

Surface Properties and Permeability of Poly(Vinylidene Fluoride)-Clays (PVDF/Clays) Composite Membranes

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Abstract. Surface properties are important factors that determine the performance of ultrafiltration membranes. This study aimed to investigate the effects of clay addition on the surface properties and membrane permeability of PVDF (poly-vinylidene fluoride) membranes. Three types of clay with different particle size were used in this study, namely montmorillonite-MMT, bentonite-BNT and cloisite 15A-CLS. The PVDF-clay composite membranes were prepared by phase inversion method using PEG as additive. The hydrophobicity of membrane surface was characterized by contact angle. The membrane permeability was determined by dead- end ultrafiltration with a trans-membrane pressure of 2 bars. In contact angle measurement, water contact angle of composite membranes is higher than PVDF membrane. The addition of clays decreased water flux but increased of Dextran rejection. The PVDF-BNT composite membranes reach highest Dextran rejection value of about 93%. The type and particle size of clay affected the hydrophobicity of membrane surface and determined the resulting membrane structure as well as the membrane performance.

1. Introduction

PVDF membranes have been widely applied in water treatment processes. PVDF membranes have many advantages including high mechanical properties and high chemical resistance [1, 2]. During their applications, low resistance to fouling often limits the use of these membranes [3]. Fouling on the membrane surface decreases its water permeability due to its surface properties.

Several factors affect the performance of an ultrafiltration membrane such as surface structure, pore size and membrane structure [4, 5]. Surface properties like membrane polarity affect the ease of interaction of water or compounds that are separated in the feed solution [6-8]. Some researchers have developed various surface modifications of PVDF membranes to produce membranes with high performance. Chemical reaction with a plasma method and addition of zwitter ionic compound which modified the surface and pore properties and its performance against the Bovine Serum Albumin (BSA) had been reported [9, 10]. Unfortunately, those modifications are often limited by hard reaction and low interference between the components of the membrane.



Fabrication of composite PVDF with inorganic filler was also developed by many researchers [11-16]. This method is widely conducted because it provides many advantages such as easy preparation, ability to modify the surface properties and improvement of membrane mechanical and thermal properties [17-19]. Some oxides had been used as fillers in PVDF membranes. Previous study showed that the addition of $\text{Mg}(\text{OH})_2$ in PVDF membranes can improve the fouling resistance against BSA and *E. coli*. [20]. Modification of PVDF with palygorskite could increase the water flux and also the abrasion of membrane surface [21].

In this study various clays were used as filler in PVDF membranes. The effects of types of clay on the surface properties and permeability of PVDF membranes have been studied. Three types of clays having different particle size were used in this research, which are bentonite (BNT), montmorillonite (MMT), and cloisite (CLS) 15A. Membranes were prepared by phase inversion method and surface properties of membranes were characterized by contact angle and surface morphology using a Scanning Electron Microscope (SEM). The membrane permeability and selectivity were characterized by water flux and rejection towards Dextran T-500.

2. Experiments

2.1. Materials

PVDF powder (Solef® 1015, solvay), polyethylene glycol (PEG)-400 (Merck), ethylene glycol (99%, Merck), n-hexane (99%, Merck), dimethylacetamide – DMAc (99%, Merck) and Dextran T-500 (Mw 500 kDa) (Pharmacosmos) were used without further purification. Three types of clay were used, which are bentonite (BNT) 180 mesh supplied by a local industry, montmorillonite and cloisite 15 A (Sigma Aldrich) with a particle size of 8.59; 13 and 24.11 μm , respectively.

2.2. Membrane Preparation

PVDF and PVDF-clay composite membranes were prepared by phase inversion method. Measured amount of PVDF, PEG 400 and clay were mixed in DMAc solvent with a composition of 17%, 5% and 1% w/w, respectively. The mixture was stirred at 60 °C for 5 h until homogeneous. The polymer mixture was sonicated with frequency 47 kHz for 1 h. The solution was spread on a glass plate and directly immersed into a coagulation bath containing water. The solid flat membranes were washed under running water to remove the residual solvent. The membrane was then stored in glycerine for further characterization. The symbols of PVDF-BNT, PVDF-CLS and PVDF-MMT denoted the composite membranes using the corresponding type of clay.

2.3. Membrane morphology and measurement of contact angle

The morphology of the surface and cross section of membranes were observed by a scanning electron microscope (JEOL JSM-6360LA) with a magnification of 5000 and 1000, respectively. The surface hydrophobicity of the membranes was characterized by contact angle (θ) measurement using drop analysis method. A piece of flat membranes was put on the sample holder. One drop of deionized water was dropped and the image was recorded. The contact angle of membrane was also measured using ethylene glycol and n-hexane as the liquid. All measurements were carried out at room temperature and the resulting images were analyzed with Image J software using drop analysis method.

2.4. Membrane characterization

The pure water flux and rejection coefficient of membranes were determined using a dead-end ultrafiltration equipment. Prior to measurement, membranes with 5 cm diameter were washed with pure water to remove glycerin. The membrane was compacted at 2 bars to get a steady flux and the permeate was collected every 5 mins; at least three data was taken to obtain an average flux for each type of membrane. The water flux was calculated using the following equation:

$$J = \frac{V}{A \times t} \quad (1)$$

where J is the water flux of membrane ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$), V is the volume of the permeate (L), A is the area of the membrane (m^2), t is the permeation time (h).

The rejection percentage was measured using the same equipment as for water flux measurement, but the feed was a T-500 Dextran solution with a concentration of 1000 ppm. The rejection was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_R} \right) \times 100 \quad (2)$$

where R is the rejection of the membrane (%), C_p and C_R are the concentration of permeate and feed solution, respectively.

3. Results and discussion

3.1. Membrane wettability

The membrane wettability can be examined by contact angle using polar and non-polar liquids. In this research, the wettability of PVDF and PVDF-clay composite membranes were analysed using polar liquids, which are water and ethylene glycol, and non-polar liquid such as n-hexane. The contact angles of water on the surface of various composite membranes were shown in Figure 1. It can be seen that the contact angles of PVDF-BNT and PVDF-CLS composite membrane were higher than the one of the pristine membrane. On the other hand, the contact angle of PVDF-MMT membrane was the lowest. The addition of BNT and CLS reached contact angle 69.2° and 76.7° respectively. It should be noted that all types of clay used in this study have similar main structure as MMT which contain negative charge in their structure. Natural BNT is MMT which still contains other natural oxides, while cloisite is MMT which has been intercalated by the addition of quaternary ammonium salt. The presence of clay on membrane surface affects the interaction between membrane and water, and also the surface roughness of membrane. The addition of oxide as a membrane component can increase the roughness of the membrane, and this has an impact on increasing the membrane hydrophobicity. On the other hand, the addition of MMT decreased the contact angle of water; it may be due to the polar nature of MMT.

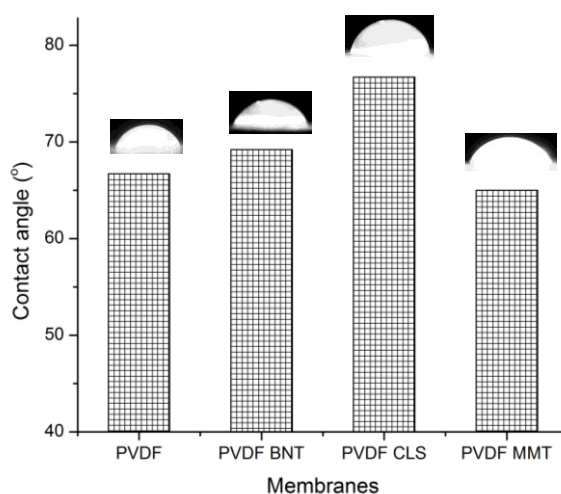


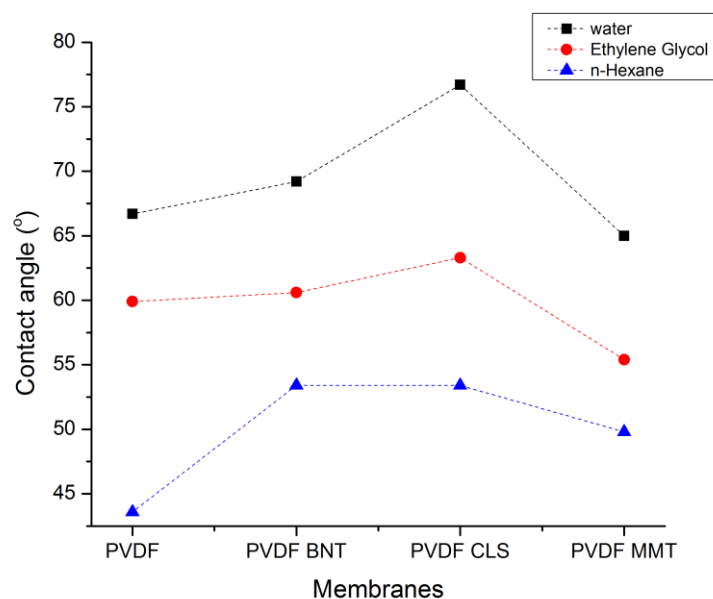
Figure 1. Contact angle of water on the surface of various composite membranes**Figure 2.** Membranes wettability of various composite membranes towards polar and non-polar liquids

Figure 2 showed membrane wettability towards polar and non-polar liquids. The contact angles of ethylene glycol have the same pattern with the one of water, while n-hexane showed a different trend. All the composite membranes gave higher values of contact angle than the pristine PVDF membrane when n-hexane was used. N-hexane contact angle of PVDF-BNT, PVDF-CLS and PVDF-MMT increased from 43.6° to 53.4°, 53.4° and 49.8° respectively. Since PVDF membrane is non-polar, its interaction with n-hexane is high, resulting in a relatively small contact angle towards n-hexane. It can be said that the addition of clay changed the surface structure of membrane and the polar properties of the membranes as well.

3.2. Membrane permeability and selectivity

Membrane permeability and selectivity were determined indirectly by measuring the water flux and rejection towards Dextran T-500. Effect of the addition of clay towards the water flux and the rejection toward Dextran T-500 solution were represented in Figure 3. The data showed that the addition of BNT and CLS in PVDF increased the water flux. PVDF-BNT and PVDF-CLS reached value peak of 13.05 L.m⁻².h⁻² and 18.15 L.m⁻².h⁻² respectively, and increased 65% and 125% from PVDF membrane. The addition of oxide into the membrane tend to increase the porosity of membranes which could enhance water permeability [22]. Meanwhile, Figure 3 also showed that similar rejection towards Dextran T-500 was obtained by PVDF and composite membranes, except the PVDF-BNT membrane. PVDF-BNT membrane reached rejection value of about 93%. The higher rejection coefficient might be due to the small particle size of BNT resulted in denser membranes than the others. Particle size of inorganic filler can effect of the membrane structure [23]. Consequently, the passage of Dextran compound across the membrane was inhibited and the rejection increased.

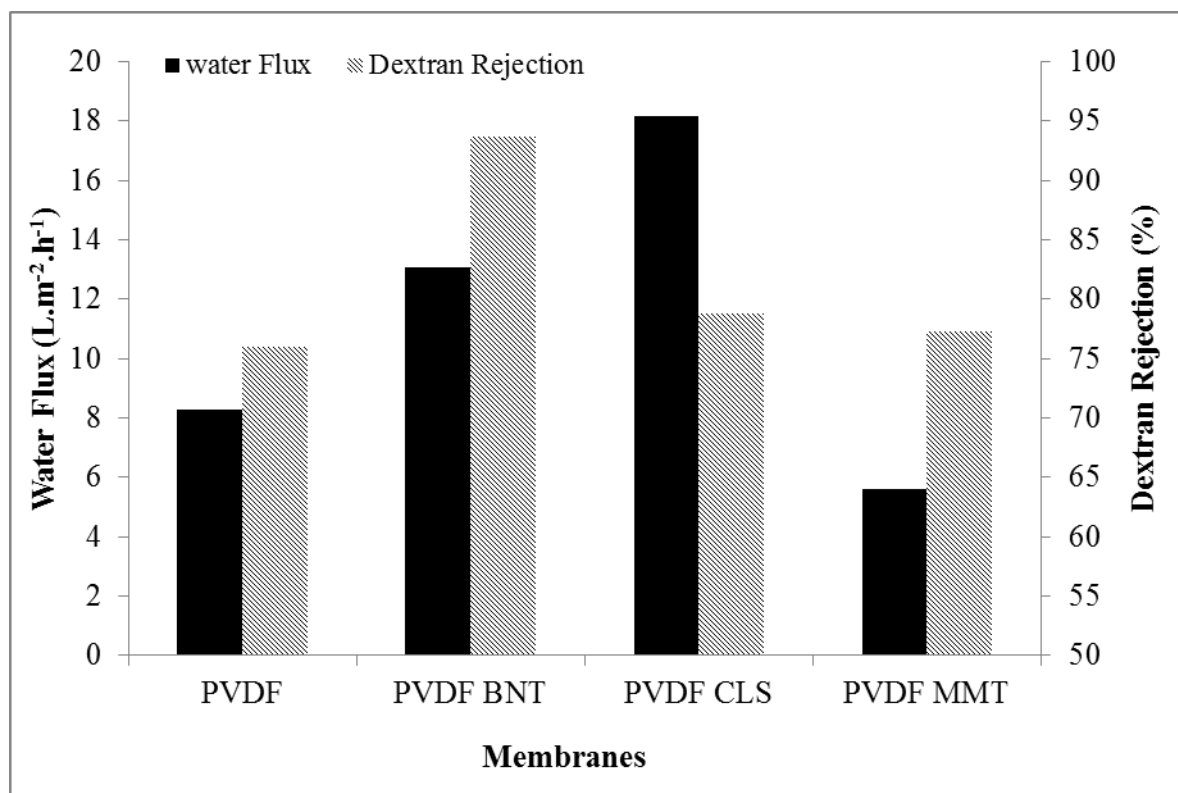


Figure 3. Water flux and Dextran T-500 rejection of pristine PVDF and various composite membranes

3.3. Membrane Morphology

The cross-section of PVDF-BNT composite membrane shown in Figure 4 indicated the presence of an asymmetrical structure; it consisted of microporous layer at the upper skin and finger-like macrovoid at the lower part of the membrane which was similar to the study by Lai *et al.* [24]. The structure is formed due to the rapid diffusion process of solvent and non-solvent during the phase inversion [25]. Figure 5 showed the difference among the morphologies of various types of membranes. The images of membrane surface looked similar one to another, but the cross-sections differed significantly. In the case of PVDF-MMT composite membrane, the addition of clay produced longer microporous layer than the pristine one which resulted in lower permeability or lower flux.

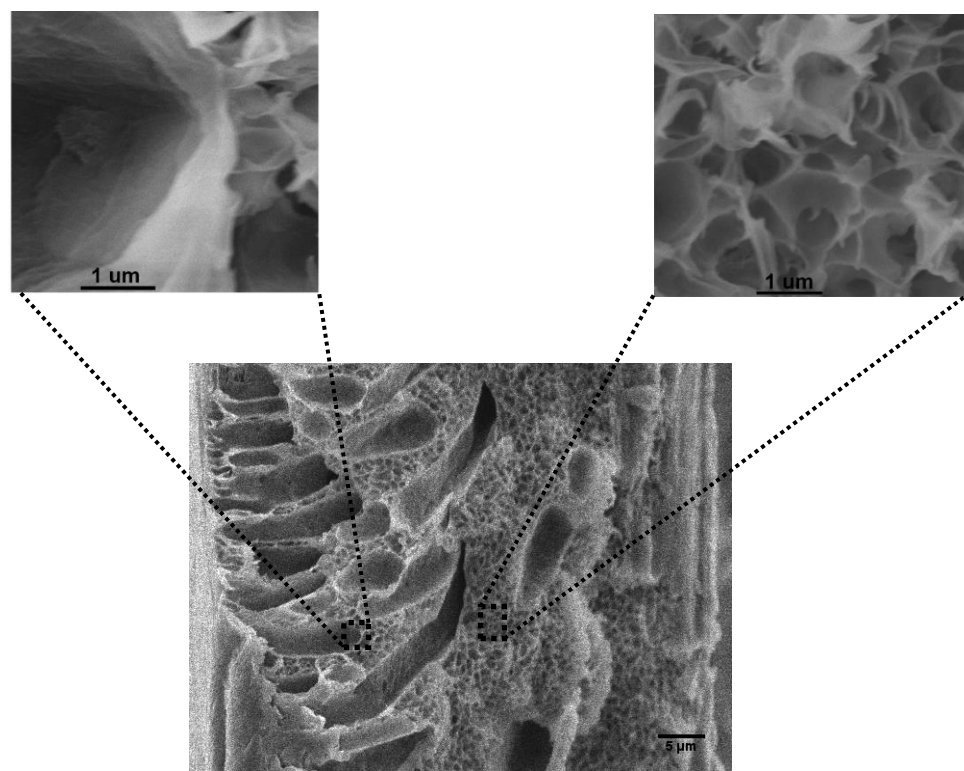
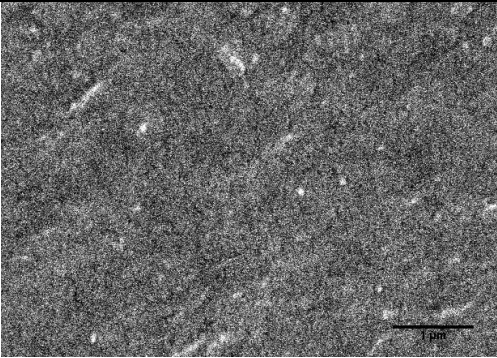

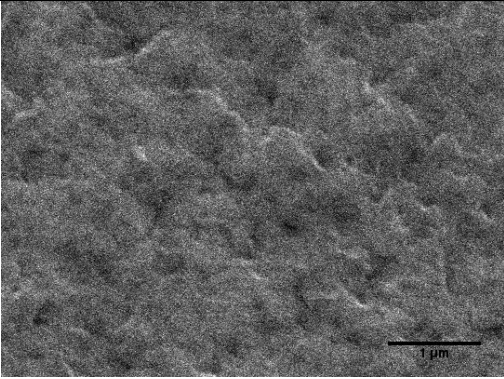
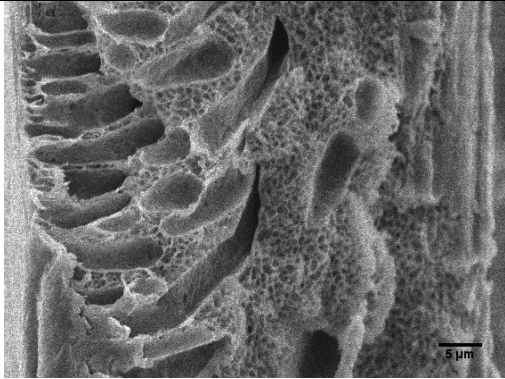


Figure 4. Cross section image of PVDF- BNT composite membrane

Membrane	Surface	Cross Section
PVDF Membrane	 SEM image showing the surface morphology of a PVDF membrane. The surface appears relatively smooth with some fine texture. A scale bar of 1 μm is present in the bottom right corner.	 SEM image showing the cross-section of a PVDF membrane. It displays a dense skin layer on top of a porous sub-layer. A scale bar of 5 μm is present in the bottom right corner.
PVDF-BNT	 SEM image showing the surface morphology of a PVDF-BNT composite membrane. The surface shows a more pronounced, wavy texture compared to the pure PVDF membrane. A scale bar of 1 μm is present in the bottom right corner.	 SEM image showing the cross-section of a PVDF-BNT composite membrane. It shows a porous structure with elongated, finger-like macrovoids. A scale bar of 5 μm is present in the bottom right corner.

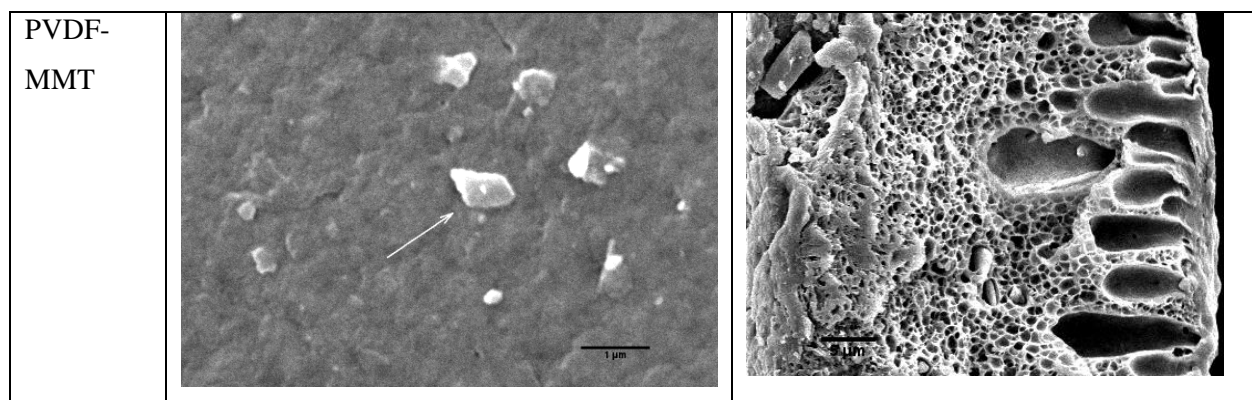


Figure 5. Surface and cross-section images of PVDF and various composite membranes

4. Conclusions

Flat sheets of various PVDF-clay composite membranes were prepared by phase inversion. The effects of clay addition on the surface properties, morphology, flux and rejection of the resulting membranes were evaluated. All membranes were found to have different asymmetric structures with spongy and finger-like pores. The addition of BNT and CLS increased the water contact angle while MMT decreased it. The negative charges of clays gave polar properties to the membrane surface, but the non-polar properties of PVDF were still dominant and resulted in lower contact angle toward n-hexane. It can be concluded that the PVDF-BNT membrane obtained the highest rejection toward Dextran T-500 (93%) compared to other composite membranes studied in this work.

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