Fabrication of Polythiourea-Copper Complex Composite Membrane and its Anti-fouling Property

M T Margarito1,2, A B Beltran1, MA Promentilla1, A Orbecido1, B Basilia1, R Damalerio1 and U Bigol3

1 Chemical Engineering Department, De La Salle University, Manila, Philippines
2 Materials Science Division, Industrial Technology Development Institute, Department of Science and Technology, Bicutan, Taguig City, Philippines
3 Environment and Biotechnology Division, Industrial Technology Development Institute, Department of Science and Technology, Bicutan, Taguig City, Philippines

marianito_margarito@dlsu.edu.ph, mtmargarito@yahoo.com

Abstract. A Composite Flat Sheet Membrane Containing Polythiourea-Copper (PTU-Cu) Complex was fabricated through a two-step phase separation involving complexation and/or crosslinking of the polymer by copper ions (Cu2+) on the first step and non-solvent induced phase separation on the second step. The surface topography of the membrane was analysed using Atomic Force Microscope (AFM) in non-contact mode. The incorporation of copper at the surface was confirmed through Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) mapping wherein other elements such as Sulfur (S), Carbon (C) and Oxygen (O) of the polymer were conducted. The fabricated membrane was rigid as shown by high value (about 2.15 GigaPascal) of measured Young’s modulus using the Pinpoint Nanomechanical Analysis Mode of AFM. In addition, the surface charge and hydrophobicity were measured using the Electrostatic Force Microscope (EFM) and water contact angle respectively. The antifouling characteristics of the membrane was evaluated through antimicrobial membrane surface contact test wherein E. coli was used as test microorganism. Other membrane properties such as pore size distribution and pure water flux were measured using a porometer and a filtration apparatus.

1. Introduction

Many researches on membrane material to reduce fouling physically incorporates nanomaterials in the dope solution through solution dispersion technique. This is to improve its antifouling performance by imparting antibacterial characteristics, reduce surface roughness and increase hydrophilicity of the surface. Nanomaterials such as silver (Ag), titania (TiO2), zinc oxide (ZnO), carbon nanotube (CNT) and copper oxide (CuO) [1] among others are used as antibacterial additive for membrane. These nanomaterials are relatively expensive and may require functionalization [2] to increase compatibility or adherence with the polymer material to prevent formation of channels in the interface which would lead to failure of the membrane. In solution dispersion technique more nanomaterials are needed to be included in the dope solution to have enough concentration at the surface to realize antifouling characteristics. There are also concerns that the nanomaterial will leach out from the membrane and into the water [3]. As a result, decrease in activity of these nanomaterial is expected due to dynamic nature of membrane filtration process and may require replenishment [4]. Contamination of water may also occur that could affect downstream processes and ultimate end use. Many of these membranes were not commercialized due to high cost, lack of long-term testing of its efficacy and concerns on the elution of nanomaterials and subsequent release in the environment.

Other strategies to incorporate antifouling material particularly at the surface of the membrane where it is desired includes grafting, plasma treatment, electroless plating [5], interfacial polymerization and
coating among others. Many of them are either complex process or in some cases also results to leaching of materials. Therefore, new strategies on membrane modification should feature simple process, improve efficacy in terms of flux and fouling mitigation, inexpensive and at the same time minimize leaching of active components to enable long term efficacy.

In this study, a composite membrane consisting of polythiourea-copper (PTU-Cu) separation layer on a PTU support was fabricated through Complexation Induced Phase Separation (CIPS) and Nonsolvent Induced Phase Separation (NIPS). Copper ions from Cupric Acetate (CuAC) solution were used in the crosslinking of the polymer through the sulfur containing group in its backbone inducing the first stage phase separation. Theoretically, the crosslinking of polymer imparts additional mechanical property while the copper imparts antibacterial characteristics. Since copper reacts chemically with the polymer, leaching could minimize. The chemical association of copper at the surface of the membrane were confirmed through SEM-EDX and its effect on the adhesion and stiffness of the membrane were measured using Pin-point TM Nanomechanical Analysis mode of AFM. Surface topography and image were both determined using FE-SEM and AFM. Surface charge distribution and water surface contact angle were also analyzed.

So far, the synthesis of PTU from p-phenylene diisothiocyanate and oxidianiline and its complexation with copper has not been performed and studied. Its properties and synthesis for application in membrane separation has not been examined in detail. The efficacy of copper in form of polymer-copper complex to inhibit fouling formation through its antibacterial characteristics were not yet evaluated. New technique has been employed in the preliminary evaluation of the membrane such as Pin-point Nanomechanical analysis to map different phase of polymers with varying stiffness and adhesion and the Electrostatic Force Microscopy (EFM) to determine the surface charge.

2. Materials and Methods

2.1. Reagents

p-phenylene diisothiocyanate (PDTC) 98 % and 4,4-Oxidianiline (ODA) 97% purity from Sigma-Aldrich were used in the synthesis of the Polythiourea (PTU). Dimethylsulfoxide (DMSO) >99.9% purity from RCI Labscan Ltd., was used as solvent for the synthesis of PTU and preparation of polymer dope solution for membrane fabrication. Cupric Acetate Monohydrate (CuAc), 98% from LOBA Chemie Pvt. Ltd. was used for the CIPS reaction.

2.2. Synthesis of Polythiourea

Polythiourea used in this study was synthesized based on the method by Ma et al., for application in capacitor dielectrics. Equimolar quantities of p-phenylene diisothiocyanate (PDTC) and oxidianiline (ODA) were reacted in Dimethyl Sulfoxide (DMSO) as solvent at room temperature for 24 hours. This forms viscous solution as a result of polymerization where repeating units of thiourea shown in figure 1 forms long molecule chain. The solution was then precipitated in hot water for 24 hours and dried in oven at 50 °C for another 24 hours.

![Thiourea repeating unit from ODA and PDTC](image-url)
2.3. Membrane Preparation

The PTU-Cu Composite membrane was prepared based on procedure by Villalobos et al. [6] with slight modification. The polymer dope solution was prepared by dissolving PTU (12%wt) in DMSO at room temperature. The solution was degassed in vacuum to allow the entrapped gas to escaped. The dope solution was then hand casted in polyester support using a casting knife with 250 microns (μm) gap. It is then immersed in 10 millimoles (mM) of Cupric Acetate in DMSO for 5 seconds where rapid thin layer precipitates at the interface through Complexation Induced Phase Separation (CIPS). The solution was then transferred to a distilled water coagulant bath where the supporting porous structure beneath the PTU-Cu layer precipitate through Non-Solvent Induced Phase Separation (NIPS). It is further immersed in the water for 24 to 48 hours to complete the solvent exchange. The membrane was then air dried for at least 24 hours prior to analysis and testing. The fabricated membrane is classified as composite membrane since the top layer is compose of dense PTU-Cu complex and the porous support layer is made up of PTU only.

Pristine PTU membrane was also prepared using the same procedure except for immersion in solution of CuAc in DMSO. The resulting membrane is classified as asymmetric membrane which consist solely of PTU polymer. Through NIPS, the membrane forms dense top separation layer underneath a porous support structure which is ideal for high flux and separation.

2.4. Membrane Characterization and Performance Evaluation

Atomic Force Microscopy. Samples of both the pristine PTU and the PTU-Cu Complex Composite membrane about 10 mm2 (square millimetres) were prepared for analysis. The surface topography and surface roughness of the membrane were measured using Park System’s Atomic Force Microscope (AFM) Model XE-100. NCHR cantilever was used in non-contact mode with scan size of 5 μm x 5 μm. Electrostatic force or the charge distribution at the surface of the membrane were mapped using Electrostatic Force Microscope (EFM) mode of AFM with NSC14/Cr-Au cantilever. The Young’s Modulus and adhesion together with the corresponding height image of the surface of the membrane at the nano level were mapped using the Park System’s AFM Model NX-20 with AC160TS cantilever in Pinpoint Nanomechanical Mode. For this analysis, different cantilever with different hardness is needed for different range of values of the Young’s Modulus.

Scanning Electron Microscopy with EDX. The membrane sample was first coated prior to analysis using the Field Emission Scanning Electron Microscopy (FE-SEM) model Helios Nanolab 600i. The surface was image at about 5,000x magnification with accelerating voltage of 5kV. The spectroscopy and distribution of the elements namely Copper (Cu), Carbon (C), Sulfur (S), Oxygen (O) and Nitrogen (N) were mapped at the surface of the membrane using Energy Dispersive X-ray (EDX).

Performance Measurement. Other performance parameters that were measured includes contact angle and pure water flux using a cross flow membrane filtration apparatus. The antibacterial performance of the membrane was evaluated through contact inhibition test using E. coli form.

3. Results and Discussion

3.1. Membrane Characterization

The result of the contact angle measurement of the PTU and PTU-Cu membrane are presented in figure 2. Higher contact angle was measured for the PTU-Cu indicating that its more hydrophobic compared
with the pristine PTU membrane. Hydrophobic membrane facilitates attachment of hydrophobic foulant and also reduces the efficacy of cleaning.

![Figure 2. Contact Angle Measurement](image)

The surface topography and average surface roughness (Ra) measurement of the membrane is shown in figure 3. Based on the image, pores are not observable at the surface and may reach nanofiltration or reverse osmosis range (<10 nanometers). This was also confirmed through measurement of pore size distribution using Porolux 100 and was not possible due to no flow at a maximum test pressure of 21 bars. Surface roughness value on the other hand shows smoother surface for the PTU-Cu membrane which is desirable to prevent fouling. Smoother surface has less surface area for the foulant to attach and thereby increase the efficacy of cleaning cycle during filtration through relaxation, shearing and backwashing.

![Figure 3. Surface Topography. (a) PTU Membrane, (b) PTU-Cu Membrane](image)

The electrostatic charge distribution and EFM phase map, Young’s modulus and adhesion force map of the membrane surface with the corresponding height image is shown in figure 4. The mean charge distribution of the PTU-Cu membrane has positive value compared with the PTU membrane which has negative value. The negative value is indicated by the negative sign of the mean phase value. The map also shows evenly distributed surface charge for both PTU and PTU-Cu except for the particles at the surface of the PTU-Cu membrane which are of relatively lower charge than the rest of the membrane. Ideally, membrane surface should have negative charge to inhibit the attraction and subsequent formation of the negative charge foulant [7].
Figure 4. Surface Charge, Adhesion and Modulus Map of PTU and PTU-Cu Membrane

The young’s modulus (YM) and adhesion map for PTU show some extreme values as depicted by lighter color in the image. Values higher than 50 Gigapascal (GP) were measured but were not considered in the calculation of the mean YM since it is beyond the range of the cantilever. These high values are concentrated in some areas and could be attributed to the different degree of polymerization. In comparison, the PTU-Cu membrane showed more uniform Young’s modulus as indicated by more uniform color contrast in the image. The mean value of YM is higher for the PTU compared to PTU-Cu. Although the copper provides crosslinking of the PTU polymer, the lower value maybe due to the thin layer of the PTU-Cu [6] on top of the PTU porous support. Liu et al. [8] has shown that YM of membrane is proportionally dependent on the thickness due to shear stress during fabrication. The rapid
complexation reaction at the interface of the PTU dope and CuAc solution creates a barrier preventing further diffusion of the Cu²⁺ into the dope solution resulting to a thin layer PTU-Cu. For the pristine PTU membrane, a relatively thicker dense separation layer may have form which is typical for a phase inversion process [9] resulting to higher value of YM and adhesion.

FESEM with EDX Analysis

The result of EDX mapping of various elements namely C, S, N, O and Cu at the surface of the PTU-Cu Membrane in Figure 4 shows uniform distribution of these elements along the membrane surface. The even distribution of copper indicates its successful incorporation at the surface through chemical bonding. The Map Sum Spectrum at the surface of the PTU-Cu Membrane in figure 6 shows around 4.7 to 5wt% copper. Based on the percentage weight of each element, the mole percentage is calculated from the wt% shown in spectra in table 1. The molecular percentage is similar to thiourea monomer with slight difference partly due to the incorporation of copper.

![Figure 5. Elemental Mapping at the Surface of the PTU-Cu Membrane: (a) SEM Image Composite Map, (b) Carbon (Kα1_2) (c) Sulfur (Kα1) (d) Copper (Lα1_2) (e) Nitrogen (Kα1_2) (f) Oxygen (Kα1)](image)

| Table 1. Calculated Mole Percentage of the PTU-Cu membrane |
|-----------------------------------------------------------|
| Element | Spectrum 1 | Spectrum 2 | Thiourea Monomer |
|--------|------------|------------|-----------------|
| C, mol%| 75.61      | 73.17      | 74.07           |
| N, mol%| 11.17      | 13.01      | 14.81           |
| S, mol%| 4.27       | 4.46       | 7.41            |
| O, mol%| 7.85       | 8.32       | 3.70            |
| Cu, mol%| 1.10       | 1.04       | -               |
3.2 Contact Inhibition Test

The result of contact inhibition test is shown in figure 7 shows positive inhibition for the PTU-Cu membrane. Furthermore, the minimal inhibition on the side of the membrane suggest minimal leaching of the components of the membrane.

3.3 Pure Water Flux

The plot of pure water flux for the membrane is plotted in figure 8. The measured stable flux is very low with values of 0.1 L/hr (Liter/hour) and 0.03 L/hr for the PTU and PTU-Cu membrane respectively at a transmembrane pressure (TMP) of 4 bars. This can be attributed to the small size of pores of the membrane.
4. Conclusion

Composite PTU-Cu Complex membrane was successfully synthesized through two-step phase separation process and was verified through SEM-EDX. Elemental mapping at the surface of the membrane shows uniform distribution of elements. EDX surface spectrum shows mole percentage similar to the thiourea monomer indicating successful polymerization of PTU.

Membrane characterization shows relatively high contact angle indicating hydrophobicity characteristic of the membrane. Furthermore, the positive surface charge of PTU-Cu membrane is not ideal to inhibit fouling formation. Cross-linking of PTU with copper causes charge reversal from negative to positive relative to the pristine PTU membrane. However, the relatively smooth surface of the PTU-Cu membrane compared to PTU membrane is ideal to minimize fouling as a result of smaller surface area for the attachment of foulant.

The mean young’s modulus for the pristine PTU membrane is relatively higher compared to the PTU-Cu composite membrane. This may be due to the thinner layer of the PTU-Cu composite membrane above the porous PTU support relative to the pristine PTU membrane.

Microbial testing shows positive contact inhibition with minimal inhibition on the side suggesting that component is not leaching out from the membrane.

The synthesized PTU-Cu composite membrane needs further development in order to increase pore size and consequently the water flux for typical water purification application. Its hydrophilicity in terms of contact angle and surface charge should also be improved further to improve its antifouling characteristics. The surface characteristics of the membrane maybe applicable for application to separation process such as membrane distillation where hydrophobic membrane is desirable.
5. References

[1] Zahid M, Rashid A, Akram S, Rehan ZA, Razzaq W. A Comprehensive Review on Polymeric Nano-Composite Membranes for Water Treatment. *J Membr Sci Technol*. 2018;08(01):1–20. Available from: https://www.omicsonline.org/open-access/a-comprehensive-review-on-polymeric-nano-composite-membranes-for-water-treatment-2155-9589-1000179-100149.html

[2] Tiraferrì A, Vecitis CD, Elimelech M. Covalent Binding of Single-Walled Carbon Nanotubes to Polyamide Membranes for Antimicrobial Surface Properties. *ACS Appl Mater Interfaces*. 2011 Aug 24 [cited 2017 Nov 4];3(8):2869–77. Available from: http://www.ncbi.nlm.nih.gov/pubmed/21714565

[3] Wang Z, Tang Y, Wang T, Liang K. Nano CuAl 2 O 4 spinel mineral as a novel antibacterial agent for PVDF membrane modification with minimized copper leachability. *J Hazard Mater*. 2019;368(September 2018):421–8. Available from: https://doi.org/10.1016/j.jhazmat.2019.01.081

[4] Mauter MS, Wang Y, Okemgbo KC, Osuji CO, Giannelis EP, Elimelech M. Antifouling ultrafiltration membranes via post-fabrication grafting of biocidal nanomaterials. *ACS Appl Mater Interfaces*. 2011;3(8):2861–8.

[5] Li R, Wu Y, Shen L, Chen J, Lin H. A novel strategy to develop antifouling and antibacterial conductive Cu/polydopamine/polyvinylidene fluoride membranes for water treatment. *J Colloid Interface Sci*. 2018;531:493–501. Available from: https://doi.org/10.1016/j.jcis.2018.07.090

[6] Villalobos LF, Karunakaran M, Peinemann KV. Complexation-induced phase separation: Preparation of composite membranes with a nanometer-thin dense skin loaded with metal ions. *Nano Lett*. 2015;15(5):3166–71.

[7] Miao Y, Guo X, Jiang W, Zhang XX, Wu B. Mechanisms of microbial community structure and biofouling shifts under multivalent cations stress in membrane bioreactors. *J Hazard Mater*. 2017;327:89–96. Available from: http://dx.doi.org/10.1016/j.jhazmat.2016.12.028

[8] Liu M, Sun J, Sun Y, Bock C, Chen Q. Thickness-dependent mechanical properties of polydimethylsiloxane membranes. *J Micromechanics Microengineering*. 2009;19(3).

[9] Machado PST, Habert AC, Borges CP. Membrane formation mechanism based on precipitation kinetics and membrane morphology: at and hollow ®ber polysulfone membranes. *J Membr Sci*. 1999;155:171–83.

6. Acknowledgments

This research was supported by the Philippine Council for Industry Energy and Emerging Technologies Research and Development (PCIEERD) and the Science Education Institute (SEI) of the Philippine Department of Science and Technology (DOST). Membrane preparation and characterization was conducted at the Advanced Device and Materials Testing Laboratory (ADMATEL) and at the Nanolab of the Materials Science Division (MSD) of the Industrial Technology Development Institute (ITDI) of DOST. Contact Inhibition was conducted at the Environment and Biotechnology Division (EBD) of ITDI. The Pin-point nanomechanical analysis on the membrane samples was conducted at the Park System’s office in Singapore by their application specialist Dr. Pan Hui-hui.