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Effect of Additive on Microstructure, Hydrophilicity and Ultrafiltration Performance of Polyethylene Terephthalate Membranes

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Abstract. Ultrafiltration is a pressure-driven separation process through a porous membrane that can separate particles or macromolecules from a solution. Ultrafiltration is mostly applied for water treatment processes in various industries such as pharmaceutical, chemical, food and beverage industries. Commercial ultrafiltration membranes are mostly fabricated from polymer materials such as polysulfone, polyethersulfone and cellulose acetate. These polymers are expensive, and for the time being they are not produced in Indonesia. In this work, polyethylene terephthalate (PET) bottle waste was used as the polymer material to prepare ultrafiltration membranes. PET is commonly used as a packaging material for foods and beverages due to its low price and excellent mechanical properties. The PET membranes were prepared via a phase-inversion technique using polyethylene glycol (PEG) as the additive. It was observed that the addition of PEG improved the flexibility and the hydrophilicity of the membranes. The water contact angle decreased to 61.5° by the addition of PEG. The microstructures of the membranes could be controlled by the molecular weight of the PEG. The result of the ultrafiltration experiment showed that the membrane with a high porosity, a large pore size and a high hydrophilicity exhibited a high water permeate flux. In the ultrafiltration experiment using a model feed solution of an aqueous solution containing Bovine Serum Albumin with a molecular weight of 66,000 Da, the membranes showed high rejection values of up to 90% with water permeate fluxes of 14.7 - 23.0 kg/(m²h).

1. Introduction

Membrane separation technology have attracted many attentions for the last few decades because of its high selectivity and low-use energy [1,2,3,4]. Reverse osmosis, nanofiltration, ultrafiltration and microfiltration membranes have been applied for various separation processes in many industries such as pharmaceutical, chemical, food, beverages, dairy, drinking water, and other industries [4]. The separation using these membranes is basically a pressure-driven separation process through a selective layer, where particles, macromolecules, ions or other solutes are retained, while smaller substances and solvents can permeate through the membranes. Among these types of membranes, ultrafiltration membranes have medium pore sizes that range from 0.001 μm to 0.1 μm , and they can retain molecules with molecular weights ranging from 500 Da to 500,000 Da. Nowadays, ultrafiltration membranes are one of the most important separation technologies for water treatment to remove microorganism, bacteria, viruses, colloidal substances, and suspended particles [4]. Commercial ultrafiltration



membranes are usually fabricated from polymers such cellulose acetate, polysulfone, or polyethersulfone. For the time being, these polymers are not produced in Indonesia, and must be imported. This condition hinders the development of cheap ultrafiltration membranes in Indonesia, meanwhile the demand of cheap ultrafiltration membranes is high.

In this study, polyethylene terephthalate (PET) bottle waste was utilized as the material to prepare ultrafiltration membranes. The aims of this work are to contribute in the efforts of plastic recycling for the environment conservation, and to develop low-cost ultrafiltration membranes. PET is abundantly produced in Indonesia as it is widely used as a packaging material mostly for foods and beverages. PET is a good packaging material because of its good transparency, good mechanical and chemical properties, as well as good gas-barrier resistance [5]. However, this single-use packaging resulted in a serious environmental problem because it produced a lot of plastic waste that is non-biodegradable. Recently, it has been reported that only 9% of plastic waste is recycled, while the remaining 91% of the plastic waste is just discarded or combusted resulting in water, soil and air pollution [6]. In spite of its excellent mechanical and chemical properties, there are only few reports about the utilization of PET for the development of separation membranes. Hao et al reported the use of PET to develop fibrous membranes by the electrospinning method, and applied the membranes as separator in lithium ion battery [7]. Other studies reported the development of track-etched PET membranes for membrane distillation [8, 9]. To the best of our knowledge, at the time being there is only one study on the use of PET for the development of ultrafiltration membranes as reported by Rajesh et al [10]. It was reported that the ultrafiltration membranes showed rejection values of about 70-90% for solute molecules with molecular weights of more than 500,000 Da (molecular weight cut off/ MWCO > 500,000 Da). Since the application of ultrafiltration membranes with MWCO larger than 500,000 Da is very limited, it is desired to develop PET ultrafiltration membranes that have high rejection values for solute molecules with lower molecular weights. To develop such kind of membranes, the source of the PET polymer and the type of additive are crucial factors in the membrane fabrication. In this study, waste of PET bottles that are commonly used as a packaging for drinking water were utilized as a polymer source to prepare ultrafiltration membranes using the phase inversion technique. The effect of the type of additive on the membrane morphology and the hydrophilicity was studied. The ultrafiltration performance of the membranes was studied by measuring the permeate flux and the rejection through an ultrafiltration experiment using pure water and an aqueous solution containing solute molecules of Bovine Serum Albumin with a molecular weight of 66,000 Da as a feed model.

2. Experimental

2.1. Materials

PET bottles that were previously used for mineral water packaging were used. Phenol, ethanol (96%) polyvinyl pyrrolidone (PVP), polyethylene glycols with molecular weights of 400, 4000, and 6000 Da (PEG 400, PEG 4000, and PEG 6000), Bovine Serum Albumin (BSA, MW: 66,000 Da) were all supplied by Merck, Germany, and were used as received. Distilled water was used.

2.2. Membrane preparation

First, the used PET bottles were washed, dried and cut to obtain small pieces of PET with a size of approximately 3 mm x 3 mm. Phenol was used as a solvent to dissolve the PET bottles. First, phenol was heated at 40°C for 20 min to liquify the solid phenol prior to be used as a solvent. Then, 4 g of the PET shards was dissolved in 15 g of phenol at 100°C until a clear homogeneous polymer solution was obtained. Meanwhile, solutions containing polyvinyl pyrrolidone (PVP) or polyethylene glycol (PEG) as the additives were prepared by dissolving 1.5 g of the additive in 5 g of phenol at 100°C. The additive solution was then blended with the PET solution at 100°C for 60 min to obtain a casting solution. Further, the casting solution was poured out onto a glass plate, and was cast using a casting knife to obtain a liquid thin film. After the casting, the glass plate was immediately immersed in a coagulation bath containing water and ethanol (1:12 v/v) as the non-solvent. The membrane was rinsed with distilled

water several times to remove the remaining residue, and then stored in a plastic container containing distilled water for further characterization.

2.3. Membrane characterization

Analysis using Scanning Electron Microscopy was carried out to study the microstructure of the PET membranes using SEM Quanta 650 equipment. The membrane sample for the SEM analysis was obtained by dipping the membrane in a liquid nitrogen and then fracturing the membrane. The membrane porosity was measured by gravimetric method through measuring the weight of the wet membrane and that of the dry membrane [11, 12]. The wet membrane was obtained by immersing the membrane in distilled water at room temperature for 24 h, whereas the dry membrane was obtained by drying the wet membrane in an oven at 110°C for 3 h. The following equation was used to determine the porosity ε [8,9]:

$$\varepsilon = \frac{(w_1 - w_2)/d_w}{((w_1 - w_2)/d_w) + w_2/d_p} \quad (1)$$

where w_1 and w_2 are the weight of the wet membrane and that of the dry membrane, respectively, whereas d_w and d_p are the density of the water and that of the polymer, respectively.

The hydrophilicity of the membranes was analyzed by measuring the water contact angle. The measurement was carried out using a water contact angle meter with the equipment type of Face CA-D (Kyowa Kaimengaku Co. Ltd, Japan).

The ultrafiltration performances of the membranes were studied by conducting ultrafiltration experiments using the experimental set up as shown in Figure 1. The membrane was placed in a membrane module having an effective membrane area of 51.8 cm². The feed solution was pure water or a phosphate-buffered saline solution containing 1000 ppm BSA as the solute model. The trans-membrane pressure was 1 bar and the temperature was room temperature. The collected permeate was weighed, and the permeate flux F was calculated from the mass of the collected permeate m , the effective membrane area A , and the time interval Δt , by using the equation below:

$$F = \frac{m}{A \Delta t} \quad (2)$$

The rejection R of the membrane was determined by measuring the BSA concentration in the permeate C_P and that in the feed solution C_F , using the following equation:

$$R = 1 - \frac{C_P}{C_F} \times 100\% \quad (3)$$

A UV-vis spectrophotometer was used to measure the BSA concentration. The measurement was carried out at a wavelength of 280 nm using a PG instrument T-60 (UK).

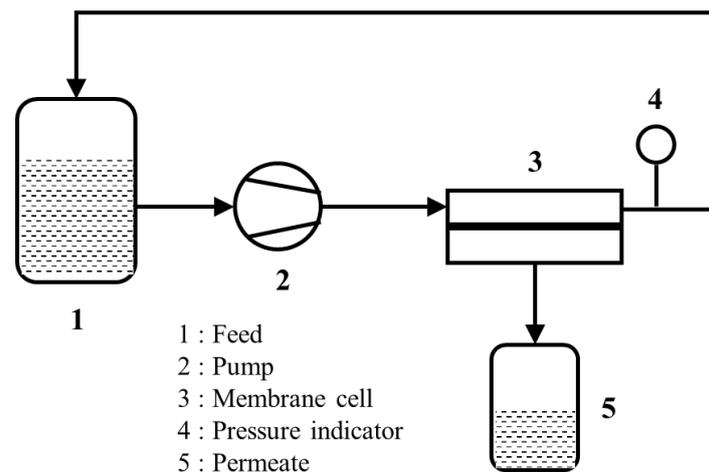


Figure 1. Ultrafiltration experimental set up.

3. Results and Discussion

The PET bottle shards and the additive (polyvinyl pyrrolidone or polyethylene glycol) were completely soluble in phenol, and the blending of both solutions resulted in clear polymer solutions. The polymer solution was then cast onto a glass plate, and was immediately submerged in the water-ethanol bath for coagulation to obtain the membranes. The average thickness of the membranes was $149 \pm 13 \mu\text{m}$. Figure 2 shows the appearance of the surfaces of the membranes. It can be seen that the surface of the PET membrane without additive (a) and that of the PET membrane with PEG 4000 additive (c) were smooth, however the surface of the PET membrane with PVP as the additive (b) contained agglomerates that were formed after the immersion of the membrane in the coagulation bath. Although PVP was completely soluble in phenol and could be blended with the PET in phenol, PVP and PET formed agglomerates during the immersion process in the coagulation bath containing water-ethanol as the non-solvent, since PVP could not easily diffuse from the PET polymer matrix into the coagulation bath. Since the use of PVP additive resulted in defects on the membrane surface, PEG was used as the additive for further experiment. Furthermore, it was observed that the PET membrane without additive was stiff, while the PET membranes with the addition of PVP or PEG showed a better flexibility. It has been known that the additives such as PVP and PEG are plasticizing agents for many polymer films that increase the flexibility of polymer films [13, 14].

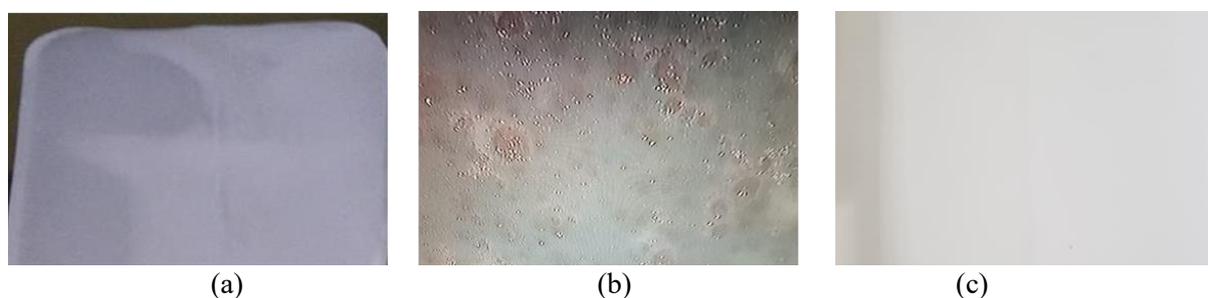


Figure 2. Photographs of the membranes (a: PET membrane without additive, b: PET membrane with PVP as the additive, c: PET membrane with PEG 4000 as the additive).

To study the influence of the additive molecular weight on the membrane performance, PET membranes were prepared using PEG 400, PEG 4000 and PEG 6000. All casting solutions were clear,

indicating that PET and PEGs were completely soluble in phenol as the solvent. Figure 3 shows the photograph of the PET membranes that were prepared using PEGs with various molecular weights. The PET membranes with PEG 400 additive and PEG 4000 additive exhibited smooth surfaces without defects, however the PET membrane with PEG 6000 showed defects in form of holes that could be clearly observed visually using bare eyes. The formation of defects in the PET-PEG 6000 membrane might be caused by the rapid diffusion of PEG 6000 from the PET polymer matrix into the coagulation bath containing the non-solvent during the immersion process. This result showed that the choice of appropriate molecular weight of the PEG additive is very critical to obtain membranes without defects. Table 1 summarizes the effect of the additive on the appearance of the casting solutions and the membranes.

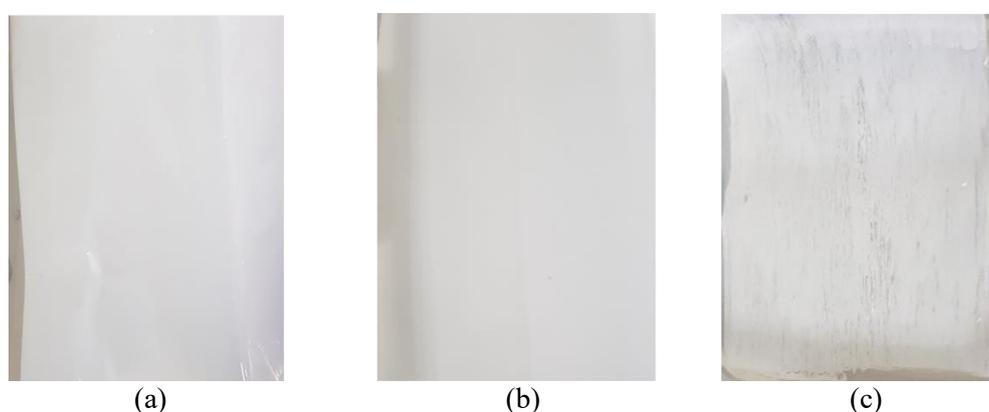


Figure 3. Photographs of the surfaces of the PET membranes using PEG additives with various molecular weights (a: PET-PEG 400, b: PET-PEG 4000, c: PET-PEG 6000).

Table 1. Summary of the appearances of the casting solutions and the membranes with various additives.

Membrane	Additive	Appearance of casting solution	Membrane appearance
PET without additive	No additive	Clear solution	The membrane was stiff
PET-PVP	PVP	Clear solution	Membrane defects; The membrane contained agglomerates on the surface
PET-PEG 400	PEG 400	Clear solution	The membrane showed no defect, and had a good flexibility
PET-PEG 4000	PEG 4000	Clear solution	The membrane showed no defect, and had a good flexibility
PET-PEG 6000	PEG 6000	Clear solution	Membrane defects; Holes were found in the membrane

Furthermore, the hydrophilicity of the membranes was analyzed by the measurement of the water contact angle. The result of the measurement of the water contact angle is listed in Table 2. There was a decline of the water contact angle when the PET membrane contained PEG additive, indicating an increment of the hydrophilicity. The addition of PEG in the PET membrane improved the hydrophilicity since PEG is known as a hydrophilic polymer. The increase in the hydrophilicity is important in the development of ultrafiltration membranes that are applied for water treatment. Similar phenomenon of increasing hydrophilicity by the addition of PEG was also reported for other polymer membranes such as polysulfone (PS) and polyether sulfone (PES) membranes [15].

Table 2. Water contact angle of the PET membranes without and with various additives

Membrane	Additive	Additive concentration (wt%)	Water contact angle (°)	Remarks
PET without additive	No additive	0	65.5 ± 1.4	
PET-PVP	PVP	5.9	-	Could not be measured due to membrane defects
PET-PEG 400	PEG 400	5.9	64.1 ± 1.6	
PET-PEG 4000	PEG 4000	5.9	61.5 ± 0.5	
PET-PEG 6000	PEG 6000	5.9	-	Could not be measured due to membrane defects

The microstructures of the membranes were then analyzed by using SEM. Figure 4 shows the SEM photographs of the cross section and the surface of the PET-PEG 400 membrane. The membrane showed an asymmetric structure consisting of a macro-porous cross section as a supporting layer and a thin smooth layer as the active surface of the membrane. Further, Figure 5 shows the SEM photographs of the PET-PEG 4000 membrane. This membrane also showed an asymmetric structure, however it can be obviously seen that the pores of the cross section of the PET-PEG 4000 membrane were larger than that of the PET-PEG 400 membrane. Since PEG has been known as a pore former [10,11], the presence of PEG in the polymer solution enhanced the formation of pores during the immersion process in the non-solvent. The pore size of the membrane was strongly affected by the molecular weight of the PEG. The membrane pore size increased with increasing molecular weight of the PEG, however it is important to be noted here that the use of PEG with too large molecular weight such as PEG 6000 resulted in membrane defect. Furthermore, the result of the determination of the membrane porosity using gravimetric method showed that the membrane PET-PEG 400 had a porosity of 76.8%, whereas the PET-PEG 4000 membrane had a higher porosity of 78.1%. Thus, increasing the molecular weight of the PEG resulted in an increment of both pore size and porosity of the membrane. Similar finding was also observed in other membranes such as polyether sulfone (PES) membrane and polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) membrane [16, 17]

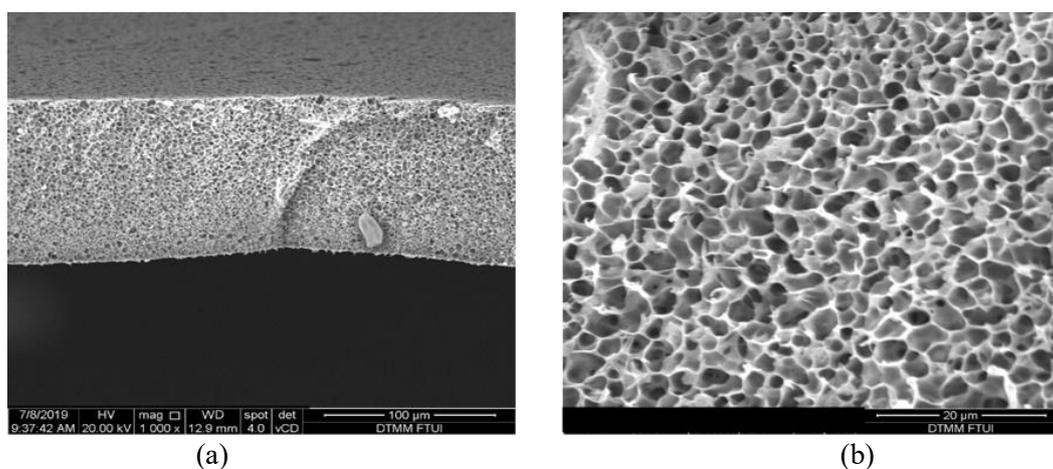


Figure 4. SEM photographs of the PET-PEG 400 membrane (a: cross section and surface, b: cross section with magnification).

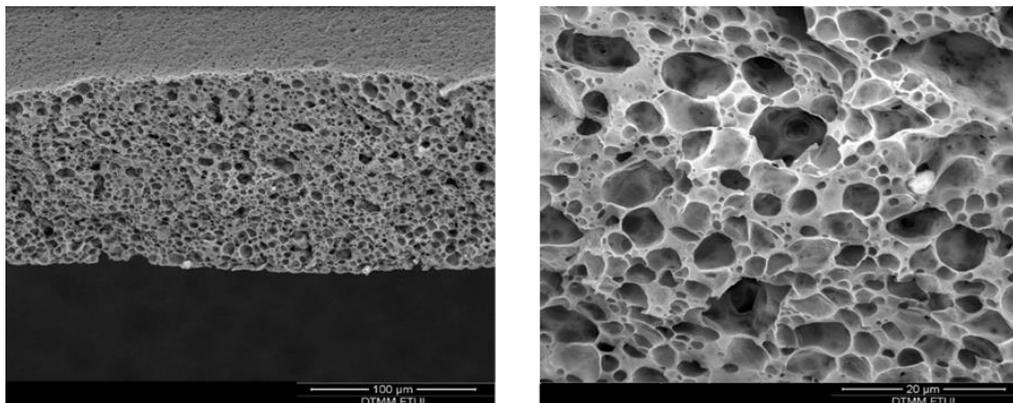


Figure 5. SEM photographs of the PET-PEG 4000 membrane (a: cross section and surface, b: cross section with magnification).

Furthermore, ultrafiltration experiments were conducted using the membranes that were successfully prepared without defects, namely the PET-PEG 400 membrane and the PET-PEG 4000 membrane. The other membranes, namely the PET membrane without additive, the PET-PVP membrane and the PET-PEG 6000 membrane could not be used for ultrafiltration experiment since the PET membrane without additive had a low flexibility and could not be fitted in the membrane module, while the PET-PVP membrane and the PET-PEG 6000 showed defects as mentioned previously. Table 3 depicts the permeate flux and the BSA rejection as a result of the ultrafiltration experiment. The values of the permeate flux and the rejection were taken after the ultrafiltration experiment reached a steady state condition. In comparison with the PET-PEG 400 membrane, the PET-PEG 4000 membrane exhibited a higher water permeate flux, because the PET-PEG 4000 membrane had larger pores as revealed by the SEM analysis and also higher porosity as mentioned above. Moreover, the PET-PEG 4000 membrane exhibited a higher hydrophilicity than the PET-PEG 400 membrane as measured using the water contact angle, thus resulting in a higher water permeate flux. On the other hand, the rejection of the PET-PEG 400 membrane against BSA molecules was 90.6%, which was higher than that of the PET-PEG 4000. This phenomenon is also in agreement with the result of the SEM analysis that showed smaller pores of the PET-PEG 400 membrane. Since the molecular weight of the BSA molecule is known to be 66,000 Da, the rejection value of 90.6% indicated that the PET-PEG 400 membrane had a molecular weight cut off (MWCO) of 66,000 Da. This showed that the rejection of this membrane is higher than that of the PET membrane reported in other study [10].

Table 3. Result of ultrafiltration experiment.

Membrane	Additive	Permeate flux (kg/m ² h)	Rejection (%)	Remarks
PET without additive	No additive	-	-	Could not be used for UF because too stiff
PET-PVP	PVP	-	-	Could not be used for UF due to defect
PET-PEG 400	PEG 400	14.7	90.6	No defect
PET-PEG 4000	PEG 4000	23.0	68.0	No defect
PET-PEG 6000	PEG 6000	-	-	Could not be used for UF due to defect

4. Conclusion

Ultrafiltration membranes were fabricated by utilizing PET bottle waste as the polymer material. Various additives were used for the membrane preparation. Polyethylene glycol (PEG) was found as a good additive for the PET membrane. It was revealed that the use of polyethylene glycol (PEG) additives such as PEG 400 and PEG 4000 improved the flexibility, the hydrophilicity and the porosity of the membranes, however PEG with a too large molecular weight (6000 Da) resulted in membrane defects. The use of PEG with a molecular weight of 400 Da or 4000 Da resulted in membranes without defects that showed good ultrafiltration performances as these membranes were able to retain Bovine Serum Albumin molecules as the solute model. The water permeate flux and the rejection of the membranes were strongly affected by the molecular weight of the PEG. The result of this study revealed that the utilization of PET bottle waste for the fabrication of ultrafiltration membranes can contribute in the plastic recycling and also in the efforts of the development of cheap ultrafiltration membranes for water treatment.

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