

## FABRICATION OF POLYETHERSULFONE MEMBRANES USING NANOCARBON AS ADDITIVE

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**ABSTRACT:** Membrane-based processes have become the most dominant technology for water or wastewater treatment. To maintain optimum performance, a membrane should have high permeability and selectivity, good hydrophilicity, in combination with stable mechanical properties. Generally, the membrane produced from pure polyethersulfone (PES) has good mechanical properties, but low hydrophilicity. Modifications of the PES membrane with hydrophilic additives can increase its hydrophilicity. Nevertheless, incorporating additives may decrease its mechanical properties. The objective of this study is to enhance the overall properties of PES membrane by incorporating nanocarbon as an additive. The goal is to obtain a membrane with high permeability and selectivity, good hydrophilicity, as well as superior mechanical properties. Four PES membranes were equipped via the dry-wet inversion method using two solvents (n-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO)). The nanocarbon additive was fabricated from palm fruit-shell biomass wastes. The results show that the type of solvent affects the pore structure of the membrane surface. The membranes prepared using the PES-NMP system have dense structures with small nodules that appear in the upper skin layer, while the membranes from the PES-DMSO system have a spherulite-like structure. The membrane structures changed significantly when the nanocarbon particles were added to the polymer solution, particularly in terms of the shape and size of the microvoids. The finger-like structure found in the membranes prepared from PES-NMP or PES-DMSO systems disappears after the nanocarbon was added to the system. Furthermore, the accretion of nanocarbon to the polymer system increases the water permeability, hydrophilicity, and mechanical properties of the resulted membrane.

**Keywords:** Membrane formation; Membrane modifying agent; Nanocarbon; Polyethersulfone

### 1. INTRODUCTION

Since the discovery of the phase inversion technique by Loeb-Sourirajan in the 1960s, various types of the membrane have been produced, and numerous modules have been developed for various industrial applications [1]. Recently, membrane mechanism has been widely utilized for water and wastewater treatment [2,3], gas separation [4], food and beverage processing [5], and in the pharmaceutical industry for enzyme and protein concentration [6]. Membrane technology offers better control of the treatment rate and product quality, thereby making it very attractive for replacing conventional separation technology, when applicable. In industrial applications, manufacturers select membranes that have good mechanical properties, high permeability, and selectivity, and that are capable of being applied at high temperatures, with resistance to extreme chemical solutions, and low fouling tendency.

Currently several types of polymer are frequently used as membrane materials, namely polyacrylonitrile (PAN), polyethersulfone (PES), poly (vinylidene fluoride) (PVDF), cellulose acetate (CA) and polysulfone (PSf) [7,8]. Among

these polymers, PES is the most widely used material for producing porous ultrafiltration membranes. In the preparation of the polymer solution, PES is completely dissolved in a polar solvent at room temperature, thereby enabling the polymer solutions to be easily configured in various membrane modules.

The current research focuses on fabricating a high-performance PES membrane with superior antifouling properties. Many authors have proposed strategies to produce a hydrophilic membrane from hydrophobic polymers. Among them are blending with hydrophilic additives [9,10], grafting the surface of the membrane with a monomer [11], and copolymerization of several polymeric additives [12]. Hydrophilic PES membranes can also be made by blending the polymer solution with chitosan [13], which can decrease the water contact angle to about 56° (highly hydrophilic properties). Other polymeric additives, such as polyvinylpyrrolidone (PVP), and polyethylene glycol (PEG) have also been explored to improve the hydrophilicity of PES membranes [14]. Through such modifications, the long-term ultrafiltration character of altered PES membranes was better than that for initial membranes.

In summary, the blending of polymeric additives in a polymer solution can improve the hydrophile level of the membrane. However, the existence of hydrophilic additives reduces the mechanical properties. The increasingly dense structure near the top and the bottom surface of the membranes is another drawback of blending with a high concentration of polymeric additives [15]. This study explored the effectiveness of non-polymeric additives as a membrane transform agent to escalate the hydrophile degree and mechanical properties of the PES membrane. Nanocarbon powder produced from oil palm shells was blended in a polymer solution. In general, this study was conducted to produce hydrophilic membranes prepared from the hydrophobic polymers with stable mechanical properties and high permeability and selectivity. The effect of the nanocarbon additive and solvent type on the resulting membrane morphologies were also studied.

## **2. METHODOLOGY**

### **2.1 Materials**

Polyethersulfone (PES, Ultrason E6020P) was purchased from BASF Co. (Ludwigshafen, Germany). Two type solvents of N-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO) were obtained from WAKO Pure Chemical Industries, Ltd. (Japan). The nanocarbon used as an additive was obtained from the Laboratory of Chemical Process, Syiah Kuala University, Indonesia. It was produced from palm shell waste. Deionized water was produced using Elix-5. This was used to conduct ultrafiltration tests and water contact angle measurements. Dextran (WM= 19.5 KDa), which was acquired from WAKO Pure Chemical, Ltd. (Japan), was used to determine the solute rejection.

### **2.2 Membrane Preparation**

Four flat-sheet membranes were prepared from dope solutions with different compositions. They were created using the non-solvent induced phase separation technique with water as a non-solvent. In this study, four dope solution formulations were used for preparing the membrane samples. The sample code and the constitution of each polymer solution are shown in Table 1. To obtain a completely homogeneous dope, the mixture of PES, solvent, and additive (if present) was stirred using a magnetic stirrer overnight at a stirring speed of 300 rpm. Later, the homogeneous solutions were kept in an oven at 30 °C for 1 hour to ensure the complete release of air bubbles. Each dope solution was molded onto a lisp at room temperature using an automatic applicator (YBA-3, Japan) at a wet

casting thickness of 700 µm. The formed sheet and the lisp were then immersed in the congealment bath containing deionized water at room temperature. The solidified membrane sheets were then rinsed and kept wet in the deionized water overnight to remove any residual solvents.

### **2.3 Analysis of membrane morphology**

The morphology of the membranes was analyzed using a scanning electron microscope (SEM, JSM-7500F, JEOL Ltd., Japan). Samples of each membrane measuring about 1 cm<sup>2</sup> were immersed in liquid nitrogen for 1 minute before they were freeze-dried (FD-1000, Eyela, Japan) overnight to remove the water content completely. For surface analysis, the samples were directly mounted on the SEM sample holder, while, for the traverse path, they were fractured in the liquid nitrogen. Furthermore, the surface and cross-section samples were coated with Pt/Pd sputtering, and the SEM image was captured at 5.0 kV with different magnification.

### **2.4 Determination of membrane hydrophilicity**

The hydrophilicity of the membrane was measured by analyzing the angle between a water drop and the membrane surface using a water contact angle meter (Kyowa CA-A, Japan). For measurement, a membrane sample from storage was directly mounted on a metal disk without any drying process. A small amount of water (0.5 µl) was dropped onto the upper skin of the membrane using a glass syringe, and within a short time, the contact angle was noted automatically with the recorder available on the measuring device. The average of at least 10 assessments was noted as the reported value.

### **2.5 Filtration Performance**

The filtration performance of the membranes was investigated by measuring the water permeability and dextran repulsion. Both tests were carried out using a dead-end filtration module (Fig. 1). A total of 300 ml of deionized water was flown through the membrane sheet installed in the module with a membrane surface area (A) of 0.00152m<sup>2</sup>. The water permeability of the membrane was calculated from the volume of water that passed through the membrane (V) during the filtration period (t) (Eq. 1).

The dextran solution of 1wt% was replaced as the feed solution for the solute rejection test. The efficiency of the dextran rejected by the membrane was calculated using Equation 2. The transmembrane pressure (P) for all the filtration experiments was set at a constant value of 0.5 atm.

Table 1 Dope solution compositions that were cast at 25 °C

Membrane Code	Polymer solution (wt%)			Non-solvent
	Polyethersulfone	Nanocarbon	Solvent	
PES1	18	-	NMP (82.0)	Water
PES2	18	-	DMSO (82.0)	Water
PES3	18	0.1	NMP (81.9)	Water
PES4	18	0.1	DMSO (81.9)	Water

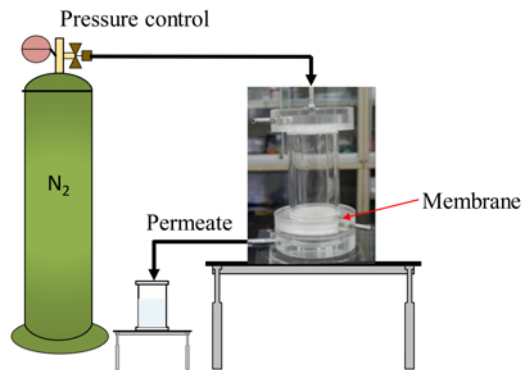


Fig. 1 Schematic of ultrafiltration module

$$\text{Water Permeability (L/m}^2\text{.hr.atm)} = \frac{V}{A.t.P} \quad (1)$$

$$\text{Solute Rejection} = \frac{(C_f - C_p)}{C_f} \times 100 \% \quad (2)$$

In which  $C_f$  and  $C_p$  are the concentration of dextran in the feed and permeate, respectively.

## 2.6 Mechanical properties

Tensile equipment (Hung Ta, Instrument Co., Ltd. Taiwan) was used to observe the mechanical properties of the membrane. The mechanical parameters investigated included the tensile strength and elongation at break. Five samples from each membrane measuring 50 mm in length were placed vertically within two pairs of clamps. The measurements for the tensile strength and elongation of the membrane was set at a stable elongation rate of 20 mm/min.

## 3. Results

### 3.1 Nanocarbon Characteristic

As explained previously, the nanocarbon used as a membrane modifying agent in this work was fabricated from palm shell waste. The particle shape and diameter obtained from the SEM measurements are shown in Fig. 2. It can be seen that the particle has an irregular form, with a diameter of about 0.60 – 1.00  $\mu\text{m}$ . Additionally, the results of the SEM-EDS analysis show the elements and compound of the particle (Table 2). Carbon dominated the

contents of the particles, with 75.32%, and 15.21% was silica.

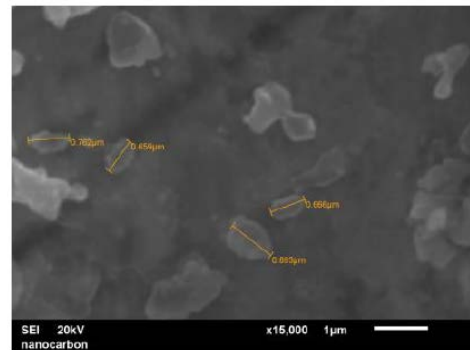


Fig. 2 SEM image of nanocarbon

Table 2 Elements and compounds of nanocarbon

Element	Mass (%)	Compound	Mass (%)
C	75.32	C	75.32
O	10.86	Al <sub>2</sub> O <sub>3</sub>	3.18
Al	1.68	SiO <sub>2</sub>	15.21
Si	7.11	CuO	6.29
Cu	5.02		
Total	100.00		100.00

### 3.2 Membrane Morphology

The SEM images showing a cross-section morphology of all the membranes samples are presented in Fig. 3. In general, the pristine membranes (without the addition of carbon powder, PES1, and PES2) consist of a dense structure near the top/bottom surfaces, a sponge-like structure with a pore size smaller than 1.0  $\mu\text{m}$ , which dominates the entire membrane cross-section, and a finger-like macro void-structure in the center of the membrane. The type of solvent affects the formation of the dense layer near the top/bottom surfaces. The PES1 has a thicker dense top-layer compared to PES2. Membrane formation in relation to the solvent used in polymer system can be explained by the solubility parameters of each component.

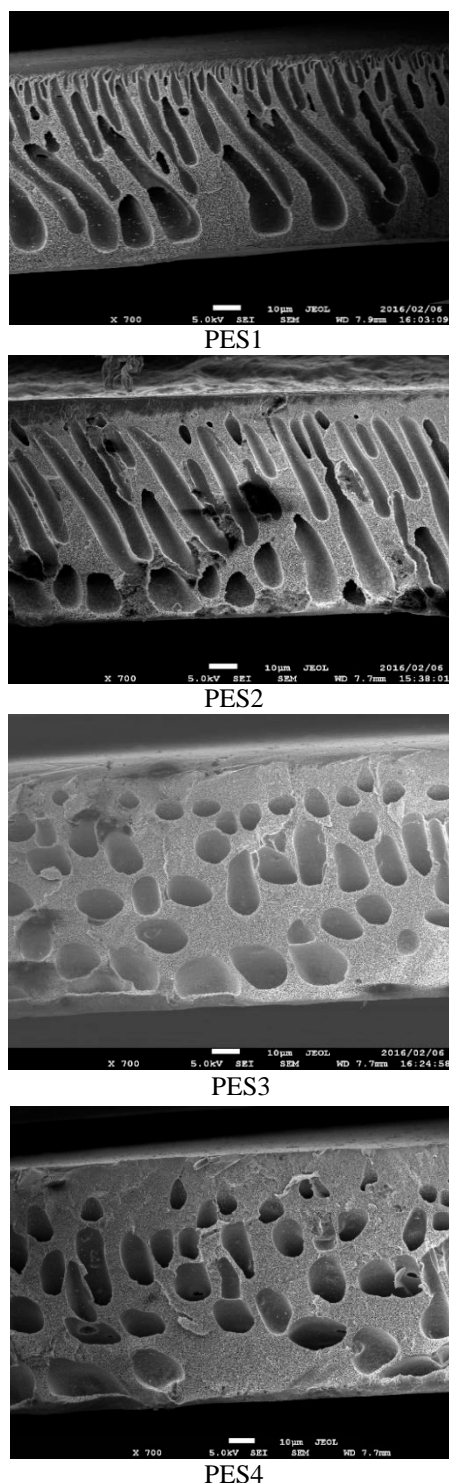


Fig. 3 SEM images showing the cross-section morphology of the fabricated membranes.

As shown in Table 3, the solubility parameters of nonsolvent (water) were closer to DMSO. The difference in solubility parameters between water and NMP is larger than between water and DMSO. During membrane solidification in the coagulation bath, the ratio of solvent outflow and nonsolvent inflow of the polymer system was large, and it may be due to the solvent leaches out of the system. In

this case, the high concentration of polymer around the top surface of membranes occurs, forming a large dense structure (Fig. 3; PES2). Studies about the effect of solvent on the membrane formation for others polymer systems have been reported by several authors [16,17].

The membrane structure changes significantly when the nanocarbon particles are added to the polymer solution. Nanocarbon suppresses the formation of macrovoids. As shown in Fig. 3, PES3 and PES4 have a distinctively different shape and size of microvoids structure. The finger-like structure found in the PES1 and PES2 disappears with the addition of 0.1 wt% of nanocarbon in the dope solution. Furthermore, the addition of nanocarbon in the polymer system also affects the formation of the top skin-layer of PES3 and PES4. The presence of nanocarbon particles in the polymer system causes changes in macro void structure and the formation of dense structures near the top surface.

Table 3 Solubility Parameter of solutions substances [18]

Substances	Solubility parameter $\delta$ (MPa <sup>1/2</sup> )
Polyethersulfone	21.9
Dimethyl sulphoxide	26.4
n-Methyl Pyrrolidone	22.9
Water	47.9

The mechanism of membrane formation by blending such kind of inorganic additives into polymer solutions is also widely explained in the literature [19,20]. In brief, the morphology changes of composite blend membranes are mostly affected by the concentration of polymer and its additives. The addition of small amounts of activated carbon nanoparticles into the polymer solution causes changes in the morphology of the polyethersulfone blend membrane.

### 3.3 Membrane hydrophilicity

The water contact angle shows the degree of membrane surface hydrophilicity. The water contact angle is determined by placing a droplet of water on the membrane surface, then the contact angle of the droplet is calculated [21]. A hydrophilic surface has a contact angle,  $\theta$ , close to  $0^\circ$ , while for a hydrophobic surface the contact angle is up to or greater than  $90^\circ$ . In hydrophilic surfaces, the liquid spontaneously passes through the membrane pores. This is contrary to the hydrophobic surfaces where less liquid could penetrate the membrane pores [21].

Table 4 Water contact angle of membrane

Membrane	Water Contact Angle ( $^{\circ}$ )
PES1	80.74 $\pm$ 1.32
PES2	80.20 $\pm$ 1.47
PES3	69.83 $\pm$ 1.63
PES4	69.78 $\pm$ 0.96

The water contact angle of all membranes is given in Table 4. The table shows that the highest contact angle is 80.74°, which belongs to PES1, the most hydrophobic among the prepared membranes. The lowest contact angle is shown by PES4 with a value of 69.83°. The decrease in the water contact angle indicates the positive impact of the nanocarbon addition in the dope solution. The nanocarbon is constituted of SiO<sub>2</sub>, which has been known to enhance the hydrophilic nature of a membrane. As reported by Shen et al.,[22], the addition of silica oxide improves the hydrophilicity of the membrane. The decrease in the contact angle for the PES3 and PES4 membranes found in this study is mostly due to the presence of silica originating from the nanocarbon additive.

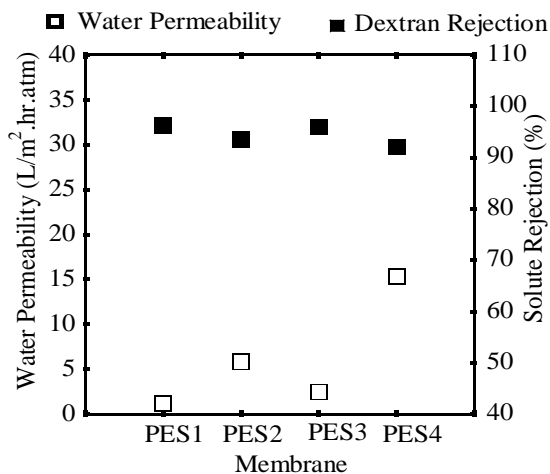


Fig. 4 Filtration performance of the membrane

### 3.4 Filtration Performance

The profiles of the permeation and solute repulsion of all the membrane systems are presented in Fig. 4. It is shown that PES1 has lower water permeability than PES2. The permeability of PES2 is even higher than PES3 (basically PES1 with the addition of nanocarbon). This finding shows that DMSO acts as a better solvent than NMP in promoting permeability. The advantages offered are so profound that the pristine membrane (PES2) is better than the one with the additive when using NMP as the solvent (PES3). The amount of water that passes through the membrane and the total of the particles rejected is related to the pore properties

of a membrane, particularly the morphology of the membrane surface.

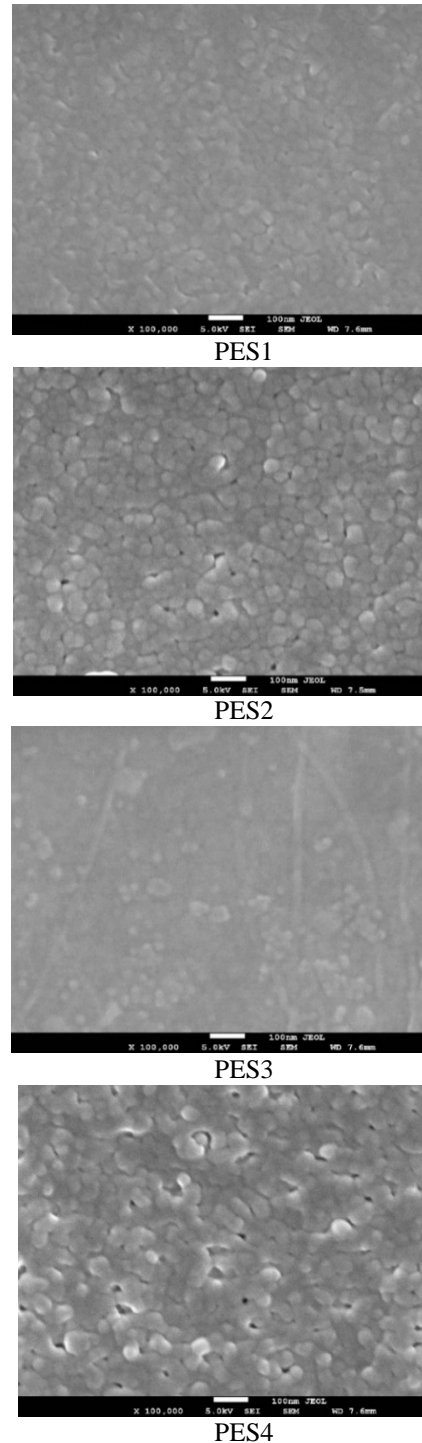


Fig. 5 SEM image of membrane surfaces

As depicted in Fig. 5, the surface morphology of membrane PES1 is dominated by a dense structure with small nodules appearing in all paths of the SEM image. In order to increase the water permeability of the PES membrane, nanocarbon was added to the polymer solution. The addition of 0.1 wt% of nanocarbon to the PES/NMP system

does not significantly contribute to the surface-pore structure, as clearly observed in Fig. 5 (for PES3). Therefore, the amount of water passed through this membrane was unaffected, and the number of dextran particles rejected was high. In this case, nanocarbon can only alter the bulk cross-section properties, but not the surface pores that often dictate the permeability.

The surface morphology of the membranes prepared from the PES/DMSO system consists of a spherulite structure at sizes of about 10 nm. Therefore, the amount of water filtrated via the PES/DMSO membrane system (PES2) was higher than the PES/NMP system. Additionally, the water permeability of the PES/DMSO membrane increases significantly after the addition of 0.1wt% nanocarbon (PES4). The average pore diameter and pore density of all the membranes were calculated based on the SEM image from Fig. 6 using *Image J software*. The surface area of the gray-scale SEM image was converted to a black-white style using the threshold menu in *Image J*. The average pore diameter of PES1, PES2, PES3, and PES4 are 1.38, 2.30, 3.40, and 7.56 nm, respectively. Considering the membrane structure presented in Fig. 5, it is understood that the increase in water permeability of the PES4 is due to the improvement of the spherulite structure on its skin layer. Moreover, increasing the pore size on the surface of PES4 is another reason for the increment in the permeability.

### 3.5 Mechanical Stability

The nanocarbon particles not only enhanced the hydrophilic nature of the membrane but also strengthened the mechanical properties of the membranes. Table 5 shows that PES1 and PES2, the pristine membranes without nanocarbon addition, have a low tensile strength of  $85.55 \pm 2.65$  and  $82.10 \pm 4.31$  M.Pa, respectively. After the addition of nanocarbon, their tensile strengths increased to about  $146.90 \pm 5.71$  and  $109.25 \pm 6.00$ , respectively (PES3, and PES4). The use of solvents also affects the tensile strength of the membranes. The PES-NMP systems have better mechanical properties than the PES-DMSO system.

In summary, nanocarbon particles have a good effect in strengthening the mechanical stability of PES membranes even with different types of solvent. The increase in mechanical properties of blend membrane is caused by a compact adhesion force between nanocarbon particles and polyethersulfone. A similar tendency of research results has been reported in case of polysulfone membranes modified with oxidized nanocarbon at a concentration of 1.0% [23].

Table 5 Mechanical properties data of the PES membranes

Membrane Code	Tensile Strength (M.Pa)	Elongation (%)
PES1	$85.55 \pm 2.65$	$80.0 \pm 1.71$
PES2	$82.10 \pm 4.31$	$60.08 \pm 2.82$
PES3	$146.90 \pm 5.71$	$80.8 \pm 0.80$
PES4	$109.25 \pm 6.00$	$63.33 \pm 1.72$

## 4. CONCLUSIONS

The nanocarbon particles obtained from the waste of palm shells were successfully embedded as an additive in the PES membranes. The characteristics and performance of the membranes were investigated including the morphology structure, water permeability, water contact angle meter, and the mechanical properties. The results showed that nanocarbon improves the membrane performance by promoting the formation of a sponge-like structure, suppressing the formation of microvoids, and promoting a good distribution of pores on the surface. When present in the membrane matrix, nanocarbon lowers the surface water contact angle and subsequently increases the hydrophilicity of the membranes. Furthermore, it leads the membranes to have higher water permeability. The nanocarbon also strengthens the membrane and increases the tensile strength from  $85.55 \pm 2.65$  up to  $146.90 \pm 5.71$  M.Pa. Overall, this study demonstrates the potential of nanocarbon as a membrane pore agent to modify the characteristics and performance of the membranes. Further studies can be done to examine the impact of nanocarbon on reducing the membrane fouling propensity.

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