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Development of Nanocomposite Polysulfone-Nanoclay Membrane with Enhanced Hydrophilicity

ABSTRACT

This research involved the development of membranes with local raw materials to suit water and wastewater treatment applications. Indigenous montmorillonite clay was surface modified with dialkyldimethyl ammonium chloride to be used as functional additive in polymeric membranes. Polysulfone (PSf) pellets were dissolved in N-methyl-pyrrolidone (NMP) and organomodified-montmorillonite (OMMT) or nanoclay was incorporated at varying concentrations up to 1.00%. Casting solutions were vacuum-mixed and degassed using a planetary mixer then casted using MEMCAST™ to produce flat sheet membranes. Characterizations include X-Ray Diffractometry, Atomic Force Microscopy, Scanning Electron Microscopy, and contact angle measurement. The exfoliation of OMMT platelet structures within the PSf matrix at 1.00% loading showed improved surface roughness and more porous morphology. Improved surface roughness was observed with an increasing value as a function of increasing OMMT concentration. Meanwhile, the morphology of the nanocomposite membranes showed three distinct layers: dense skin layer, porous finger-like layer, and sponge-like structured layer. Moreover, the contact angle of the membranes decreased by 13.7% with 1.00% addition. This enhancement in hydrophilicity could affect properties like permeate flux and membrane fouling, which could play an important role in the functional performance of synthesized membranes with nanoclay additives. One-way ANOVA revealed that the change in OMMT concentration has significant effect on the surface roughness and contact angles of the membranes at 95% confidence level.

Keywords: *nanoclay, polymeric membrane, surface properties, hydrophilicity*

Blessie Basilia[1*]
Sharyjel Cayabyab[1*]
Edmar Casa[1]
Alvin Kim Collera[1]
Persia Ada de Yro[1]
Marianito Margarito[1]
Lumen Milo[1]
Mar Christian Que[1]
Vivian Lagura[1]
Brigida Visaya[1]

[1] Industrial Technology Development Institute, Materials Science Division, Suri St., Gen. Santos Ave., Department of Science and Technology (DOST) Cpd., Bicutan, Taguig City, Philippines

*corresponding authors:
basiliablessie@gmail.com
srcayabyab@gmail.com

INTRODUCTION

One of the major challenges worldwide is the rising demand for safe and sustainable water supply (*Elimelech and Phillip 2011*). In 2015, the World Health Organization (*2018*) reported 844 million people who lack basic drinking water services and projected that by 2025, half of the world's population would be living in water-stressed areas. Factors that have greatly contributed to this are the growing world population, global climate change, and water quality deterioration (*Qu et al. 2013*). Ultimately, certain parts of the world with low-income and middle-income economies experience more pronounced effects due to the lack of access to technologies for water treatment (*Qu et al. 2013; Theron et al. 2008*).

The Philippines, being listed in the lower middle-income economies (*United Nations 2018*), has nine million out of 101 million Filipinos who use unsafe and unsustainable water (*Water.org 2019*). Although the country has numerous water sources such as rivers, seas, lakes, reservoirs, other groundwater resources, or even rainfall and wastewater (*Greenpeace Southeast Asia 2007*), the purity of water for human consumption is inadequate (*Geise et al. 2010*). To meet the growing demand for quality water supply, development of technologies for the protection of existing freshwater resources (*Pendergast and Hoek 2011*) and treatment of unconventional water resources are still greatly considered.

Numerous advancements in water treatment have emerged over time. One of the most commonly used technologies in purifying and producing quality water is membrane technology because of its energy efficiency (*Geise et al. 2010*), high removal efficiency, cost effectiveness (*Jhaveri and Murthy 2016*), no thermal input requirement, and regeneration of used up material (*Pendergast and Hoek 2011*). Membrane technology is known for using at least a layer of thin semi-permeable material (*Singh 2015*) when a driving force such as pressure, vapour pressure, electric potential, concentration or temperature (*Fane et al. 2011*) is applied. Use on water and wastewater treatment covers the removal of microorganisms, bacteria, particles, organic materials, to the removal of ions and dissolved non-ions (*Le and Nunes 2016*).

There are several classifications by which the membranes are characterized. Membranes are classified according to structure; it could be dense, porous, and/or composite. Under porous membranes, structures could be symmetric or asymmetric (*Ladewig and Al-Shaeli 2017*). Membrane structures greatly affect the application in which membranes could be used for. In pressure driven membranes, intended use of final product, variation in pore sizes (*Pendergast and Hoek 2011*), molecular weights of compounds being filtered (*GEA Process Engineering 2012*) and required pressure (*Cui et al. 2010*) would vary applications such as particle filtration, microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

Another classification of membranes is the type of material. Different membrane materials include inorganic membranes (ceramic and metals), polymeric membranes, biological membranes, which are barriers within or around a living organism's cell (*Ladewig and Al-Shaeli 2017*), and composite membranes that is consist at least two layers of different polymeric materials. Among these membranes, polymeric membranes are widely used in water treatment due to ease of preparation, low cost, high efficiency with low energy requirement, and flexibility in different membrane configurations (*Ladewig and Al-Shaeli 2017*). Examples of polymeric membranes include polysulfone (PSf), polyamide (PA), and polyvinylidene difluoride (PVDF).

These polymeric membranes are usually fabricated via phase inversion (PI) method. This method is a thermodynamic and kinetic process (*Ma et al. 2011*) that involves transforming the polymer from its solution state to its solid state (*Mulder 2000; Pendergast and Hoek 2011*). Transformation is accomplished via immersion precipitation, thermally-induced phase separation, evaporation-induced phase separation, and vapour-induced phase separation (*Lalia et al. 2013*). These fabrication processes involve the homogenous dissolution of the polymer in the form of pellets or powders in a solvent such as n-methyl-2-pyrrolidone (NMP) and dimethylacetamide and use of a nonsolvent (typically water) coagulation bath to form the membranes (*Lalia et al. 2013*). The solvent in the homogenous solution is exchanged with the nonsolvent to form the membrane structure (*Ma et al. 2011; Pendergast and Hoek 2011*). For immersion precipitation, the polymer solvent is immersed in the coagulation bath; for the thermally-induced phase separation and temperature plays a role in the demixing of the solution; for the evaporation-induced phase separation, volatile solvent is used, thus is allowed to evaporate; and for the vapour-induced phase separation, membranes are formed via the exposure of polymer solution in the atmosphere with nonsolvent (*Lalia et al. 2013*). The membranes fabricated using these techniques could either be in the form of spiral wound, tubular, flat sheet membranes, or hollow fiber membranes (G*EA Process Engineering 2012*).

Recent strategies in membrane technology have been employed and studied to achieve desired membrane properties. These include the development of mixed matrix nanocomposite membranes where nanomaterials are dispersed onto polymeric matrix (*Esfahani et al. 2018*). This technique aims to combine properties from both materials, specifically the unique characteristics of the nanomaterials and the processability of the polymeric membrane (*Esfahani et al. 2018*). Conventional nanocomposite membranes are mostly fabricated using PI method; with the incorporation of organic, inorganic, biomaterial, and hybrid material combining at least two material types (*Yin and Deng 2015*). Some of the properties that are generally enhanced with the incorporation of the nanomaterials are hydrophilicity, charge density, porosity, antibacterial properties, photocatalytic properties, chemical stability, and mechanical integrity of the developed membranes (*Esfahani et al. 2018; Yin and Deng 2015*).

Polysulfone-based membranes are commonly used in ultrafiltration processes due to its excellent heat resistance, chemical compatibility and resistance to wide pH range (*Ganesh et al. 2011*) and high mechanical integrity (*Fan et al. 2008*). To address the hydrophobicity of PSf (*Ganesh et al. 2013; Fan et al. 2008*), surface coating, surface grafting, and incorporation of hydrophilic additives (*Zhao et al. 2012*) are explored. Typically, clays impart hydrophilicity and mechanical property on PSf membranes due to attached hydrophilic -OH groups in the clay structure (*Yin and Deng 2015*). In this study, organo-montmorillonite clay that could act as nanofillers are incorporated in PSf membranes.

MATERIALS AND METHODS

The study was conducted from December 2017-May 2018 covering the period of experimentation and characterization. PSf pellets (average molecular weight Mw ~35000 g mol^{-1} and average number molecular weight Mn ~16000 g mol^{-1}) supplied by Sigma-Aldrich were oven-dried for 4 hours at 99.85^{o}C. Organically modified montmorillonite clay was processed at the Department of Science and Technology. The method used to process the locally sourced raw bentonite is as follows: the raw bentonite was beneficiated to obtain montmorillonite then organically modified to enhance compatibility with the polymeric matrix (*Basilia 2004*). The modifier used was di-(hydrogenated tallow) dimethyl ammonium chloride (DHTDMAC) with molecular weight of 567-573 g mol^{-1}. The montmorillonite used in the study was first organically modified using quaternary alkyl ammonium salt, specifically di-(hydrogenated tallow) dimethyl ammonium chloride. The inorganic ions in the montmorillonite were exchanged with the alkylammonium ions, therefore modifying the different properties of the clay The inorganic ions in the montmorillonite were exchanged with the alkylammonium ions, therefore modifying the different properties of the clay (**Figure 1**). The organo-modified montmorillonite (OMMT) was also oven-dried for 4 hours at 99.85^{o}C. N-methyl-2-pyrrolidone (NMP), in which PSf was dissolved, was supplied by Sigma-Aldrich.

Different casting solutions were prepared by mixing the different materials in a vacuum mixer. Different materials were weighed accordingly (**Table 1**). For the preparation of the control solution, a quarter of the total PSf pellets was added every half an hour of mixing in the vacuum mixer (*Rodrigues 2016*). For the preparation of solutions with clay additives, OMMT was initially dispersed in the NMP. The solution was sonicated for half an hour and then PSf pellets were added. The casting solutions were degassed for at least half an hour (*Rodrigues 2016*).

The solutions were automatically casted on stainless steel substrates using the MEMCAST™ machine with 100 µm thick casting knife. The casted solutions were then immersed on water coagulation bath. The membranes were immersed for 24 hours to allow complete exchange of solvent (NMP) and nonsolvent (water) phases (*Rodrigues 2016*). Fabricated flat sheet membranes were air-dried then stored in a dessicator for characterization.

Table 1. The different formulations of different casting solutions used.

Formulation	Weight Percentage (%)		Wt. % Clay Based on PSf
	PSf	NMP	
Control	18.0	82.0	0.00
0.25 OMMT	18.0	82.0	0.25
0.50 OMMT	18.0	82.0	0.50
0.75 OMMT	18.0	82.0	0.75
1.00 OMMT	18.0	82.0	1.00

Characterizations on the OMMT included imaging using Transmission Electron Microscope (TEM, JEOL JEM-2100F), determination of basal spacing using X-ray Diffractometer (LabX XRD-6000 by Shimadzu), determination of cation exchange capacity and percent montmorillonite purity of the OMMT.

The topography of different samples was generated using Atomic Force Microscope (AFM, Park Systems XE-100). The microscope used was in noncontact mode. The scan size and scan rate for all samples were 5µm x 5µm and 0.3 Hz, respectively.

The effect on the structure of the clay nanofillers was evaluated using the XRD (LabX XRD-6000 by Shimadzu) with scan rate of 1^{o} min^{-1}. Plots of the intensity in auxiliary units against 2theta in radians were generated for the different membranes.

The membranes were immersed in water before cryo-snapping in liquid nitrogen. Samples were viewed under Scanning Electron Microscope (SEM). The contact angles of the different membranes were measured using the Face Contact Angle Meter (Kyowa Interface Science Co. Ltd) to get the effect on the hydrophilicity (*Asadollahi et al. 2017*). Five measurement readings were taken for each membrane to get the average contact angle.

RESULTS AND DISCUSSION

The cation exchange capacity (CEC) of the raw bentonite increased from 43.0 meq per 100g to 84.0 meq per 100g. The increase in the basal spacing of the clay or the dispersed thickness of the clay platelets was 3.66 nm. The interlayer spacing and consequently the basal spacing could bring about intercalation, exfoliation, or intrusion of polymeric chains (*Basilia 2004, Shah et al. 2017*). The OMMT has 99.9% montmorillonite purity.

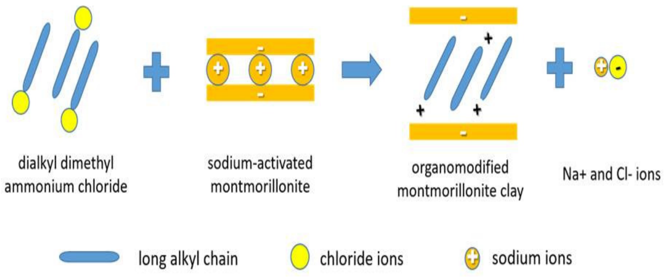

Figure 1. Schematic diagram of organo-modification of montmorillonite clay (*Basilia 2004; Luo et. al. 2015*).

The morphological structure of the OMMT in the TEM image shows the stacked clay platelets of the OMMT (**Figure 2**).

The surface roughness values were reported as roughness average (Ra) and calculated using the formula stored in the software of the (**Figure 3**). It can be observed that the surface roughness of the membrane increases as as a function of increased OMMT concentration up to 0.75%. This could be due to the long alkyl chains from the OMMT segments that were dispersed on the surfaces of the membranes. However, at 1.00% OMMT loading, the surface roughness had a lower value (13.229 nm) than at 0.75% OMMT loading. At higher concentrations, obstruction is caused by agglomerated clay structures. It will lead to resistance to diffusion of solvent and nonsolvent molecules during phase inversion causing the decrease in surface roughness (*Baig et al. 2019*). As the surface roughness of the membrane changes, it momentarily affects the static contact angle measurement resulting in an increase in hydrophilicity (*Wang et al. 2012*). One-way Analysis of Variance (ANOVA) at 95% confidence level revealed that the weight percent OMMT significantly affects the average surface roughness.

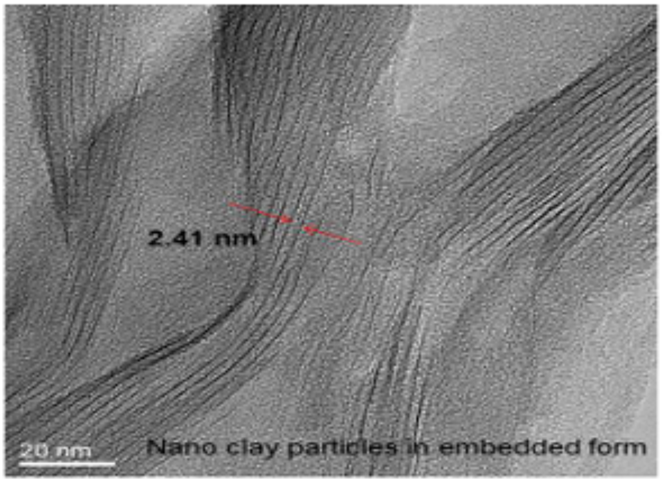

Figure 2. Morphological structure of organomodified-montmorillonite using Transmission Electron Microscopy imaging (JEOL JEM-2100F).

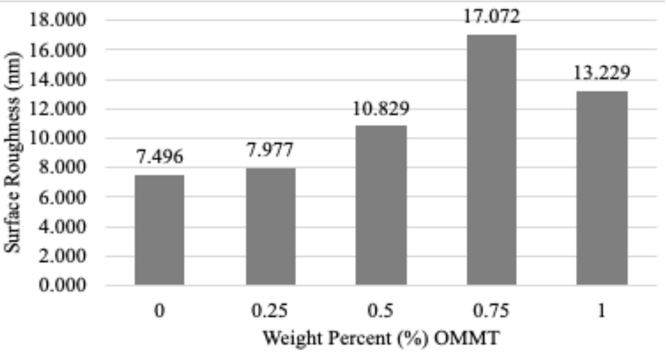

Figure 3. Different surface roughness of Polysulfone-organomodified-montmorillonite membranes as measured from the atomic force microscope (XE-100 Model by Park Systems).

Analysis using XRD gave information on the average distance between the nanolayers and relative stacking order (**Figure 4**). Organomodification of the montmorillonite intends to increase the basal spacing of the clay platelets but not to disrupt spatial separation of the layers. Exfoliation of nanoclay structures was observed within the PSf matrix at a clay loading of up to 1.00% (**Figure 4**). This could be due to the intrusion of polymer chains into the clay platelet structures. For 0.25% and 0.50% clay loading, a peak was observed at around π/10 radians (2theta). However, this peak was no longer observed for 0.75% and 1.00% clay loading indicating exfoliation of the clay platelets.

The fabricated flat sheet membranes show an asymmetric pore structure with a dense skin layer, a porous finger-like layer, and a layer with sponge-like structures (**Figure 5**). It was observed that the pore size and pore density on the sponge-like structures vary with different nanoclay concentrations (**Figure 6**). The addition of OMMT in the polymeric membranes affected the exchange of NMP with water consequently changing the membrane morphology (*Rodrigues 2016; Wijmans et al. 1985*).

It could also be observed that the porosity of the walls of the finger-like structures of the different membranes increased as the clay concentration increased (**Figure 7**), similar to the observation of *Monticelli et al.* (*2007*). The

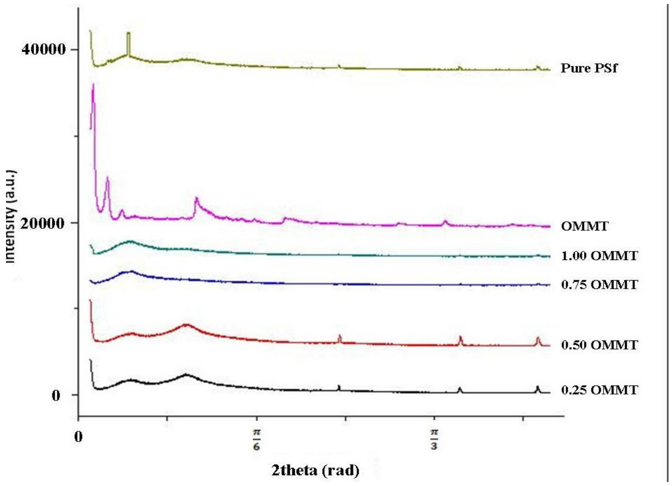

Figure 4. X-ray diffractometry results of organomodified-montmorillonite powders, pure Polysulfone, and Polysulfone- organomodified-montmorillonite membranes using (LabX XRD-6000 by Shimadzu).

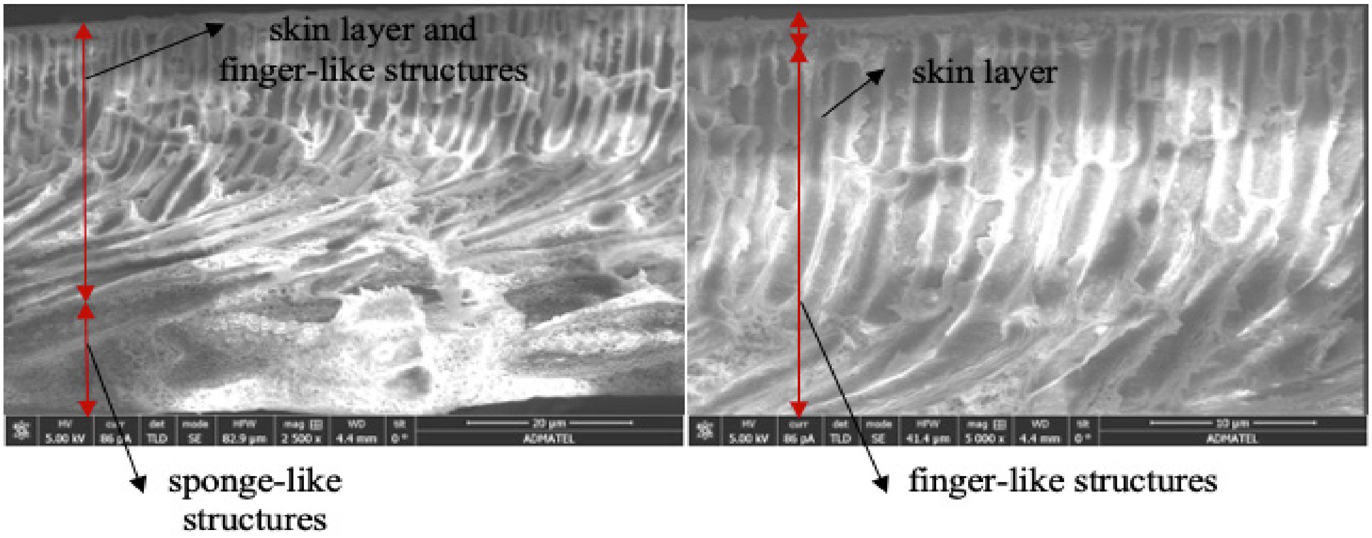

Figure 5. Cross-sectional Scanning Electron Microspcope images of pure Polysulfone at 5.00kV at 2500x (left) and 5000x (right).

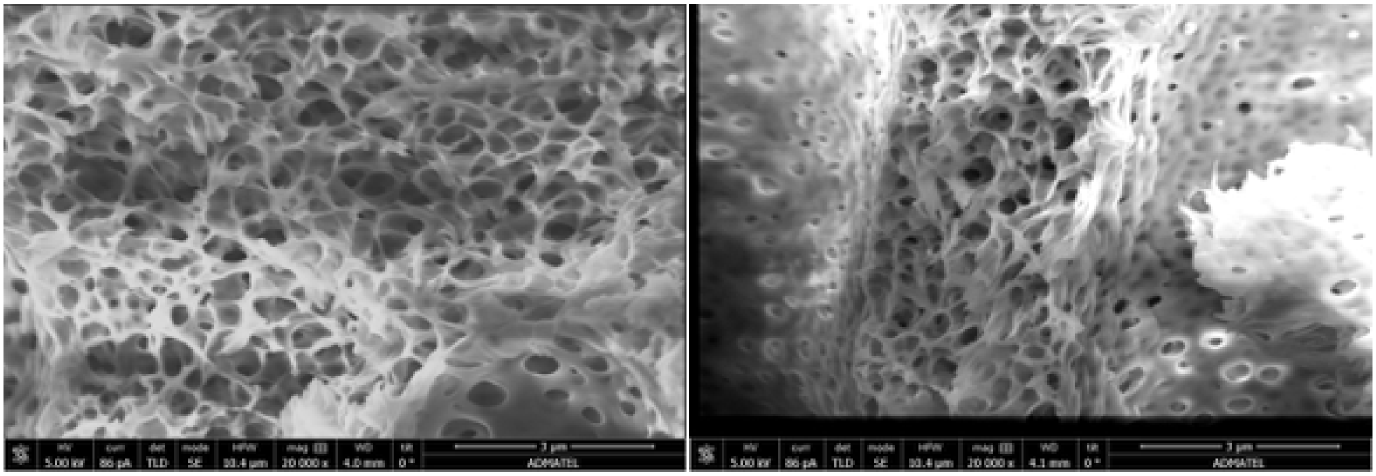

Figure 6. Cross-sectional Scanning Electron Microspcope images of Polysulfone-organomodified-montmorillonite membranes at 5.00kV: 0.25% organomodified-montmorillonite (OMMT) (left) and 1.00% OMMT (right) at 20 000x.

change in the characteristics of the finger-like structures could be due to the increase in the viscosity with OMMT addition, thereby affecting the formation of the membrane layers during coagulation. Also, clay layers could remain well-dispersed during immersion in the coagulation bath (*Monticelli et al. 2007*), therefore developing the asymmetric morphological pore structure. The dispersion behavior of clay layers was observed from the XRD results showing exfoliation in the developed membranes. Nanoclay structures hastened the rate of solvent/nonsolvent exchange, which resulted in the formation of skin layers with decreased pore size and more porous finger-like structures (*Rezaei-DashtArzhandi et al. 2015; Yin and Deng 2015*), consequently affecting the hydrophilicity of the entire PSf membranes.

It was observed that there is a decreasing trend in the contact angle of the membranes as the OMMT loading was increased (**Figure 8**). With OMMT addition, there was a decrease in a magnitude of 13.7% at 1.00% nanoclay suggesting the development of more hydrophilic membranes. This enhancement of hydrophilicity is brought about by presence of -OH groups in the OMMT (*Yin and Deng 2015*), the platelet structure of OMMT (*Wang et al. 2012*), and the interaction of the clay with the structures on the surface of the polymer matrix (*Tran et al. 2012*).

It should also be noted that this decreasing trend in the contact angle can be caused by the increase in the surface roughness of the membranes as the percentage of nanoclay increases. According to *Wenzel* (*1936*), rough surfaces have higher wettability. For a certain unit area of a material, a rough surface has higher actual

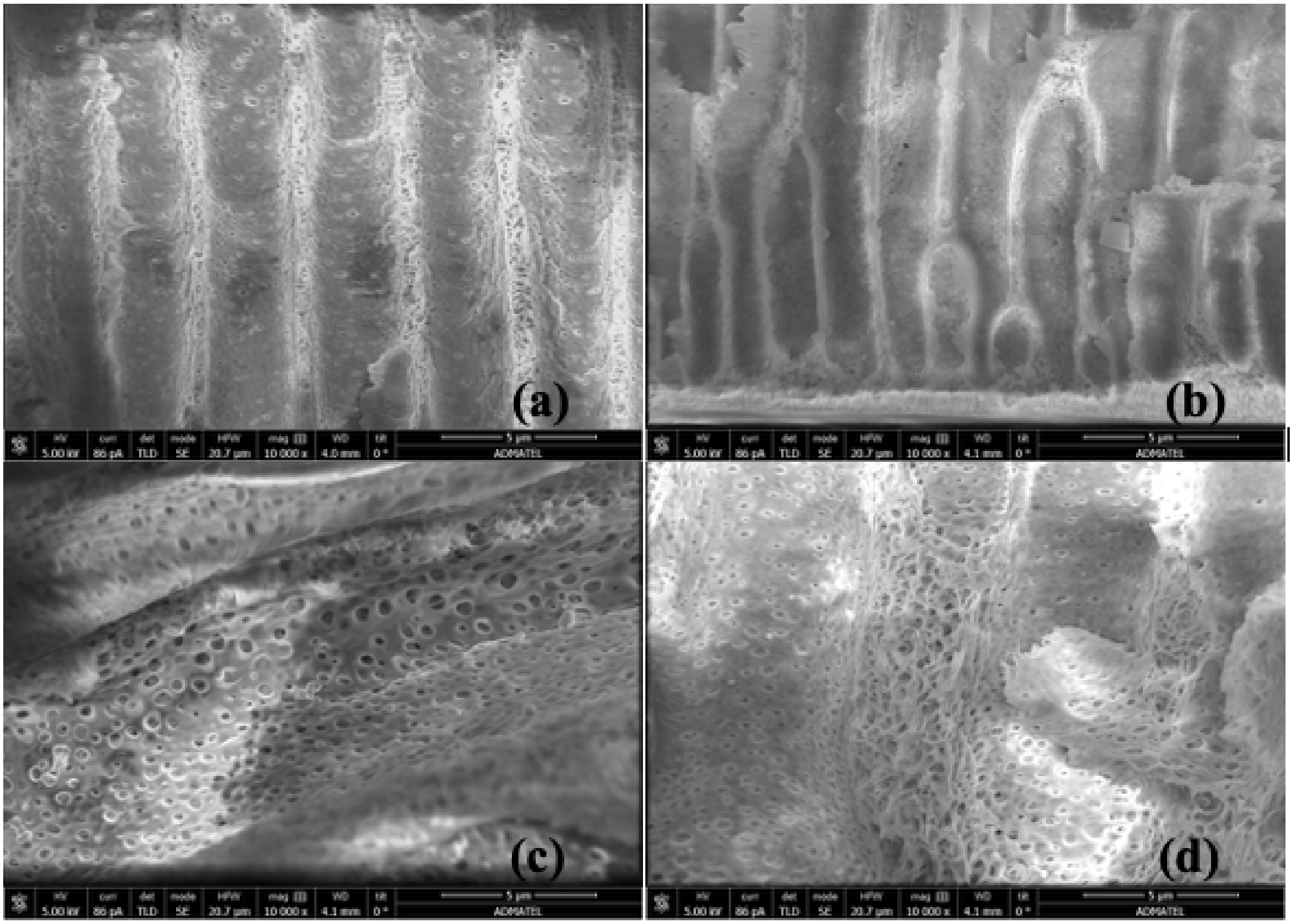

Figure 7. Cross-sectional Scanning Electron Microspcope images of Polysulfone-organomodified-montmorillonite membranes (OMMT) at 5.00kV: (a) 0.25 OMMT, (b) 0.50 OMMT, (c) 0.75 OMMT, and (d) 1.00 OMMT at 10 000x magnification.

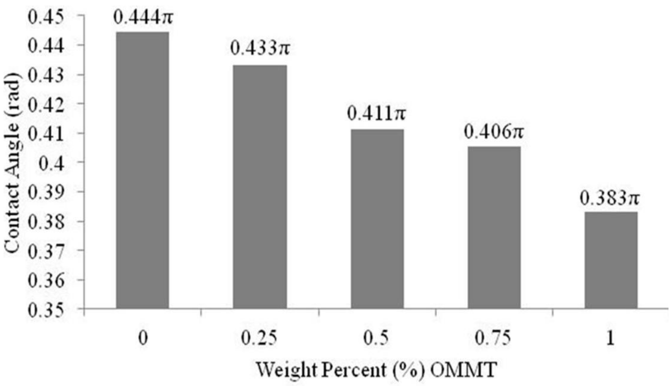

Figure 8. Different average contact angles of Polysulfone-organomodified-montmorillonite membranes measured using Face Contact Angle Meter from Kyowa Interface Science Co. Ltd.

area than a smooth surface; and the spreading/wetting of the liquid over the area is governed by the change in the energy of the wetted surface and the free liquid (*Wenzel 1936*). Thus, with higher actual area there is a greater net decrease in energy for wetting the surfaces (*Wenzel 1936*) and consequently, a lower contact angle. One-way ANOVA showed that increasing the weight of percent OMMT had a significant effect in the contact angle of the different membranes.

CONCLUSIONS AND RECOMMENDATIONS

The developed polymeric membranes with organo-modified montmorillonite clay showed changes in the surface properties such as improved surface roughness and more porous morphological structure, which resulted to a lower surface tension. This phenomenon yielded an exfoliated nanocomposite membrane with enhanced hydrophilicity. In effect, this could relate to the improvement on properties such as membrane fouling, permeance, and rejection ability that could impact several water treatment applications (*Yin and Deng 2015*). This study could play an important role in relating the functional performance of polymeric membranes particularly with the use of functional additives.

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