EFFECT OF TETRAOCTYLPHOSPHONIUM BROMIDE (TOP-Br) ON CHARACTERISTICS AND MORPHOLOGY OF PVDF/TOP-Br NANOCOMPOSITE MEMBRANE

A. Ali[1*], N. A. Sani[2], M. Awang[3], M. A. A. Abdullah[4], N. S. Mohamed[5],
[1,2,3,5] School of Ocean Engineering Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.
[4]School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
[*]Corresponding author; Tel.: (+06) 09-6683833, Fax: (+06) 09–6683991, E-mail: asmadi@umt.edu.my

ABSTRACT: *Polyvinylidene fluoride (PVDF) membrane is categorized as hydrophobic membrane that leads to a low membrane flux and easily fouled during membrane operation process. The addition of nanoparticles into the membrane matrix is an efficient way in adjusting membrane properties, thus improve membrane hydrophilicity and performance with more effective antifouling capabilities. In this study, the PVDF/TOP-Br nanocomposite membrane was prepared by blending method with addition of different TOP-Br clay dosage. Flat sheet asymmetric PVDF/TOP-Br nanocomposite membranes were prepared via phase inversion method. Membrane characterization were performed using scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis and mechanical properties. The introduction of TOP-Br provided better dispersion and formation of exfoliated layers of clays in PVDF membrane. The results revealed that an increase in the clay content make the membrane become more porous, thin skin layer and increase the porosity of the membrane nanocomposite thus increase their hydrophilicity. The composite membrane also showed greater stiffness compared to pure PVDF membrane.*

Keywords: Polyvinylidene chloride membrane, Nanoclay, Polymer Nanocomposite, Morphology

1. INTRODUCTION

Polyvinylidene fluoride (PVDF) has been used in various application in ultrafiltration processes due to its excellent chemical resistance, thermal stability and mechanical properties. However, the PVDF membrane has highly hydrophobic nature. This nature of membrane can lead to the deposition of solute or particle on a membrane surface or in membrane pores, causes a serious fouling and also a rapid decline in permeation flux [1]. The hydrophobicity of PVDF membrane has limited the application of the commercial PVDF membrane in various applications.

Thus, it is necessary to improve the hydrophilicity of PVDF membrane by chemical or physical modification, surface grafting polymerization, coating and blending with hydrophilic polymer [2]. Among these methods, blending with inorganic materials especially nanoparticles has attracted much interest due to their simple operation and efficient method for designing new materials to improve performance of the hydrophobic membranes [3]. Montmorillonite is one of the most familiar natural clay used in the preparation of polymer clay nanocomposite membrane because of its ability to be dispersed in the polymeric matrices at nanoscopic level [4] and only a small amount of this material was needed in the fabrication of nanocomposites. Another advantage of this silicate nanoparticles is its ability to form intercalated or exfoliated structure in the resultant nanocomposite membrane. However, the clay minerals required a certain modification to compatibilize their surface chemistry due to the naturally hydrophilic. Incorporating organically modified clays would exhibit good interaction at the filler and polymer by cationic exchange reaction with alkylammonium or alkylphosphonium surfactant that will also lead to the expansion of interlayer space of clay [5].

Several polymeric PVDF blend membranes have been fabricated and investigated by many researchers related to the compatibility of its hydrophobic nature with commercially modified clay minerals.

In this study, the preparation of PVDF/clay nanocomposite membrane using organically modified clay by the blending method were investigated. In previous study, the clays with the ammonium based modifier have been used extensively in PVDF nanocomposite membranes but the behavior of nanocomposite membrane with phosphonium based clay has not been studied. The purpose of this study is to prepare flat sheet PVDF/clay nanocomposite membranes by phase inversion method. The effect of clay dosage on morphology, the permeation characteristics and mechanical properties of the prepared membranes were investigated in detail.

2. MATERIAL AND METHODS

Materials. All materials used were of analytical grade. The membranes were fabricated from the dope solution of polyvinylidene fluoride (PVDF) as the base polymer and N-methyl-2-pyrrolidone (NMP) as a solvent. The alkylphosphonium montmorillonite clay was prepared via cation ion exchange between sodium ions of Na^+ MMT and tetraoctylphosphonium bromide (TOP-Br) ions and act as inorganic filler [6]. Bovine serum albumin (BSA) was used for the evaluation of membrane performance. Distilled water was also used throughout the experiments**.**

Membrane preparation. The membranes were prepared via phase inversion method as described by Ali et al [7]. Different TOP-Br clay content (0.2, 0.4, 0.6, 0.8 and 1.0 mass %) were added to a 17/83 wt% of polymer/solvent solution and homogenous dispersion were prepared by mechanical stirring for 6 h at 70 ^{0}C. Membrane were fabricated via phase inversion technique where the solution was casted on a glass plate with 150 µm thickness and immediately immersed in a coagulation bath. A flat sheet membrane was obtained and it was stored in distilled water for 24 h in order to remove excess solvent in the fabricated membrane. The membrane were stored in distilled water for prior usage.

Membrane characterizations. XRD patterns of nanocomposite membranes were obtained by X-Ray diffractometer under the following conditions 40 kV-30 mA; CuKα radiation (λ=1.78897 Å); at the rate of 0.02^0/s in the range of 1-10^0 (2θ).

Fourier transform infrared spectroscopy (FTIR) was used to determine the chemical functional groups of the membrane surface. The membrane were placed on the sample holder and all spectra were recorded in the wave number range around 4000-400 cm^{-1}.

The morphology and the structure of the prepared membranes were examined by a scanning electron microscopy (SEM) at Institute of Oceanography, Universiti Malaysia Terengganu (UMT). The samples of the membrane were frozen in liquid nitrogen and fractured. The surface then were sputtering with gold and viewed with the microscope at 10 kV.

Tensile strength and elongation at break of membranes were carried out using a universal testing machine (Shimadzu EZ-500 NLX) at room temperature and extension rate of 2 mm/min.

A thermogravimetric analysis (TGA) was carried out in a Pyris 6 PerkinElmer instrument at Makmal Berpusat, Universiti Malaysia Terengganu with nitrogen atmosphere heated were from 25 to 900 ^{0}C at a rate of 10^{0}C min^{-1}.

3. RESULTS AND DISCUSSION

XRD Analysis. XRD is a method to study the dispersion of clay minerals inside the polymer matrix and the patterns can be useful in studying the exfoliation and intercalation of nanostructure. The XRD pattern of TOP-Br clay, native PVDF and PVDF/TOP-Br nanocomposite membranes with different clay concentrations are shown in Figure 1.

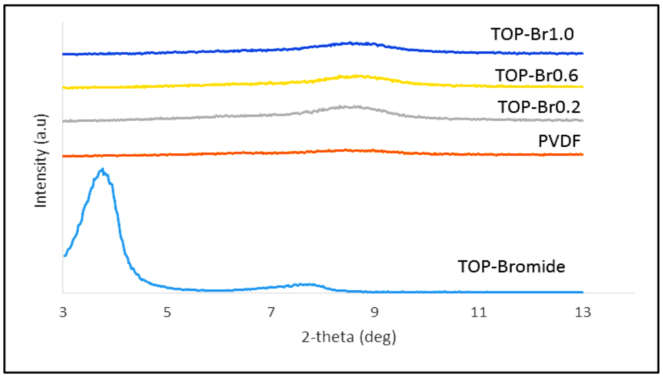

Figure (1) X-Rray diffraction patterns of TOP-Br clay, native PVDF and PVDF/TOP-Br nanocomposite membrane with various clay contents.

The TOP-Br clay shows a diffraction peak at 2θ=3.73^0, which according to the Bragg's law (nλ=2d.sinθ), implied a basal

spacing of 2.36 nm. An increase in the basal spacing of organoclays depends on the length of the alkyl chains and packing density, in addition to conformational arrangement of the surfactant molecule between layers of the clay [8].

It is observed that the PVDF membrane does not show any specific peak due to its structure. The crystalline peak of PVDF/TOP-Br 0.2, 0.6 and 1.0 wt% nanocomposite membranes is almost disappeared and there is no obvious peak of the clay was found in the XRD pattern. This shows that the clay particles were exfoliated and were diffused inside the polymer chains. Nanocomposite membranes with a good dispersion of clay were formed. Generally, the clay content in an exfoliated structure is much lower, resulted in a formation of a well dispersed polymer/clay nanocomposite [9].

FTIR Analysis. FTIR is employed to investigate the chemical composition of membranes. Figure 2 shows the FTIR spectra of pure PVDF and PVDF/TOP-Br nanocomposite membranes. The chemical structure of pure PVDF shows the bands located between 3022 – 2980 cm^{-1} corresponded to the CH_2 symmetric and asymmetric vibration of PVDF. The C - C band of PVDF was observed at 1185 cm^{-1}. The peaks at 878 and 840 cm^{-1} were related to C – C – C asymmetrical stretching vibration and CF stretching vibration of PVDF.

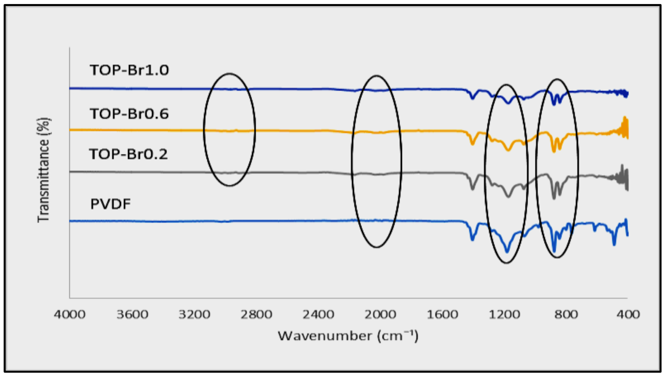

Figure (2) FTIR patterns of native PVDF and PVDF/TOP-Br nanocomposite membrane with various clay contents.

In the FTIR spectra of PVDF/TOP-Br nanocomposite membranes, the characteristic absorption peaks of the pure PVDF membrane were retained and the intensities bands had decrease. However, there was a new peak at 3340 cm^{-1} that could be observed. The occurrence of this vibration peak is due to the O – H stretching vibration of TOP-Br clay. Moreover, the bands at less than 500cm^{-1} is might be due to the halogens compounds in the sample.

Membrane Morphology. SEM analysis is important techniques to study the membrane morphology and qualitative information regarding surface and cross sectional morphology of the prepared membranes. The SEM images of cross section structure of the prepared membranes at different concentration of APMMT are shown in Figure 3.

It can be seen from Fig 3 that all the membranes were asymmetric structure which consist of a dense top surface layer and a porous sub layer. The top surface layer or the skin layer acts as a separation layer which control the separation process and selectivity of the membrane. The sub layer plays a role as the support layer that acts as mechanical support.

Figure 2(a) shows the cross section structure of native PVDF membrane has a thick skin layer consists of finger like structures and macrovoids structure at the bottom surface layer. A spongy structure also form beneath the skin layer and sub layer of native membrane.

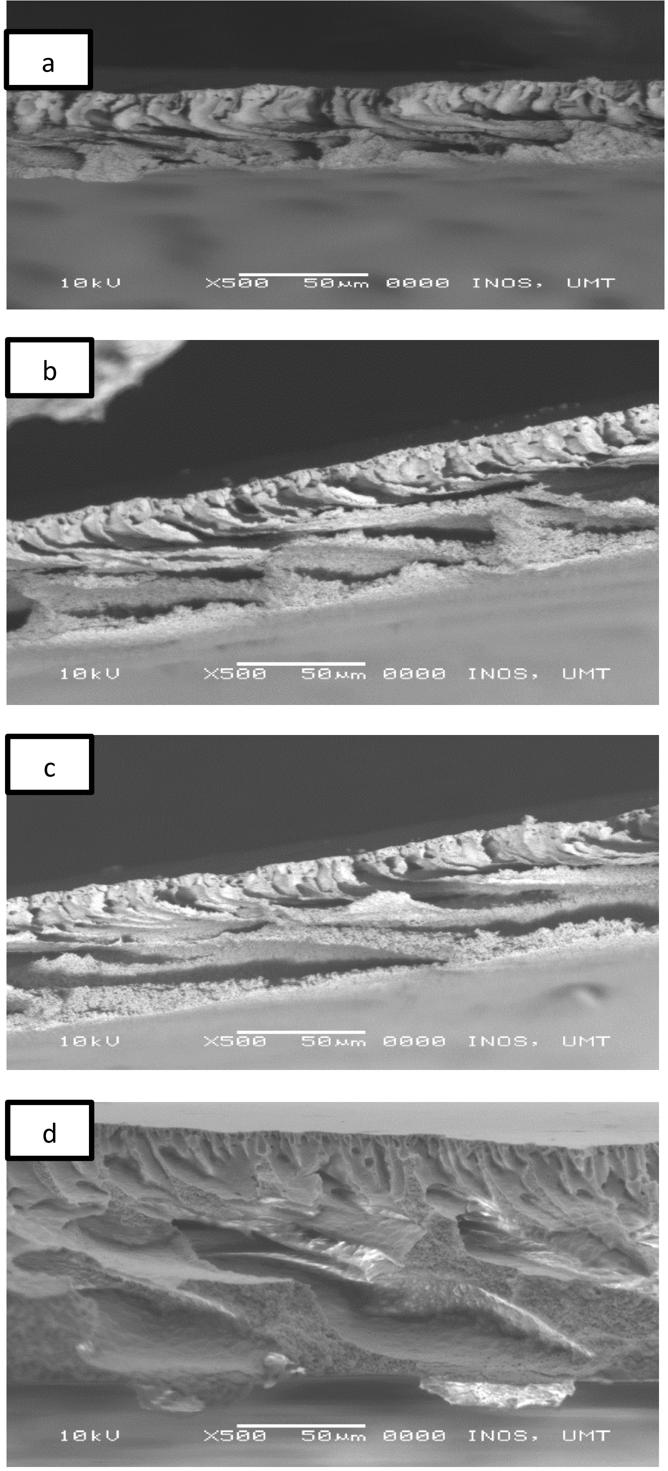

Figure (3) SEM cross section images of PVDF/TOP Br nanocomposite membranes with (a) 0, (b) 0.2, (c) 0.6 and (d) 1.0 wt% of TOP-Br

Figure 3(b), (c) and (d) represents the morphology structure of PVDF/TOP-Br at various clay concentration. Addition of TOP-Br clay increased the number of finger like pores and improved the size of macrovoids in the support layer. At the same time, the length of finger like structure was found shorter but the large void were found larger and more remarkable. The present of TOP-Br caused less dense spongy structure formed and decrease the thickness of skin layer in nanocomposite membranes. This makes the sub layer membrane become more porous and increase the porosity of membranes.

The change in the pore size and porosity occurs due to the instantaneous demixing of membrane casting solution and rapid precipitation of polymer matrix [10]. The addition of hydrophilic material into the hydrophobic polymer will promote instantaneous demixing process [11]. The finger like structure has a tendency to be changed to macrovoids structure if higher concentration of clay been used. Many types of hydrophilic groups will increase the rapid mass transfer between the solvent and non-solvent during phase inversion. Thus, larger pore channel would formed due to the rapid mass transfer [12].

Mechanical Properties. Tensile strength and strain at break are two important parameters to describe the mechanical properties of membranes. Tensile strength is the maximum stress that a material can withstand while being stretched or pulled before failing or breaking. Strain at break is a measure related to material ductility.

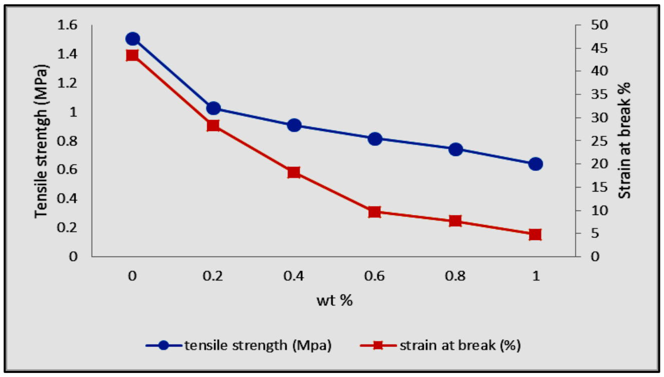

Figure 4. Tensile strength and strain at break of PVDF/TOP-Br nanocomposite membranes with various clay content

The effect of clay content on the mechanical strength of PVDF/TOP-Br nanocomposite membranes was shown in Figure 4. It is observed that as the clay content increase, the tensile strength decreased from 3.87 MPa for native membrane to 0.73 MPa for PVDF/TOP-Br1.0 and strain at break decreased from 42.28% for native membrane to 7.03% for PVDF/TOP-Br1.0 nanocomposite membrane. These results can be explained through the membrane morphology as shown in Figure 3 where the structure with large macrovoids increased the porosity thus weakened the strength of the membranes.

The presence of clay is usually known by the nanocomposites becoming more brittle, causing a decrease in strain at break

[13]. Adding the TOP-Br clay into PVDF membrane will cause the membrane ductility to decline. This phenomenon is likely due to layered silicate aggregation, which prevents the formation of nanostructured systems and collapsed the clay layer [13]. The same result has been observed for other polymer/Na montmorillonite nanocomposite membrane where it would take only a small amount of the undispersed organoclay to create the effects that were observed for tensile strength and strain at break [14].

Thermogravimetruc Analysis. Figure 5 presents the thermal decomposition graphs for different PVDF/TOP-Br nanocomposite membranes in comparing with the pure PVDF membrane. All of the membrane have two degradation stages during the thermal degradation process. The first degradation process occurred at 350-500 ^{0}C due to desorption of water and moisture that present in the polymer nanocomposite. The second stage which occurred after 500 ^{0}C corresponded to the burn off of carbonaceous residue [15]. As the clay content increases the temperature of decomposition reduces.

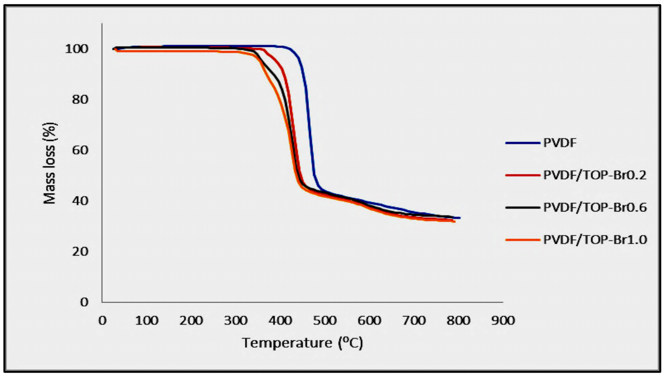

Figure 5. TGA curves of PVDF/TOP-Br nanocomposite membranes with various clay content.

A studies from Leite et al [9] also noted this weakening in thermal stability in their PVDF/clay nanocomposite membranes, which have lower activation energy compared to the pure PVDF membrane. A small amount of additives are able to catalyze the thermal decomposition rate of PVDF [14]. Despite the small loading in the membrane, the presence of TOP-Br caused the decomposition of the PVDF/clay nanocomposite started to break down and occur at a lower temperature. The degradation is due to the natural occurring minerals being highly degraded and hence releasing free water. The water in the interlayer space disappeared when temperature reachs 300^{0}C. This in turns increased the degradation material and mass loss rate of decomposition products.

4. CONCLUSIONS

Nanocomposite PVDF membranes were prepared by addition of TOP-Br clay in the dope solution at different clay dosage by the blending method and wet phase inversion method. Effect of clay dosage were investigated on the morphology, structure, and mechanical properties. All the membranes were found to have asymmetric structure and resulted in membranes with thinner skin layer and larger macrovoids due to the addition of TOP-Br clay compared to native PVDF membranes. XRD analysis shows that the good dispersion of nanoclay and formation of exfoliation structure. The thermal decomposition of the nanocomposite membrane occurred at a lower temperature compared to the native membrane.

5. ACKNOWLEDGEMENT

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[*] Corresponding author; Tel: (+06) 09-6683833, Fax: (+06) 09–668399, E-mail: asmadi@umt.edu.my