Fabrication Membrane of Titanium Dioxide (TiO2) Blended Polyethersulfone (PES) and Polyvinilidene Fluoride (PVDF): Characterization, Mechanical Properties and Water Treatment

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Fabrication Membrane of *Titanium Dioxide* (TiO_2) Blended *Polyethersulfone* (PES) and *Polyvinilidene Fluoride* (PVDF): Characterization, Mechanical Properties and Water Treatment

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Abstract. In this research, Polyethersulfone (PES) and Polyvinylidene Fluoride (PVDF) with the addition of a Titanium Dioxide (TiO_2) blended membrane were prepared using the DC 15000 V electric field method. The mechanical properties of membranes and water treatment performance was investigated. The surface mixture of Polyethersulfone (PES) and Polyvinylidene Fluoride (PVDF) membranes is characterized using SEM, the membrane pore size shrinks and forms evenly with the addition of Titanium Dioxide (TiO_2) and DC electric field methods. Tensile tests were carried out to obtain the mechanical properties of Polyethersulfone (PES) and Polyvinylidene Fluoride (PVDF) by adding Titanium Dioxide (TiO_2) mixture membrane, which showed an increase in optimal tensile strength to 3.86 MPa at a concentration of 30% Polyethersulfone (PES) and also increased to 1.15 MPa at 20% Polyvinylidene Fluoride (PVDF). The membrane surface was examined using contact angle measurements, which in the mixed membrane Polyethersulfone (PES) and Polyvinylidene Fluoride (PVDF) showed a decrease in the angle between the range of 43º - 46º. Therefore, hydrophilicity makes it possible to suppress the permeate flux of pure water. Making membranes with the addition of Titanium Dioxide (TiO_2), and assisted by DC electric fields opens up new ways to increase membrane strength, hydrophilicity, shrink and make pore sizes evenly formed.

Introduction

The growing of world population has an impact on healthy water resources which makes healthy and potable water become a luxury item for more than 2.1 billion people worldwide who do not have access to safe water treatment [1]. The needs of clean drinking water is one of the special concerns for the world. Just like in the case when the United Nations (UN) and the World Bank gave the warning about global water crisis, where 40 percent of the world's population lacks of clean water[2]. Membrane technology has become an efficient separation technology [3] in several recent years due to its adaptability, low energy requirements[4] and the quality of water[5] produced. Polymer-based membranes is one of the most widely used membranes in the industry[4] because of their low cost and good performance, but behind these advantages polymer membranes have low mechanical and thermal resistance[3].

Polyethersulfone (PES) and Polyvinylidene Fluoride (PVDF) polymers are one of the most widely used materials for membrane manufacture [1,6]. However, the hydrophobic characteristics of PES and PVDF will result the poor membrane contamination in water treatment, which is a challenge for their use in industry [7]. PES is one of the water filtration membrane fabrication polymers commonly used because it has many beneficial properties including excellent mechanical properties, high dimensional stability, thermal stability, exceptional oxidative and hydrolytic stability, mechanical resistance, and tolerance to solvents [7]. PVDF is a type of polymer that has high mechanical stability and thermal stability and stable, has resistance to chemicals so it is suitable to be used in membrane composing materials[3]. In addition PVDF is a piezoelectric polymer which has the highest dielectric constant [8]. Apart from these extraordinary characteristics, PES and PVDF are hydrophobic [5,9]. However, PES and PVDF membranes can be modified to be more hydrophilic by grafting, coating and mixing methods [1]. The mixing method is the easiest method out of the three methods above.

Recent studies have focused on the addition of Titanium dioxide (TiO_2) to polymers. TiO_2 as an addictive substance that can increase fouling resistance has been confirmed by many studies [10]. TiO_2 is a nanoparticle that can increase the hydrophilicity, self-cleaning, and antibacterial of the membrane itself. Besides that TiO_2 has stability properties, non-toxic, low price and superhydrophilicity [11]. As we know that polymers such as PES and PVDF have high hydrophobic properties so that by mixing TiO_2 is expected to increase the hydrophilicity of the membrane [12,13].

Membrane modification is prepared through the electric field method assuming the electric field method will suppress agglomeration that occurs due to the addition of TiO_2 to PES and PVDF. In the study[14] confirmed that the addition of 5000V electric field made Graphe Oxide (GO) evenly distributed to the membrane with the addition of a low GO concentration. Therefore the concentration that will be used for TiO_2 is only 1wt%. However, the electric field voltage is increased up to 15000V with asumption the greater voltage applied, the smaller agglomeration that will occur on the membrane and also TiO_2 can increase the electrical conductivity of the polymer electrolyte on the membrane [15].

Experimental

Materials

Polyethersulfone (PES, 20,25,30wt%), Polyvinylidene Fluoride (PVDF, 10,15,20wt%), N,N-Dimethylformamide (DMF), Titanium Dioxide (TiO_2, 1wt%) obtained from aldrich Chemical and used without purification Furthermore. The solution is stirred mechanically for 8 hours to obtain a perfect homogeneous solution. The flat-sheet method with the modification of the 15000 V DC electric field is different from the flat-sheet method in general, where the use of an electric field will be placed between two copper plates in the membrane molding process.

Membrane Preparation

In this study, flat membrane sheets were prepared without any prior material purification process. The DMF mixture solvent is mechanically stirred at 40º. Then the PES polymer (20wt%, 25wt%, 30wt%) and PVDF (10wt%, 15wt%, 20wt%) are mixed slowly into the solvent. After the mixture of polymers and solvents has been homogeneous and does not form lumps, add the addictive substance TiO_2 1wt%. Each solvent was stirred at a speed of 100 rpm and with a span of 8 hours using a magnetic stirrer (FAITHFUL Magnetic Stirrer SH-3, Palembang, Indonesia). The prepared solvent will be formed using the copper plate flat-sheet method with electric field modification for 3 minutes before immersion in deionized water.

Results and Discussions

Contact Angle

The hydrophilicity of a membrane surface can be investigated using water contact angles. The water contact angle is used to analyze the hydrophilicity of a membrane. The hydrophilicity of the membrane has a significant impact on water treatment performance and the antifouling ability of themembrane itself. Contact angle Membrane mixture of PES and PVDF with the addition of TiO_2 is shown in Fig. 1. A low membrane contact angle identifies that the addition of TiO_2 nanoparticles and the use of a 15000 V DC electric field can increase the hydrophilicity of a membrane[16]. With the addition of 1wt% TiO_2 at each concentration of PES and PVDF the contact angle is reduced (44º, 43º, and 44º) and (41º, 43º, and 46º). The highest hydrophilicity was obtained from mixing 1wt% TiO_2 with 10wt% PVDF which reached 41º then 43º for mixing 1wt% TiO_2 with 25wt% PES. A mixture of PES and PVDF membranes with the addition of TiO_2 using the electric field method can achieve similar or even lower contact angles compared to previous studie [17,18]

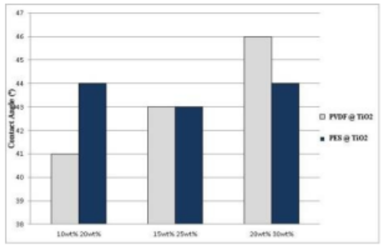
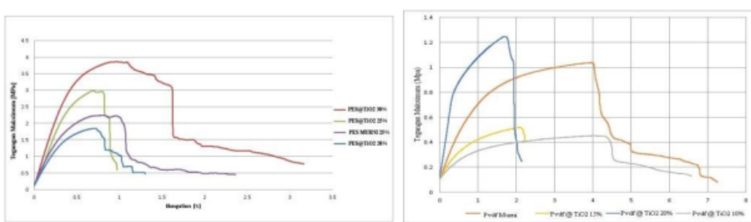


Fig. 1. Contact angle of the mixed membrane by the electric field method Tensile Strength

Mechanical testing using ZWICK ROEL Material Testing Machine (Type BT2-FR020TH.A60, Bangka Belitung, Indonesia). The tensile strength and elongation of the membrane are parameters that can explain the mechanical properties of the membrane. Tensile tests carried out on PES and PVDF @ TiO_2 membranes with composition (20, 25, 30wt%) and (10, 15, 20wt%) and compared with pure PES and PVDF membranes are shown in Fig. 2. It can be seen in Fig. 2 that (a) the higher the concentration of PES, the more resilient, this is contrary to the PVDF membrane in Fig. 2 (b) the higher the PVDF concentration, the more brittle the membrane is. The average tensile strength value is obtained by carrying out 3 tests. For the tensile strength of PES @ TiO_2, this shows an increase in value from 1.84 MPa to 2.99 MPa when specimens with PES fiber composition increase from 20wt% to 25wt%. Then the tensile strength at the composition of 30wt%, increased to 3.86 MPa. and for tensile strength PVDF @ TiO_2 showed an increase in value from 0.453 MPa to 0.5 MPa when the specimens with PVDF fiber composition increased from 10wt% to 15wt%, the tensile strength at the composition of 20wt%, increased to 1.1533 MPa. As a result, the effect of adding TiO_2 on PES and PVDF significantly increases the mechanical strength of the membrane, which also influences membrane life[19].

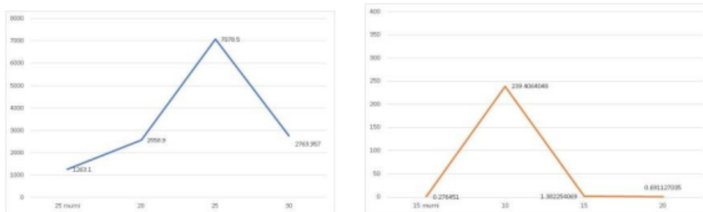


(a) (b)

Fig. 2. Tensile Strength of Membranes: (a) PES (b) PVDF

Water Treatment Perfomance

Water treatment performance is characterized using clean water permeability. The flux value of each polymer concentration produced during the 1 hour test was recorded and membrane decay that occurred after the test was also analyzed. Dead-end system with an effective membrane area of cm^2 is used to analyze the performance of the prepared membrane. The membrane is tested at 1-2 bar pressure for 1 hour and at ambient temperature. Water treatment performance of PES and PVDF @ TiO_2 membranes with the use of an electric field is shown in Fig. 3. In fig. 3 (a) PES @ TiO_2 membrane at a concentration of 25wt%, PES @ TiO_2 shows a maximum flux value of 7078.5 L / mm^2.h , due to agglomeration in the microstructure at the time of membrane formation, then at a concentration of 20 & 30wt% PES @ TiO_2 showed an increase of 3.85%, from 2558.9 L / mm^2.h to 2763,957 L / mm^2.h. in fig. 3 (b) PVDF @ TiO_2 mixed membrane, the permeability of pure water is reduced. Concentration of 10% PVDF @ TiO_2 shows a high flux of 239.41 L / mm^2.h, which is caused by the pore size formed on the membrane unevenly and many agglomeration occurs later at a concentration of 15wt% and 20wt% shows a flux value of 1.38 and 0.69 L / mm^2.h. The addition of TiO_2 to the membrane increases the hydrophilicity which is very influential resulting in the low value of pure water flux [20].

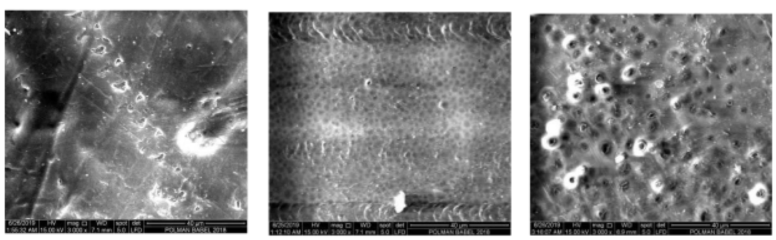


(a) (b)

Fig.3. Water treatment performance: (a) PES (b) PVDF

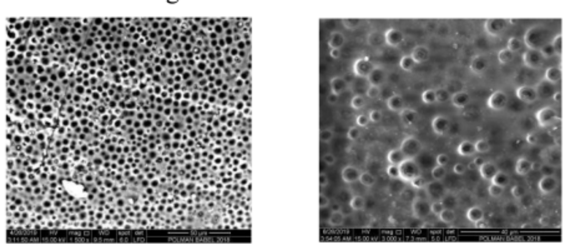
Morphological Characteristics

The front surface of the membrane is characterized using Inspect S50 (FEI Company, Bangka Belitung, Indonesia). The structure of the PES @ TiO_2 membrane with different weight concentrations was prepared by adding the DC electric field observed with SEM. In fig. 4, the concentrations of 20wt% and 30wt% show the smooth pore surface observed below 3000 times magnification. This confirms that the addition of 15000V DC electric current helps in pore smoothing of the membrane. However it is the opposite at a concentration of 25wt% where there is a lot of agglomeration in the membrane and the formation of uneven pore sizes on the membrane surface. Fig. 5 presents a comparison for PES polymers without the addition of TiO_2 to the forming process. The results observed at 1500 times magnification and 3000 times magnification get maximum results where the surface pores are formed very evenly and almost no agglomeration occurs on the membrane surface.



(a) (b) (c)

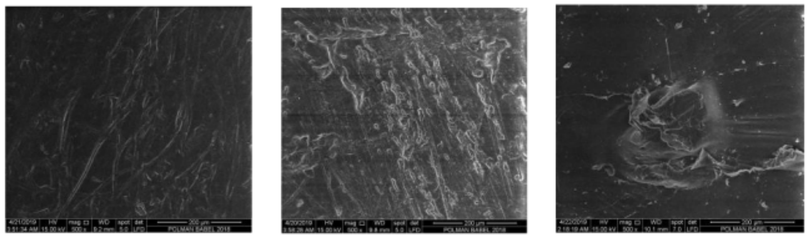
Fig.4. PES @ TiO_2 Membrane Surface Addition of Electric Field: (a) 20wt%, (b) 30wt%, (c)25wt% Magnification of 3000 times



(a) (b)

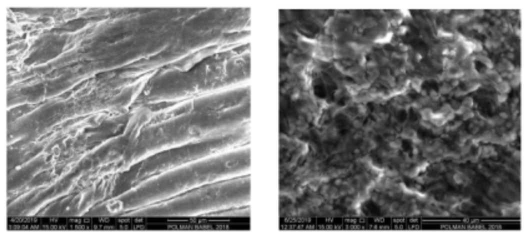
Fig.5. Pure PES Membrane Surface 25wt% Electric Field Addition: (a) 1500 times magnification, 3000 times magnification

Fig.6 presents the surface structure of the PVDF @ TiO_2 membrane with concentrations of 10wt%, 15wt%, 20wt% and the addition of a DC electric field observed with SEM. The picture shows the smooth surface results without pores and agglomeration of the membrane was observed with magnification 500 times. This confirms that the pore structure of the membrane is very tight and TiO_2 is spread evenly on the polymer. Then in Fig. 7 presents a comparison of pure PVDF without the addition of TiO_2 during the membrane manufacturing process. The results were observed at an enlargement of 1500 times and magnification of 3000 times, there is a lot of agglomeration that occurs but the pore structure on the membrane surface is very tight and smooth.



(a) (b) (c)

Fig.6. PVDF @ TiO_2 Membrane Surface Electric Field Additions: (a) 10wt%, (b) 15wt%, (c)20wt% 500 times magnification



(a) (b)

Fig.7. Pure PVDF Membrane Surface 15wt% Addition of Electric Field: (a) 1500 times magnification, (b) 3000 times magnification

Conclusion

The mixture of PES and PVDF membranes with the addition of TiO_2 was successfully made using the 15000 volt DC electric field method. The influence of TiO_2 and electric fields over the specified PES and PVDF membrane concentration ranges was investigated starting from the mechanical properties of the membrane to the performance of water treatment. Observation using SEM shows that with the addition of TiO_2 and electric field, the membrane morphological structure has an even and smooth pore size from low to high concentrations, this is directly proportional to the tensile strength of PES and PVDF membranes the higher the concentration the greater the maximum stress obtained. For the addition of TiO_2 can increase the hydrophilicity of the membrane, the optimal value obtained for PES membranes is 43^0 and for PVDF membranes up to 41^0 but this is very contrary to pure water flux, the higher the hydrophilicity of eating the lower the value of pure water flux the results of research show that the addition of TiO_2 and the use of a 15000 volt DC Electric Field are one of the effective methods to improve the mechanical properties of membranes and water treatment performance with low TiO_2 concentrations.

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