

Modification of polyethersulfone hollow fiber membrane with different polymeric additives

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(Received May 30, 2015, Revised March 10, 2016, Accepted April 16, 2016)

Abstract. The improvement of fouling resistance of porous polymeric membrane is one of the most important targets in membrane preparation for water purification in many process like wastewater treatment. Membranes can be modified by various techniques, including the treatment of polymer material, blending of hydrophilic polymer into polymer solution, and post treatment of fabricated membrane. This research proposed the modifications of morphology and surface property of hydrophobic membrane by blending polyethersulfone (PES) with three polymeric additives, polyvinylpyrrolidone (PVP), Pluronic F127 (Plu), and Tetronic 1307 (Tet). PES hollow fiber membranes were fabricated via dry-wet spinning process by using a spinneret with inner and outer diameter of 0.7 and 1.0 mm, respectively. The morphology changes of PES blend membrane by those additives, as well as the change of performance in ultrafiltration module were comparatively observed. The surface structure of membranes was characterized by atomic force microscopy and Fourier transform infra red spectroscopy. The cross section morphology of PES blend hollow fiber membranes was investigated by scanning electron microscopy. The results showed that all polymeric additives blended in this system affected to improve the performances of PES membrane. The ultra-filtration experiment confirmed that PES-PVP membrane showed the best performance among the three membranes on the basis of filtration stability.

Keywords: polymeric additive; ultrafiltration; solute rejection; water permeability

1. Introduction

The improvement of fouling resistance is an important target of membrane modification, particularly when the hydrophobic polymer such polysulfone (PSf) and polyethersulfone (PES) being used as a membrane material (Pagidi *et al.* 2014, Kumar and Ulbricht 2014, Nie *et al.* 2012, Han *et al.* 2013, Lang *et al.* 2013, Kumar *et al.* 2015, Esfandian *et al.* 2016). Fouling consisting of reversible and irreversible deposition of a material onto or into the membrane causes loss of flux, increases filtration resistance, and reduces membrane life. Consequently, running cost increases due to high chemical consumption for flushing and frequent membrane replacement. Therefore, reducing of membrane fouling is a crucial issue for many researchers and membrane manufacturers. Many studies have been conducted to improve the hydrophilic property of

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hydrophobic polymer in order to minimize the membrane fouling. Larsson *et al.* (1996) reported the reduction of protein adsorption on the surface of hydrophobic methylated silica using amphiphilic polymer Pluronic PE9400 composing of poly(ethylene oxide) (PEO) and poly(propylene oxide)(PPO) blocks. The sterical prevention of protein adsorption on the surface of modified material was observed. Proteins are one of foulants which affect on the membrane life time. Intensive investigation on the addition of Pluronic as a surface modifying agent and pore forming agent has been carried out by a research group of Jiang (Wang *et al.* 2006, Lv *et al.* 2007). Hydrophilic-flat-sheet membrane with remarkable fouling resistance was successfully fabricated by blending various molecular weight of Pluronic into polymer solution.

In our previous study, a tetrafunctional block polymer Tetronic 1307 (Tet) was successfully blended as a third component in order to produce high hydrophilicity of PES hollow fiber membrane (Arahman *et al.* 2008). The existence of PEO segment contained in Tetronic 1307 contributed to the decrease of water contact angle, designating that the fabricated membrane became more hydrophilic. In relation to fouling investigation, the results summarized that the ratio of permeability recovery of PES blend membrane with 7wt% of Tet increases twice in compare to that of unmodified PES membrane (Arahman *et al.* 2009). Another attractive hydrophilic polymer such as polyvinylpyrrolidone (PVP) has also been investigated as an additive to improve hydrophilicity of hydrophobic membrane. Several authors have reported that blending of PVP into PES polymer solutions could produce hydrophilic PES membrane with higher porosity and pore distribution, and competitive rejection of foulant that is different from the properties of unmodified membrane (Malek *et al.* 2012, Basri *et al.* 2011, Marchese *et al.* 2003).

In brief, hydrophilic polymer, i.e., Pluronic, Tetronic, and PVP, have been confirmed as potential additives in the fabrication of PES UF membrane via NIPS and thermally induced phase separation (TIPS) procedure with improved the permeability and hydrophilic property (Han *et al.* 2013, Lang *et al.* 2013, Malek *et al.* 2012, Arahman 2014). Those additives are useful in improving surface hydrophilicity of resulted membrane as well as membrane performances in overall. However, it is difficult to ensure the best additive could appropriately be selected for membrane modification based on the reported results in previous experiments. This is mainly due to the spinning or casting conditions i.e., polymer flow rate, bore fluid flow rate and composition, air gap distance, take-up velocity, spinneret dimension, and coagulation composition which are different from one experimental report to another. Moreover, the environmental characteristics such as temperature and humidity also determine the structure of fabricated membrane. A comprehensive study in relation to this work is required in order to obtain a better understanding on the PES hollow fiber membrane performance modified with those three kinds of additives. Therefore, the objective of this study is to investigate the effect of three kinds of polymeric additives as a membrane modifying agent on the morphology and the ultrafiltration performance of PES hollow fiber membrane. All of spinning conditions, including temperature, polymer flow rate, additive composition, bore fluid flow rate, take-up speed of winder, air gap distance, and coagulation bath composition were kept to be similar.

2. Experimental

2.1 Materials

The material used for membrane preparation was polymer PES Ultrason E6020 P (Mw = 65,000). Additives of Surfactant Tetronic 1307 (MW 18000), and Pluronic F127 (Plu) (MW 12600)

were purchased from BASF Co. Another additive, PVP (Mw 30,000) obtained from SIGMA ALDRICH (Steinheim, Germany) also used for membrane modifying agent. Undehydrated solvent N-methyl-2-pyrrolidone (NMP) was obtained from WAKO Pure Chemical Industries, Ltd. (Japan). Humic acid (HA) with molecular weight of 77,000 obtained from SIGMA ALDRICH (Germany) was used as the agent for fouling investigation. High quality of pure water produced by an Elix-5 system (Millipore) was used in the membrane preparation and ultrafiltration experiment. Dextran (Mw =10,000; 20,000; 40,000; and 77,000) purchased from WAKO Pure Chemical, Ltd. (Japan) was used as a particle to determine the molecular weight cut off (MWCO) of membrane

2.2 Membrane preparation

PES unmodified membrane from the system of PES/NMP and three types of PES modified membrane with Plu, PVP, and Tet were fabricated by dry-wet spinning in which water was used as non-solvents to induce phase separation as a procedure explained in our previous works (Arahman *et al.* 2009). To prepare dope solutions, at first, PES was mixed in NMP at 25°C for overnight to ensure the solution became homogeneous. After that, three kinds of additives were dissolved into PES/NMP solution. The compositions of dope solutions are shown in Table 1.

The homogenous solution was flown from a dope vessel, extruded via a spinneret and immersed in coagulation bath containing water with air gap distance of 5 cm. The polymer flow rate was kept constant by a gear pump at 0.0584 ms⁻¹ for all systems. Water was used as inner coagulant at a flow rate of 13.2 ms⁻¹. The solidified membrane was entwined on a cylinder spindle at a take-up speed of 0.22 ms⁻¹. Finally, the resulted hollow fiber membrane was kept in deionized water to release solvent in the membrane.

2.3 Membrane characterization

A scanning electron microscope (SEM) (FE-SEM, JSM-7500F, JEOL Ltd., Japan) was used to investigate the morphology of fabricated PES membrane. The image was recorded with an accelerating voltage of 10 kV. A freeze dryer (FD-1000, Eyela, Japan) was used to dry membrane sample in order to remove water completely. Subsequently, the membrane was immersed in liquid nitrogen for fracture process. Before imaging with SEM, the fractured membrane sample was coated with Pt/Pd sputtering.

The change in chemical structure of unmodified and modified membranes was analyzed using Fourier transform infrared (FTIR) spectroscopy (FTIR-8100A, Shimadzu co., Ltd., Japan). The mechanical properties of fabricated membrane before and after modification by additives was measured using a tensile apparatus (AGS-J, Shimadzu Co., Japan). The analyzed parameter included elongation and tensile strength.

Table 1 Dope solution composition

Code	Polymer solution (wt%)			Non-solvent	Bore fluid composition
	Polymer	Additive	Solvent		
PES	PES (18)	-	NMP (82)	Water	Water
PES-Plu	PES (18)	Pluronic F-127 (2)	NMP (80)	Water	Water
PES-PVP	PES(18)	PVP (2)	NMP (80)	Water	Water
PES-Tet	PES (18)	Tetronic 1307 (2)	NMP (80)	Water	Water

Hollow fiber membrane was cut in approximately 7 cm length, and put on between two clip panels vertically with the distance of 50 mm. The mechanical parameter of membrane can be observed by extend of membrane with clip panel at elongation rate of 50 mm/min until the membranes was broken. The data of mechanical properties were obtained as averages of 5 measurements for each sample.

2.4 Filtration performances

Filtration characteristic of the fabricated membranes was characterized by measuring water permeability of deionized water and relative permeability of humic acid (HA) solution. The ultrafiltration module was set up as laboratory scale of single hollow fiber module described in our previous work (Arahman *et al.* 2012). Feed solution with flow rate of 0.05 ms^{-1} was forced into a module packed by using peristaltic pump at membrane pressure (P) of 0.5 atm. A pressure driven inside flow filtration model was conducted by using a 150 mm length of single membrane with inner diameter of 0.96 mm. The volume of permeate (V) was collected every five minutes (t), and the water permeability (J_w) was calculated on the basis of the inner surface area (A) of the hollow fiber membrane by using the following equation

$$J_w = \frac{V}{AtP} \quad (1)$$

In the measurement of a relative permeability of HA solution, at first deionized (DI) water was permeated as a feed solution for one hour filtration, and the averages water permeability J_0 was measured. Then, HA solution with a concentration of 100 ppm and pH of 7.0 ± 1 was permeated as a feed solution for two hours of fouling filtration. Sodium dihydrogen phosphate and disodium hydrogen phosphate solution were used to adjust the pH of HA solutions. The filtrate of HA solution was collected every 5 minutes, and the permeability of HA solution J_1 was measured. Relative permeability and rejection of HA solution during two hours filtration were calculated by using Eqs. (2) and (3), respectively.

$$\text{Relative permeability} = \frac{J_1}{J_0} \quad (2)$$

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

where C_P and C_R are the concentration of humic acid in permeate and retentate, which is analyzed by a spectrophotometer (Shimadzu, UV-Vis 1800, Japan) at a wavelength of 254 nm.

In order to evaluate the tendency of membrane permeability before and after filtrated with humic solution, the permeability recovery ratio (PRR) was measured. After two hours filtration with humic acid solution, the module was flowed with deionized water as feed solution under the constant transmembrane pressure. At this filtration stage, the constant water permeability J_2 was measured at the end of filtration after 1 hr. The PRR is defined by Eq. (4).

$$PRR = \frac{J_2}{J_0} \times 100\% \quad (4)$$

2.5 Determination of MWCO of membrane

The molecular weight cut off (MWCO) is one of the important parameter for membrane characterization. For MWCO investigation in this work, a 200 ppm dextran solution with molecular weight of 10,000, 20,000, 40,000, and 77,000 Da were filtrated by using single sheet hollow fiber membrane module. The concentration of dextran in permeate (CP) and in retentate (CR) was analyzed by the UV-Vis spectrophotometer (Shimadzu, UV-Vis 1800, Japan). The MWCO of all fabricated membranes were determined from the rejection of dextran solution.

3. Results and discussion

3.1 Membrane morphology

In order to understand the effect of the existence of polymeric additives as a pore maker agent on the structures of the PES membrane, the morphology of all fabricated membranes was observed by FE SEM. Fig. 1 indicates the SEM image of enlarged cross-section of membrane formed by PES/NMP solution and the modified membrane formed by PES/NMP/Plu. F-127, PES/NMP/PVP, and PES/NMP/Tet.1307 solutions. In all cases, fingerlike, macro-void structure was clearly formed around outer and inner surfaces of the hollow fiber membranes. It is well understood that, in membrane preparation via NIPS process, the pore volume and pore structure are mainly determined by diffusion process of non-solvent into the polymer solution, and diffusion of solvent into the coagulation bath (Smolders *et al.* 1992). The phenomenon easily occurs on subsurface of membrane; hence the fingerlike structures are formed in this layer as seen in Figs. 1(a)-(d). Large sponge structure is configured in the centre path of unmodified hollow fiber membrane, as indicated in Fig. 1(a).

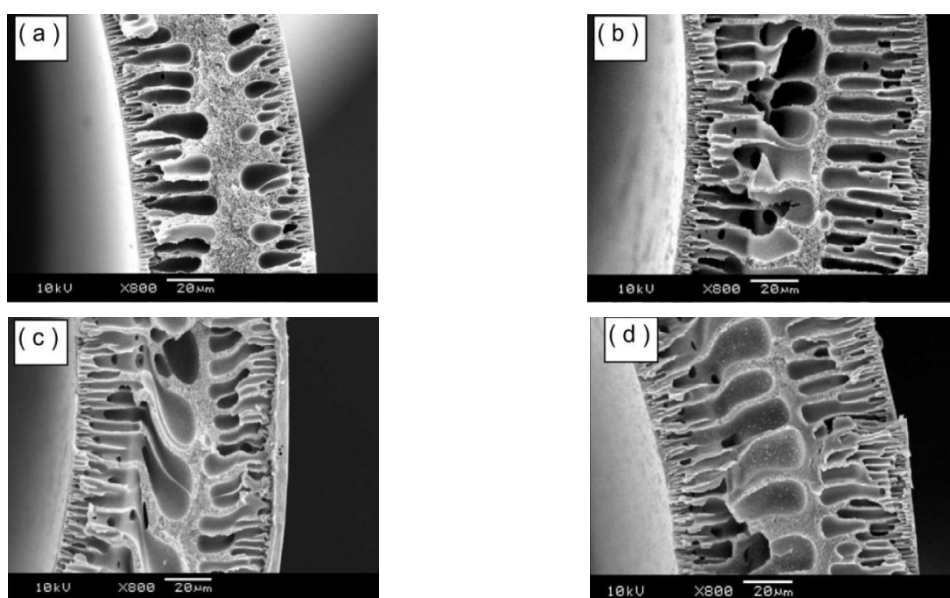


Fig. 1 Cross-section morphology of PES hollow fiber membrane imaged by SEM. (a) PES; (b). PES-Plu; (c) PES-PVP; (d) PES-Tet

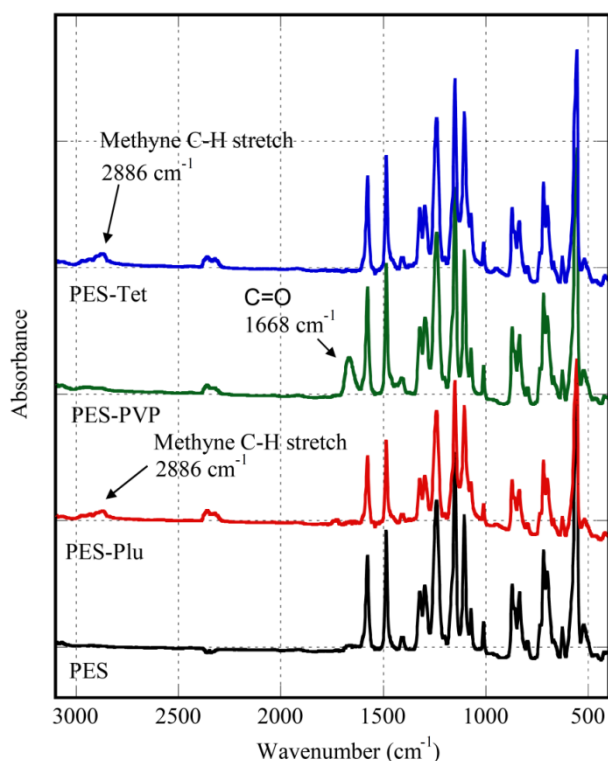


Fig. 2 FTIR spectra of the original PES and modified PES membranes

In membrane modification process, increasing pore density with most stable pore size is the most necessary. Sponge structure formed in the center path of fabricated membrane is related to the filtration performance and mechanical properties. Membranes with large sponge structure are superior in mechanical properties. However, its filtration performances are limited, because of low water permeability (Loh and Wong 2014, Fang *et al.* 2015). The effect of membrane morphology on the membrane properties and its filtration performances are discussed in Section 3.3-3.5. The addition of membrane modifying agent into polymer solution results in the increase of number and length of fingerlike structure, as shown in Figs. 1(b)-(d). Sponge structure in the center path of PES unmodified membrane (Fig. 1(a)) significantly decreased in the PES modified membrane in all systems.

3.2 FTIR spectroscopy

It is important to ensure the influence of polymeric additives on the surface property of fabricated membrane. Therefore, FTIR measurement was carried out to confirm the existence of polymeric additive on the surface layer of PES blend membranes. Fig. 2 shows the results of FTIR measurement. The IR spectra of PES unmodified membrane showed the remarkable bands at 1577 cm^{-1} , and 1460 cm^{-1} assigned to by aromatic bands of PES polymer. The presence of polymeric additives Plu and Tet as a surface modifying agent in blend membrane system showed an additive new small peak in the band of $2200\text{-}2400\text{ cm}^{-1}$. This peak is attributed to the stretching vibration of methyne C-H and skeletal C-C vibration of surfactant Pluronic / Tetronic (Arahman *et al.* 2009). In

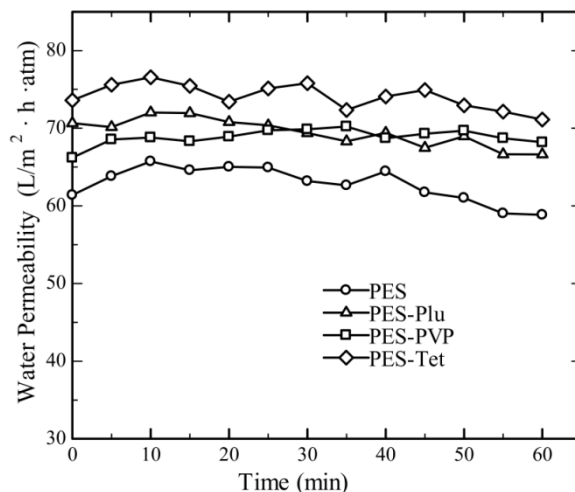


Fig. 3 Time course of pure water permeability of membranes

case of the PES membrane modified with PVP, a new moderate bands appear at 1600 cm^{-1} in correlating to the C = O and N-C stretching vibration of polyvinyl pyrrolidone. The appearing of these peaks indicated that polymeric additive exist also on the membrane surface.

For all modified PES membrane, another peak also appeared at wave number of $2240\text{--}2400\text{ cm}^{-1}$ which corresponds to the aliphatic nitrile group (Coateds 2000). The existence of these functional groups on base membrane surface brought slightly change of the modified membrane hydrophilicity. Thus, we can conclude that the appearance of these peaks prove that the modified PES membrane with tetronic, pluronic and PVP had improved the hydrophilicity of the modified membrane.

3.3 Filtration performances

The results of filtration experiments with deionized water for all membranes prepared from the system of PES, PES-Plu, PES-PVP, and PES-Tet are shown in Fig. 3. The initial water permeability was different among the four types of membranes. PES original indicated the lowest water permeability compared with other blend membrane. The addition of 2wt% of polymeric additives in the polymer solution brought the increase of water permeability of all PES modified membrane. According to SEM analysis as shown in Fig. 1, its can be confirmed that addition of Plu, Tet, or PVP in the dope solution can improve the number and length of macrovoid. This is the reason for the increase of water permeability of PES-Plu, PES-PVP, and PES-Tet membranes.

Humic acid is widely used as a fouling agent in membrane filtration. Humic acids refer to the fraction of humic substances which contained in soils and appear in surface water in low concentration as a product of decomposition of lignin, carbohydrate and protein (Nystrom *et al.* 1996). In this work, humic acid solutions of 100 ppm were used as fouling agent to observe the flux tendency of four types of hollow fiber membrane. Fig. 4 indicates the decrease of relative permeability (J/J_0) of PES unmodified membrane and PES modified membrane with additives as a function of filtration time. It is showed that the reduction of relative permeability of PES original membrane was significantly taken place. The decrease of relative permeability of this membrane was about 60% after two hours of filtrations.

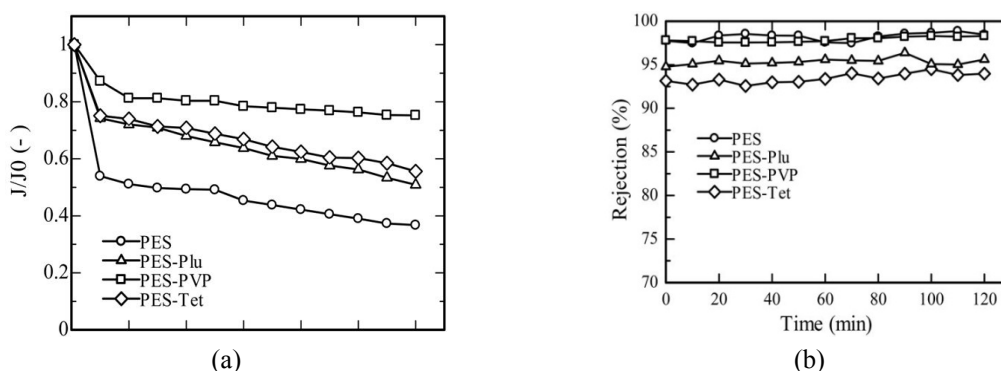


Fig. 4 (a) Relative permeability; and (b) solute rejection; of PES hollow fiber membrane by using humic acid solution of 100 ppm as a function of filtration time

Table 2 Permeability recovery ratio of fabricated membrane

Membrane system	PES	PES-Plu	PES-PVP	PES-Tet
PRR (%)	56.32	74.10	85.50	78.21

The relative permeability decline of the unmodified PES membrane was influenced by adsorption of humic acid molecules on the surface due to its hydrophobic property of this membrane. A certain amount of humic acid molecules are adsorbed onto the pore surface, and it could result to cake layer formation on the inner surface of membrane (Arahman *et al.* 2009). Otherwise, at the same experimental condition, the relative permeability of PES membrane modified with either Plu. F127 or Tet. 1307 was higher than that of the original PES membrane. The addition of Plu. F-127 and Tet. 1307 into polymer solution brought the increase of membrane hydrophilicity, as presented in previous work (Smolders *et al.* 1992). Membrane with high hydrophilicity property could reduce the adsorption of humic acid molecule into pore surface of membrane. As a consequence, the formation of fouling layer can be minimized. Therefore, the relative permeability of this membrane does not change significantly.

PES-PVP membrane indicated the best performances for the most stable relative permeability. The permeability reduction of this membrane after two hours filtrated with humic acid solution is approximately 20%. PES-PVP membrane also has a good performance for permeability recovery ratio as shown in Table 2. PVP is a well known additive as membrane-modifying agent both for controlling membrane structure, and membrane hydrophilicity (Pagidi *et al.* 2014, Wienk *et al.* 1995). The existence of this additive on the system will make the PES membrane becoming more hydrophilic, resulting in improving of the fouling resistance and more stable water permeability. In Fig. 4, the rejections of humic acid solution were also plotted. In all cases, the rejection of humic acid solution was higher than 90%.

3.4 The MWCO's membrane

Measurement of molecular weight cut off (MWCO) is one of the frequent techniques used to estimate the average pore size of fabricated membrane. The MWCO of membrane mean the molecular weight of solute rejected for 90% (Chen *et al.* 2014). In this work, MWCO were

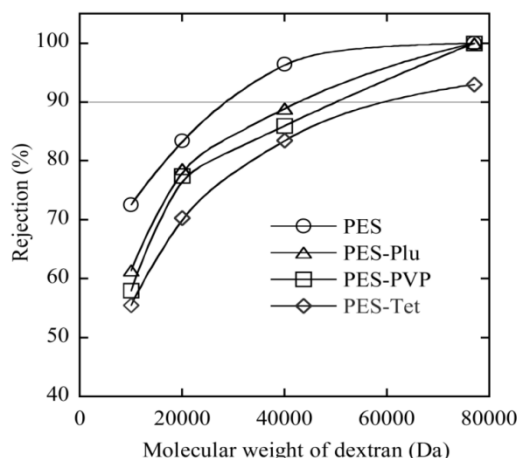


Fig. 5 Rejection of dextran solution with different molecular weight

determined by rejection experiment using 200 ppm of dextran solution with different molecular weight. Rejection experiment was conducted for all membranes at 25°C under 0.5 atm. Fig. 5 shows the rejection curve of all types of membrane at various molecular weight of dextran. The rejection of dextran were different in one and other membranes. According to the rejection data of all experimental condition as plotted in Fig. 5, the MWCO of membranes can be determined as 27,000, 42,000, 50,000, and 60,000 Da for PES, PES-Plu, PES-PVP, and PES-Tet membranes, respectively.

3.5 Mechanical properties

The results of mechanical properties investigation for membranes prepared from PES/NMP and PES/NMP blended with polymeric additives are indicated in Table 3. Based on the results, it can be observed that an addition of polymeric surfactant into the polymer solution causes a decrease in tensile strength and elongation. The decrease of mechanical properties of PES blended membrane can be explained by SEM results as indicated in Fig. 1. PES blended membrane with polymeric additives has macro-void structure larger than that of PES original membrane. This is because of entangling interaction between polymer polyethersulfone and polymeric additives which results in an increase in membrane-pore size. Consequently, these phenomena caused the decrease in mechanical properties of PES blend membrane.

In many cases, the addition of polymeric additives into polymer solution brought a significant

Table 3 Mechanical properties of the original PES and modified PES membranes

Membrane code	Mechanical properties	
	Tensile strength [MPa]	Elongation [%]
PES	8.32	88.17
PES-Plu	3.90	43.39
PES-PVP	6.79	59.97
PES-Tet	4.50	51.08

impact on the mechanical properties of the resulted membrane. Those effects depended on the types and concentration of polymer and additives. Loh and Wong (2014) investigated the effect of addition of 0.5wt% Pluronic F127 on the mechanical properties of hollow fiber membrane prepared from 18wt% of poly(vinylidene fluoride) (PVDF). They found that the tensile strength of blended PVDF membrane was about 48%, less than PVDF pristine membrane. Vilakati *et al.* (2014) summarized the reducing of the mechanical properties of polysulfone (PSf) membrane modified with 0.5wt% of PVP. The tensile strength of the modified membrane was about 42%, less than initial value of unmodified PSf membrane. Decreasing of the mechanical properties of these membrane may be attributed to the filtration time, particularly when hypochlorite solutions are used as a backwash solution (Arahman *et al.* 2009).

4. Conclusions

Polyethersulfone (PES) hollow fiber membrane with improved water permeability has been successfully prepared by addition of 2wt% of Tetronic 1307, PVP, or Pluronic F127. The study was focused on the influence of those additives in objectives to improve the filtration stability of PES membrane by using pure water and humic acid solution of 100 ppm. SEM investigation showed that the morphology change of modified membrane was significantly observed. FTIR observation confirmed the existence of hydrophilic segment on the outer surface of membrane. Overall, the results indicates that the Pluronic F127, PVP, and Tetronic 1307 are usable as a membrane modifying agent. The modified PES membrane with PVP show the most stable of relative permeability of humic acid solution.

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