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EFFECT OF BENTONITE AS FILLER IN COMPOSITE MEMBRANE PERFORMANCE POLYVINYLIDENE FLUORIDE (PVDF)-POLYMETHYLMETHACRYLATE (PMMA)

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Abstract. *The effect of bentonite as filler on the performance of the composite membrane of PVDF-PMMA has been performed. This study was conducted to determine the performance PVDF-PMMA composite membranes and membrane applications PVDF-PMMA-Bentonite on oily wastes. Bentonite is obtained from North Aceh while PVDF membrane-PMMA by phase inversion method. This study uses an oily waste water model was made by mixing surfactant tween 80 with concentration of 2% with palm oil and gas oil. Membrane PVDF-PMMA-Bentonite is analyzing using cell ultrafiltration (flux test), FTIR and SEM-EDX. The results showed that the value of flux with the addition of bentonite is greater than without bentonite. Good flux values contained in the PVDF-PMMA-Bentonite (1:1:2) amounted to 32.143 $L/m^2.h.bar$ with permeability of 21.428 $L/m^2.h$. FTIR characterization analysis results show that bentonite can add to pore at wave number 1520 cm^{-1} and 1660 cm^{-1} SEM and EDX results showed regular shape and uniform pore.*

Keywords: *Membrane, bentonite, filler, FTIR, SEM-EDX, Oily wastewater*

I INTRODUCTION

Membrane technology is broadly used for drinking water desalination, waste cooking oil processing, medical purposes, and gas separation in chemical industry. Moreover, it is also applied in the field of alternative energy which is a basic part in fuel cell. Supplying membrane for chemical uses is a major challenge in the membrane study field. Generally, membrane can be created from organic and inorganic compounds. Furthermore, the most important point is that membrane does not have negative impact to the environment because separating process by using membrane does not need additional chemical compound. Polyvinylidene flouride (PVDF) can be used as a material in making process of membrane. PVDF is a polymer with high polarity and electrolyte absorbent [3]. A shortfall of PVDF is that it has high crystallinity such that the produced membrane is fragile and easily broken. However, the high crystallinity of PVDF can be decreased through blending method which is a simple method to modify the polymer matrix. Some polymers such as polyethylene oxide (PEO), polyacrylonitrile (PAN), polydimethylsiloxane (PDMS), and polymethyl methacrylate (PMMA) have been used as PVDF matrix mix [4]. In this research, PMMA was used to create composite together with PVDF. PMMA has characteristics which are like transparent plastic, have good collision strength and temperature resistance. PMMA membrane has low stereoregularity making it amorf, resistant to aqueous inorganic reagent including alkali and acid. Utilized of PVDF-PMMA membrane was also conducted by Ochoa *et al.*,[3]. They investigated the hydrophilicity effect to the separation of oil waste emulsion by using the PVDF-PMMA membrane and organic additive which was PVP (polyvinylpyrrolidone). The membrane's performance was counted by the presence of COD *(*Chemical Oxygen Demand) decrease to the variation of PMMA concentration, which reached 90% of the rejection value. Creating PVDF-PMMA membrane by adding bentonite as a filler is still researcher's choice to increase the membrane's performance. Filler is used to increase the hardness and the elastic modulus, modify the values of the strength, toughness, stability, heat and electricity conductivity [4].

Bentonite is a good absorbent. The existence of pore space between the clay mineral bonds and unbalanced electrical load in the ions makes bentonite beneficial as excavation trench for many purposes [5]. The effort in separating oil-water emulsion is not yet optimally carried out. In order to support it, this research concerns on developing PVDF-PMMA composite membrane by adding the bentonite as the filler. The addition of bentonite is expected to increase the membrane's performance resulting high flux value and rejection coefficient. The produced membrane was characterized by evaluating its flux value, FTIR, and SEM-EDX. Furthermore, membrane in the optimum condition was tested against the oil emulsion separation. The produced membrane has been applied to resolve the environmental contamination. The oil contamination in low or high concentration has happened as a serious problem. Therefore, this research is an effort in creating a technology for solving the separation problem in low-cost and easy way as well as without further impact [6].

II METODOLOGY

The materials which were used in this research are bentonite, aceton, PVDF (polyvinylidenefluoride), PMMA (polymethyl methacrylate), DMAc (N-N dimethylacetamide), dextran, H_2SO_4, aquades, oil waste, gasoline, and tween 80.

Bentonite activity
Natural bentonite in the form of boulder was broken up by using porcelain and then sieved to produce particles of 170 mesh. Bentonite powder was put into HCL of 10 mL and stirred by using magnetic stirrer on a hot plate for 2 hours at temperature of 40^{o}C. Thereafter, it was washed and filtered with aquades up to pH>4. The filtrate was discarded while the wet bentonite sediment was dried in the oven at temperature of 105^{o}C for 4 hours hence the pure bentonite was obtained. The resulting bentonite was not characterized but it was directly used to make membrane.

Composite membrane of PVDF-PMMA-bentonite variation
PVDF-PMMA-bentonite membrane was producing based on the research conducted by Ochoa [3]. In the research, it used phase inversion method by dissolving PVDF and PMMA with and without adding the bentonite in DMAc solution as much as 10 mL. The solution was stirred by using magnetic stirrer until it become homogeneous at temperature of 40^{o}C. Furthermore, dope solution was poured on rectangular glass plate and set aside for 60 sec at room temperature. This step aimed to let the solvent evaporate. Hereafter, soaking process was taken in the coagulation tub containing aquades for 24 h and then it was stored for membrane's performance test.

Membrane's performance test
Membrane's performance test was carried out through evaluating the flux by using ultrafiltration module. The test was conducted in the chemistry laboratory of LIPI (*Lembaga Ilmu Penelitian Indonesia*), Bandung. In the working system of ultrafiltration module, a feed (water) was inserted in the ultrafiltration module by using the funnel pipette with a small hole of diameter 0.5-2 mm at pressure of 0.1-5 bar, then the stirring rotation was set until it was stable. Permeate would come out through the bottom hose while the retentate would remain stuck in the ultrafiltration module.

III RESULTS AND DISCUSSION

Membrane synthesis
Producing of PVDF-PMMA membrane was done through phase inversion. Polymer was dissolved in DMAc solvent at temperature of 40^{o}C, then bentonite was added as filler at composition of 1, 2 and 3 (% b/b). The concentration ratio of PVDF-PMMA-Bentonite can be observed in Table 1. The concentration's variation was determined based on the optimal condition presented in previous research conducted by Ochoa (2003), which was PVDF-PMMA 7:3 (% b/b) and PVDF-PMMA 1:1 (% b/b) [7]. Table 1 presents the variation of bentonite's compositions which produced PVDF-PMMA membrane with different visual properties. PVDF-PMMA membrane was measured by using the micrometer and its thickness ranges between 0.011-0.013 mm, while PVDF-PMMA membrane with the addition of bentonite has thickness ranging between 0.015-0.02 mm. These results were caused by higher density in the membrane due to the addition of bentonite. The more the bentonite was added, the thicker the membrane was. In Table 1, it is also can be learned that all variations of the PVDF-PMMA membranes before and after the addition of bentonite are hydrophobic. There are some hydrophobic polymer; PVDF (polyvinylidenefluoride), PS (polysulfonate) and PP (polypropylene) [2].

Table 1 Comparison of various concentrations of PVDF-PMMA-Bentonite variation

PVDF:PMMA:Bentonite (% b/b)	PVDF	PMMA	Bentonite	Visual Properties of Membrane
7:3:0	1.19	0.51	0	Thin, hydrophobic, white, smooth, glossy
7:3:1	1.19	0.51	0.2	Thin, hydrophobic, white, smooth, less shiny
7:3:2	1.19	0.51	0.4	Thick, hydrophobic, white, slightly rough, less shiny
7:3:3	1.19	0.51	0.6	Thick, hydrophobic, white, slightly rough, less shiny
1:1:0	0.85	0.85	0	Thin, hydrophobic, white, smooth, glossy
1:1:1	0.85	0.85	0.2	Thin, hydrophobic, white, smooth, less shiny
1:1:2	0.85	0.85	0.4	Thin, hydrophobic, white, smooth, shiny
1:1:3	0.85	0.85	0.6	Thick, hydrophobic, white, slightly rough

The hydrophobic property in this research came from C-F bond in the stable PVDF polymer structure. Visually, among the resulting membranes before and after the addition of bentonite, PVDF-PMMA membrane at concentration of 1:1:2 (% b/b) with the addition of bentonite at 0.4 was the finest with thickness at 0.015 mm. The produced membrane was white, had smooth surface, and shined as shown in Figure 1. This result happened because of complete interaction between the polymer and the bentonite or compatible (even) intermixture.

Figure 1 PVDF-PMMA-Bentonite membrane

Membrane's performance

In this research, the membrane's performance was determined through the flux and selectivity parameters by counting the rejection coefficient (R). The value of flux of the PVDF:PMMA membrane of 1:1 (% b/b) without bentonite was 0.848 $L/m^2.h$, after the bentonite was added the flux decreased as much as 3.957 $L/m^2.h$, while the value of flux of the PVDF:PMMA membrane of 7:3 (% b/b) was 0.329, after bentonite was added it became 0.019 $L/m^2.h$ (Table 2). This happened because the bentonite had filled the PVDF:PMMA membrane's pores such that water would not easily pass it and the flux rate became smaller. This result resonances what was stated by DPU (1983), which is that filler would fill the pores among particles in order to reduce hollow spaces and increase the density and stability of mass [8].

The rejection coefficient was determined by dextran break-out test at molecule mass 19.500, 506.000 g mol^{-1}. The rejection coefficient value has purpose to evaluate the membrane's performance in restraining the dissolved particles. Small rejection coefficient shows big sized pores. Ultrafiltration membrane should have high value of the rejection coefficient (R) to make a perfect separation process. Therefore, bentonite is a suitable filler to be used in the ultrafiltration membrane because bentonite is a crystal in the form of powder such that the surface area would be wider. High rejection coefficient (R) via dexstran on molecule mass of 506.000 g/mol was at PVDF:PMMA:Bentonite variation 7:3:2 (% b/b), which was 82% with flux 0,019 $L/bar.m^2$ and variation 1:1:2 (% b/b) is 83% with flux 0.072 $L/bar.m^2$.

Table 2 Performance of PVDF-PMMA-Bentonite membrane.

Ultrafiltration membrane PVDF: PMMMA:B	Flux ($L/m^2 \cdot h$) P=1 bar	Rejection (%)	
		19.500 g/mol	506.000 g/mol
1:1	0.848	78.5310	82.6311
1:1:1	3.957	78.0000	82.6514
1:1:2	0.072	77.9778	83.0585
1:1:3	0.009	77.7750	82.5146
7:3	0.329	77.8140	82.5602
7:3:1	Large	77.6970	82.1538
7:3:2	0.019	77.8520	82.3090
7:3:3	Large	77.9690	82.8642

Application on oil-water emulsion

Figure 2 shows that the flux decreases over time. The flux value, which was initially 22 $L/m^2.h$ at pressure of 1 bar, of the PVDF-PMMA-Bentonite membrane of 1:1:2 (% b/b) decreased to 4 L/m^2.hour. This happened due to membrane's condition which had not experienced compacting because on the membrane's surface there had not been many particles sticking to the membrane wall yet such that the streaming feed passing through the membrane was not restrained. Constant flux was reached at time of 45 and 60 min, it was caused by the compacting happened on membrane since there were more solute particles sticking on the membrane wall's surface. The same situation did not happen on PVDF-PMMA-Bentonite membrane of 7:3:2 (% b/b). The initial flux decreased from 9

L/m^2h to 4.9 L/m^2h but the constant flux had not reached yet at 60 min. According to Mahmud [3], the decreasing on flux is caused by clogged membrane's pores due to micro particulate matter such that it causes fouling and more compacting to the membrane's structure, which restrains the streaming feed from passing through it. Therefore, from these two variations, PVDF-PMMA-Bentonite membranes of 1:1:2 (% b/b) and 7:3:2 (% b/b), the membrane of 1:1:2 (% b/b) would be used to the oil-water emulsion test.

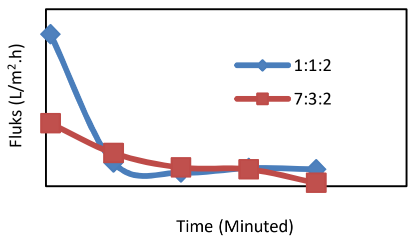

Figure 2 Water flux with respect to time.

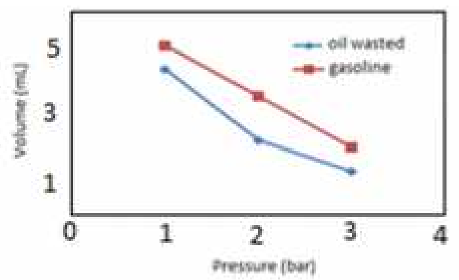

Figure 3 Relationship between pressure and volume of oil wasted and gasoline.

Figure 3 exhibits that increases on the pressure cause decreases on the flux of the oil wasted and gasoline. The flux of the oil wasted which was initially at pressure of 0.5 bar decreased from 4.2 mL to 2.1 mL as the pressure increased, while gasoline decreased from 5 mL to 3.5 mL. The flux decrease happened due to the interaction between the membrane and the hydrophobic property of the oil-water emulsion, the size of emulsifier molecules were smaller than the size of membrane's pores such that it caused fouling on the membrane. Hydrophobic membrane was polar such that emulsifier molecules would be more strongly absorbed by water than by oil. Therefore, the surface tension decreased more such that the water could be easily passed through the membrane's pores. If high pressure was applied then the streaming rate of the waste oil and gasoline passing through the membrane's pores at high speed would cause more accumulated oil drops, whether on the surface or on the membrane, which resulted pore clogging or concentration polarization. Concentration polarization caused a decrease on flux as the pressure increased [9].

Analysis of function cluster

Characterization using FTIR aims to analyse the function cluster of the membrane with and without the filler (bentonite). Resulting FTIR spectrum can be observed in Figure 4. It shows the comparison of FTIR spectrum from PVDF-PMMA membrane without and with the addition of filler (bentonite).

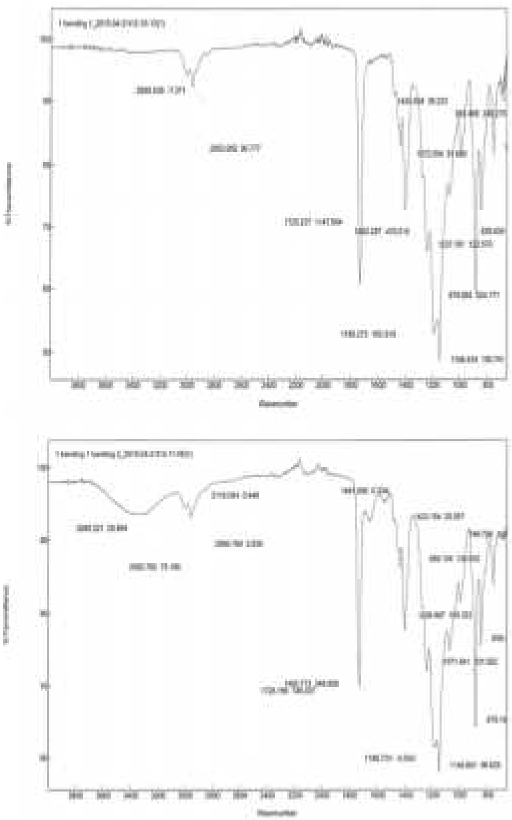

Figure 4 Spectrum of FTIR of PVDF-PMMA membrane without bentonite (up) and with bentonite (down)

FTIR spectrum shows no significant difference but only on some peaks which present absorption at wave numbers 1520 cm^{-1} and 1660 cm^{-1}. This results agree with the one based on a research conducted by Upriatna and Pramono (2005) stating that vibration at wave numbers of 1500-1700 cm^{-1} showed interaction between inter-layer phase and bentonite. Wave number of 1520 cm^{-1} is extended peak of Si-O or Al-O from the bentonite, while wave number of 1660 cm^{-1} is crumpled peak of H-O-H from the water molecules absorbed in the bentonite's surface. Based on the FTIR spectrum, it can be learned that bentonite fill the PVDF-PMMA membrane in inter-layer phase way, which is interaction between PVDF-PMMA membrane and active side of the bentonite. The occurrence of new absorbing peaks shows that the bentonite has successfully filled the PVDF-PMMA membrane such that it can be filler on the PVDF-PMMA membrane.

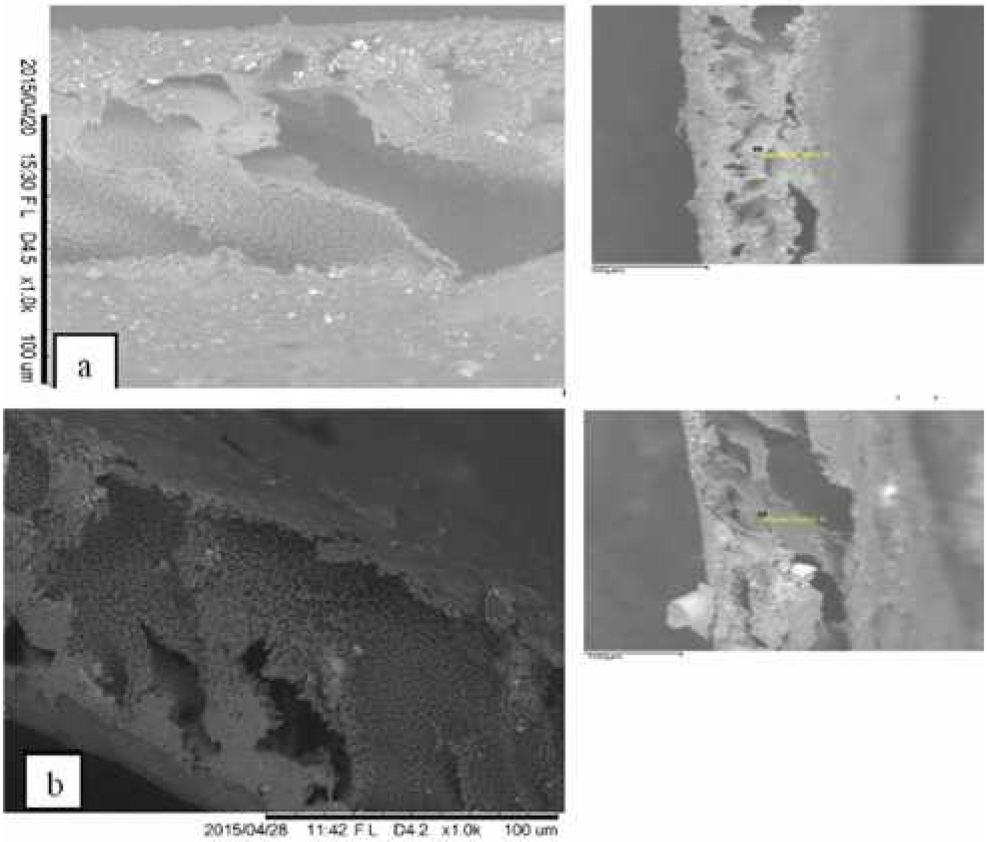

Figure 5 Surface structure of composite PVDF:PMMA membrane (a) without bentonite (b) with bentonite

Membrane's morphology

Results of Scanning Electron Microskop (SEM) with 1000 time magnification shows that there is difference between cross sections of the PVDF-PMMA membrane without filler and with the bentonite filler (Figure 5). On both figures, it can observed the difference in surface structure and density of the pores, Figure (5b) shows bigger hole than Figure (5a), this is due to that bentonite consists of Si and Fe elements, but clumps in the Figure (5b) are decreasing compared to the ones in Figure (5a), it is caused by wide pore surface of the bentonite.

CONCLUSION

Bentonite can be used as filler which takes role to increase the performance of PVDF-PMMA membrane. PVDF-PMMA membrane has optimum properties visually and characteristically. PVDF-PMMA membrane has good performance at membrane composition of 1:1:2 (% b/b) which gives flux value of 0.848 $L/m^2.h$ and rejection factor of 82.631% without addition of bentonite and flux value of 0.072 $L/m^2.h$ and rejection factor 83.058% with addition of bentonite. Characterization of PVDF-PMMA membrane with bentonite by using FTIR shows that bentonite fills the PVDF-PMMA membrane in inter-layer phase way which is interaction between PVDF-PMMA membrane and active side of the bentonite. It is indicated by the absorption at wave number 1520 cm^{-1} and 1660 cm^{-1} which comes from the bentonite. The SEM-EDX analysis result shows that PVDF-PMMA membrane after the addition of filler (bentonite) has asymmetrical shape and smooth surface.

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