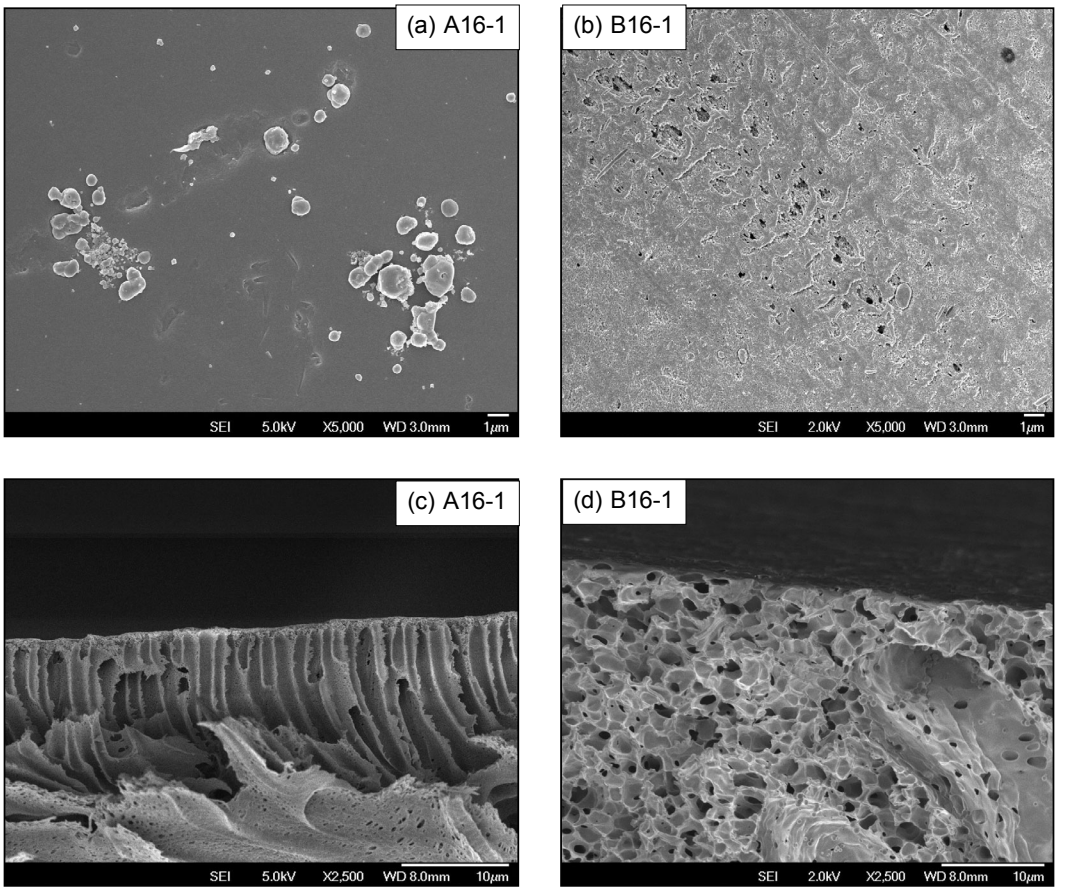

Figure 2 Images of PES-$AgNO_3$ composite

d) at magnification 2500×. Table 2 lists the morphology and properties of resultant composites.

For A16-1 composite, FE-SEM imaging revealed silver particles with diameters in the range 100 – 500 nm on the surface as shown in Figure 2(a). EDX analysis confirmed the weight is ~0.16%. In contrast, no silver particles were observed from the top surface of B16-1 composite, Figure 2(b). Pores were observed in FE-SEM image Figure 2(b) at magnification 5000× but none were observed in A16-1, Figure 2(a). It has been demonstrated that DMF can reduce Ag^+ ions to the zero-valent metal (Ag^0) at room temperature [23]. Probably in B16-1 composite, Ag^+ has been reduced to Ag^0 and the heavy particles tend to leach out from the composite during the phase inversion process.

Cross sectional images of A16-1 composite in Figure 2(c) shown a finger-like structure while cross sectional images of B16-1 composite in Figure 2(d) revealed a mixture of finger-like and spongy structure with voids. B16-1 composites showed high permeability as depicted in Figure 3 due to their morphology and it has also affect the rejection performance of composite as compared to A16-1, as listed in Table 2.

Table 2 Morphology and properties of the PES-$AgNO_3$ composite

PES/$AgNO_3$ flat sheet	Morphology (cross section)	$AgNO_3$ % (EDX)	PWP (max) ($Lm^{-2}hr^{-1}$)	Rejection(%)
A16-1(NMP)	Finger-like	0.16	1044	55
B16-1(DMF)	Mix (finger-like & spongy with voids)	–	5411	51

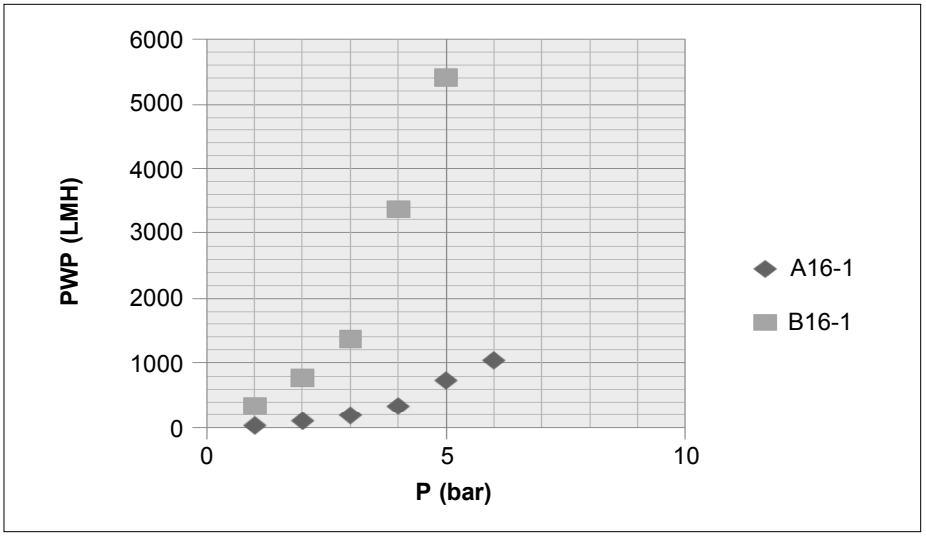

Figure 3 Pure water permeability ($Lm^{-2}hr^{-1}$) against pressure (bar) for composites

Pastoriza-Santos suggested an equation to explain the reduction of silver by DMF solvent [24]:

$$HCONMe_2 + 2Ag^+ + H_2O \rightarrow 2Ag^0 + Me_2NCOOH + 2H^+ \quad (3)$$

4.0 CONCLUSION

The effect of adding silver nitrate to PES casting solution on some properties of the resulting composite composites has been investigated. The preliminary results indicate that asymmetric PES-$AgNO_3$ composite composites made with DMF solvents produces mixed spongy and finger-like with voids morphology structure with high permeability as compared to PES-$AgNO_3$ made with NMP solvents. Further works in proving the oxidation state of silver in composite structure so as to prove the antibacterial property of this PES/$AgNO_3$ composite are still in progress.

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