

Synthesis and Characterization of Polysulfone/Montmorillonite (PSF/MMT) Mixed Matrix Membrane for Gas Separation

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Abstract. In this paper, flat sheet polysulfone (PSF) membrane and polysulfone/montmorillonite (PSF/MMT) mixed matrix membranes with different MMT contents were prepared by dry-wet phase inversion method. *N*-methyl-2-pyrrolidone (NMP) and deionized water were used as a solvent and coagulant, respectively. The morphology and structure of membranes were analyzed by scanning electron microscope. Thermogravimetric analysis was also performed to examine the thermal decomposition of the synthesized membrane. Results showed that MMT had a good dispersion in the PSF matrix.

Introduction

Membrane is commercially used in industry for many gas separation processes [1]. According to Susanto and Unbriht [2], polymeric membranes are dominant in many industrial applications due to the availability of materials, extensive polymer properties, ease of processing, high packing density and cost effectiveness. Despite all these advantages, polymeric membranes very often are not sufficiently permselective; so that they fall below the Robeson upper bound line [3]. In addition, polymeric membranes cannot withstand high temperature and aggressive chemical environment. On the other hand, inorganic materials are often extremely permselective, easy to clean, thermally and chemically resistant. Nevertheless, their use is limited as they are usually expensive, brittle, and difficult to be prepared in a reproducible way.

Mixed matrix membranes (MMMs) are hybrid membranes consisting of inorganic nanofillers dispersed in a polymer matrix [4]. They present a viable opportunity to enhance the separation capabilities of polymeric membranes; combining the high permselectivity of the filler (e.g. zeolite, nanoclay, carbon molecular sieves) with an ease of production of polymeric membranes [5].

Polysulfone (PSF) is one of the most commonly used membrane material for gas separation. It has excellent thermal, chemical and mechanical properties; and wide pH tolerance which gives an advantage to PSF in many industrial applications [6]. Nevertheless, the intrinsic permselectivities achieved by PSF membranes need to be improved.

Montmorillonite (MMT), a type of nanoclay, has been employed predominantly in the synthesis of polymer-clay nanocomposite since it is a naturally occurring mineral that is commercially available and inexpensive [7]. This aluminosilicate material shows promise as inorganic filler to enhance the barrier properties of polymeric materials [8], as they create a maze or 'tortuous path' that retards the progress of the large molecules through the polymeric matrix. There is also evidence that the nano-sized clay increase the gas diffusion properties of the membrane [9].

Over the past few decades, less attention has been devoted to incorporating nanoclay as fillers in MMMs for gas separation [10]. Hence, the present study aimed to prepare PSF/MMT nanocomposite membranes with different filler concentration by dry/wet phase inversion method. The effects of clay loading on the morphology and thermal properties of the MMM were investigated in detail. By understanding the morphology and physical features, the porosity and filtration performance of the membrane can be predicted. The synthesized membranes are subsequently characterized by using various analytical tools.

Experimental

Raw Material. A commercial Udel® Polysulfone, purchased from Solvay Advanced Polymers was used as the polymer matrix. *N*-methyl-2-pyrrolidone (NMP) supplied by Merck Sdn. Bhd. was used as the solvent, while deionized water was used as the non-solvent. The MMT was purchased from Sigma Aldrich. All materials were used without further purification.

Fabrication of Asymmetric Flat Sheet Mixed Matrix Membrane. In this paper, two types of membranes were prepared: neat PSF membrane and PSF/MMT MMM. The casting dope solutions were prepared by mixing 20wt% of PSF polymer with 80wt% NMP. Then, different MMT concentration (0wt%, 1wt%, 3wt%, and 5wt%) was added to the casting solution and stirred at 50°C until the polymer and clay dissolved in the solution. The solution was further stirred for 24 hours at room temperature to ensure complete dissolution of polymer and clay. The mixed solution was degassed by using ultrasonic degasser for at least 4 hours to remove trapped air bubbles, and then left standing for 1 day. Before casting, the mixture was further sonicated for 30 minutes and left standing for another 30 minutes to ensure homogenous dispersion of clay. The degassed solution was then poured onto a flat, levelled glass plate and cast into a thin film. The cast solution is slowly evaporated at ambient condition for 15 minutes. Then, the film is immersed in an aqueous bath at 25°C for 1 day. Finally, the membrane was washed with distilled water and dried for 24 hours at 60°C.

Mixed Matrix Membrane Characterization. Thermal gravimetric analysis (TGA) was performed on the membranes using a thermo-gravimetric analyser (Model: Perkin Elmer TGA-7). The samples were heated from 30 to 800°C at a heating rate of 10°C min⁻¹, with a nitrogen flow rate of 50 mL min⁻¹. The glass transition temperature (T_g) of the MMMs was measured using differential scanning calorimetry (DSC) (Perkin Elmer, DSC Pyris-1). The membrane sample was heated at temperature ranges of 30–350°C at a heating rate of 10°C min⁻¹. The sample was then cooled from 350 to 30°C at a cooling rate of 10°C min⁻¹. The same procedure was repeated in the next heating cycle. T_g of the sample was determined as the midpoint temperature of the transition region in the second heating cycle. Field emission scanning electron microscopic (FESEM) study was made using VPFESEM, model Zeiss Supra55VP. The membrane samples were fractured in liquid nitrogen and mounted on a stainless steel stand with carbon tape and then coated with 15nm of gold using a sputter coater.

Results and Discussion

Characterization of MMMs using Thermal Gravimetric Analysis.

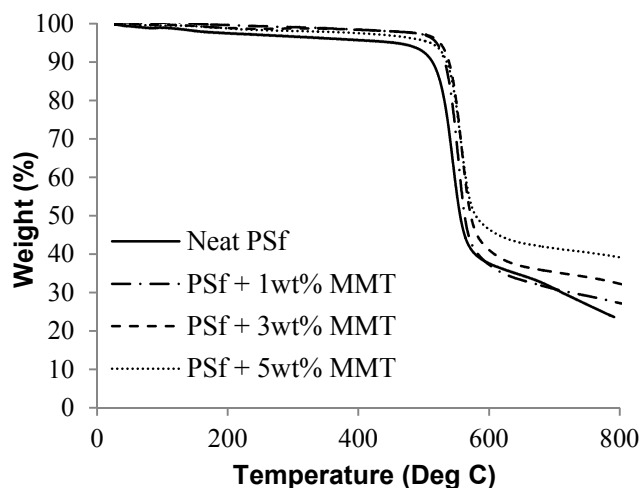


Fig. 1. TG curves of the membrane samples

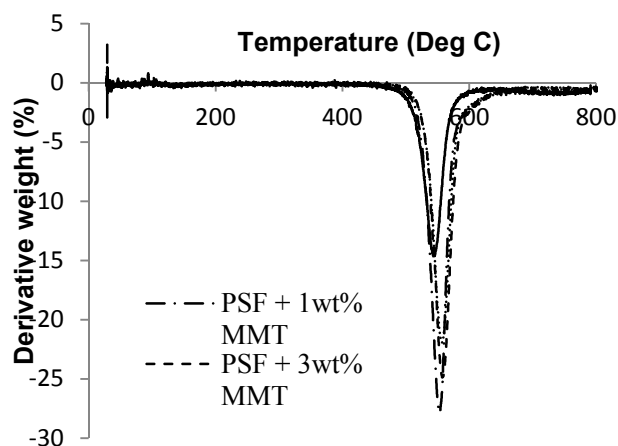


Fig. 2. DTG curves of the membrane samples

Fig. 1 and Fig. 2 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the following samples: neat PSF membrane, PSF/1wt% MMT MMM, PSF/3wt% MMT MMM, and PSF/5wt% MMT MMM. TGA was performed to analyze the thermal stability of the membranes [11]. The DTG curves show the decomposition temperature of the four membranes: 541°C for neat PSF membrane, 551°C for PSF/1wt% MMT MMM, 556°C for PSF/3wt% MMT MMM and 554°C for PSF/5wt% MMT MMM. The onset decomposition temperature of the neat PSF membrane was observed from the TG curve at $520 \pm 2^\circ\text{C}$, while the MMMs at approximately $530 \pm 2^\circ\text{C}$. Compared to neat PSF membrane, all MMMs exhibited higher decomposition temperature, with PSF/3wt% MMT MMM showing the highest decomposition temperature (556°C).

The improvement of the decomposition temperature for all MMMs resulted from the resistance created by clay's layered morphology which retarded the diffusion of oxygen into the polymer matrix [12]. As the clay loading increases, more heat is absorbed in the MMMs during heating up, thus delayed the decomposition. As a result, the decomposition temperature was raised for all MMMs [10]. This behavior is similar with the results reported by Bikiaris in his study [13] which suggested that enhanced thermal stability is closely related to the interactions between the clay particles and the polymer matrices. Reduction in decomposition temperature of PSF/MMT MMM of 3wt% clay to 5wt% is believed to be due to formation of agglomerates in the MMM (Figure 3). The inference is in agreement with Bikiaris's study [13] which supported the theory that formation of aggregates may cause thermal stability deterioration.

Characterization of MMMs using differential scanning calorimetry. The glass transition temperature, T_g of the neat PSF membrane, PSF/1wt% MMT MMM, PSF/3wt% MMT MMM and PSF/5wt% MMT MMM was measured using DSC (Table 1). The T_g of all MMMs is higher than that of neat PSF membrane. Introduction of 1wt% MMT into PSF serves to substantially increase the T_g by 9.73%. At 3wt% and 5wt% MMT loading, an even higher T_g over that of PSF is evident. This can be explained in terms of exfoliated dispersion of MMT in the polymer matrix [14]. Addition of stiff clay platelets acts as reinforcement to polymer chains at a molecular level; consequently obstructs the localized motions of polymer chains. This resulted in an increase in T_g , signifying that the MMT caused the structure of the membrane to become more crystalline and less amorphous.

Table 1. Glass transition temperature for the fabricated membranes

Membranes	T_g ($^\circ\text{C}$)
Neat PSF	183.74 ± 0.1
PSF/1wt% MMT	201.62 ± 0.1
PSF/3wt% MMT	207.61 ± 0.1
PSF/5wt% MMT	210.10 ± 0.1

Field emission scanning electron microscope of mixed matrix membranes.

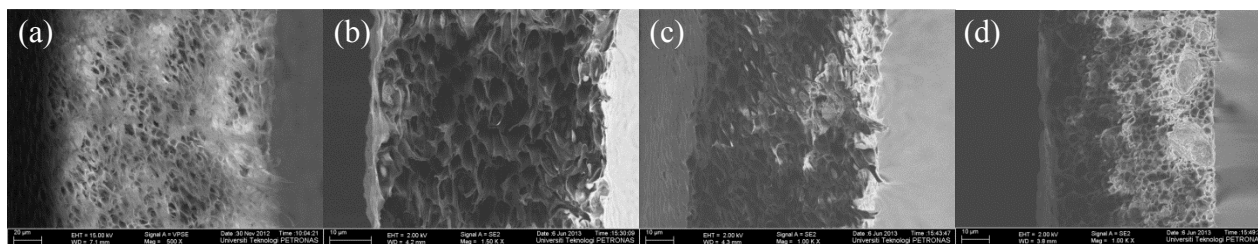


Fig. 3. FESEM micrographs for cross sectional view of membranes: (a) neat PSF (b) PSF/1wt% MMT (c) PSF/ PSF/3wt% MMT (d) PSF/5wt% MMT

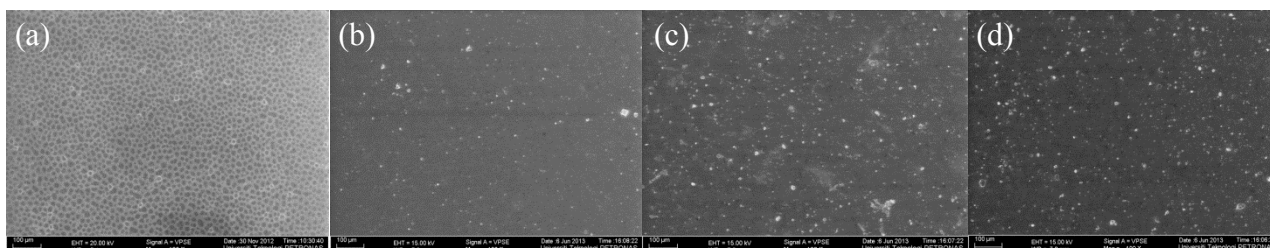


Fig. 4. FESEM micrographs for top surface view of membranes: (a) neat PSF (b) PSF/1wt% MMT (c) PSF/3wt% MMT (d) PSF/5wt% MMT

Fig. 3 shows the FESEM images for the cross section of neat PSF membrane and PSF/ MMT MMMs at different clay loading; Fig. 4 shows the micrographs of the skin surface. The measured thickness of the membrane is between 60 to 80 μ m. The thickness and structure of the MMM is closely related to the polymer concentration and viscosity of the casting dope [15,16] as well as the evaporation rate during casting [17]. From the FESEM images, thin and porous asymmetric membranes were successfully formed through dry/wet phase inversion technique.

Fig. 4 shows the dispersion of the filler at the skin surface of the MMM. Fine and homogenous distribution of clay was observed. The even distribution of clay is aided by the small nano-sized particle and the sonication process. Study by Aaron et al. [16] concluded that smaller particles such as sub-micron and nano sized particles will fit in the skin layer better than larger particles. In addition, nano-sized nonporous fillers such as MMT will provide higher polymer-particle interfacial area and improved interface contact.

Fig. 3(b) illustrates the morphology of PSF/MMT MMM with 1wt% clay loading. Weak organic-inorganic interaction caused voids to form in the polymer-filler interface [9]. Besides, the nucleation of the non-solvent/ polymer around the filler during phase separation process might also contribute to the defects [5]. From Fig. 3(c) and 3(d), particles agglomeration can be observed. As the clay content in the MMM increased, the particle cluster became more significant and bigger agglomerates were formed. Many literatures reported that bigger aggregates caused poor adhesion, consequently larger voids were formed [5,10,18,19]. Interestingly, the FESEM result contradicted with previous studies. MMM with 3wt% and 5wt% of clay content shows better adhesion between PSF and MMT, forming smaller void. PSF/5wt% MMT MMM is believed to have formed rigidified polymer layer around the nanoparticles. Moore and Koros [20] described interface voids and matrix rigidification as interface defects which resulted from the stresses due to reduction in free volume during solvent evaporation. This resulted in high permeability since gas molecules can pass through the nano-gap between polymer and clay, subsequently reduces selectivity; while rigidified polymer layer will result in higher selectivity, but low permeability [10,20]. The latter phenomenon is more favourable unless the rigidified polymer permeability is so low that it significantly affects the membrane performance [5].

Conclusion

PSF membrane and PSF/MMT MMM were fabricated using dry/wet phase inversion method. The casting dope was prepared at fixed polymer-solvent ratio, while MMT loading was manipulated (1wt%, 3wt% and 5wt%). TGA results showed enhancement of thermal stability of MMM compared to the neat PSF membrane. Thin asymmetric membrane with dense skin layer and porous sub-structure was observed from FESEM images. The study concluded that higher clay loading resulted in bigger agglomeration but smaller voids, which contradicted with previous studies. This might be due to formation of matrix rigidification. We note that, in order to prove the inference made from the morphology of the MMMs, gas permeation test can be conducted. Based on the reported results, PSF/MMT MMM is expected to have better selectivity and permeability compared to neat polymer membrane. Besides, the interaction between different types of nanofillers with the polymer is an interesting topic for future studies.

Acknowledgements

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