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EFFECT OF TETRAOCTYLPHOSPHONIUM BROMIDE (TOPBR) CLAY COMPOSITION ON POLYVINYLIDENE FLUORIDE (PVDF) NANOCOMPOSITE ULTRAFILTRATION MEMBRANE

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ABSTRACT

Nanocomposite membranes containing polyvinylidene fluoride (PVDF) and tetraoctylphosphonium bromide clay (TOPBr) were prepared by phase inversion method. Different TOPBr and PVDF contents were used in order to investigate the effect of TOPBr clay composition on the membrane properties. The morphology of PVDF/TOPBr nanocomposite ultrafiltration (UF) membrane was characterized by scanning electron microscopy (SEM) and hydrophilicity of the nanocomposite membrane was evaluated in terms of water content, porosity and pure water flux (PWF). The results revealed that the increasing of TOPBr clay content produced more porous nanocomposite membrane due to the formation of many finger like pores and microvoids. The hydrophilicity of the membranes was strongly enhanced by increasing the contents of TOPBr clay.

Keywords: Polyvinylidene fluoride; Nanocomposite membrane; Ultrafiltration; Hydrophilicity; Clay

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1. INTRODUCTION

Polyvinylidene fluoride (PVDF) membrane is one of the most popular polymeric membranes that widely used in UF membrane separation process at industries because of their excellent chemical resistance, good mechanical and thermal properties [1]. However, the hydrophobicity of PVDF could lead to low water flux and also the adsorption of foulants onto membrane surface which can cause the decrease of permeation flux [2]. Therefore, a lot of effort has been expended on hydrophilic modification of PVDF membranes through some surface modification and blending methods.

Recently, blending with inorganic materials such as nanoclays have been favored as the great method in producing high hydrophilicity surface of the membrane. Montmorillonite (MMT) is one of the most familiar natural clays used in the preparation of polymer clay nanocomposite membranes because of its ability to be dispersed in the polymeric matrices at nanoscopic level and only a small amount of this material was needed in the fabrication of nanocomposites membrane [3][4].

Study by Dong [5] has reported that the addition of tiny amount of inorganic clay into the polymer matrix shows an outstanding effect on morphology and performance of membranes. However, several researchers reported the original state of MMT which is a hydrophilic material found to be less compatible with most hydrophobic engineering polymer membranes resulted in severe membrane fouling and decline of barrier permeability in their application of membrane separation process [6][4].

In order to attain the compatibility with the hydrophobic polymer, organophilic MMT or modified MMT was used to replace natural clay in the preparation of clay nanocomposite membranes. Certain modification is needed for clay minerals to compatibilize their surface chemistry due to its hydrophilicity in nature. Incorporating organically modified clays would exhibit good interaction at the polymer and filler interfaces of the silicate layers [3].

Hence in this study, the preparation of PVDF/MMT nanocomposite membranes using organically modified clay, tetraoctylphosphonium bromide (TOPBr) by blending method were investigated. To the best of our knowledge, there is no study has been conducted focusing on this potential modified clay blended with polymer in nanocomposite UF membrane. The purpose of this study was to prepare flat sheet PVDF/TOPBr nanocomposite

UF membrane by phase inversion technique and characterize its characteristics and performance. The effect of TOPBr clay on water contet, porosity, pure water permeation and morphology of nanocomposite membrane with different polymer concentration were explored.

1. Experimental

1.1 Materials

Commercial grade PVDF materials (Solef® 6008) pellets was supplied by Solvay Solexis and tetraoctylphosphonium bromide (TOPBr) clay were used for nanocomposite UF membrane preparation. The modified clay, TOPBr was prepared according to Ali's [7] works. *N*-Methyl-2-Pyrrolidone (NMP) from MERCK Schuchard OHG, Germany was used as solvent in the preparation of nanocomposite membrane. Distilled water also was used throughout the experiment.

1.2 Membrane Preparation

Different TOPBr clay contents (0.4 and 0.8 wt %) were added into 15/85 wt% and 17/83 wt% of polymer/solvent solution, and marked as PV/TB 15 and PV/TB 17, respectively. These homogeneous dispersions were prepared by mechanical stirring. Membranes were fabricated via phase inversion technique where the solution was cast on a glass plate with 150 µm thickness and then, immediately immersed into a coagulation bath. A flat sheet membrane was obtained and it was stored for 24 h in order to remove excess solvent in the fabricated membrane. The membranes were stored in distilled water for prior usage.

1.3 Membrane Characterizations

1.3.1 Water Content and Porosity

The water content of the native PVDF and PVDF/TOPBr nanocomposite UF membrane was evaluated for water absorption capacity and calculated by Eq. 1:

$$A = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100\% \quad (1)$$

where A is the water content (wt%), W_{wet} is the wet weight of membrane (mg) and W_{dry} is the dry weight of membrane (mg). The water content of the membranes was determined by

soaking the membrane in water for 24 h at room temperature. The weight of the wet PVDF/TOPBr membrane was first measured after mopping the membranes with a blotting paper and then dried in an oven at 75°C for 48 h. The porosity of membranes was evaluated using the expression below:

$$Porosity = \frac{(W_1 - W_2/d_{water})}{V} \times 100\% \quad (2)$$

where W_1 and W_2 are the mass of membrane in wet and dry states (mg), d_{water} is the density of water at room temperature (mg/ml) and V *is* the volume of the membrane in wet state (ml).

1.3.2 Pure Water Flux and Permeability Coefficient

Pure water flux is important for the determination of membrane stability and hydraulic properties. Distilled water was used to determine pure water flux of each membranes using a dead-end filtration cell. Membrane were then subjected to pure water flux test with varying operating pressure in the range of 1 to 5 bar. Membrane permeability coefficient can be determined by subjecting these membranes at various pressure towards its pure water fluxes.

1.3.3 Membrane Morphology

The cross sectional morphologies for all fabricated membrane were characterized by using a scanning electron microscope (SEM Model JSM 6380LA) located at at Institute of Oceanography (INOS), Universiti Malaysia Terengganu. The membrane samples were fractured in liquid nitrogen and sputtered with gold before transfer and analysed by using the microscope.

2. RESULTS AND DISCUSSION

2.1Water Content and Porosity

Hydrophilicity of membrane is related to the water content of membrane [8]. Hydrophilicity and porosity are two important parameters for membrane in the separation process and membrane permeation. They also have close relationship with the morphology and pure water flux of membranes [6]. The percentage of water content and porosity was calculated using equation (1) and equation (2) respectively. All the results obtained for native PVDF

membranes and PVDF/TOPBr nanocomposite ultrafiltration membrane were plotted as shown in Fig. 1(a) and (b).

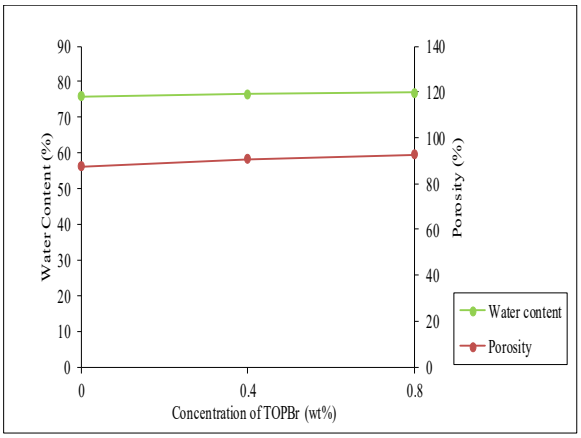

Fig.1(a). Water content and porosity at different concentration of TOPBr for PV/TB 15 membranes

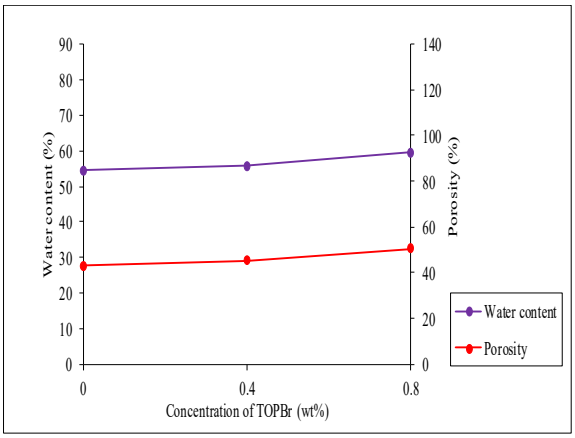

Fig.1(b). Water content and porosity at different concentration of TOPBr for PV/TB 17 membrane

By referring to Fig.1(a) and (b), the water content and porosity increased with the addition of TOPBr clay. The value of water content and porosity for native PVDF membrane, PV/TB 15-0 were 75.9% and 87.33% respectively. With the increases in clay amount from 0.4 wt% to 0.8 wt%, water content increased from 76.43% for PV/TB 15-4 to 77.02% for PV/TB 15-8 membrane. Membrane porosity also increased from 90.62% to 92.57%. Meanwhile, PV/TB 17-0 depicted 54.44% in water content and 43.19% in porosity. Both the water content and

porosity were observed to increase from PV/TB 17-4 of 55.88% and 45.23% to 59.55% and 50.49% for PV/TB 17-8 membrane.

All the obtained results revealed that when the amount of clay increased, the water content and porosity of PVDF/TOPBr membranes also increased. The increment in water content because of the detachment of polymer chains from the silica surface which led to interface voids. Furthermore, this causes an increase in void volume resulting in the formation of bigger size pores on the membrane surface and increases the water uptake in the pores [8]. The incorporation of clay to the membrane dope improved the inflow rate of water and accelerated the exchange process between the solvent in polymer dope and non-solvent in coagulation bath and consequently increased the ratio of water content and porosity of fabricated membranes [6]. Among all the fabricated membranes, PV/TB 15-8 yield the highest water content and porosity.

2.2 Pure Water Flux

PWP test was employed to measure the permeability of native PVDF membranes and PVDF/TOPBr nanocomposite ultrafiltration membrane at different pressures. Each piece of the fabricated membrane was tested at least three times to ensure the consistency of results obtained. Fig. 2(a) and (b) showed the graph of pure water flux versus pressure with different composition of PVDF/TOPBr nanocomposite ultrafiltration membrane.

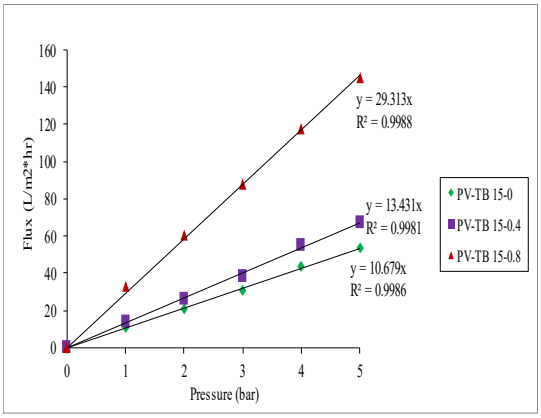

Fig.2 (a). Pure water flux of PV/TB 15 nanocomposite ultrafiltration membrane with different TOPBr composition

From the graphs, it can be observed that all the membranes possessed linear profile. This revealed that the pure water flux is directly proportional to the applied pressure. All the fabricated membranes had lowest flux at lowest applied pressure which is at 1 bar. When the applied pressure increased from 1 to 5 bar, the pure water flux of membranes shows an increment pattern gradually. The slopes of the graphs indicating the permeability coefficient of PVDF/TOPBr nanocomposite ultrafiltration membranes. The results of permeability coefficient and regression coefficient were summarized in Table 1(a) and (b) accordingly.

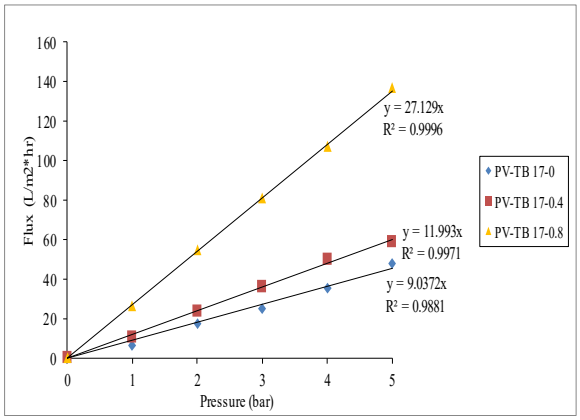

Fig.2 (b). Pure water flux of PV/TP-17 nanocomposite ultrafiltration membranes with different TOPBr composition.

Table 1(a). Permeability and regression coefficient for PV/TB 15 membrane

Membrane	**Permeability Coefficient ($L/m^2.hr.bar$)**	**Regression Coefficient (R^2)**
PV/TB 15-0	10.679	0.9986
PV/TB 15-4	13.431	0.9981
PV/TB 15-8	29.313	0.9988

Table 1(b). Permeability and regression coefficient for PV/TB 17 MMT membrane

Membrane	Permeability Coefficient ($L/m^2.hr.bar$)	Regression Coefficient (R^2)
PV/TB 17-0	9.0372	0.9881
PV/TB 17-4	11.993	0.9971
PV/TB 17-8	27.129	0.9996

As shown in the tables, all the membrane exhibited increment in pure water flux as the composition of clay increased. For example, permeability coefficient for PV/TB 15-0 was 10.679 L/m^2.hr.bar and after the addition of 0.8 wt% clay, the permeability coefficient increased to 29.313 L/m^2.hr.bar for PV-TB 15-8 membrane. According to Rajabi et al. (2014), incorporation of hydrophilic clay into the casting solution enhances the water affinity of polymeric casted films towards water compared to native PVDF membrane resulting in increasing of the penetration velocity of water into the fabricated membrane. Moreover, the increase of water flux is attributed to the asymmetric and opened structure of membrane as well as the improvement of membrane's hydrophilicity and porosity once clay is added [9].

Besides, polymer concentration also affected towards the permeability of membranes. It was observed than when the polymer concentration increased from 15 wt% to 17 wt%, the pure water flux decreased. The permeability coefficient obtained for all PV-TB 15 were greater as compared to PV-TB 17 membranes. The water flux of the membrane decreases with the increase of total polymer concentration [10]. Generally, the increases in concentration of polymer in solution will lead to the decrease of membrane's pore size and effective porosity [11].

2.3 Membrane Morphology

The SEM images of cross section structure of the all prepared membranes are shown in Fig. 3 and Fig 4. All fabricated membrane shown asymmetric structure. The membranes consisted of two layers which are skin active layer and supporting layer. Both layers provided important roles in membrane transport property. Skin active layer controls the selectivity and separation

process whereas the support layer lies below acts as a supporting structure. The porosity of the supporting structure is generally much greater as compared to top thin layer [12].

As shown in Fig. 3(a) and Fig. 4(a), the native PVDF membrane has dense spongy structure due to its hydrophobic properties. Membrane with the polymer composition of 17 wt% exhibited spongier than 15 wt% of polymer membrane. Higher polymer concentration increased the viscosity of the dope solution, leading to the formation of dense spongy membrane. This is because dope solution with high viscosity can obstruct the diffusional exchange rate of solvent and non-solvent in sub-layer, inducing fast phase separation at skin layer and slows the precipitation rate of the sub-layer. Therefore, this lead to the formation of asymmetric membrane with dense and thick skin layer supported by a closed cell sub-layer [11].

With the incorporation of TOPBr nanoclays, a drastic change in membrane morphology was observed. As the composition clay was added into the native membrane, the membrane structure became porous with the presence of many open pore or microvoids. Anadão [13] has explained that when the concentration of clay increases, the nanocomposite membrane be more porous with formation of microvoids. Moreover, the membranes were noticed to increase in the number of finger-like pores as the content of clay increases. This caused the membrane sub-layer to become more porous and increased its porosity. Membranes with predominantly large diameter, unhindered finger-like internal pore structure are most appropriate for achieving high water permeability during water or wastewater treatment [14].

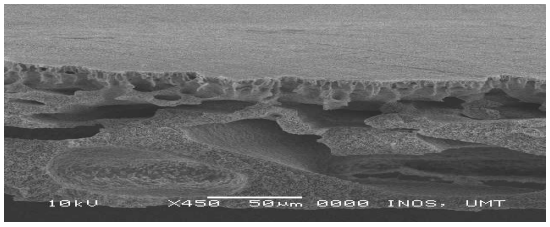

Fig.3(a). Cross section morphology of PV/TB 15-0 membrane

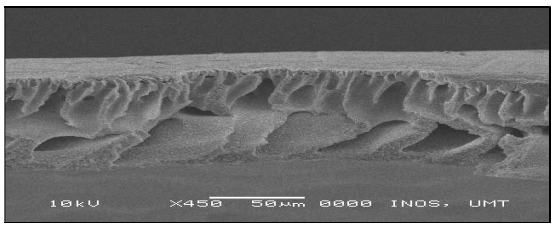

Fig.3(b). Cross section morphology of PV/TB 15-4 membrane

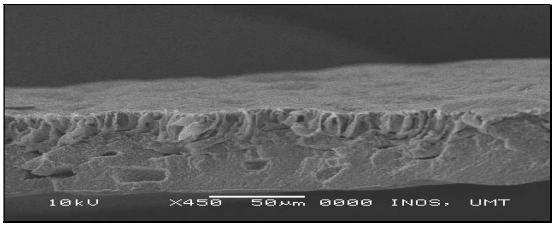

Fig.3(c). Cross section morphology of PV/TB 15-8 membrane

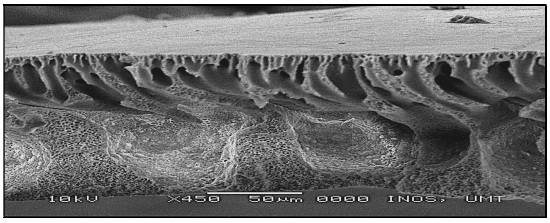

Fig.4(a). Cross section morphology of PV/TB 17-0 membrane

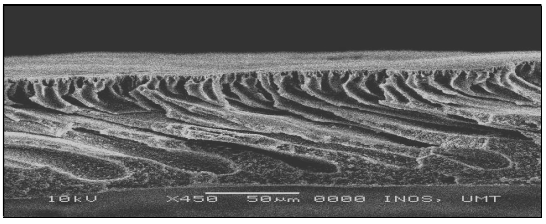

Fig.4(b). Cross section morphology of PV/TB 17-4 membrane

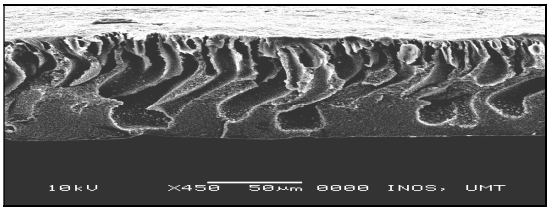

Fig.4 (c). Cross section morphology of PV/TB 17-8 membrane

3. CONCLUSION

The hydrophilicity of the PVDF/TOPBr nanocomposite ultrafiltration membrane were improved by the increment contents of TOPBr nanoclays, which can be illuminated from the increasing in water content, porosity and pure water flux as well as the permeability coefficients of all nanocomposite membrane in comparing with the native membrane. The improvement in hydrophilicity properties of PVDF/TOPBr nanocomposite membrane showed these membranes have better anti-fouling characteristics than the native PVDF membrane.

4. ACKNOWLEDGEMENTS

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