Accelerated Hydrothermal Degradation and Biodegradation of Electrospun Polycaprolactone Montmorillonite Nanofiber Membrane

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Abstract *– The nanocomposite of montmorillonite (MMT) clay and polycaprolactone (PCL) have been reported to successfully serve as a reusable adsorbent of heavy metal from wastewater from metal extraction. In this study, the degradability of the electrospun polycaprolactone (PCL) nanofiber membrane, as support material to MMT, was evaluated through accelerated hydrothermal degradation and biodegradation as a continuous effort to be able to appropriately discard the spent adsorbent materials. In the hydrothermal conditions, the membranes were immersed in NaOH solution and* H_2O *at 35* ^oC *and 45* ^oC *at specific durations. While for the biodegradation, alkali-treated and untreated membranes were buried in two separate media, i.e. soil and compost, to evaluate the natural decomposition. The extent of degradation measured via gravimetry showed that the alkali-treated membranes subjected to hydrothermal degradation had the highest weight loss that ranged from 27% to 96% after 24 hours of immersion. The membranes buried in compost had weight loss ranging from 77% up to 100% after three (3) weeks of being in the ground. Compared to membrane made of pristine PCL polymer, it was also shown that MMT improved the degradability of the membrane such that 96% of weight loss was already observed after 24 hours of hydrothermal immersion and 100% weight loss after three (3) weeks of ground covering. This could have been brought about by the decrease in the degree crystallinity of the support polymer which was almost 30% lower compared to the pristine material. It was also found that biodegradation in compost was better than in soil such that a maximum weight loss of 100% in compost was observed compared to 70% weight loss in soil after 3 weeks. The former was found to contain 180 times more microorganisms than soil which could be responsible for the higher biodegradation performance. These results would be useful in establishing protocols for the disposal of PCL and its derivatives after being used in various applications not just in wastewater treatment but also in other applications like biomedical devices in the medical industry.*

Keywords—Degradation, Polycaprolactone, Montmorillonite, Nanocomposite Membrane, Biodegradation, Hydrothermal Degradation, Nanofiber Membrane

I. INTRODUCTION

The montmorillonite clay composite had been known to immobilize heavy metal contaminants, i.e., arsenic, from aqueous solution [1]. But direct application of adsorbent particles present difficulty in collecting saturated materials. To address this, Araño et al. [2] incorporated the particles in an electrospun polycaprolactone (PCL) nanofiber membrane. Polycaprolactone is a biodegradable polymer that can be formed to membrane at low temperatures [3], [4] making it a viable matrix of MMT. The membrane production techniques available are phase inversion, interfacial polymerization, stretching, track-etching, and electrospinning [5]. Among these techniques, the electrospinning process offers a feasible approach in fixing the MMT particles in the membrane while exposing active sorption areas.

The electrospinning process utilizes a solution that passes through a capillary tube ejecting a stream of fibers onto an electrically conducting collector. The fibers were attracted to the collector through the potential difference between the capillary tip and the collector [6]. Numerous studies [2], [7]–[10] had been reported on the successful synthesis of the PCL-nanoclay as composite membrane through the electrospinning process.

The wide use of PCL could also be attributed to its biodegradability. The degradation behavior of PCL has been extensively investigated under enzymatic [11]–[17] or hydrolytic [18]–[21] conditions. Lu and co-authors [22] noted that both enzymatic and hydrolytic degradation could occur in the presence of microorganism and in simulated seawater. The enzymatic degradation is proposed to undergo a two-step process; (i) the attraction of enzymes to the PCL caused by the surface potential and (ii) the enzyme catalyzed hydrolysis reaction that is dependent on the nature and concentration of enzyme [23]. The route of hydrolytic degradation can proceed from the surface of the material and followed by diffusion-controlled reaction [20]. In both mechanisms, the degradation rate was depressed by the increase in crystallinity of PCL [14], [19]–[21], [24]–[26]. Moreover, Kim et al. [13] reported that the soil covering position affects the degradation rate in the presence of enzyme.

The incorporation of organically modified montmorillonite in PCL by melt mixing and improvement in the mechanical property [27] and thermal stability [28] of PCL-clay composite were reported. Meanwhile, Franca and co-authors [29] showed that the molded PCL-montmorillonite products were not susceptible to hydrolytic degradation. This shows that processing conditions would introduce defects and alters the crystallinity, thereby affecting the degradability of PCL. The aim of this work was to evaluate the degradability of the electrospun PCL nanofiber membrane with MMT fillers and further correlate this to the effect of the addition of MMT to the crystallinity of the PCL polymer matrix. Alkali treatment, degradation technique, and medium of the degradation were also evaluated.

1.1 Experimental Procedure

Preparation of Nanofiber Composite Membrane

The nanofiber composite membrane preparation was adapted from the procedure of Masih et al. [3], Dela Cruz et al. [5], and Araño et al. [1], [2], [30]. All MMT used were sourced from Southern Clay Products. The sodium in montmorillonite with a trade name of Cloisite Na^+ was exchanged with iron using reagent-grade anhydrous ferric chloride ($FeCl_3$) from Techno Pharchem and were hydrolyzed with reagent-grade NaOH to produce the iron-modified montmorillonite (MMT). The modified MMT was electrospun with 80,000 average molecular weight polycaprolactone (PCL) from Sigma Aldrich as the supporting polymer at 3% and 90% w/w, respectively. A 7 wt% of organically modified montmorillonite, i.e. Cloisite 25A, was used to stabilize the PCL-MMT electrospinning suspension in dichloromethane solvent. A horizontal electrospinning set-up with a 20 kV voltage source and rotating drum collector were utilized to produce the PCL-MMT nanofiber membrane with 0.09 to 0.17 mm thickness and fiber diameters of 500 nm and 300 nm for PCL and PCL-MMT [5], respectively. The drum angular velocity and syringe tip to collector distance were maintained at 7.3 rad/s and 100 mm, respectively.

To investigate the occurrence or morphology of MMT in the nanofiber, the electrospun PCL-MMT was observed using the Hitachi SU-3500 scanning electron microscope (SEM) coupled with energy dispersive x-ray (EDX) for compositional analysis. The behavior of electrospun nanofiber membrane upon exposure to heat was also observed using a Q200 differential scanning calorimeter from TA Instruments following a heat-cool-heat thermal profile of 5-10 mg nanofiber membrane heated at 10 °C/min from -40°C to 300 °C. The heat of fusion of PCL ($\Delta H_{f\ 100\%}$) and PCL-MMT (ΔH_f) were also obtained from the DSC thermogram and was used to estimate their degree of crystallinity, X_c , by applying Eq. 1 [31] and Eq. 2 [32], respectively. The $\Delta H_{f\ 100\%}$ is equivalent to 139.5 J/g and was taken

$$X_{c_{PCL}} = \frac{\Delta H_f}{\Delta H_{f_{100\%}}} x\ 100 \qquad \text{Eq. 1}$$

$$X_{c_{PCL-FeMMT}} = \frac{\Delta H_f}{\Delta H_{f_{100\%}}\ x \left(1 - \frac{wt\%_{filler}}{100}\right)} x\ 100 \qquad \text{Eq. 2}$$

as the heat of fusion of 100% crystalline PCL [33], and $wt\%_{filler}$ is the total amount of nanofiber membrane.

Hydrothermal Degradation Test

An accelerated degradation test was performed with 1M NaOH as the degradation media and at thermal conditions of 35°C and 45°C, which was maintained inside a Memmert UF-55 oven. A 4 cm^2 membrane was enclosed in a polyester cloth for ease of retrieval and immersed in NaOH solution for 24 hours. A total of 3 replicates were collected every 8 hours and were washed thoroughly with distilled water and stored in a desiccator for a week to dry. The retained weight after the hydrothermal degradation were measured thereafter.

Biodegradation Test

The biodegradation test was done by covering a 4 cm^2 membrane enclosed in a polyester cloth in soil and compost medium. The media were placed in polypropylene containers with drain holes. The soil was acquired from a small-scale mining site in Itogon Benguet, Philippines, with the coordinates of 16°22.681'N, 120°37.743'E to resemble the actual disposal site, and the compost was from the Materials Recovery Facility of the University of the Philippines, Quezon City, Philippines. The organic component of the soil and compost media was determined using ultraviolet-visible spectrometer (UV-Vis) PerkinElmer LAMBDA 25 following the Walkley-Black Method. The nitrogen content was estimated through the Kjeldahl method and the bacteria and fungi content were counted using the Galaxy 230 Colony Counter from Rocker Scientific. No replicate was done on measuring the organic component and the nitrogen content of the biodegradation media.

The membrane in the polyester cloth were buried at a depth of 4 – 6 cm. Water content in the soil or compost medium was maintained by watering it with 100 mL of distilled water every 3 days. The samples in 3 replicates were recovered at a predetermined interval for 3 weeks. The collected samples were then washed thoroughly with distilled water and dried inside a desiccator for a week prior to examination. The alkali pre-treatment was carried out immersing the membrane in a 1 M NaOH for 8 hours before biodegradation. The exposure of a high pH solution were widely applied to accelerate the degradation PCL [34], [35]. The retrieved samples underwent visual inspection and dried in desiccator for a week prior to obtaining the weight.

II. RESULTS AND DISCUSSION

The electrospun nanofiber membranes were subjected to morphological analysis to investigate variation in microstructure and occurrence of the MMT filler in the nanofiber membrane. The micrographs of nanofibers with and without MMT filler are shown in Figure 1. Both micrographs show entangled nanofibers that makes the membrane with fiber diameters varying from micrometer to nanometer range [2]. A distribution of white specks can also be observed on the PCL-MMT nanofiber membrane. An EDX analysis revealed the particles to be agglomerates of MMT given the detection of Si, Al, Mg, and Fe elements in Figure 2. These elements were similarly found in montmorillonite structure [36] and the modification of the material by replacing the Na ions in the interlayer spacing as well as at the edges of the nanoclay structure with Fe [37]. These membranes were subjected to different degradation conditions to determine the effect of adding MMT to the system.

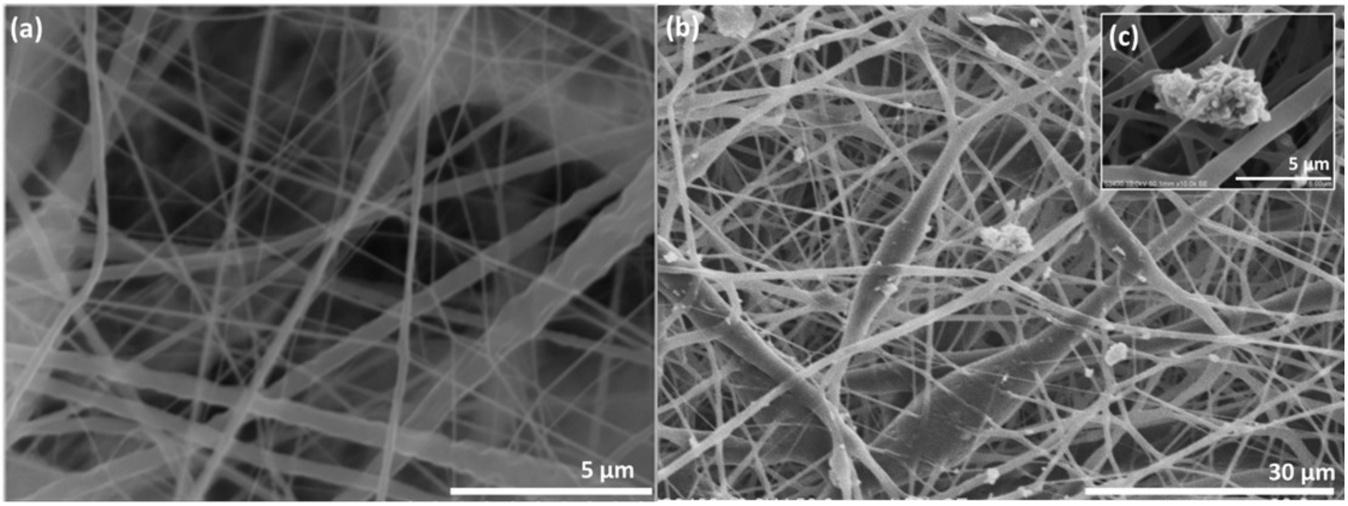
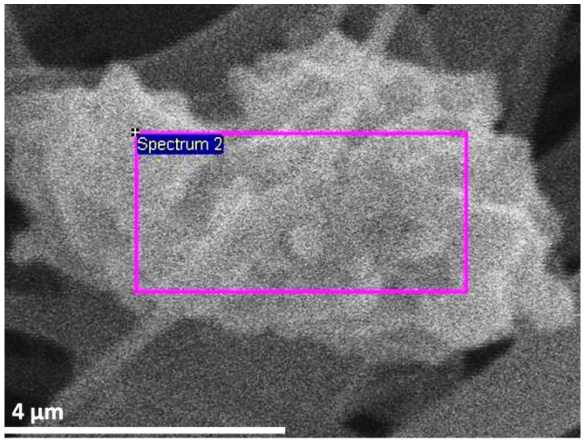


Figure 1. Morphological variation between (a) PCL nanofiber, (b) PCL-MMT nanofiber, and (c) an inset showing MMT in PCL-MMT as observed under the SEM at different magnification.



Element	Weight %
Fe	47.54
O	28.27
Ca	9.27
Na	4.44
Si	3.66
Mg	3.58
Al	3.24
Total	**100.00**

Figure 2. Composition of the agglomerate observed in Figure 1 as determined from energy dispersive X-ray spectroscopy. Specific area of analysis is indicated by the area enclosed by the purple box.

Hydrothermal Degradation

The hydrothermal degradation test was conducted on the nanofiber membranes and the resulting degradation performance are shown in Figure 3. The membranes exhibited varying degrees of degradation at different immersion medium, time and temperature. At eight (8) hours immersion in both water and NaOH, no appreciable physical damage was observed yet. After sixteen (16) hours, holes were already visible particularly on PCL-MMT immersed in NaOH at 35 °C and 45 °C, and PCL in NaOH at 45 °C. The PCL in NaOH at 35 °C only exhibited holes after 24 hours while the rest almost completely degraded at this time. The corresponding average weight loss of the hydrothermally treated samples with are presented in Figure 4. All samples, PCL and PCL-MMT membranes, immersed in NaOH solution exhibited a higher final weight loss as compared to their counterparts immersed in water. This is expected because NaOH has been reported to promote ester hydrolysis [34], [35], which is the typical mechanism of PCL degradation. In contrast, the samples immersed in water showed no hydrolysis reaction in the immersion experiment because of the relatively low level, between 3 to 7 wt. %, of recorded weight loss [29]. Meanwhile, the addition of MMT brought a relatively much higher increase in the weight loss of samples as exhibited by the 100% weight loss of PCL-MMT membrane in comparison to the 35% weight loss of PCL membrane subjected to 24 hours of hydrothermal alkali treatment at 45°C. The presence of MMT was reported to decrease the fiber diameter by almost 200 nm [2]. The large surface area-to-volume ratio of PLC-MMT membrane made it more susceptible to degradation than the PCL membrane [38]. Finally, an increase in 10 °C of temperature resulted in a reduction of weight. This observation suggests a diffusion-controlled reaction accelerated by a higher temperature [21]. Moreover, the slight weight gain observed when samples were immersed in water can be explained by the absorption of water in PCL as reported by Franca et al. [29] where it was associated to the swelling of PCL.

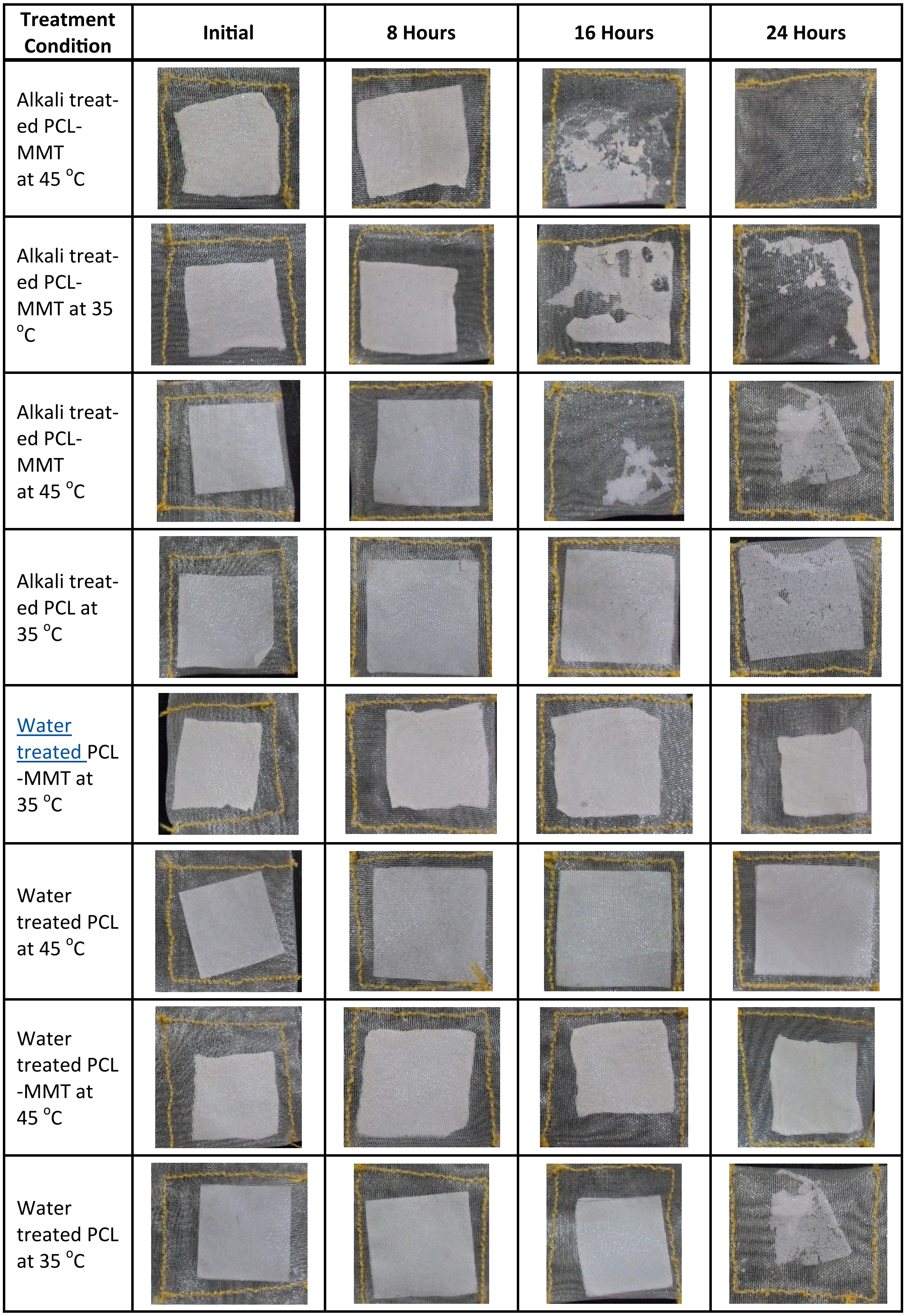


Figure 3 Macrographs of the nanofiber membrane before and after exposure to different solution condition, temperature, and immersion time.

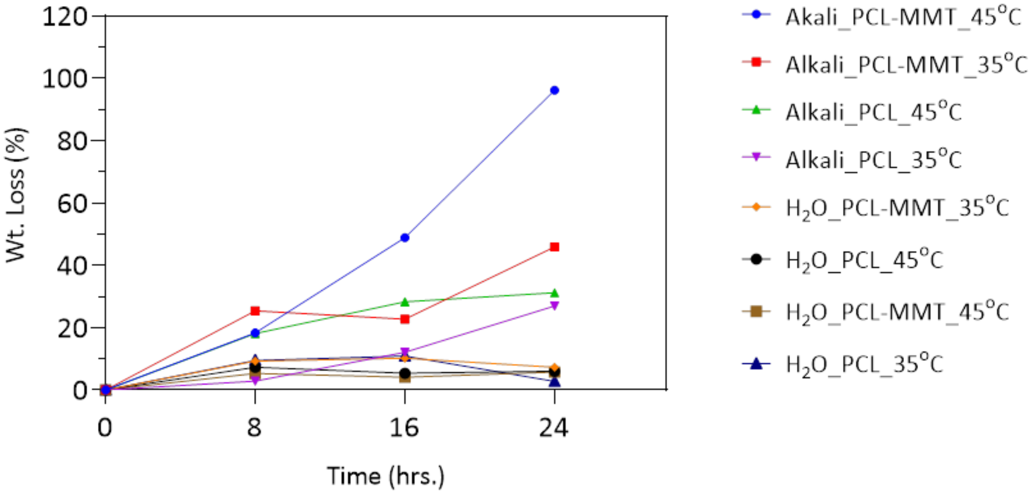


Figure 4. The average weight loss in the hydrothermal degradation of nanofiber membrane immersed in alkaline solution and in water at 35 oC and 45 oC over time.

Biodegradation

The ground covering test was conducted to evaluate the degradation of the material in a more cost-effective and environmental approach. The use of natural medium, i.e. soil and compost, closely resembles the natural degradation set-up in the mine sites where the spent adsorbent membrane will eventually be generated. The macrographs showing extent of degradation over 3 weeks is shown in Figure 5. After one (1) week, the membranes already exhibited signs of degradation manifested by the presence of holes in random locations on the membrane. On the 2nd week, most of the membranes have completely degraded leaving few patches from the original membrane. Finally, the samples after the 3rd week had already been completely degraded except for the alkali treated PCL-MMT buried in soil medium. The equivalent weight of the degraded nanofiber membranes was recorded, and the average weight loss is presented in Figure 6. The membranes embedded in compost all exhibited a high overall reduction in weight after three weeks compared to their counterparts covered with soil. An exception to the trend is however observed for the alkali-treated PCL-MMT that has a lower weight loss of 77% compared to the untreated PCL-MMT that exhibited 100% weight loss after three weeks in compost. Alkali-treatment is seen to accelerate the degradation of PCL-MMT membranes but not of PCL membranes. In fact, the high pH treatment seemed to have delayed biodegradation of PCL membranes in the biodegradation set-up.

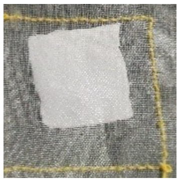
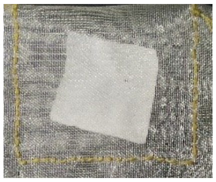
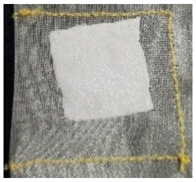
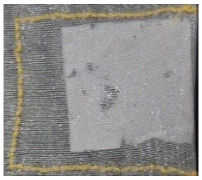
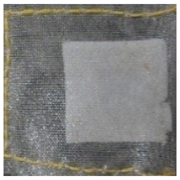
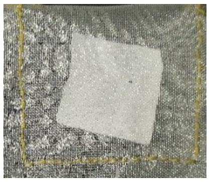
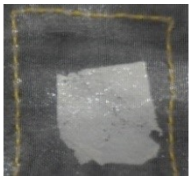
Treatment Condition	Initial	Week 1	Week 2	Week 3
Alkali treated PCL-MMT in Compost				
Alkali treated PCL-MMT in Soil				
PCL-MMT in Compost				
PCL in Compost				
Alkali treated PCL in Compost				
PCL-MMT in Soil				
PCL in Soil				
Alkali treated PCL in Soil				

Figure 5. Macrographs of the different types of nanofiber membranes before and after the exposure in different ground conditions and ground covering duration.

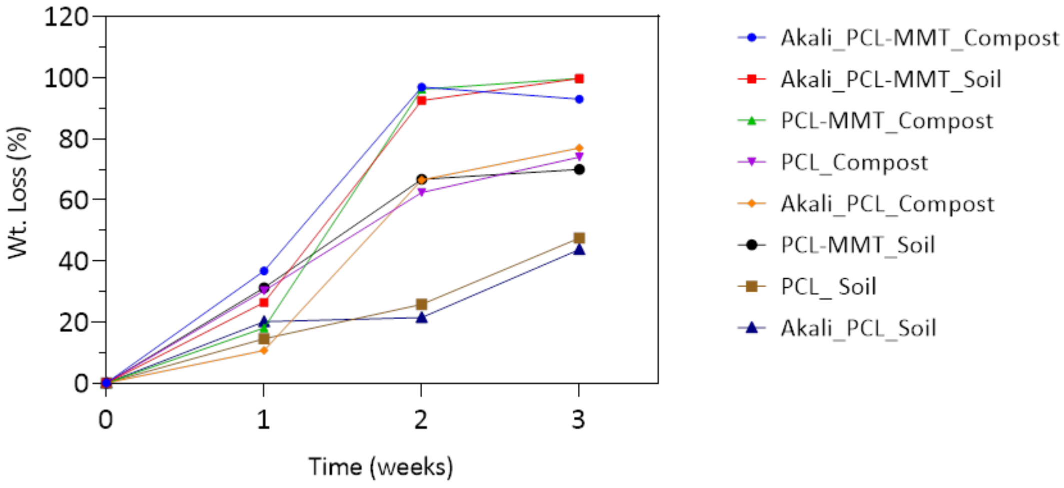


Figure 6. The average weight loss in the biodegradation of nanofiber membrane with and without alkali -treatment and covered by soil and compost over time

To distinguish the difference between the quality of soil and compost as biodegradation medium, their physiochemical properties were determined and summarized in Table 1. The compost medium contains 180 times more microorganisms than soil medium. These microorganisms, like bacteria and fungi, produce enzymes that drive the degradation of polyesters [14], [35]. In addition, the compost has almost 9 times more organic matter hence, microorganisms can thrive in it more leading to more enzymes available for the degradation reaction. Therefore, the high weight losses of samples buried in compost and soil should be an enzymatically driven degradation [11], [12], [16]. The alkali pre-treated membranes were expected to heighten the weight loss due to biodegradation after one (1) week because of the exposure of the membrane surface to hydroxide ions that enhances the hydrolysis process [39]. But such was not observed in the time interval selected. It is possible that presence of hydroxide is not favorable to the microorganisms and may have caused their death [39], [40] in the region close to surfaces of the alkali-treated membranes.

Table 1. Physiochemical properties of degradation media for the ground covering test.

Medium	**pH**	**% Organic Matter**	**% Nitrogen**	**Bacteria (CFU/g)**	**Fungi (CFU/g)**
Soil	8.3	0.64	0.03	4.20×10^5	3.20×10^3
Compost	8.3	5.67	0.39	7.50×10^7	1.20×10^6

In order to understand the difference in the degradation behavior of PCL and PCL-MMT composite nanofiber membranes, which is thought to be a consequence of the decrease in the degree of crystallinity of PCL upon addition of MMT, the degree of crystallinity was estimated from their enthalpy of fusion using Eq. 1 and Eq. 2. The DSC thermogram of PCL and PCL MMT is presented in Figure 7 and the summary of thermal properties is listed in Table 2. The crystallization temperature, T_x, of PCL shifted to a lower value from 33.3 °C to 30.5 °C upon the addition of Fe-MMT while a negligible change in melting temperature can be observed. The estimated enthalpy of melting, ΔH_f, of PCL and PCL-MMT are 64.5 J/g and 40.7 J/g, respectively. These correspond to a degree of crystallinity of 46.2% for PCL nanofiber membrane and 32.4% for PCL-MMT nanofiber membrane. The reduction of crystalline region in the PCL suggests an increase in readily degradable amorphous region [14], [15], [20], [35], [41], which explains the high weight loss of membranes containing MMT in Figure 4 and Figure 6. The amorphous region contains loose polymer chains making it more susceptible to chemical attack and therefore degrades easily [42].

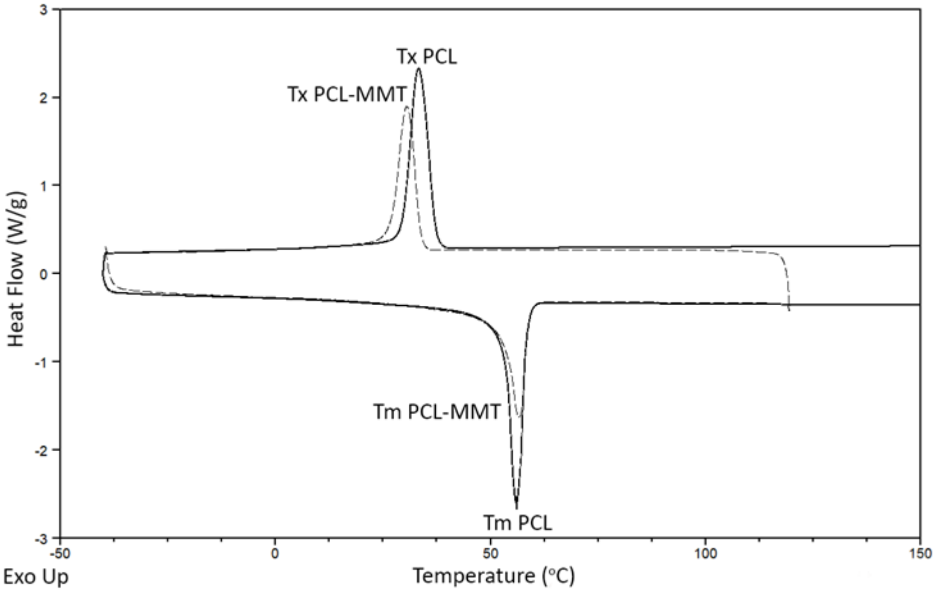


Figure 7. DSC curves of PCL-MMT (broken line) and PCL (solid line) showing the positive exothermic crsytallization peaks and the negative endothermic melting peaks.

Table 2. Thermal properties and degree of crystallinity of the PCL and PCL-MMT nanofiber membranes obtained from the DSC curves.

Sample	**Melting Temp, Tm (°C)**	**Crystallization Temp., Tx (°C)**	**ΔH_f (J/g)**	**X_C (%)**
PCL	56.1	33.3	64.5	46.2
PCL MMT	56.6	30.5	40.7	32.4

III. CONCLUSION

The synthesized PCL nanofiber composite membrane was successfully shown to be degraded through hydrothermal method and biodegradation methods. Hydrothermal degradation is accelerated in alkali solutions and thermal activation wherein 100% weight loss of the PCL-MMT membrane was obtained when immersed in alkali solution at 45 °C for 24 hours compared to only 50% weight loss when done at 35 °C and less than 10% weight loss when immersed in water. In the case of biodegradation of the adsorbent membrane, it was shown that highest degradation was achieved in membranes covered in compost such that 100% weight loss can be achieved after three weeks of degradation. The high microbial population in compost is thought to be responsible for this difference given that the compost had 180 times more microbial population than soil from the mine site. Alkali-treatment, however, showed a delaying effect to degradation such that alkali-treated PCL-MMT buried in soil had only 77% weight loss after three weeks of being in the ground while the untreated PCL-MMT buried in soil exhibited 100% weight loss. In both hydrothermal degradation and biodegradation, it was shown that addition of MMT to PCL membrane accelerated degradation and this was supported by the fact that addition of MMT decreased the degree of crystallinity of PCL matrix. These findings are favorable for the management of waste obtained from the treatment of wastewater from metal extraction. Being able to degrade the adsorbent material in three weeks using biodegradation or in 24 hours using hydrothermal method will prevent accumulation of solid waste from spent adsorbent membranes.

IV. ACKNOWLEDGEMENTS

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References

[1] D. Masih, Y. Izumi, K. Aika, and Y. Seida, "Optimization of an iron intercalated montmorillonite preparation for the removal of arsenic at low concentrations," *Eng. Life Sci.*, vol. 7, no. 1, pp. 52–60, 2007.

[2] K. Araño, M. L. Dela Cruz, E. M. Dela Pena, and L. J. Diaz, "Qualitative Analysis of the Effect of Polymer Solution and Suspension Properties on the Electrospinning of Nanocomposite Fibers," *Adv. Mater. Res.*, vol. 686, pp. 65–70, 2013.

[3] R. M. Mohamed and K. Yusoh, "A Review on the Recent Research of Polycaprolactone (PCL)," *Adv. Mater. Res.*, vol. 1134, pp. 249–255, 2015.

[4] L. S. Nair and C. T. Laurencin, "Biodegradable polymers as biomaterials," *Progress in Polymer Science (Oxford)*, vol. 32, no. 8–9. pp. 762–798, 2007.

[5] B. S. Lalia, V. Kochkodan, R. Hashaikeh, and N. Hilal, "A review on membrane fabrication: Structure, properties and performance relationship," *Desalination*, vol. 326, pp. 77–95, Oct. 2013.

[6] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, and S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites," *Compos. Sci. Technol.*, vol. 63, no. 15, pp. 2223–2253, Nov. 2003.

[7] G. Nitya, G. T. Nair, U. Mony, K. P. Chennazhi, and S. V. Nair, "In vitro evaluation of electrospun PCL/nanoclay composite scaffold for bone tissue engineering," *J. Mater. Sci. Mater. Med.*, vol. 23, no. 7, pp. 1749–1761, 2012.

[8] J. H. Roque-Ruiz, E. A. Cabrera-Ontiveros, J. Torres-Pérez, and S. Y. Reyes-López, "Preparation of PCL/Clay and PVA/Clay Electrospun Fibers for Cadmium (Cd+2), Chromium (Cr+3), Copper (Cu+2) and Lead (Pb+2) Removal from Water," *Water. Air. Soil Pollut.*, vol. 227, no. 8, 2016.

[9] Y. Dong, C. Qian, J. Lu, and Y. Fu, "Clay montmorillonite-poly(e-caprolactone) electrospun microfiber/epoxy composites with triple shape memory effect," *Pigment Resin Technol.*, vol. 47, no. 1, pp. 29–37, Jan. 2018.

[10] A. K. Gaharwar *et al.*, "Nanoclay-Enriched Poly(ε-caprolactone) Electrospun Scaffolds for Osteogenic Differentiation of Human Mesenchymal Stem Cells," *Tissue Eng. Part A*, vol. 20, no. 15–16, pp. 2088–2101, 2014.

[11] M. Shimao, "Biodegradation of plastics," *Curr. Opin. Biotechnol.*, vol. 12, no. 3, pp. 242–247, 2001.

[12] V. Toncheva, A. Van Den Buicke, E. Schacht, L. J. Mergaert, and J. Swings, "Synthesis and Environmental Degradation of Polyesters Based on Poly (-caprolactone)," *J. Enviroment Polym. Degrad.*, vol. 4, no. 2, pp. 71–83, 1996.

[13] Y. C. Kim, H. S. Jun, H. N. Chang, and S. I. Woo, "Effect of polymer position in nutrient-salt agar medium on fungal degradation of polycaprolactone," *Korean J. Chem. Eng.*, vol. 12, no. 3, pp. 320–324, 1995.

[14] T. Hayashi, H. Kanai, and T. Hayashi, "Enzymatic degradation of poly(ε-caprolactone) fibers in vitro.," *Polymer Journal*, vol. 33, no. 1. pp. 38–41, 2001.

[15] V. K. Khatiwala, N. Shekhar, S. Aggarwal, and U. K. Mandal, "Biodegradation of Poly(ε-caprolactone) (PCL) Film by Alcaligenes faecalis," *J. Polym. Environ.*, vol. 16, no. 1, pp. 61–67, 2008.

[16] M. Rutkowska *et al.*, "Biodegradation of Modified Poly(ε-caprolactone) in Different Environments," *Polish J. Environ. Stud.*, vol. 11, no. 4, pp. 413–420, 2002.

[17] D. Chen, H. Chen, J. Bei, and S. Wang, "Hydrolytic Degradation of Polyester- Polyether Block Copolymer Based on Polycaprolactone/Poly(ethylene glycol)/ Polylactide," *Polym. Int.*, vol. 276, no. July 1999, pp. 269–276, 2000.

[18] H. Tsuji and K. Suzuyoshi, "Environmental degradation of biodegradable polyesters. IV. The effects of pores and surface hydrophilicity on the biodegradation of poly(εcaprolactone) and poly[(R)-3-hydroxybutyrate] films in controlled seawater," *J. Appl. Polym. Sci.*, vol. 90, no. 2, pp. 587–593, 2003.

[19] J. M. Meseguer-Dueñas, J. Más-Estellés, I. Castilla-Cortázar, J. L. Escobar Ivirico, and A. Vidaurre, "Alkaline degradation study of linear and network poly(ε-caprolactone)," *J. Mater. Sci. Mater. Med.*, vol. 22, no. 1, pp. 11–18, 2011.

[20] M. A. Woodruff and D. W. Hutmacher, "The return of a forgotten polymer—Polycaprolactone in the 21st century," *Prog. Polym. Sci.*, vol. 35, no. 10, pp. 1217–1256, Oct. 2010.

[21] C. X. Lam, S. H. Teoh, and D. W. Hutmacher, "Comparison of the degradation of polycaprolactone and polycaprolactone–(β-tricalcium phosphate) scaffolds in alkaline medium," *Polym. Int.*, vol. 56, no. 6, pp. 718–728, Jun. 2007.

[22] B. Lu *et al.*, "Comparison of PCL degradation in different aquatic environments: Effects of bacteria and inorganic salts," *Polym. Degrad. Stab.*, vol. 150, no. November 2017, pp. 133–139, 2018.

[23] J. Zeng, X. Chen, Q. Liang, X. Xu, and X. Jing, "Enzymatic degradation of poly(L-lactide) and poly(ε-caprolactone) electrospun fibers," *Macromol. Biosci.*, vol. 4, no. 12, pp. 1118–1125, 2004.

[24] L. A. Bosworth and S. Downes, "Physicochemical characterisation of degrading polycaprolactone scaffolds," *Polym. Degrad. Stab.*, vol. 95, no. 12, pp. 2269–2276, 2010.

[25] A. Banerjee, K. Chatterjee, and G. Madras, "Enzymatic degradation of polymers: a brief review," *Mater. Sci. Technol.*, vol. 30, no. 5, pp. 567–573, 2014.

[26] A. Höglund, M. Hakkarainen, and A. C. Albertsson, "Degradation profile of poly(ε;-caprolactone)-the influence of macroscopic and macromolecular biomaterial design," *J. Macromol. Sci. Part A Pure Appl. Chem.*, vol. 44, no. 9, pp. 1041–1046, 2007.

[27] S. Kumar, A. Mishra, and K. Chatterjee, "Effect of organically modified clay on mechanical properties, cytotoxicity and bactericidal properties of poly(ε-caprolactone) nanocomposites," *Mater. Res. Express*, vol. 1, no. 4, 2015.

[28] L. N. Ludueña, J. M. Kenny, A. Vázquez, and V. A. Alvarez, "Effect of clay organic modifier on the final performance of PCL/clay nanocomposites," *Mater. Sci. Eng. A*, vol. 529, no. 1, pp. 215–223, 2011.

[29] D. C. França *et al.*, "Hydrolytic and Thermal Degradation of PCL and PCL/Bentonite Compounds," *Mater. Res.*, vol. 19, no. 3, pp. 618–627, 2016.

[30] M. L. Dela Cruz, K. Arano, E. M. Dela Pena, and L. J. Diaz, "Nanoclay-supported zero-valent iron as an efficient adsorbent material for arsenic," *Adv. Mater. Res.*, vol. 686, pp. 296–304, 2013.

[31] A. Heimowska, M. Morawska, and A. Bocho-janiszewska, "Biodegradation of poly (ε -caprolactone) in natural water environments," pp. 120–126, 2017.

[32] K. Fukushima, D. Tabuani, C. Abbate, M. Arena, and L. Ferreri, "Effect of sepiolite on the biodegradation of poly (lactic acid) and polycaprolactone," *Polym. Degrad. Stab.*, vol. 95, no. 10, pp. 2049–2056, 2010.

[33] Q. Guo and G. Groeninckx, "Crystallization kinetics of poly(ε-caprolactone) in miscible thermosetting polymer blends of epoxy resin and poly(ε-caprolactone)," *Polymer (Guildf).*, vol. 42, no. 21, pp. 8647–8655, 2001.

[34] M. Bartnikowski, T. R. Dargaville, S. Ivanovski, and D. W. Hutmacher, "Degradation mechanisms of polycaprolactone in the context of chemistry, geometry and environment," *Prog. Polym. Sci.*, vol. 96, pp. 1–20, Sep. 2019.

[35] N. C. Billingham, *Degradable polymers: Principles and applications*, vol. 53. 1996.

[36] J. L. Marco-Brown, C. M. Barbosa-Lema, R. M. Torres Sánchez, R. C. Mercader, and M. dos Santos Afonso, "Adsorption of picloram herbicide on iron oxide pillared montmorillonite," *Appl. Clay Sci.*, vol. 58, pp. 25–33, 2012.

[37] M. Vinuth, H. S. B. Naik, B. M. Vinoda, H. Gururaj, N. Thomas, and G. Arunkumar, "Enhanced removal of methylene blue dye in aqueous solution using eco-friendly Fe(III)-montmorillonite," *Mater. Today Proc.*, vol. 4, no. 2, pp. 424–433, 2017.

[38] R. L. Dahlin, F. K. Kasper, and A. G. Mikos, "Polymeric nanofibers in tissue engineering," *Tissue Eng. Part B. Rev.*, vol. 17, no. 5, pp. 349–364, Oct. 2011.

[39] D. Rosner, "Traceability of cleaning agents and disinfectants," in *Handbook of Hygiene Control in the Food Industry*, Woodhead Publishing, 2005, pp. 672–683.

[40] C. E. Starliper, B. J. Watten, D. D. Iwanowicz, P. A. Green, N. L. Bassett, and C. R. Adams, "Efficacy of pH elevation as a bactericidal strategy for treating ballast water of freight carriers," *J. Adv. Res.*, vol. 6, no. 3, pp. 501–509, May 2015.

[41] M. J. Jenkins and K. L. Harrison, "The effect of crystalline morphology on the degradation of polycaprolactone in a solution of phosphate buffer and lipase," *Polym. Adv. Technol.*, vol. 19, no. 12, pp. 1901–1906, Dec. 2008.

[42] Y. Tokiwa, B. P. Calabia, C. U. Ugwu, and S. Aiba, "Biodegradability of plastics," *Int. J. Mol. Sci.*, vol. 10, no. 9, pp. 3722–3742, Aug. 2009.

Appendix

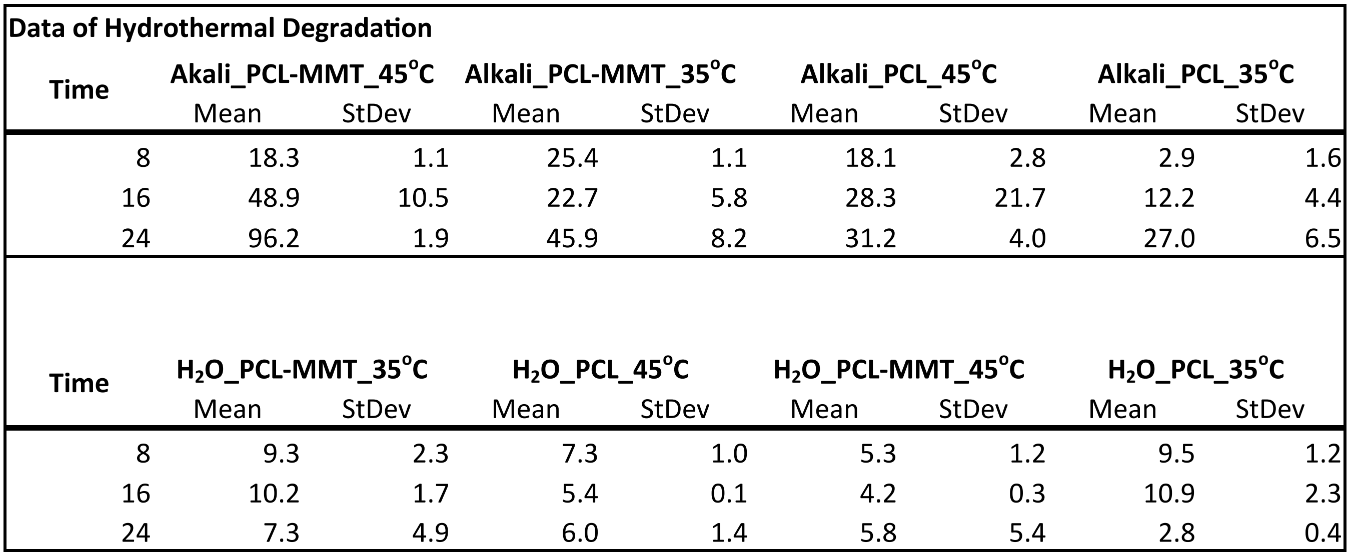
Weight loss of due to hydrothermal degradation with standard deviation represented by the error bars

Data of Biodegradation

Time	Akali_PCL-MMT_Compost		Akali_PCL-MMT_Soil		PCL-MMT_Compost		PCL_Compost	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
1	36.8	12.9	26.4	10.8	18.1	9.8	30.3	27.1
2	96.9	4.6	92.5	11.9	96.2	3.7	62.4	35.8
3	93.0	12.2	99.7	0.5	99.7	0.5	74.0	39.6

Time	Akali_PCL_Compost		PCL-MMT_Soil		PCL_ Soil		Akali_PCL_Soil	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
1	10.7	3.5	31.2	2.8	14.5	2.1	20.1	10.1
2	66.5	20.3	66.7	29.0	25.8	3.1	21.5	4.8
3	77.0	23.4	70.0	25.2	47.5	27.1	43.7	22.8

Weight loss of due to biodegradation with standard deviation represented by the error bars



Data of Hydrothermal Degradation

Time	**Akali_PCL-MMT_45^{o}C**		**Alkali_PCL-MMT_35^{o}C**		**Alkali_PCL_45^{o}C**		**Alkali_PCL_35^{o}C**	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
8	18.3	1.1	25.4	1.1	18.1	2.8	2.9	1.6
16	48.9	10.5	22.7	5.8	28.3	21.7	12.2	4.4
24	96.2	1.9	45.9	8.2	31.2	4.0	27.0	6.5

Time	**H_2O_PCL-MMT_35^{o}C**		**H_2O_PCL_45^{o}C**		**H_2O_PCL-MMT_45^{o}C**		**H_2O_PCL_35^{o}C**	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
8	9.3	2.3	7.3	1.0	5.3	1.2	9.5	1.2
16	10.2	1.7	5.4	0.1	4.2	0.3	10.9	2.3
24	7.3	4.9	6.0	1.4	5.8	5.4	2.8	0.4