

# Synthesis of Iron-Modified Montmorillonite as Filler for Electrospun Nanocomposite Fibers

Khrysllyn Araño, Dela Cruz, Michael Leo, Dela Pena, Eden May, Leslie Joy Diaz

**Abstract**—Montmorillonite (MMT) is a very abundant clay mineral and is versatile such that it can be chemically or physically altered by changing the ions between the sheets of its layered structure. This clay mineral can be prepared into functional nanoparticles that can be used as fillers in other nanomaterials such as nanofibers to achieve special properties. In this study, two types of iron-modified MMT, Iron-MMT (FeMMT) and Zero Valent Iron-MMT (ZVIMMT) were synthesized via ion exchange technique. The modified clay was incorporated in polymer nanofibers which were produced using a process called electrospinning. ICP analysis confirmed that clay modification was successful where there is an observed decrease in the concentration of Na and an increase in the concentration of Fe after ion exchange. XRD analysis also confirmed that modification took place because of the changes in the d-spacing of Na-MMT from 11.5 Å to 13.6 Å and 12.6 Å after synthesis of FeMMT and ZVIMMT, respectively. SEM images of the electrospun nanofibers revealed that the ZVIMMT-filled fibers have a smaller average diameter than the FeMMT-filled fibers because of the lower resistance of the suspensions of the former to the elongation force from the applied electric field. The resistance to the electric field was measured by getting the bulk voltage of the suspensions.

**Keywords**—Electrospinning, nanofibers, montmorillonite.

## I. INTRODUCTION

MONTMORILLONITE (MMT) is one of the most widely available and naturally occurring clay minerals with deposits found in many countries. One of the more common forms of MMT is Sodium MMT (Na-MMT) which has a characteristic white color. Its microstructure allows it to be chemically or physically modified to make it suitable for a specific application. One way of modifying MMT is by substituting the inorganic ions in its layered structure with other cations through ion exchange reactions [1]-[3].

Since MMT can be obtained as nanoparticles, they can be used in combination with other materials to achieve special properties. Nanofibers filled with nanoparticles or nanoclays have been the subject of interest in a number of studies. Nanofibers particularly have become an attractive material in the last few decades due to their outstanding properties such as high surface area to volume ratio by virtue of their very small diameter, which typically ranges from 50-1000nm [4]. Nanofibers are produced by a process called electrospinning which utilizes high voltage electric field, i.e. 10-25 kV to generate fibers with diameters in the nano-scale from a polymer solution or polymer melt [5].

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The objective of this study is to synthesize iron-modified MMT, specifically FeMMT and ZVIMMT from Na-MMT and incorporate the modified nanoclay in a polymer for the production of nanocomposite fibers via electrospinning. Properties of the electrospun fibers were investigated to identify which of the two nanoclays would yield fibers with smaller diameters and desirable morphology.

## II. METHODOLOGY

### A. Synthesis of FeMMT and ZVIMMT

The base clay mineral for the production of FeMMT and ZVIMMT was Na-MMT. Na-MMT was dispersed in distilled water followed by the addition of FeCl<sub>3</sub>. NaOH was then added to the suspension. Stirring was performed after addition of FeCl<sub>3</sub> as well as NaOH. After stirring for an extended period of time, the suspension was filtered and dried in vacuum oven to produce FeMMT. The same procedure was performed for the production of ZVIMMT except for an added step between NaOH addition and filtration. Between the said steps, sodium borohydride (NaBH<sub>4</sub>) was added to reduce Fe to its zero valent form.

Inductively-coupled plasma (ICP) and x-ray diffraction (XRD) analyses were both employed to confirm the modification of clay.

### B. Electrospinning of the Nanocomposite Fibers

Polymer solutions of polycaprolactone (PCL) were prepared using dichloromethane (DCM) as the solvent. The iron-modified clay was added to form a suspension which was then electrospun to produce nanocomposite fibers.

Scanning electron microscope (SEM) imaging was performed to examine the morphology of the fibers, and determine the fiber diameter using a freeware for image analysis, i.e. Image J. The bulk voltage of the suspensions used in electrospinning were measured and correlated with the fiber diameter.

## III. RESULTS AND DISCUSSION

Modification of Na-MMT to FeMMT and ZVIMMT via ion exchange technique was successfully performed as primarily indicated by the change in color of the material. Fig. 1 shows that the initial white color of Na-MMT changed to brown and black signifying the presence of iron in FeMMT and ZVIMMT, respectively.



Fig. 1 (a) Na-MMT, (b) FeMMT, (c) ZVIMMT

Fig. 2 shows the change in the concentration of Na and Fe in the MMT particles obtained from ICP analysis. The initial 22450 ppm concentration of Na decreased to 2710 ppm after the synthesis of FeMMT. Similarly, the concentration of Na also decreased to 16700 ppm for ZVIMMT. The opposite effect was observed for Fe as it increased from 4530 ppm to 105000 and 101333 ppm for FeMMT and ZVIMMT, respectively. The results suggest that Fe successfully replaced the Na ions in the clay structure. One factor that permits ion exchange is the charge of the ions involved. Since Fe has a larger charge number than Na, the former has a higher replacing power which allowed its ions to replace those of Na.

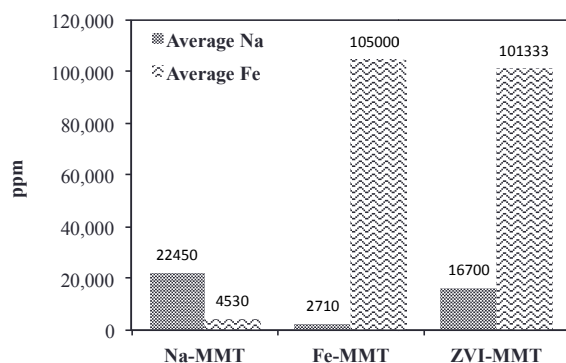


Fig. 2 ICP analysis of the MMT particles showing the amount of Na and Fe

XRD analysis also suggests that clay modification took place as indicated by the changes in the d-spacing of the material. Fig. 3 shows that Na-MMT has an interlayer spacing of 11.5 Å which increased to 13.6 Å and 12.6 Å after the synthesis of FeMMT and ZVIMMT, respectively. The increase in d-spacing is due to the oxide layer attached on the surface of the Fe particles that replaced the Na ions.

SEM imaging revealed that the nanofibers filled with FeMMT particles have larger diameters than those of ZVIMMT-filled fibers as shown in Figs. 4 (a) and (b). The average fiber diameter of FeMMT-filled fibers is 296.67 nm while that of the ZVIMMT-filled fibers is 245.13 nm.

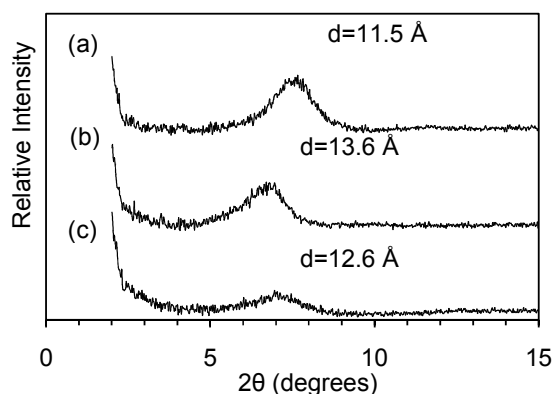
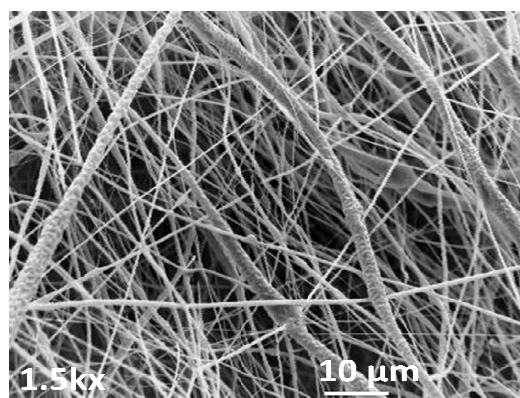
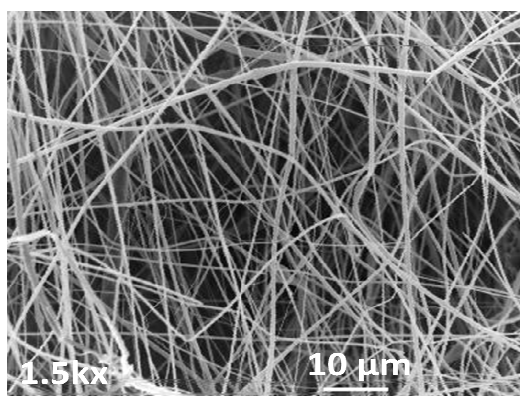


Fig. 3 XRD patterns of (a) Na-MMT (b) FeMMT and (c) ZVIMMT



(a)



(b)

Fig. 4 SEM micrograph of (a) FeMMT and (b) ZVIMMT-filled nanofibers taken at 1.5kx

The measured diameter of the electrospun fibers suggests that the valence state of Fe in the modified clay influenced the electrospinning of the polymer-clay suspension which resulted in finer fibers when the zero valent form of Fe was present. Bulk voltage measurement of the suspensions prior to electrospinning showed that ZVIMMT and FeMMT particles produced suspensions with 1.6 mV and 162.7 mV bulk

voltages, respectively. The bulk voltage can be used to estimate the conductivity of the suspension such that FeMMT-polycaprolactone suspension would exhibit a higher conductivity relative to the ZVIMMT suspension. Increase in conductivity essentially lowered the ability of the suspension to generate electrostatic charge upon application of high voltage, which is key factor in electrospinning along with surface tension and viscosity. Hence, ZVIMMT suspension resulted in finer fibers due to its lower suspension conductivity.

#### IV. CONCLUSION

FeMMT and ZVIMMT were successfully synthesized from Na-MMT via ion exchange technique as confirmed by the decrease in the amount of Na and increase in the amount of Fe in MMT. Results also suggest that Fe was able to replace Na in between the MMT layers based on the observed increase in the d-spacing of the clay after modification.

SEM images of the electrospun nanofibers showed that ZVIMMT particles produced finer fibers. The lower bulk voltage of the ZVIMMT suspension suggests that the valence state of Fe affected the electrical resistance of the suspension and its ability to generate electrostatic charge upon application of high voltage.

#### ACKNOWLEDGMENT

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