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Investigation of the dispersion of nanoclays into PVDF for enhancement of physical membrane properties

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Abstract

Polymer membranes are extensively used for water treatment but they wear irreversibly over time, especially when used in treatment of waters containing abrasive substances such as in seawater pretreatment. Novel nanocomposite membranes may be a cost effective approach to improving membrane physical endurance. Various methods of dispersing commercially available Cloisite® 30B nanoparticles in 1-methyl-2-pyrrolidinone (NMP) were investigated and the respective particle sizes were measured by nanoparticle sizer. Ultrasonication dispersed the nanoparticles to the smallest size in the shortest period of time. Flat sheet poly(vinylidene fluoride) (PVDF)/nanoclay membranes with 6.25 wt % clay loading were cast by phase inversion. The morphology and the structure of the membrane were characterized by scanning electron microscopy (SEM), combustion testing and thermogravimetric analysis (TGA). Porous membrane with fingerlike macrovoids was fabricated and 1.7 wt% of nanoclay was incorporated into the final product as shown by TGA. The composite membrane showed greater stiffness compared to pure PVDF membrane.

Keywords: Dispersion; Poly(vinylidene fluoride); Nanoclay; Ultrafiltration; Membrane fabrication

1. Introduction

Membrane technology has been utilised in the water industry for more than 40 years [1]. The most common applications include producing usable water from surface waters, seawater and brackish water, as well as treating domestic and industrial wastewaters. Membrane systems are used to replace procedures such as sedimentation and granular filtration [2] that are usually found in a conventional water treatment plant. Membrane systems require less space and consistently produce high quality water. The ability to rapidly and continuously remove contaminants and pathogens promptly makes membrane technology more attractive [3].

Poly(vinylidene fluoride) (PVDF) plays an important role in various industries, such as pulp and paper, nuclear-waste processing and chemical processing [4], owing to its excellent chemical and physical properties. Its strong chemical resistance against corrosive chemicals including acids, bases, oxidants and halogens [5], and its toughness makes it an excellent polymeric membrane material and popular among various industries. PVDF membrane is widely used in water treatment for the same reasons, but it also has the ability to be controllably porous, an essential feature for microfiltration and ultrafiltration applications.

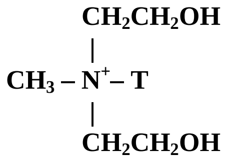
Despite the robustness of the material, membrane fouling and wearing are some major problems encountered in the water industry. Fouling results in obstruction of water transport through the membrane and it may occur by particle deposition, adsorption of organic molecules, inorganic deposits, as well as microbial adhesion and growth [3]. In particular, inorganic deposits such as clay minerals are associated with membrane damage through abrasion as their crystalline structure is compressed against the membrane surface by increased operating pressures [6]. In the presence of abrasive materials, especially in applications to treat raw water samples such as seawater, physical durability is needed to ensure sufficiently long operational life.

To address the issues of fouling and to improve the mechanical performance of current commercial membranes, inorganic materials are being included into the polymer matrix. In this paper, various methods were investigated for their suitability to disperse nanoparticles uniformly. Composite PVDF/nanoclay flat sheet membranes were cast and characterized for the composition of the inorganic nanomaterials, as well as measures of improved mechanical strength which will lead to improved physical membrane strength.

2. Experimental

2.1. *Materials*

The powdered PVDF used was a commercial product Solef® 1015 (specific gravity = 1.78, T_g = 140°C) obtained from Solvay Solexis. The nanoclay used in this study was commercially available Cloisite® 30B, a natural montmorillonite modified with a quaternary ammonium salt supplied by Southern Clay Products. The organic modifier is a methyl tallow bis-2-hydroxyethyl ammonium ion as show in Figure 1. The solvent used was biotech grade (≥99.5%) 1-methyl-2-pyrrolidinone (NMP) from Sigma-Aldrich.



$$\begin{array}{rl} & \mathbf{CH_2CH_2OH} \\ & | \\ \mathbf{CH_3 -} & \mathbf{N^+ - T} \\ & | \\ & \mathbf{CH_2CH_2OH} \end{array}$$

Where T is Tallow (~65% C18; ~30% C16; ~5% C14)

Anion: Chloride

Figure 1. Organic modifier used in Cloisite® 30B

2.2. *Casting solution and dispersions*

Three different instruments were used to disperse Cloisite® 30B into NMP: (1) ultrasonication in an ultrasonic bath, (2) Thinky Mixer ARE-250, a planetary centrifugal mixer, at 2000 rpm and (3) overhead stirrer from VELP Scientifica at 200 rpm. The mass ratio of Cloisite® 30B to NMP used was 1:84. This was based on the ratio to mix with PVDF at a later stage for membrane fabrication.

PVDF membrane dope consisted of 15 wt% of PVDF and 85 wt% of NMP while the composite membrane dope was prepared by mixing 1 wt% of Cloisite® 30B, 15 wt% of PVDF and 84 wt% of NMP. This is to achieve a mass ratio of 1:15 nanoclay to PVDF (6.25 wt%) in the final membrane. Each dope solution was then heated in a 90°C oil bath and stirred with an overhead stirrer at 200 rpm for 24 hours.

2.3. *Membrane preparation*

The dope was coated on a glass substrate with a Doctor blade to form thin films between 300 μm and 400 μm in thickness. The membrane was then formed through phase inversion by immersion in deionised water at 60°C for 15 minutes. A portion of the membranes were soaked overnight in a 15 wt% glycerol/water solution in order to preserve their porous structure. The membranes were dried in a thermostat cabinet at 30°C for 48 hours.

2.4. Characterization of dispersions

Zetasizer Nano ZS from Malvern Instruments, a Dynamic Light Scattering (DLS) instrument, was used to measure the size and the size distribution of the nanoparticles. Small samples were taken from the dispersions at various time intervals and diluted with NMP to about 0.02 wt%, so as to be in the concentration range suitable for Zetasizer operation. Multiple Zetasizer measurements were taken for each sample, and the average recorded.

2.5. Characterization of membranes

Membranes were characterized by scanning electron microscope (SEM), combustion testing and thermogravimetric analysis (TGA).

SEM images were taken with a Nikon/JEOL NeoScope JCM-5000. Membrane samples were mounted onto the 25 mm height sample holder and fixed in place with adhesive carbon tape. No other preparation was performed.

TGA was performed using a PerkinElmer TGA 7. Cloisite® 30B, PVDF and composite membrane samples were heated from 50 to 850°C at a rate of 20°C/min under air.

Mechanical properties including elongation at maximum load, tensile strength, Young's modulus and modulus of toughness of the membranes were measured using an Instron 5500R tensile testing instrument at 20ºC. The initial gauge length was 20 mm and the testing speed was 400 mm/min. At least 3 samples of each type of membranes were tested.

3. Results and Discussion

3.1. Particle size distribution

Figure 2 demonstrates the Z-average size, which is the intensity-weighted mean diameter derived from the cumulants analysis, of the nanoparticles versus the mixing time with 3 different mixing methods. The supplier's product data sheet of Cloisite® 30B indicates the typical dry particle sizes as follow: 10% less than 2 µm, 50% less than 6 µm and 90% less than 13 µm. Although the Z-average size only reflects the actual particle size if the sample is monomodal, spherical and monodisperse, it is able to show the general trend that the overall particle size decreases over time with all 3 mixing methods.

Ultrasonication appears to be the best method in terms of dispersing the particles to the smallest size within the shortest period of time. Prolonged stirring at a lower speed may be a more economical way to disperse the nanoparticles, but gradual breakdown of size after 15 hours reduced the particle size to about 480 nm, which is still larger than the size achieved after 2 hours with the ultrasonication method (265 nm).

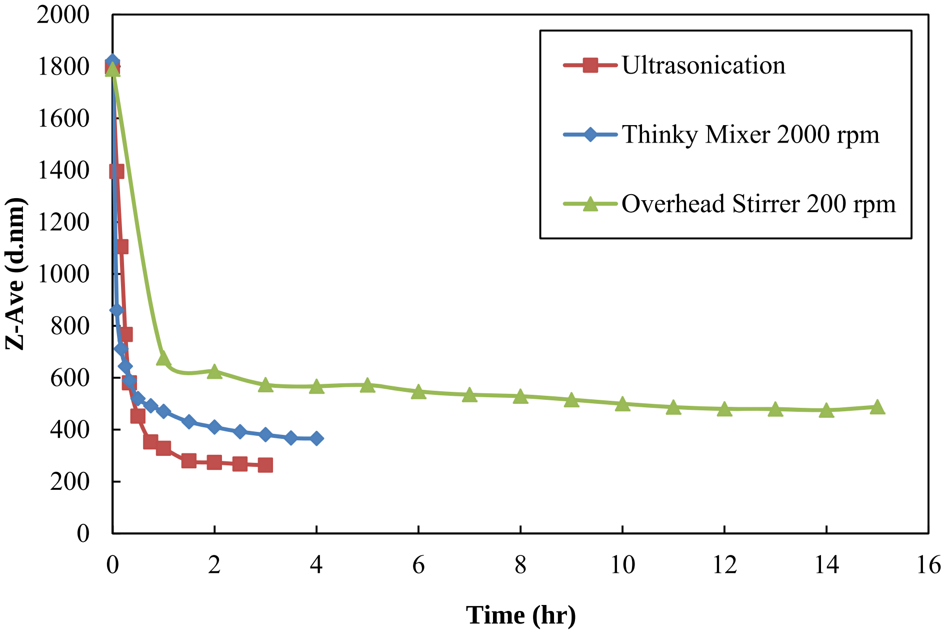


Figure 2. Z-average particle size of Cloisite® 30B dispersed in NMP vs mixing time

Figure 3 shows the size distribution by intensity using ultrasonication as the dispersion method. Readings at 0 and 5 minutes are excluded from the graph as large particles were present in the initial period and these skewed the distribution curves significantly. It was observed that as time progressed, the particle size reduced and a narrower distribution range was measured. It is also noted that ultrasonication for 1 hour gave the highest dispersion rate of the particles. After the 1 hour mark, the particle size decreased slowly and eventually remained at about 300 nm.

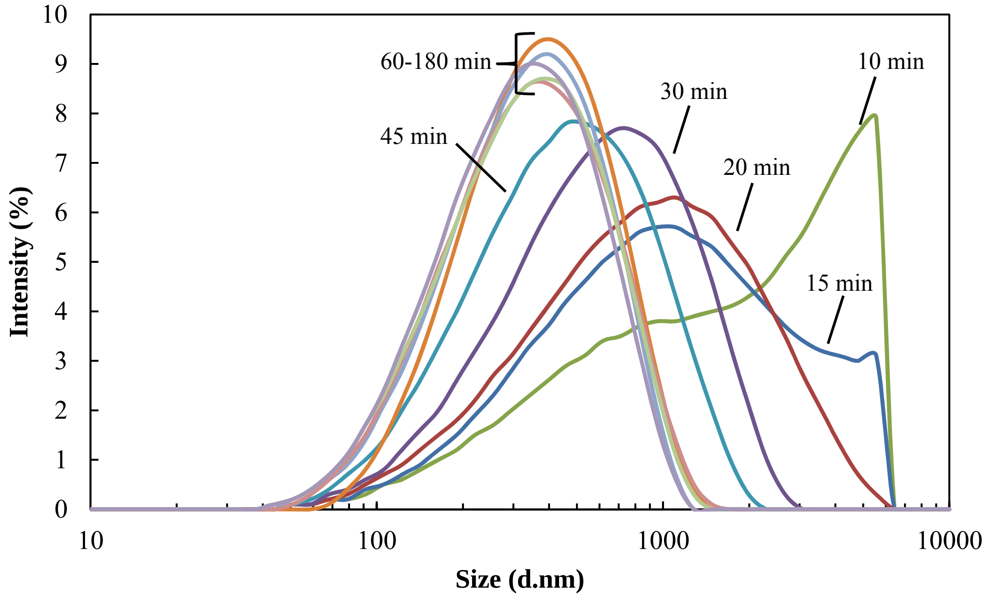


Figure 3. Size Distribution by intensity with ultrasonication

While it would be ideal to study the dispersion of clay particles in the casting solution as well, it is not feasible in this situation. Upon diluting the dope to the concentration required by the particle sizer, temperature would drop below the original dope temperature of 90°C, which causes PVDF to precipitate. Our key aim of this study was to observe at least qualitatively, the optimum technique and parameters to effectively disperse nanoparticles in NMP.

3.2. *Membrane morphology*

Figure 4 illustrates the top surface morphology of the PVDF/nanoclay composite flat sheet membrane. The sample appears to have a porous structure with pores less than 1 μm. The edge of a membrane sample was torn to reveal the inner core structure of the membrane as shown in Figure 5. Fingerlike macrovoids and circular pores were observed. These structural features of the membrane are typical for membranes made by phase inversion [7].

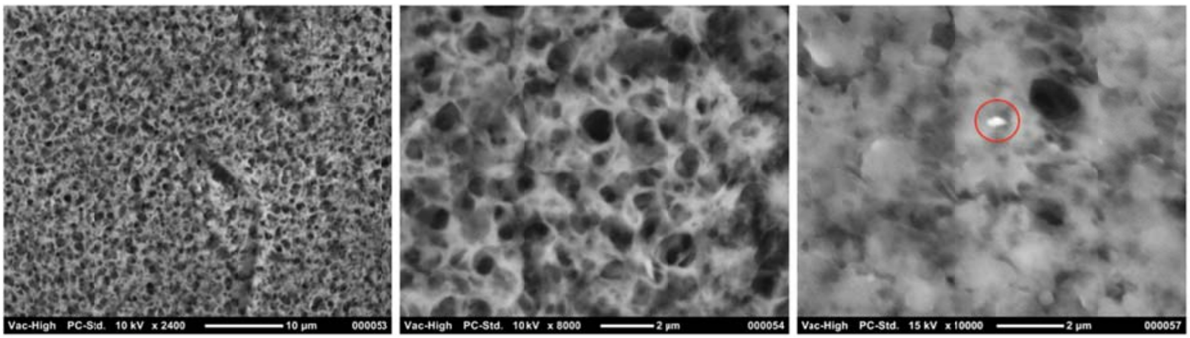


Figure 4. SEM micrographs of the top surface of a PVDF/Cloisite® 30B membrane with increasing magnification (left to right). Right image is close-up of the 'dense' region observed in the middle image.

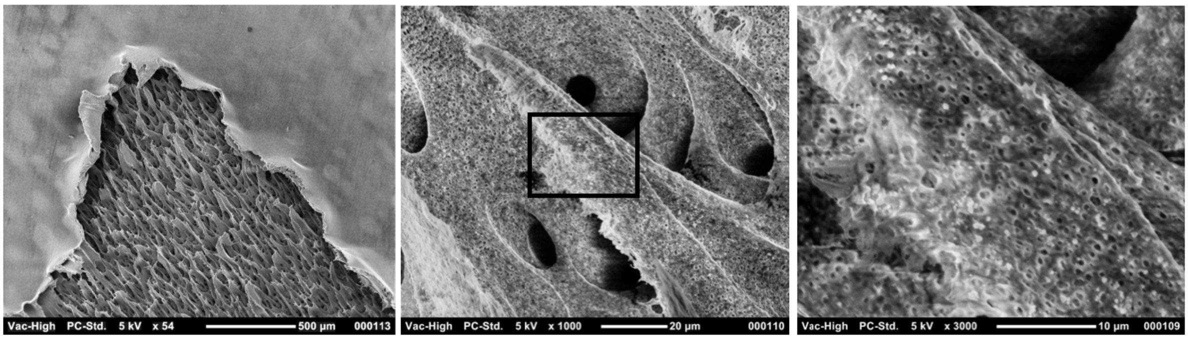


Figure 5. SEM micrographs of the inner core of a PVDF/Cloisite® 30B membrane with increasing magnification (left to right).

The dispersion of nanoparticles appears to have been effective in making defect free (as observed by SEM) membranes. Despite the relatively large size of the particles detected in the NMP dispersion discussed in Section 3.1, it is expected that further breakdown of the particles into nanoparticles occurred as this is commonly observed in nanocomposite research [8]. There are possibly 200 nm particles as annotated in the red circle in the right image of Figure 4. However, the dense regions of the membrane in this case were larger than the measured nanoparticles as well as the pores. As such, even if the particles were in this size range or clumped together, they did not appear to alter the membrane structure.

The presence of nanoparticles is usually detected via TEM or x-ray scattering [9, 10], and this is the subject of ongoing work in this project. Also, our future work will explore the testing on both flat sheet and hollow fibre membranes (flux, rejection and fouling performance).

3.3. *TGA*

Figure 6 shows the TGA results of Cloisite® 30B, PVDF and PVDF/nanoclay membranes and Table 1 summarizes the residual weight percentage of each material remaining after TGA which translates to the inorganic component of the materials. It is shown that 69.2% of the nanoclay is inorganic and was left as residue after thermal decomposition. This figure matches with the 30% weight loss on ignition stated on the supplier's product data sheet of Cloisite® 30B. Both original and composite membranes exhibited a two-step weight loss, which are attributed to the decomposition of the polymer. The 30% organic fraction of Cloisite® 30B (where Cloisite® 30B contributed to 1.9 wt% of the entire membrane) is too small to contribute to the weight loss peaks in the TGA curve. Thermal decomposition of the composite membrane occurred at a lower temperature compared to the original PVDF membrane. Other researchers have found the addition of inorganic material into PVDF increases the temperature of thermal degradation [7, 11], which is the opposite of our findings. In their work, they used purely inorganic materials such as $CaCO_3$, silica (including SBA-15). Cloisite® 30B contains 30.5% organic content which started to decompose at a lower temperature than pure PVDF (i.e. 250°C and 450°C respectively), this may explain the reason for the reduced thermal stability. Even though small in content, the decomposition of the Cloisite® 30B has brought forward the decomposition of the composite PVDF/nanoclay. Despite this effect, the organic modifier in Cloisite® 30B is needed for the compatibility of the inorganic nanoparticles with the polymer structure.

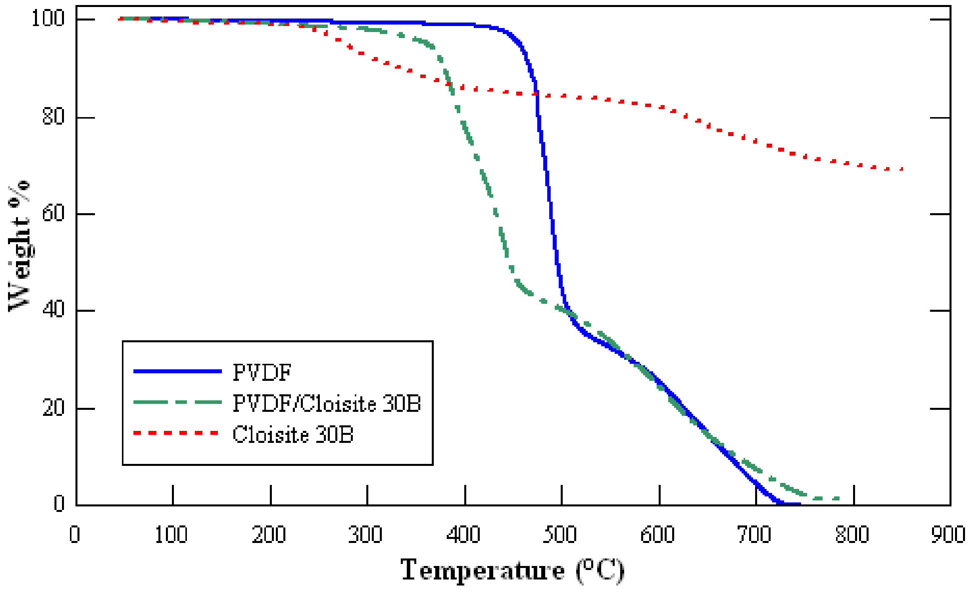


Figure 6. TGA thermograms of Cloisite® 30B, original PVDF and PVDF/nanoclay membranes

Table 1. Tabulated TGA data showing weight remaining after heating to 850°C

Material	Weight remaining %
Cloisite® 30B	69.2
PVDF membrane	0.0
PVDF/Cloisite® 30B membrane	1.2

The TGA curve shows that there was 1.2 wt% of residue left after thermal decomposition of the PVDF/nanoclay membrane while the pure PVDF membrane left no residue. Table 2 compares the nanoparticle content of the dope and membrane measured by TGA. Based on the dope preparation procedure, the total inorganic contribution in the casting dope would be

4.3%. Alternatively, 1.4 wt% of inorganic component indicates 1.7 wt% of nanoclay loading has been successfully incorporated into the membrane.

Table 2. Tabulated inorganic and nanoclay weight contribution

Material	Inorganic wt%	Cloisite® 30B wt%
Original dope (PVDF/nanoclay)	4.3*	6.25
PVDF/nanoclay membrane by TGA	1.2	1.7

* Calculated based on the residue of Cloisite® 30B after TGA.

It is noted in Table 2 that the nanoclay loading in the final product shown by TGA is considerably lower than that of the initial dope. Further investigations will consider this discrepancy with the aim of establishing a procedure to incorporate a greater percentage of nanoparticles into the membrane.

3.4. Mechanical properties

The testing results of mechanical properties including tensile strength, elongation at maximum load, Young's modulus and modulus of toughness are listed in Table 3. It was observed that the composite membrane exhibits higher Young's modulus than the pure PVDF membrane, which indicates the introduction of nanoclay provides extra stiffness to the polymer matrix. On the other hand, the PVDF/nanoclay membrane demonstrated a smaller modulus of toughness (the area under the stress-strain curve), showing it is less tough than the PVDF membrane.

Table 3. Mechanical properties of membranes

Membrane	Tensile strength (MPa)	Elongation at max load (%)	Young's modulus (MPa)	Modulus of toughness (MPa)
PVDF	4.9 ± 0.1	144 ± 16	10 ± 2	6.8 ± 0.8
PVDF/nanoclay	4.5 ± 0.1	75 ± 9	17 ± 1	3.0 ± 0.3

This work has established the procedures for mixing commercial nanoparticles into PVDF membranes, explored their effect on membrane structure, and final content within the polymer. The mechanical properties indicated a stiffer yet less tough material is made as a result of their addition. Further works will investigate various nanoclay loadings to understand its effect to the toughness and stiffness of the membrane. Membrane performance under scouring and/or high fouling conditions is also to be explored in future work.

4. Conclusions

Cloisite® 30B was dispersed in NMP with various methods. Ultrasonication was the fastest and most effective reducer of particle size in dispersing the clay into the smallest particle size within the shortest mixing time. Flat sheet PVDF/nanoclay composite membranes were cast by phase inversion. SEM images confirmed the porous structure of the membranes. Inorganic residue was left behind after both TGA and combustion testing, indicating that nanoclay was present in the membrane despite a lower loading than the original dope. The incorporation of nanoclay gave extra stiffness to the membrane and a lower toughness. Future work will address an improved procedure to incorporate a greater amount of the nanoparticles into the membrane, and membrane performance will be tested.

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