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Fabrication and Characterization of Polycaprolactone / Nanozeolite Membrane Films via Phase Inversion Technique

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Abstract. This research focused on the fabrication and characterization of polycaprolactone (PCL)/nanozeolite(NZ) membrane films. PCL/NZ membrane blends were produced at varying amounts of NZ (0 wt. %, 0.5 wt. % and 1.0 wt. %).The membranes produced were characterized using a.) Scanning Electron Microscopy (SEM) in determining the surface morphologies, b.) UTM to evaluate the effect of NZ addition on the tensile strength of PCL, and c.)contact angle goniometer to investigate the effect of NZ on the wettability of PCL/NZ membrane blends. Upon characterization, the SEM result showed that increasing NZ concentration increased the presence of pores and pore-like structures on the PCL/NZ system. Also, the tensile strength of the PCL/NZ blend improved with the addition of NZ. Lastly, the contact angle measurements obtained showed enhanced membrane hydrophilicity because of the hydrophilic NZ present on the matrix. The incorporation of NZ on PCL generally improved its properties based the different characterizations conducted.

1. Introduction
Tremendous amounts of plastic materials are being produced and utilized each year due to numerous desirable properties being exhibit by this type of materials. Plastic materials are being used in many industries such electronics, construction, medicine and automotive because of their good performance throughout their service life and durable mechanical properties when exposed to weathering and harsh environments [1]. But accompanied by the increasing plastic material utilization is its increasing detrimental effect on the environment due to improper disposal of plastic waste. With this as a concern, consumers are shifting to the use of biodegradable polymers which addresses the disposal issues of plastic materials that usually ends in landfills [2].

Due to catastrophic environmental impact of plastic wastes, researchers focused on biodegradable plastics derived from renewable biomass which can be biologically degraded into components that are not harmful to the environment. In this regard, the production for biodegradable plastics increases due to its diverse applications [3]. One of the biodegradable plastics that has promising mechanical properties, and high potential for wide applications is polycaprolactone (PCL) [4]. But despite its good

characteristics, considering that it is a biodegradable polymer, PCL still needs improvement in terms of its technical performance, especially when compared to several conventional polymers [2]. Due to this reason, enhancement of polymer properties can be done by fabricating nanocomposites through the addition of nanofillers[2,5].

Several studies concerning on the improvement of PCL properties were conducted by researchers. In particular, fabrication of nanofibrousnanocomposite of PCL using nanofillers were studied by other researchers as a potential material for wastewater treatment. In the study conducted by Irandoost et *al*., (2019)[6], they fabricated PCL nanofibrousnanocomposites by incorporating nanoclay and nanozeolite (NZ) to improve its Pb^{2+} adsorption from the prepared aqueous solution. They found out that increasing clay minerals concentrations resulted to the increase in the Pb^{2+} adsorption by the PCL nanofibrousnanocomposite. Furthermore, improvement of heavy metal adsorption of electrospunnanofibers by nanoclay addition is evident in the study of Tolentino et *al*. (2019)[7]. In their study, incorporation of iron-modified NZ to the cellulose acetate matrix increased its adsorption capacity for the removal of Ni^{2+} ions from simulated wastewater.

Most researchers focus on heavy metal removal application of PCL reinforced with nanoclays through adsorption experiments. But the interaction of between PCL and nanoclays, such as NZ, as well as the mechanical properties should also be taken into account. The aim of this study was to produce PCL/NZ reinforced membrane films. Specifically, the objectives of this study were the following: a.) fabricate PCL/NZ membrane films at different NZ loadings through hand-casting method; b.) characterize the surface morphologies and cross-sections of the membrane films produced through Scanning Electron Microscopy (SEM); c.) determine the mechanical properties of the membranes by means of Universal Testing Machine (UTM); and lastly, d.) investigate membrane-water interaction through the use of contact angle goniometer.

This research can be a fundamental study for PCL/NZnanocomposite and can serve as a basis in determining the potential application for similar component systems.

2. Methodology

Different membrane blends were fabricated using PCL and NZ. PCL was first added to the solvent n-methyl-2-pyrollidone (NMP) with constant stirring until a homogeneous mixture was produced. Then, varying amounts of nanozeolite were added to produce different PCL/NZ blends (0 wt. % or pure PCL, 0.5 wt. % NZ and 1.0 wt. % NZ). The resulting mixtures continuously stirred and heated to 100°C until homogenization occurred. The mixtures were cooled down to room temperature to remove the bubbles brought about by the constant stirring. Hand-casting process was done by pouring each resulting mixture on the glass plate, and was spread evenly using a casting knife with 30 μm thickness. The films produced were immersed in the coagulation bath containing deionized water for 20 minutes to facilitate membrane formation. The membranes produced were set aside and air-dried for 24 hours. Characterization of the different membrane blends produced were conducted using the following techniques: a.) SEM (Hitachi S-3400N) for surface morphology and cross-section analyses; b.) UTM (Shimadzu UTM Model AGS-IKNX) for mechanical properties determination; and lastly, c.)contact angle goniometer (Theta Optical Tensiometer) for wettability assessment. Statistical analysis (ANOVA and post hoc test) of the contact angle measurements were also done to further verify the significance of NZ addition on PCL in terms of wettability.

3. Results and discussion

3.1. Surface morphology and cross-section analysis

Based on the results of SEM imaging (Figure 1), considering both the surface morphology and the cross-sectional image obtained, the appearance of pores was observed upon the addition of NZ on PCL. Moreover, the presence of pores or pore-like structures was evident with increasing NZ concentration (comparing Figure 1.a and Figure 1.b). Going in to detail, this phenomenon was due to the membrane fabrication technique that was used, which was phase inversion or phase separation process. Initially, PCL is a hydrophobic material due to its long hydrocarbon chains. Meanwhile, NZ is hydrophilic primarily because of the hydroxyl groups (-OH) present on its structure. During the phase inversion

process, wherein the casted mixture was placed in the coagulation bath, the PCL/NZ mixture tend to attract water molecules on its system due to hydrophilic NZ that was present. In addition to this, the solvent for the PCL/NZ mixture used was NMP, which has a good miscibility with water. These factors can be correlated to the phase inversion exchange rate between the solvent, NMP, and water. This resulted to a higher possibility of having PCL/NZ (polymer) – water interaction. Once the membranes produced were removed from the coagulation bath and air-dried, the water molecules that underwent phase inversion with the solvent in the PCL/NZ system evaporated which produced to void spaces in the membrane system, and were regarded as pores[8].
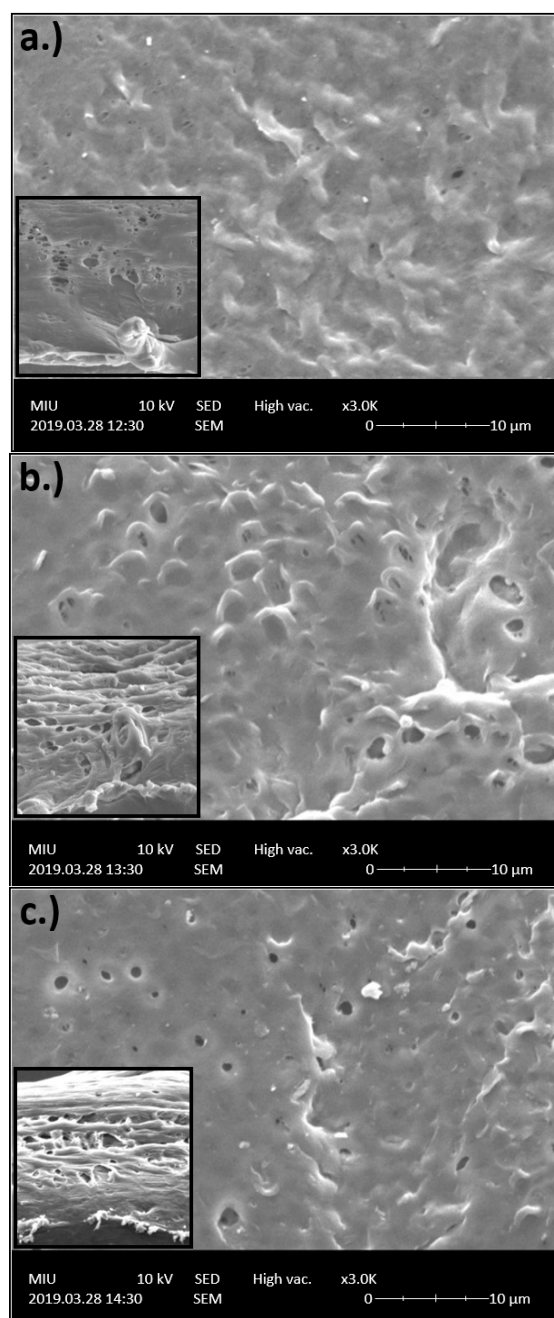

Figure 1.SEM images of the different membrane blends a.)pure PCL, b.) 0.5 wt. % NZ, and c.) 1.0 wt. % NZ at 3000x magnification (surface morphology and cross-section).

3.2. Determination of mechanical properties

To investigate the mechanical properties of the different membrane blends produced, specifically the tensile strength, a UTM was utilized. Based on the results obtained which was shown in Figure 2, the incorporation of NZ on PCL resulted to the increase on the membrane's tensile strength. Improved membrane tensile strength can be attributed to the strong interfacial bonding present between NZ particles and PCL polymeric chains [8].
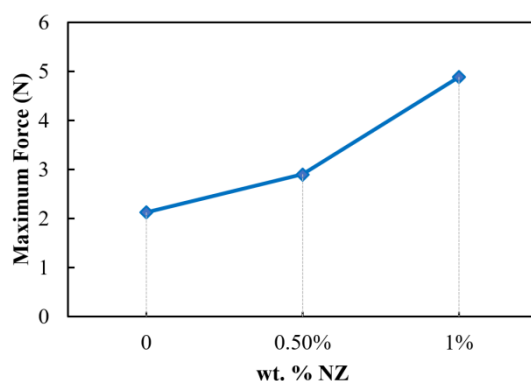

Figure 2. The tensile strength of the different membrane blends from the UTM.

3.3. Assessment of the membranes' wettability

The water contact angle for each membrane blend was measured using the goniometer. The results (Figure 3) showed that the addition of NZ particles on the PCL polymer matrix caused a significant decrease in terms of contact angle measurement. This decrease in contact angle measurement means increase in the membrane's hydrophilicity. Initially, pure PCL is hydrophobic in nature but upon the addition of the hydrophilic NZ, it can be seen that PCL/NZ membranes tend to become hydrophilic. NZ particles significantly increased the surface hydrophilicity of the PCL, which can be a great membrane property for wastewater treatment application since this would mean increase in water flux and antifouling ability [7,8]. Furthermore, the presence of NZ having -OH groups on the membrane's surface influenced its hydrophilic property. The -OH groups on the surface tend to form intermolecular attraction between the water molecules, primarily hydrogen bonding.
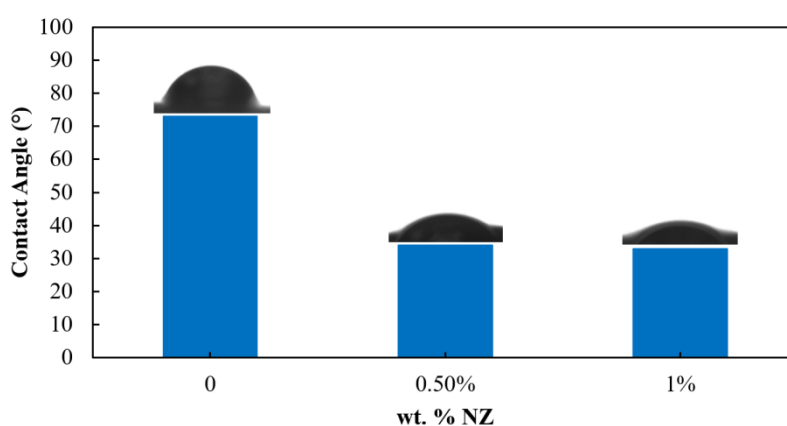

Figure 3. Contact angle measurement of the membrane blends.

3.4. Statistical analysis of the contact angle measurements

To confirm if the decrease in the contact angle measurements were statistically significant, ANOVA was conducted. The null hypothesis considered was no significant difference between the contact angle measurements obtained. Based on the result of the statistical analysis with 95% confidence level, the *p*-value was found to be less than 0.05. Thus, the decrease in the contact angle measurement due to NZ addition statistically significant. In order to determine where the significance between the measurements came from, a post hoc test was done. Based on the statistical computation, there was a significant difference between pure PCL and each of the blend. This further mean that aside from the

result of the contact angle measurement, the effect of the incorporation of NZ on PCL was statistically significant. Introducing NZ on PCL matrix really caused a significant effect in terms of the membranes' wettability.

4. Conclusion

The results of the study justified the objectives of the experiment. Different PCL/NZ membrane blends with varying NZ concentration were fabricated by hand-casting method through phase inversion technique. It was found out from the SEM results that increasing the concentration of NZ on the membrane facilitated the increase in the formation of pores in the membrane. The results from the UTM showed that the presence of NZ particles on PCL polymeric matrix can improve its tensile strength by means of forming interfacial bonds. With regards to the data from the goniometer, it was found that adding NZ on PCL significantly increased the hydrophilicity of the membrane due to the hydrophilic nature of NZ. This was further supported by the statistical analysis that was conducted.

5. References

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