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JUDUL : **MODIFICATION OF NANOFILLER TO IMPROVE THE FINAL PROPERTIES OF POLYLACTIC ACID (PLA) NANOCOMPOSITES**

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MODIFICATION OF NANOFILLER TO IMPROVE THE FINAL PROPERTIES OF POLYLACTIC ACID (PLA) NANOCOMPOSITES

LATISHA ANTHONY

Thesis submitted in partial fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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I hereby declare that the work in this thesis entitled "Modification of Nanofiller to Improve the Final Properties of Polylactic Acid (PLA) Nanocomposites" is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Special dedication to God the Almighty, my supervisor,
parents, family members and friends for your
continuous guidance, support and aid.

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"In ordinary life we hardly realize that we receive a great deal more than we give, and that it is only with gratitude that life becomes rich." -Dietrich Bonhoeffer

ABSTRACT

Modifications of nanoclay were prepared from pristine clays and organoclays with Transition Metal Ions (TMIs), Ferum, Copper and Nickel using different solvents. The first part of the experiment focuses on determining the viability of Ethanol as a solvent in the modification process as well as its efficiency in aiding the adsorption of TMIs in comparison to solvents such as Methanol and Dioxane. The composition and structure of the modified nanoclay were characterized using Atomic Absorption Spectroscopy (AAS), Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). From the AAS results, it was determined that Ethanol was a viable solvent for the nanoclay modification and proved to be extremely efficient for Copper ions especially. SEM and FTIR results proved that modified nanoclays had smoother surfaces for pristine clays or montmorilonite (MMT) which proved that the modification was successful. The same modifications performed on organoclayswere proven to be unsuccessful. The modified samples were then intercalated in Polylactic Acid (PLA) polymer matrices to form polymer nanocomposites (PNC). The biodegradability and thermal stability of the Polymer nanocomposites were tested and its performance is compared against a polymer nanocomposite intercalated with pure (unmodified) nanoclay. The PNC were formed using solution intercalation method with 1,4-Dichloroethane as a solvent. Both the biodegradability and thermal stability also showed positive improvements. Biodegradibility is hypothesized to have increased due to the characteristics of transition metal ion which are easily oxidized. The ions with higher electronegativity showed the least improvement when intercalated into the polymer matrices. Thermal stability also increased significantly, due to the transition metal ions hindering the pristine clay within the polymer matrices from decomposing easily. Further research will be required to commercialize findings.

Keywords: Modification, Nanoclay, Montmorillonite, Organoclay, Transition Metal Ions (TMIs), Solution Intercalation, Polylactic Acid (PLA) , Polymer Nanocomposites (PNC), Characterize, Scanning Electron Microscopy (SEM), Atomic Absorption Spectrometry (AAS), Fourier Transform Infrared (FTIR), Thermal Stability, Biodegradibility,

ABSTRAK

Ubahsuaian tanah bersaiz nano (nanoclay);- montmorilonite (*pristine clay*) dan organoclays, dengan Ion Logam Peralihan(TMIs) seperti Ferum, Kuprum dan Nikel menggunakan pelarut yang berbeza telah disediakan. Bahagian pertama eksperimen tertumpu kepada pembuktian kemampuan Etanol sebagai pelarut dalam proses pengubahsuaian serta kecekapan dalam membantu penjerapan TMIs berbanding dengan pelarut seperti Metanol dan Dioxana. Komposisi dan struktur nanoclay yang telah diubah suai dicirikan menggunakan Spektroskopi Serapan Atom (AAS), Fourier Transform Infrared (FTIR) dan Mikroskopi Imbasan Elektron (SEM). Dari keputusan AAS, ia telah ditentukan bahawa Etanol merupakan pelarut yang sesuai digunakan bagi pengubahsuaian nanoclay dan terbukti sebagai sangat efisien untuk penjerapan ion Kuprum terutamanya. Keputusan SEM dan FTIR membuktikan bahawa pengubahsuai montmorillonite(pristine clay) menyebabkan permukaan menjadi lebih licin daripada montmorillonite (MMT) yang asli Keputusan ini tidak sama dengan keputusan yang diperolehi untuk organoclay. Sampel yang diubah suai kemudiannya dicampurkan dalam matriks polimer Polylactic Asid (PLA) untuk membentuk polimer dengan komposit bersaiz nano (PNC). Penguraian Biologik (biodegradability) dan kestabilan haba PNC telah diuji dan dibandingkan dengan prestasi PNC yang telah dicampurakan dengan nanoclay asli (tidak diubahsuai). PNC telah dibentuk menggunakan kaedah interkalasi larutan dengan menggunakan 1,4-Dikloroetana sebagai pelarut. Kedua-dua penguraian biologik dan kestabilan haba juga menunjukkan peningkatan yang positif dari segi persembahan. Penguraian biologik mungkin telah dipercepatkan disebabkan ciri-ciri ion logam peralihan yang mudah dioksidakan. Ion yang lebih elektronegatif menyebakan peguraian lebih lambat apabila diinterkalasi ke dalam matriks polimer. Kestabilan termal juga meningkat dengan ketara, ini kerana ion-ion logam peralihan menghalang nanoclay dalam PNC daripada terurai dengan mudah. Penyelidikan lanjut diperlukan untuk mengkomersilkan penemuan.

Kata Kunci: Pengubahsuaian, Tanah Bersaiz Nano (Nanoclay), Ion Logam Peralihan (Tmis), Interkalasi Larutan, Asid Polylactic (PLA) , Polimer Dengan Komposit Bersaiz Nano (PNC), Dicirikan, Microskopi Imbasan Elektron (SEM), Spektrometri Penyerapan Atom (AAS), Fourier Transform Infrared (FTIR), Kestabilan Terma, Penguraian Biologik

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LIST OF SYMBOLS

%	Percentage
°C	Degree celsius
Min	Minute
µm	Micrometer
Mm	Milimeter
Cm	Centimeter
W	Waat
G	Gram
Mg	Miligram
M	Meter
S	Second
mL	Mililiter
L	Liter
Ppm	Part per million
v/v	volume to volume ratio

LIST OF ABBREVIATIONS

Fe	Ferum
Ni	Nickel
Cu	Copper
TMIs	Transition Metal Ions
PLA	Polylactic Acid
PNC	Polymer Nanocomposite
MMT	Montmorrilonite
TGA	Thermal Gravimetry Analyzer
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
AAS	Atomic Absorption Spectrometry
MW	Molecular weight

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

1.1.1 Background of Polylactic Acid (PLA)

Polylactic acid or polylactide ,PLA is a type of biodegradable thermoplastic that is produced from renewable resources. It is primarily generated from dextrose, a natural sugar derived from the starch in kernels of corn. Other agricultural raw materials, such as rice, sugar beets, sugar cane, wheat and sweet potatoes, can also serve as sources for the starch or sugars used to make this biopolymer. (Averous, 2008) This means that the production of PLA can be tailored to use dominant, locally available crops. For instance, the usage of sugar canes to produce PLA in Malaysia.

Conventionally, most of the plastic products used daily are petroleum-based. Recently though, the usage of this biopolymer is garnering more favor as it boasts the ability to have clear and strong properties similar to that of oil-based plastics but with an added advantage of being commercially compostable. PLA also requires 65 percent less energy to produce and generates 68 percent fewer greenhouse gasses in comparison with traditional oil-based plastics. (Kingsland, 2010)

It is used in many fields including that of biomedicine, pharmaceutical and food packaging. Because it is biodegradable, it is primarily used in the development of bioplastic products such as loose-fill packaging, compost bags, and disposable tableware. In the food packaging industry, PLA is used to produce biodegradable and compostable disposable cups that can hold cold beverages and as the lining in cups for hot beverages. Oligolactic Acid (OLA), a shorter polymer of lactic acid is also being used as a surfactant on the pharmaceutical industry (Averous, 2008)

1.1.2 Background of Nanoclay

Nanoclays are organoclay nanoparticles of layered mineral silicates. It is divided into several types such as montmorillonite , bentonite, koalinite, and hectorite. When used in polymer nanocomposites, they have a large range of attractive applications such as rheological modifiers and gas absorbents. Montmorillonite nanoclay is the most common form of nanoclay and is in pure form. (Alexandre, 2000)

Closite Na^+ is a type of montmorillonite that consists of 1 nm thick aluminosilicate layers surface-substituted with metal cations, Na^+ and stacked in 10 µm-sized multilayered stacks. The dispersion of montmorillonite in a polymer matrix to form polymer-clay nanocomposite depends on how the surface of the clay layers are modified,. Within the nanocomposite individual clay layers fully separate to form plate-like nanoparticles with very high aspect ratio. (Olad, 2011)

Cloisite C20 is an organically modified nanoclay which has layered magnesium aluminum silicate platelets. The platelets are surface modified with dialkyldimethylammonium chloride also known as hydrogenated tallow. The alkyl from this structure is derived from hydrogenated tallow to allow complete dispersion into and provide miscibility with the thermoplastic systems for which they were designed to improve. (Southern Clay Product Bulletin, 2011)

1.1.3 Background of Clay/Polymer nanocomposites

Polymer nanocomposites(PNC) are a new class of materials which has promising potential future applications such as high-performance materials. The main feature of the polymer nanocomposite basically consists of a host polymer that is reinforced with approximately 5%wt nanosized inorganic fillers. The nanofiller will significantly impact the overall macroscopic properties of the host polymer.

There are three major classes of polymer nanocomposites that can be obtained by the use of different nanofillers; which are Clay/Polymer Nanocomposites, Metal/Polymer Nanocomposites, and Carbon Nanotubes/Polymer Nanocomposites

In the clay/polymer nanocomposite, typically smectite-type clays are used as fillers. Montmorillonite layered structures and other forms of nanoclay are dispersed in a host polymer matrix. Based on the type of bonding between the polymer chain and the silicate layer, new material showing improvement in different macroscopic aspects are achieved. (Gacitua, et. al., 2005) These macroscopic properties may include higher tensile strength and better heat and chemical resistance.

1.1.4 Background of surface modification

The main goal of this experiment is to modify the surface of nanoclay and to disperse it as a filler within PLA to form a nanocomposite. Surface modification refers to the modification reaction that occurs at the surface of a material that brings about physical, chemical or biological characteristics different from the ones originally found on the surface of a material.

The modification can be done by several different methods including:

Table 1.1: Methods of Surface Modification

Physical	Chemical	Radiation
• Physical adsorption • Langmuir-Blodgett film	• Oxidation by strong acids • Ozone treatment • Chemisorption • Flame treatment	• Plasma (glow discharge) • Corona discharge • Photo-activation (UV) • Laser • Ion/Electron beam • γ-irradiation

(Source: Loh, et al.,1995)

Nanoclay is naturally hydrophillic and is held together strong by electrostatic forces. This makes it poorly suited to mix and interact with polymer matrices. Therefore, the clay needs to be treated before it can be used to make a polymer nanocomposite. The most common way of treating clay in order to make it more compatible with polymer matrices, is through ion exchange.

1.2 PROBLEM STATEMENT

PLA is being increasingly used in industries as one of the most efficient thermoplastics. Even so, PLA is still subject to common problems such as fatigue and low maximum continuous working temperature (approximately 50º C). This narrows down its applications especially in heavy duty industries.

But most importantly, the usage/creation of this polymer nanocomposite will generate waste which could lead to pollution. If the product is biodegradable it will spend a shorter duration of time as waste, thus eliminating potential pollution.

1.3 OBJECTIVE

The objectives of this study are:-

I. To modify the surface of nanoclay filler by using transition metal ions.
II. To study the structure and characteristicss of the modified nanoclay.
III. To study the properties of PLA polymer by using the modified nanoclay as a filler.
IV. To draw a comparison between the properties of modified-nanoclay filled PLA polymer with unmodified-nanoclay filled PLA

1.4 SCOPE OF STUDY

In order to meet with the objectives of this project, the scope of study is narrowed down to the following:

I. To modify the surface of nanoclay, Cloisite Na^+ and Cloisite C20 with copper, nickel and ferum salts using the solution intercalation method.
II. To determine the best solvent-metal ion pairing to be used for the modification as well as to prove ethanol is a viable alternative for currently used solvents, dioxane and methanol.
III. To determine the structure of modified nanoclay and compare it with the structure of unmodified nanoclay.
IV. To determine the thermal stability and biodegradibility of modified nanoclay-filled PLA polymer and compare it with the properties of unmodified nanoclay-filled PLA polymer.

1.5 RATIONALE AND SIGNIFICANCE

This experiment is done in order to enhance the desirable properties of conventional PLA nanocomposites in terms of biodegradability. It is also done to prove that ethanol is a viable, less toxic alternative solvent that can be used to perform the surface modification. Quickening the biodegradability of bioplastics is also better for the environment as a material that requires a shorter period to biodegrade means will spend a shorter period time being waste products. Essentially, it will serve as more environmentally-friendly option in comparison to conventional oil-based plastics. of nanoclay.

In terms of applications, a higher thermal stability will significantly widen the usage of PLA nanocomposites in industries especially heavy duty industries which require equipments to withstand extremely high temperatures. This study will primarily be focusing on finding an alternative for conventional nanoclay polymer composites which is more biodegradeable, and yet is comparable in terms of thermal stability.

1.6 CONCLUSION

This experiment is done is hopes of discovering a more adept and commercially suited polymer nanocomposite using surface modification techniques to modify the structure of the polymer filler, nanoclay. The organoclay in this research will be modified using transition metal ions.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

The primary goal of the current research is to modify the surface of the nanoclay filler and test the properties of the PLA nanocomposite using the modified nanoclay as a reinforcement agent. The current research will primarily be focusing on using transition metal ions (i.e Copper $^{2+}$ ions from Copper salts) to modify the surface of nanoclay, Cloisite Na^+ and Cloisite C20A. Based on the focal point of this research, the primary raw material used can be identified as nanoclay, PLA, and transition metal ions.

2.1 POLYLACTIC ACID (PLA)

Polylactic acid (PLA) is a thermoplastic polymer that when in a solid state can be either semicrystalline or totally amorphous. Lactic acid (2-hydroxy propionic acid) is the most common form of the acid. PLA is an unique polymer that in some ways behaves similar to PET, but also to a certain extent performs a lot like polypropylene (PP). Ultimately, it can be considered as the polymer with the broadest range of applications because of its ability to be crystallized, modified, filled, copolymerized, and processed in most polymer processing equipment. It can beformed into transparent films, fibers, or injection molded into preforms like bottles. (Henton, et al., 2005). But in spite of these characteristics its commercial viability has been limited by high production costs which is approximately greater than $2/lb.

The PLA synthesis process begins with lactic acid which is produced by the fermentation of dextrose. This is followed by a continuous condensation reaction which will lead to the production of low molecular weight PLA prepolymer. Next, the low molecular weight prepolymer is then converted to high molecular weight polymers by using ring-opening polymerization. The process is depicted in the following Figure 2.1.

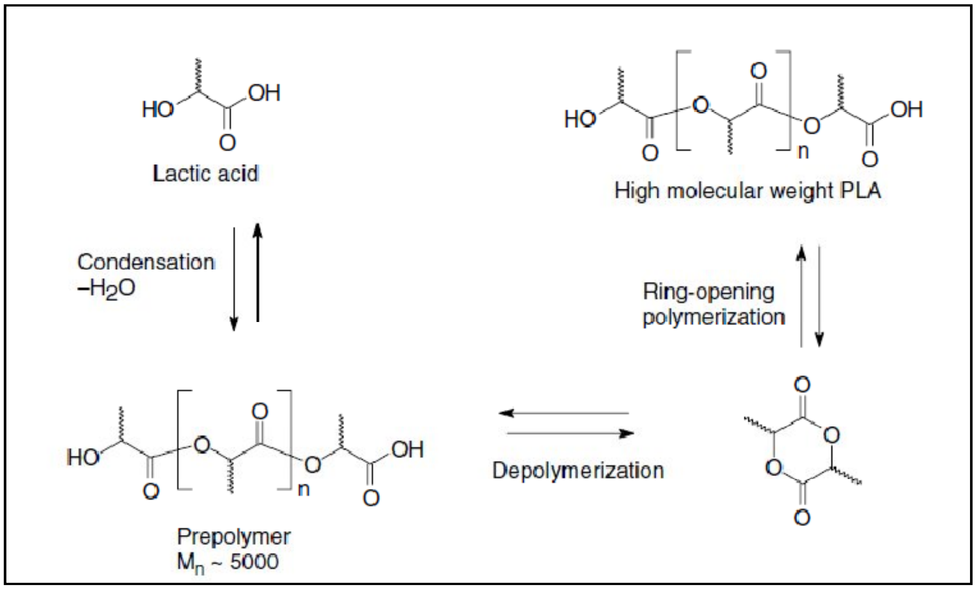
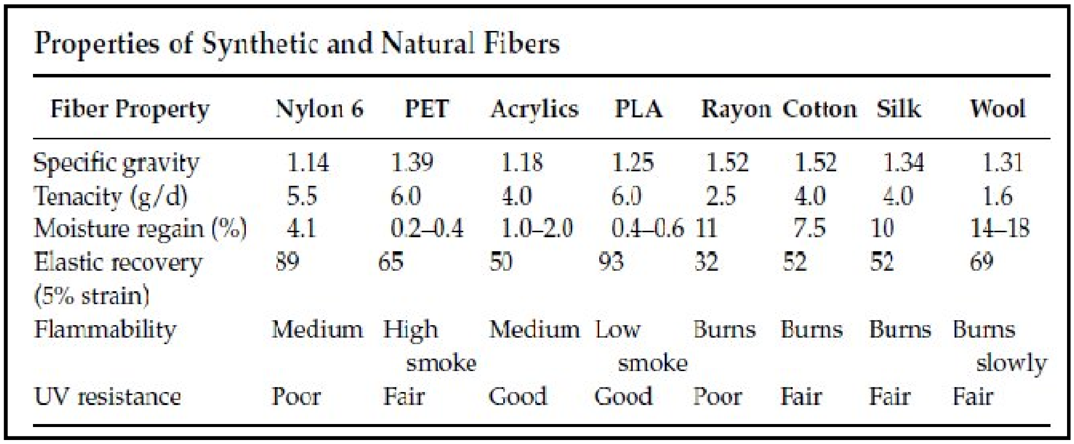


Figure 2.1: Synthesis of Polylactic Acid

(Source: Averous, 2008)

There are several reviews that detail the properties and characteristics of PLA. The physical characteristics of PLA are greatly dependent on its transition temperatures for common qualities such as density, heat capacity, and mechanical properties. When in the solid state PLA can either be amorphous or semicrystalline, depending on its stereochemistry. For amorphous PLAs, the glass transition (*T*g) determines the maximum usable temperature for commercial applications. When in the semicrystalline state, both the *T*g , which is approximately 58 °C and the melting point ,*T*m, which ranges from 130°–230°C are important when determining the usable temperature for various applications. Above the *T*g , amorphous PLAs will behave as a viscous fluid upon further heating. While below the *T*g, PLA will behave as a glass until cooled to its β transition temperature of approximately -45°C. (Henton, et. al, 005). The properties of PLA compared to other polymers are listed in Table 2.1.

Table 2.1: Properties Comparison Chart of PLA and Other Polymers.



Properties of Synthetic and Natural Fibers

Fiber Property	Nylon 6	PET	Acrylics	PLA	Rayon	Cotton	Silk	Wool
Specific gravity	1.14	1.39	1.18	1.25	1.52	1.52	1.34	1.31
Tenacity (g/d)	5.5	6.0	4.0	6.0	2.5	4.0	4.0	1.6
Moisture regain (%)	4.1	0.2–0.4	1.0–2.0	0.4–0.6	11	7.5	10	14–18
Elastic recovery (5% strain)	89	65	50	93	32	52	52	69
Flammability	Medium	High smoke	Medium	Low smoke	Burns	Burns	Burns	Burns slowly
UV resistance	Poor	Fair	Good	Good	Poor	Fair	Fair	Fair

(Source: Henton, et al., 2005)

PLA has a wide range of applications, such as woven shirts, microwavable trays, hot-fill applications and even engineering plastics. Since these blends have good structure (form)-stability and visual transparency it becomes useful as low-end packaging material. PLA is also used in biomedical applications such as in sutures, stents, drug delivery devices and as a material for tissue engineering. Because it is biodegradable, it can also be employed in the preparation of bioplastics which can be used to manufacture loose-fill packaging, compost bags, food packaging, and disposable tableware. PLA is also extremely useful when spun into fibers. These fibers are the starting material for various products such as upholstery, disposable garments, awnings, and diapers. . (Averous, 2008)

2.2 NANO-SIZED ORGANOCLAY (NANOCLAY)

One of the primary nanofillers used in polymer nanocomposites (PNC) are nanoclays. Cloisite Na$^+$ *(*Na$^+$MMT*)* and Closite C20A are types of nanoclay. Cloisite Na$^+$, is a type of natural,pure unmodified montmorillonite which consists of aluminosilicate layers which have been surface-substituted with metal cation, Na$^+$. It is made up of smectite clay minerals and has a plate-like structure. Even though the individual platelet thicknesses are generally only around one nanometer (one-billionth of a meter), nanoclay still has an extremely high aspect ratio. **(**Olad, 2011). This results in a montmorillonite that is hydrophilic in nature.

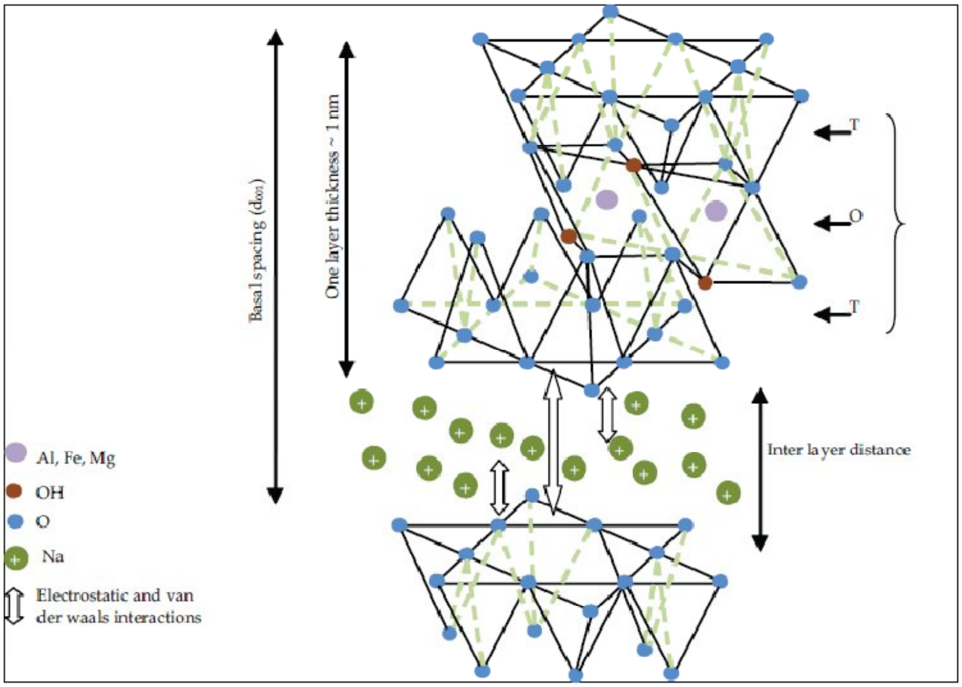


Figure 2.2: Layered Silicate Structure of Montmorillonite

(Source: Olad, 2011)

Nanotubes or Carbon nanotubes are a group of carbon molecules tubular in shape provided which have very paricular properties. The nanotubes are structured cylindrically with each of its ends covered by half a fullerene molecule. Its diameter is only a few nanometers, but its length may reach several millimeters. Several types of nanotubes exist; but they can be divided in two main categories which are single-walled (SWNT) and multi-walled (MWNT). In terms of their electrical properties, nanotubes can be either excellent conductors or insulators depending on their structure. Thermal conductivity performance is also excellent in the axial direction but remains very low in the lateral direction.. (Khare, & Bose, 2005)

Though both nanotubes and nonoclay are potentially useful fillers for polymers, this research will be focusing on the use of nanoclay (Closite Na^+) instead of carbon nanotubes. This is due to the cost efficiency and cost competitiveness of nanoclay in comparison with nanotubes. The significantly lower cost of nanoclay will make it a more appropriate option for large scale industrial usage.

2.3 CLAY/POLYMER NANOCOMPOSITE

Nanocomposites are prepared by dispersing a less than 5wt% nanoclay into a polymer which offers tremendous improvement in performance of the polymer. Usually smectite-type clays such as (MMT) and hectorite are used as fillers. The process of dispersing clay into a polymer structure is called exfoliation .Exfoliation is aided by the use of surface compatibilization or suface modification chemistry, which basically increases the distance between the stacks of plate-like structure in nanoclay to the extent that it may be separated easily by mechanical shear or heating.(Gacitua, et al., 2005). Nanocomposites also show excellent mechanical properties when compared to the pure polymer in terms of tensile strength, heat and chemical resistance.

Generally, a well-developed polymer/clay nanocomposite results in increased mechanical strength compared to the pure polymer matrix since uniform dispersion of the nano-sized clay particles produces a high interfacial area and ionic bonds between the nanoclay and host polymer. Currently there are several polymer nanocomposites in the market that uses clay as a filler. The applications as well as the improvement in properties brought forth by the introduction of clay into the nanocomposite are listed in Table 2.2:-

Table 2.2: List of Commercially Available Clay/Polymer Nanocomposite

APPLICATION	IMPROVEMENT OF PROPERTIES
Nylon 6 Films and Bottles	• Oxygen and CO_2 barrier • Water vapor barrier • UV transmission • Thermal stability • Stiffness • Down-gauging • Clarity • Anti-tack
Polyolefin Injection Mold	• Thermal stability • Shrinkage / warpage reduction • Stiffness • Solvent / chemical resistance • Flame resistance • Weight reduction • Fiberglass reduction • Thin-walling • Scratch and mar • Anti-bloom
Epoxy	• Higher Tg • Stiffness • Solvent / chemical resistance • Flame resistance • Rheology control • Scratch and mar • Anti-bloom

Polyolefin Films, Bottles and Sheet	• Oxygen and CO_2 barrier • Melt Strength • Thermal stability • Stiffness • Down-gauging • Melt fracture reduction

(Source: Okomoto, 2003)

In this research, the development of polymer nanocomposites aims to provide a better balance of these properties. The focus, essentially is to increase the mechanical properties such as the thermal stability of the polymer nanocomposite. The modified clay which uses transition metal ions, when used as a reinforcement agent should provide higher thermal stability when compared to PLA/Clay nanocomposite using unmodified clay.

2.4 SOLUTION INTERCALATION METHOD

There are three techniques used to disperse the clay within the host polymer, which are in-situ polymerization, solution intercalation and melt processing.(Gacitua, et al., 2005) Solution induced intercalation method basically solubilizes the polymer in an organic solvent, before dispersing the cay in the obtained solution and subsequently either evaporating the solvent or precipitating the polymer. These techiniques are illustrated from Figure 2.3 to Figure 2.5.

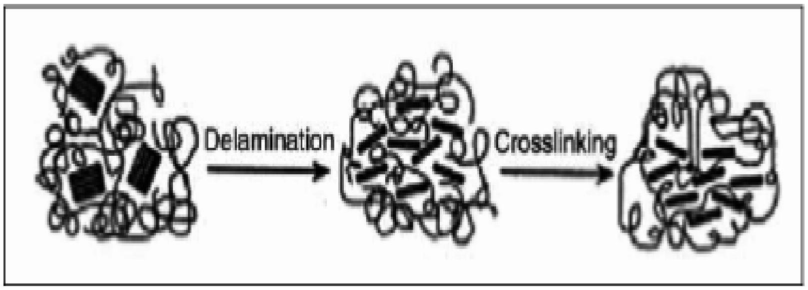


Figure 2.3: Solution Intercalation Method

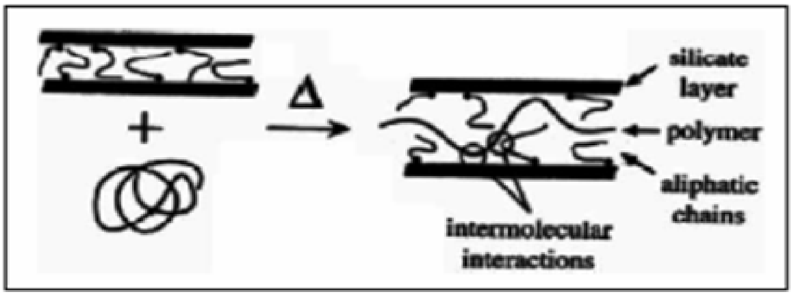


Figure 2.4: In-situ Polymerization Method

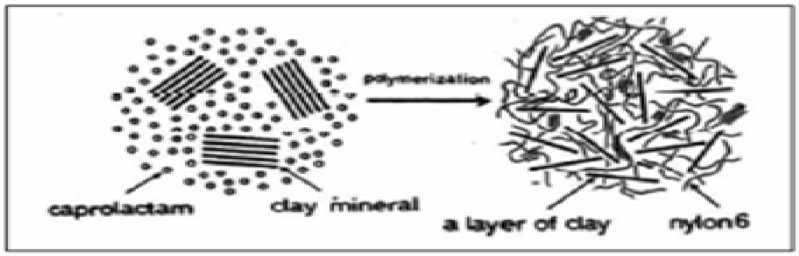


Figure 2.5: Melt Intercalation Method

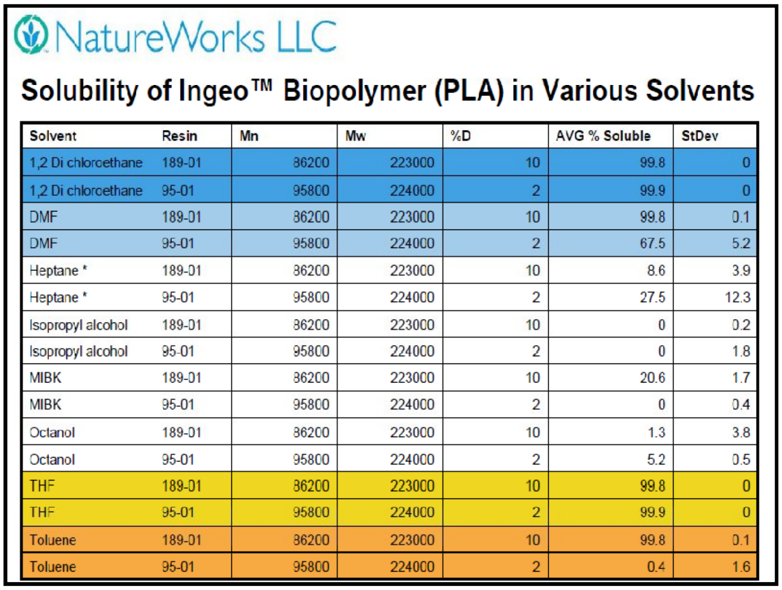
(Source: Gacitua, 2005)

In situ intercalative polymerization basically occurs when the polymer is formed between the layers by swelling the layer hosts within the monomer solution. In melt intercalation polymers, and layered hosts are annealed above the softening point of the polymer. This method is the most popular method used to prepare nanocomposites (Gordon, et. al., 2007)

In another research, it was explained how the the dispersion of modified nanoclay in Polyurethane was better than the dispersion of ordinary Cloisite Na^+. The method employed to disperse the clay in the polymer host was solution casting using a chosen solvent. In order for this method to work the polymer needs to be able to be dissolved within the solvent.. (Widya, et. al., 2005).

Usually the solvent proposed to disperse clay in the PLA polymer matrix is chloroform. The sample is then added with a few drops of methanol which will function as a co-solvent. Due to safety concerns, the chloroform is swapped with 1,2 Dichloroethane which is less hazardous in comparison to chloroform. The new solvent was chosen based on the list of solvents produced by NatureWorks LLC as seen in Table 2.3. Next, the polymer is dissolved and the clay is mixed within the solvent, the polymer nanocomposite is then precipitated out by reluxing and then using an ultrasonic water bath. This method is chosen because it gives clearer peaks in the XRD graph compared to melt intercalation method.(Maji, et al, 2009). This result can be seen in Figure 2.6.

Table 2.3: List of PLA Solvents



NatureWorks LLC

Solubility of Ingeo™ Biopolymer (PLA) in Various Solvents

Solvent	Resin	Mn	Mw	%D	AVG % Soluble	StDev
1,2 Di chloroethane	189-01	86200	223000	10	99.8	0
1,2 Di chloroethane	95-01	95800	224000	2	99.9	0
DMF	189-01	86200	223000	10	99.8	0.1
DMF	95-01	95800	224000	2	67.5	5.2
Heptane *	189-01	86200	223000	10	8.6	3.9
Heptane *	95-01	95800	224000	2	27.5	12.3
Isopropyl alcohol	189-01	86200	223000	10	0	0.2
Isopropyl alcohol	95-01	95800	224000	2	0	1.8
MIBK	189-01	86200	223000	10	20.6	1.7
MIBK	95-01	95800	224000	2	0	0.4
Octanol	189-01	86200	223000	10	1.3	3.8
Octanol	95-01	95800	224000	2	5.2	0.5
THF	189-01	86200	223000	10	99.8	0
THF	95-01	95800	224000	2	99.9	0
Toluene	189-01	86200	223000	10	99.8	0.1
Toluene	95-01	95800	224000	2	0.4	1.6

(Source: NatureWorks LLC, 2010)

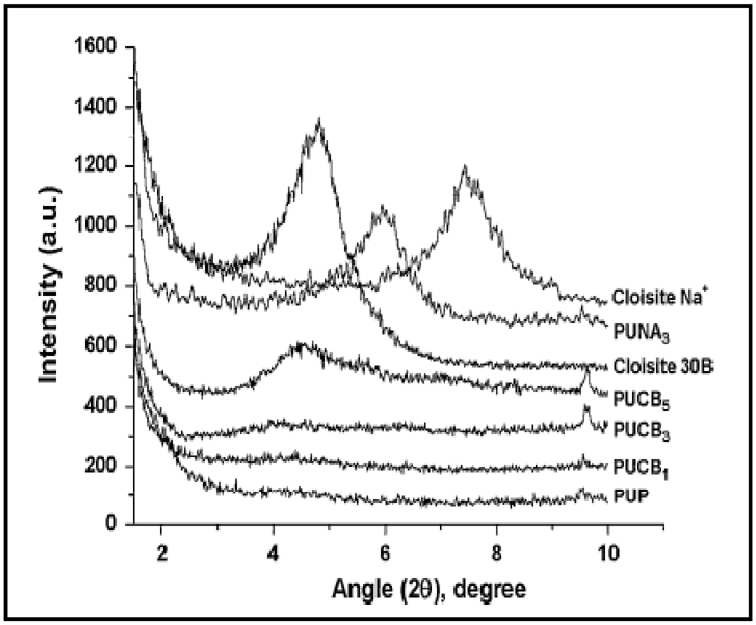


Figure 2.6: Comparison of XRD Graph for Solution and Melt Intercalation

(Source: Maji, et.al., 2009)

2.5 SURFACE MODIFICATION

Prior to dispersing, the clay needs to be first pretreated due to its hydrophilic nature. Unfortunately, most polymers are hydrophobic and consequently are not compatible with hydrophilic clays. Organophilic clay can be formed from normally hydrophilic clay by modifying the surface of the clay by attaching a new functional group to the outer plane or by replacing the current functional group with a different one (ion-exchange). Since polymers are generally organophilic, unmodified nanoclay are difficult to disperse. (Zhang, 2008)

The hydrophilic nature of clay is not the only reason which causes this nanofiller to be not quite suited for mixing and interacting with polymer matrices;- the electrostatic force which holds the stacks of clay platelets tightly together is also a cause behind the poor dispersion quality of naturally occurring montmorillonite. This strong electrostatic force is due to positively charged ions being attracted to the net negative charge within the clay structure. These positive ions will shared between the layers of aluminosilicate causing the stacks of plate-like structure within the morphology of the nanofiller to be bound together strongly. Through clay surface modification, montmorillonite is transformed from being hydrophilic to being organophilic and, therefore, compatible with conventional polymers. Surface compatibilization is also known as “intercalation”. Once the nanoclay has been successfully modified it will provide for better dispersion in the polymer matrix. (Zhang, 2008)

Due to these reasons, clay is treated prior to use in the production of nanocomposite. Making a composite out of untreated clay would be extremely ineffective as most of the clay will be unable to properly interact with the polymer matrices. One of the easiest ways to modify the surface of the clay is by using ion exchange. Thus, the clay was modified with Copper^{2+} ions using this method. (Nawani, 2007).

There were four choices of solvent and transition metal ion (TMI) salts proposed in this research which were to be used with pristine clay (Cloisite Na^{+}). These options are listed below in Table 2.4

Table 2.4: List of Solvent and Corresponding TMI Salts

SOLVENT	TMI SALTS	CONCENTRATION
Water	Copper (II) Sulphate	0.3 M
Methanol	Copper (II) Chloride	0.3 M
Ethanol	Copper (II) Chloride	0.3 M
Dioxane	Copper (II) Nitrate	0.3 M

The quality of the dispersion was observed by using Scanning Electron Microscope (SEM) and it was found that the results acquired from this research which proposed the usage of solution intercalation method was quite encouraging. Figure 2.7 below is a SEM image acquired once the modification was successful.

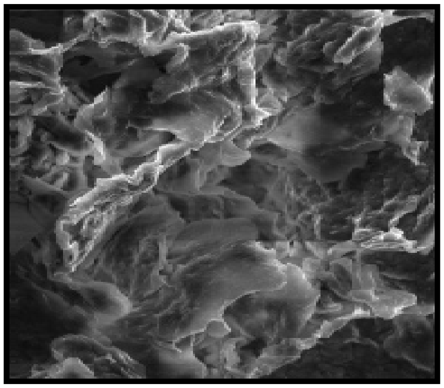


Figure 2.7: SEM Image of Modified Clay

(Source: Nawani, 2007)

From the results, it was also noted that the onset temperature of the thermally induced weight loss in TMI-modified organoclays was significantly higher. The drastically higher thermal stability of TMI-modified organoclays can be attributed to the charring processes which were enhanced by the presence of catalytically active TMIs. This high thermal stability of TMI-modified organoclays will make it an effective flame resisting agent. (Jia, et al., 2010)

2.6 EXPERIMENTAL METHODOLOGY AND ANALYSIS

Three tests will be conducted in regards to the polymer nanocomposite generated through this research. These tests include a biodegradability test, a fatigue resistance test as well a thermal stability test. A biodegradability test was chosen in line with the global interest that is moving toward environmental-friendly products. Biodegradable plastics are anticipated to offer significant economic and industrial growth potential (Lazenby, 2011). The biodegradability of products helps to reduce pollution and as such shows significant growth potential especially in end-users industries.

There are two primary methods use to test the biodegradability of the polymer nanocomposite which are takes into consideration hydrolytic degradation and enzymatic degradation. In the hydrolytic degradation test, a sample of the polymer is immersed in a phosphate buffer solution. The sample is the left for an incubation period about one week. The amount of weight loss of the polymer nanocomposite sample will signify the biodegradability of the sample. (Yoon, 2005). Enzymatic degradation is usually tested using soil burial techniques. This test requires the polymer nanocomposite to be buried in compost at 55°C and left to incubate. The problem with the soil burial test is that it is heavily influenced by outside conditions such as weather and humidity. (Quynh, et al., 2007) For the current research, the soil burial test will not be used.This is because preparation of the compost used in soil burial test requires a long duration. Due to the time constraint of the research, hydrolytic degradation method is chosen.

The biodegradability is expected to increase as the modification will be using transition metal ions. It has been noted that biodegradability of PLA nanocomposites increase due to the transition metal ions which are present as impurities in the nanofiller. This is because the Cu^{2+} ions act as a catalyst to accelerate the decomposition of PLA. (Bochini, et al, 2009). The two most common industrial problems are fatigue and low thermal stability. Therefore, it is important that the polymer nanocomposite produced during this research takes into account these issues. In regards to thermal stability, the improvement in property is not only important in the industrial point of view but also because similar thermal stability enhancements are difficult to achieve by reinforcement of conventional fillers. By treating organoclays with transition metal ions, the thermal stability of the nanofiller will increase thus increasing the thermal stability of the polymer nanocomposite. The thermal stability test is carried out using thermogravimetric analysis based on ASTM D-648 standards.

2.7 CONCLUSION

The literature was studied and analyzed in order to find a suitable research scope and effective experimental methods. Though, some unconventional methods were also utilized through the course of the research, the principle and overall effect of the methods were made sure to be indentical. The literature was useful when trying to gauge expected results as well as when trying analyzed acquired data.

CHAPTER 3

METHODOLOGY

3.0 INTRODUCTION

The main objective of the research is to use modified organoclay as a filler in polymer nanocomposites in order to improve its final properties. The modification will be done using solution dispersion method. Verification of the modification is done through FTIR, AAS and SEM testing (Hoidy, 2010). The succefully modified clay is then intercalated into polymer matrices and then tested again to determine its final properties.

3.1 INSTRUMENTS & EQUIPMENT

Ultrasonic Water Bath, Scanning Electron Microscope (SEM), Thermogravimetric Analyzer (TGA), Fourier Transform Infrared Spectroscopy (FTIR), Atomic Absorption Spectrometer (AAS), weighing scale, oven

3.2 MATERIALS

Nanoclay Cloisite Na^+ and Cloisite C20A were purchased from Southern Clay Products, Inc. Transition metal ion salts Copper (II) Chloride, Nickel Chloride and Ferum (III) Chloride were purchased from SIGMA-ALDRICH. Pellets of Polylactic acid (PLA) polymer were procured from Southern Clay Inc. Ethanol, Methanol and 1,2-Dicholoroethane were acquired from Merck Germany. Distilled water and Dioxane used were from laboratory resources.

3.3 APPPARATUS

Beaker 10mL, 250mL, 500mL and 1L, glass rod, parafilm, magnetic stir bar, aluminum foil, membrane filter, syringe, measuring cylinder 250ml and 10ml, volumetric flask 10ml and 50ml, filter paper, funnel, petri dish, spatula, 20mL universal bottles, vial 2 ml and 10ml, micropippete 1000µl and 100µl with tips, stopper, dropper, Schott bottle 100ml, sealed bags, vacuum filtration apparatus, magnetic hot plate, mortar and pestle, plastic weighing boats, centrifuge tubes, test tube stand.

3.4 METHODOLOGY

3.4.1 Modification of Nanoclay using Solution Intercalation Method

The main objective of the research is to use modified Cloisite Na^+ and Cloisite C20A as a filler in polymer nanocomposites in order to improve its final properties. Following that, it is only appropriate if the experiment begins with the modification of the nanoclay.

3.4.1.1 Pre-treatment Phase of Nanoclay

Prior to the modification stage, the clay has to first undergo a pre-treatment phase. During this stage, the clay needs to be washed thoroughly to remove residual impurities. The nanoclay sample is mixed with ethanol at an approximated solvent to clay ratio of 20 ml to 1g. The suspension is then stirred vigorously for 8 hours at a temperature of approximately 50-60°C. The resulting slurry is kept in a 1 M NaCl which was prepared from solid Sodium Chloride salt. The solution is left for 48 hours to allow the removal of exchangeable ion contaminants. Finally the slurry is filtered and dried in an oven for 12 hours at 60°C.

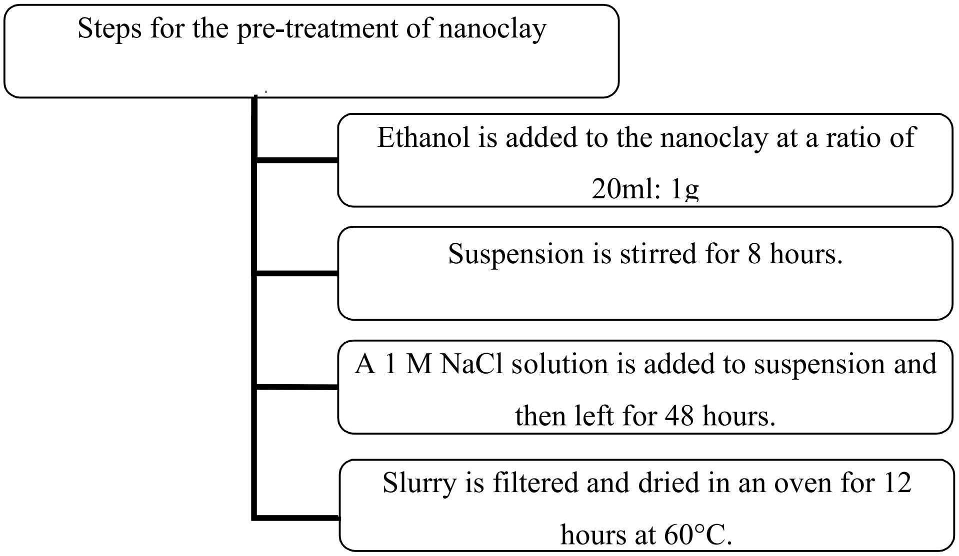


Figure 3.1: Pretreatment of Nanoclay Steps

Figure 3.2: Ethanol and Nanoclay Slurry

3.4.1.2 Preparation of Metal Ion Solution and Surface Modification Phase

Once the clay has been dried, it is ready to be treated with 0.30 M of the desired metal ion salts. In this experiment we will focus on three types of metal ions which are Copper $^{2+}$, Ni^{+} and Fe^{3+}.

Based on the molecular weight of each of the metal ion salts, the desired weight of material required to produce a 250 ml, 0.3M solution is determined and recorded in Table 3.1. Figure 3.5.1.2 shows the prepared solutions.

Table 3.1: Calculated Mass of Transition Metal Salt Required

Salt	Molecular Weight (g/mol)	Weight Required (g)
Copper (II) Chloride, $CuCl_2$	134.45	10.08
Nickel Chloride, $NiCl_2$	129.59	9.72
Ferum Chloride, $FeCl_3$	162.30	12.17

Figure 3.3: Transition Metal Ion Salt Solutions

To prepare the solutions seen above, the required amount of metal salt needed is first weighed and then dissolved in dioxane (solvent). The solution is stirred for 1-2 hours prior to the addition of Cloisite Na$^+$. For this experiment approximately 10g of pre-treated Cloisite Na$^+$ was used for every 250ml of metal ion solution. Once the clay is added, the solution is stirred for 5-6 hours and then left for 24 hours. During stirring, it is necessary to use a closed container to prevent the evaporation of the solution. After the treatment, the sample needs to be filtered, washed, and dried once again in an oven for 12 hours at 80ºC. (Nawani, 2007). The above procedure is repeated for the following combination of solvent-clay-metal ions as listed in Table 3.2.

Table 3.2: Prepared Clay-Solvent-Metal Ion Combinations

Nanoclay	Solvent	Metal Ions
Cloisite Na$^+$	Dioxane	Copper
		Nickel
		Ferum
	Ethanol	Copper
		Nickel
		Ferum
	Methanol	Copper
		Nickel
		Ferum
Cloisite Na$^+$	Dioxane	Copper
		Nickel
		Ferum
	Ethanol	Copper
		Nickel
		Ferum
	Methanol	Copper
		Nickel
		Ferum

3.4.2 Adsorption Intensity Testing Using Soil Leaching Procedures and Atomic Adsorption Spectrometry

The variability in the intensity of adsorption of the transition metal ions unto the surface of nanoclay due to the utilization of different solvents are tested in this stage. This step is done to prove that ethanol is a viable solvent to be used during the surface modification by solution intercalation phase.

3.4.2.1Soil Leaching Stage

In this step, first the soil leaching medium is prepared. The medium used is 0.05M Ethylenediaminetetraacetic acid, EDTA which is prepared by first weighing 14.612g of EDTA powder, which has a molecular weight of 292.24g/mol. The EDTA is then dissolved into 1000mL of Ultrapure Water. The recovery rate of heavy metals using this medium is approximately 97% (Hwang, Park & Namkoong, 2007).

5g of clay is placed in a schott bottle, and he 0.05M EDTA solution is added to it at a ratio of 10mL:1g. The bottle is then placed in an ultrasonic waterbath for 12 minutes at 60kW to leach the adsorbed metal ions back out of the surface of the nanoclay. Method is shown in Figure 3.5.2.1(a). This step is done to prove that the metal ions had attached itself to the surface of the nanoclay as well as to determine the concentration and amount of metal ions that had been adsorbed unto the surface of the nanoclay. The remaining solution is filtered once using vacuum filtration with 1μm filter paper.

Figure 3.4: Soil Leaching Equipment

3.4.2.2 Atomic Adsorption Spectrometry Testing

Before running the sample in AAS, it is first filtered using an 0.22µm syring filter. This is shown in Figure 3.5.2.2. Then 100µL of sample clay leachate is then diluted with ultrapure water to 10mL, which is a dilution factor of 100. The standards for each metal ions to be tested is also prepared using serial dilution method, with the first standard being prepared at a concentration of 10ppm. The stock solution provided has a concentration of 1000ppm. Therefore, the amount of stock solution needed can be calculated through the usage of the following formulae:

$$M_1V_1 = M_2V_2 \text{ ------------------- } (1)$$

M_1 = concentration of stock solution
= 1000ppm
M_2 = concentration of the first standard
= 10ppm
V_2 = volume of standard needed
= 10mL

Therefore the V_1, volume of stock solution needed $= \frac{10\text{ppm} \times 10\text{mL}}{1000\text{ppm}}$

$= 0.1$ mL

$= 100$ µL

Subsequent standards prepared are 5ppm, 2.5ppm, 1.25ppm and a blank. This is done by pouring 5mL of the prepared 10mL, 100ppm standard into a new centrifuge tube and diluting it with 5mL of ultra pure water. This will provide for a 5ppm standard solution. This dilution step is repeated for subsequent standards.

The summary of the standards and samples ran through AAS is shown in Table 3.3

Table 3.3: Summary of AAS Samples

Transition Metal Ions	Standard	Sample
Cu/Ni/Fe	10.00 ppm 5.00 ppm 2.50 ppm 1.25 ppm 0.00 ppm	C20 in Dioxane
		MMT in Dioxane
		C20 in Ethanol
		MMT in Ethanol
		C20 in Methanol
		MMT in Methanol

The concentration values acquired are times with the dilution factor and clay leaching recovery rate.

Therefore actual concentration of sample;-

Actual concentration = AAS reading x dilution factor x clay leaching recovery rate

Given: Dilution factor = 100
Recovery rate = 97%

Actual Concentration = AAS reading x 100 x 0.97 --------------------- (2)

Figure 3.5: Preparation Step for AAS

3.4.3 Morphology Study Using Scanning Electron Microscopy (SEM)

A SEM test was carried out to check the surface of the modified nanoclay. An uncharacteristically rough surface is not suitable to be made commercial and proves the quality of modification is sub-par.

For this test, the clay must be in the form of fine clay. Therefore the clay is pounded using a mortar and pestle and subsequently, dried in the oven for 30-45 minutes at 60°C. Then the clay is dispersed on a petri dish and divided into four sections as in Figure 3.6.

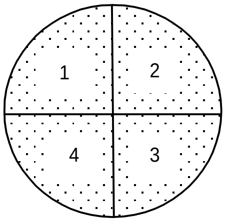


Figure 3.6: Dispersed Nanoclay on Petri Dish

Samples from all four sections are gathered and mixed together. This portion of the nanoclay is then inserted in a 2mL vial. SEM testing was conducted by the central lab. The equipment is as seen in Figure 3.7. SEM Images will be taken using a back-scattering detector.

Figure 3.7: SEM Equipment

3.4.4 FTIR Testing of Modified Nanoclay

This test was carried out using the FTIR made available at the FKKSA Laboratory. The FTIR was run using the SMART Collector (Diffuse Reflectance) head. The background of the samples was all set based on standard KBr. Once the background was completed, the readings for the samples were taken. Powdered samples were used for this test. Samples are made sure to be in line with the read beam to ensure accurate readings. The graph displayed will show the different level of absorbance between various peaks. Figure 3.8 shows the equipment used in the FTIR analysis.

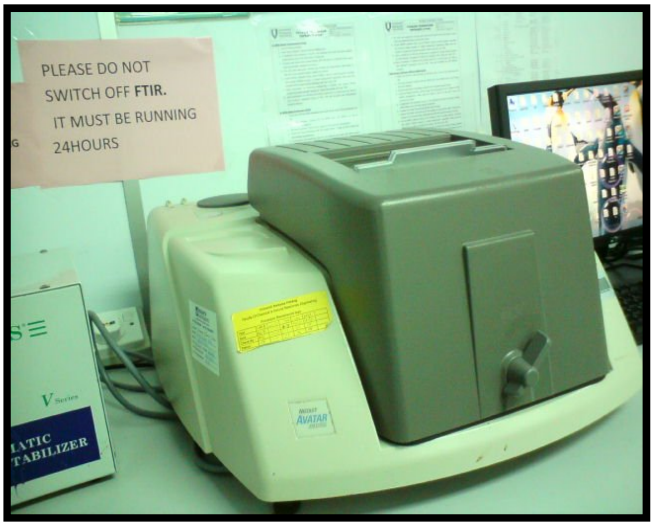


Figure 3.8: Fourrier Transform Infrared Analyzer

3.4.5 Production of Polymer Nanocomposite

After the modification stage is confirmed to be successful. The modified nanofiller will then be dispersed in Polylactic Acid to form a polymer nanocomposite. This step begins by dissolving the 57g of PLA pellets in 100 ml of 1,2 Dichloroethane. This solution is left for 24h to aid dissolution. Then 3g finely powdered modified Closite Na$^+$ was then then added into the solution. It must be ensured that the nanofiller makes up for $\leq$ 5wt% of the total PLA and nanoclay weight, in compliance with standard polymer nanocomposite standards. The resulting mixture is refuxed for 1 hour and then stirred vigorously stirred for 3 hours. Finally, the nanocomposite is poured into a Petri dish and left to dry. The thin layer of nanocomposite is then formed into granulates. The steps are repeated for all modified Cloisite C20 and Cloisite Na$^+$. Figure 3.9 and Figure 3.10 show the steps which are involved.

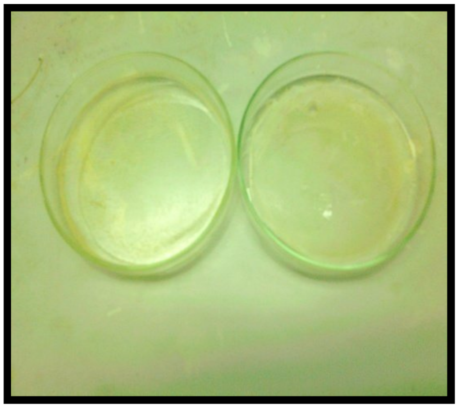


Figure 3.9: Polymer nanoclay solution poured into petri

Figure 3.10: Formed polymer nanocomposite plastic

3.4.6 Testing of Polymer Nanocomposite

3.4.6.1 Hydrolytic Degradation Testing

To test the biodegradability, the hydolytic degradation of PLA is used. Samples of 300 mg of PLA/clay nanocomposite granulates were immersed in 0.13M, pH 7.4 phosphate buffer solution at 37 degrees °C, as seen in Figure 3.11. After an incubation period of 10 days, the granulates are taken out and washed with distilled water and finally dried to a constant weight in vacuum conditions. The degree of biodegradation will be evaluated by measuring weight loss after 10 days. Test results are compared with weight loss of a control sample that consists of pure PLA granulates.(Quynh, et al., 2007)

Figure 3.11: Polymer Nanocomposites Immersed in Phosphate Buffer

3.4.6.2 Thermal Stability Testing

Lastly, a test is conducted using a thermogravimetric analyzer (TGA) to test the thermal stability of the polymer nanocomposite. For this test, the samples were heated from 35°C to 400°C at a rate of 10°C/min under a nitrogen atmosphere with a nitrogen flow rate of 20ml/min (Chow, et. al., 2009). All tests mentioned above will also be conducted for a sample of PLA nanocomposite using unmodified Cloisite Na^+ and Cloisite C20 to prove the improvement in the final properties of the polymer nanocomposite. Figure 3.12 show the equipment used for the thermal stability test.

Figure 3.12: Thermal Gravimetry Analyzer

CHAPTER 4

RESULTS AND DISCUSSIONS

4.0 INTRODUCTION

This chapter presents all the finding and data acquired throughout the course of this experiment. The results are also discussed in depth, so that it may be used to support and prove the objectives and scopes of this research. The discussion and findings encompass results from equipments such as Atomic Adsorption Spectrometer (AAS), Scanning Electron Microscopy (SEM), Thermal Gravimetry Analyzer(TGA) and Fourrier Transform Infrared (FTIR).

4.1 ATOMIC ADSORPTION SPECTROMETER (AAS) RESULTS AND DISCUSSION

In the Atomic Adsorption Spectrometer Test, the concentration and amount of transition metal ions that have attached itself to the surface of the nanoclay are tested. Each sample was prepared using different solvent/clay/transition metal ion pairing. The purpose of this test is to specifically proof the feasibility of using ethanol as a solvent for the proposed transition metal ions. The metal ions are able to attach themselves through ion exchange with the free moving cations in between the silicate layers. This is in accordance to Le Chateliers law which indicates when there is an excess of one ion or charged atom, the equilibrium will shift to accommodate the excess ions. Thus, the charged metal ions will substitute the cations. Once Ethanol is proven to be a viable solvent, the research will be carried on using modifications which utilized Ethanol as a solvent. The concentration values acquired through AAS are summarized in Table 4.1.

Table 4.1: AAS Results for Soil Leachate (Diluted Factor:100)

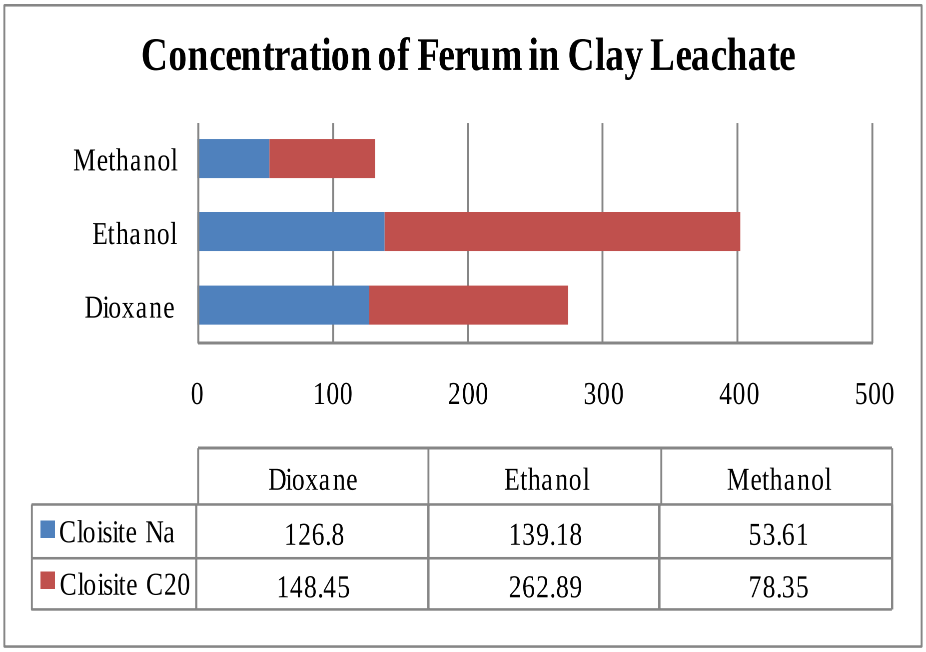
Transition Metal Ion	Solvent	Cloisite Na^+ Concentration (ppm)	Closite C20 Concentration (ppm)
Copper	Dioxane	0.91	1.76
	Ethanol	1.05	1.98
	Methanol	1.99	2.52
Ferum	Dioxane	1.23	1.44
	Ethanol	1.35	2.55
	Methanol	0.52	0.76
Nickel	Dioxane	1.67	2.57
	Ethanol	1.21	2.14
	Methanol	0.79	2.01

For all preceeding tests, the sample leachates were diluted with 1:100 V/V ratio. Therefore all concentration values acquired through AAS needs to be multiplied by 100 and divided with 0.97;- which accounts for the recovery rate of transition metal ions through soil leaching using EDTA has a medium. The calculated values of the concentration are listed in Table 4.2.

Table 4.2: Actual Concentration of Transition Metal Ion in 5g of clay

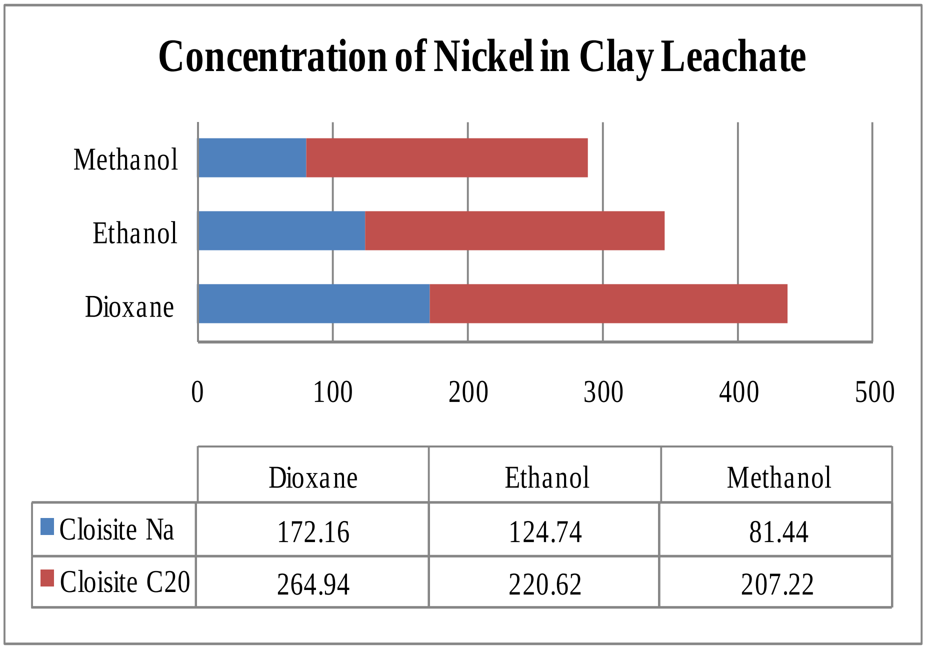
Clay	Solvent	Ferum (ppm)	Nickel (ppm)	Copper (ppm)
Cloisite Na^+	Dioxane	126.80	172.16	93.81
	Ethanol	139.18	124.74	108.25
	Methanol	53.61	81.44	205.15
Cloisite C20	Dioxane	148.45	264.94	181.44
	Ethanol	262.89	220.62	204.12
	Methanol	78.35	207.22	259.79

Graphs showing the difference in the amount of transition metal ion adsorbed on the surface of nanoclay using various solvents are plotted. Also, a comparison between the amount of transition metal ion adsorbed based on clay type is also discussed. Figures 1 till 5, represent the amount of a particular metal ion present in the nanoclay, when prepared using different solvents. The subsequent Figures 4.1 till 4.5 represent the efficiency of a particular solvent in aiding the attachment of different transition metal ions on the surface of the nanoclay.



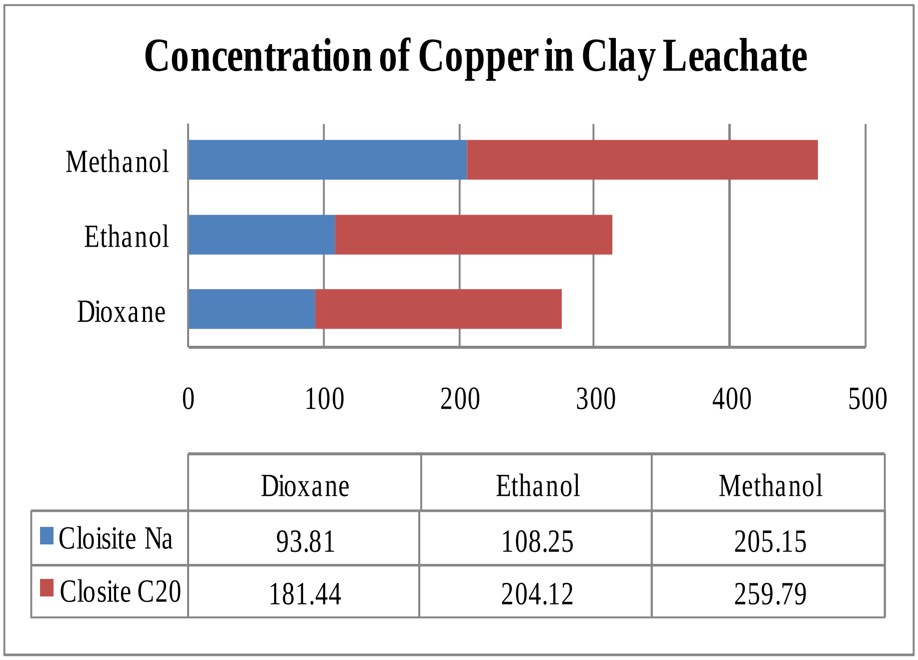
	Dioxane	Ethanol	Methanol
🟦 Cloisite Na	126.8	139.18	53.61
🟥 Cloisite C20	148.45	262.89	78.35

Figure 4.1: Amount of Ferum Present in Modified Organoclay Leachate



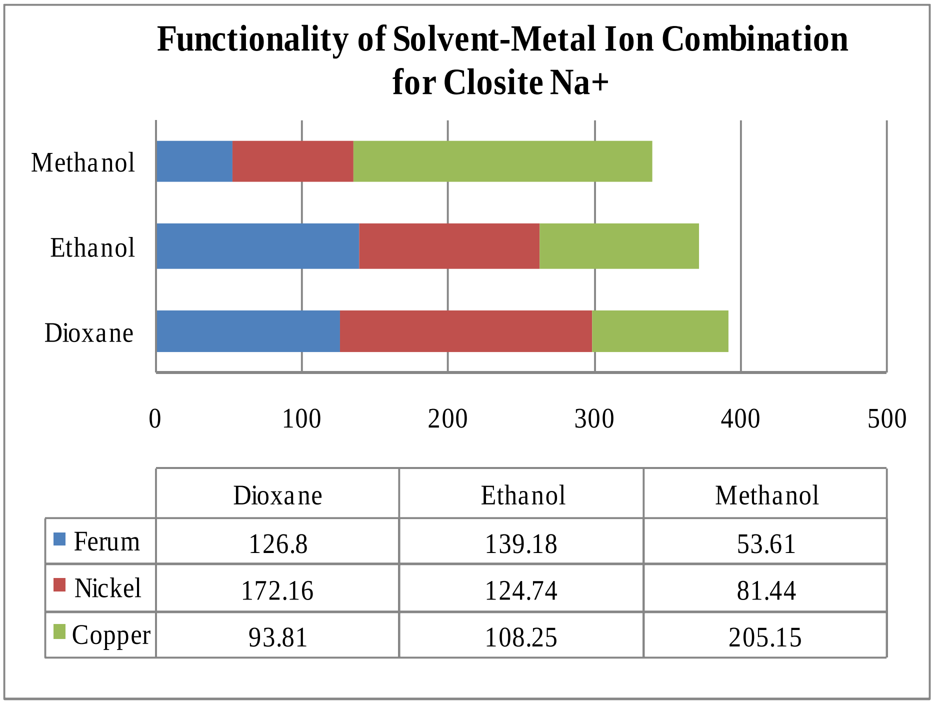
	Dioxane	Ethanol	Methanol
🟦 Cloisite Na	172.16	124.74	81.44
🟥 Cloisite C20	264.94	220.62	207.22

Figure 4.2: Amount of Nickel Present in Modified Organoclay Leachate



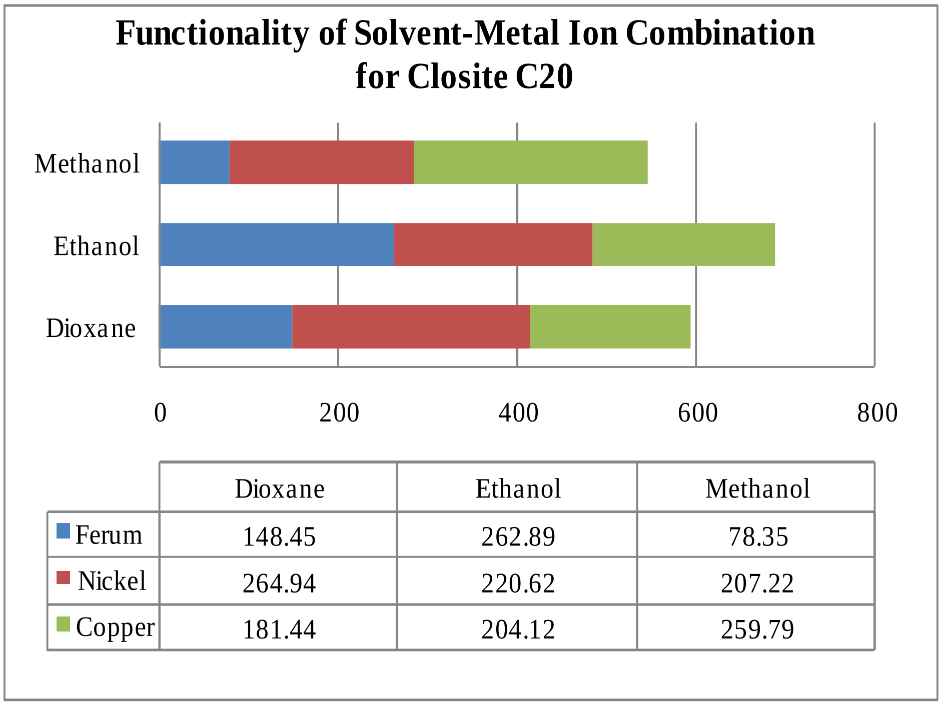
	Dioxane	Ethanol	Methanol
🟦 Cloisite Na	93.81	108.25	205.15
🟥 Closite C20	181.44	204.12	259.79

Figure 4.3: Amount of Copper Present in Modified Organoclay Leachate



	Dioxane	Ethanol	Methanol
🟦 Ferum	126.8	139.18	53.61
🟥 Nickel	172.16	124.74	81.44
🟩 Copper	93.81	108.25	205.15

Figure 4.4: Efficiency of Solvent to aid attachment of Metal ions to pristine clay (Cloisite Na^+/MMT)



	Dioxane	Ethanol	Methanol
🟦 Ferum	148.45	262.89	78.35
🟥 Nickel	264.94	220.62	207.22
🟩 Copper	181.44	204.12	259.79

Figure 4.5: Efficiency of Solvent to aid attachment of Metal ions to organoclay (Cloisite C20)

From the plotted graphs, it can be seen that ethanol is a viable option when modifying using solution dispersion method. For Cloisite Na^+, modifications using ethanol as a solvent showed the best adsorption for Ferum ions. The level of adsorption was even greater than the proposed solvents, methanol and dioxane. For Nickel and Copper, it showed mediocre level of adsorption, being slightly less than Dioxane for Nickel and Methanol for Copper. For Cloisite C20, the efficiency of adsorption for different transition metal ions is similar to that of Cloisite Na^+

4.2 SCANNING ELECTRON MICROSCOPY (SEM) RESULTS AND DISCUSSION

4.2.1 Modified Cloisite Na^+ (1000x magnification)

The Figures 4.6 till Figure 4.9 show the SEM images that were taken at 1000x magnification for modified and unmodified Cloisite Na^+.

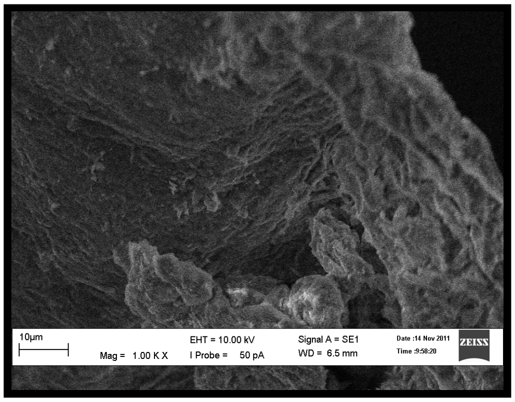


Figure 4.6: Modified Cloisite Na^+ with Nickel 1000x

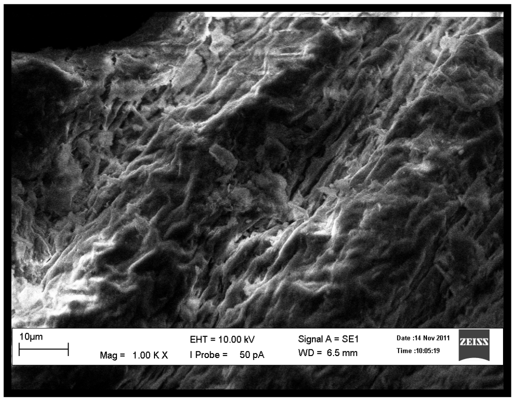


Figure 4.7: Modified Cloisite Na^+ with Copper 1000x

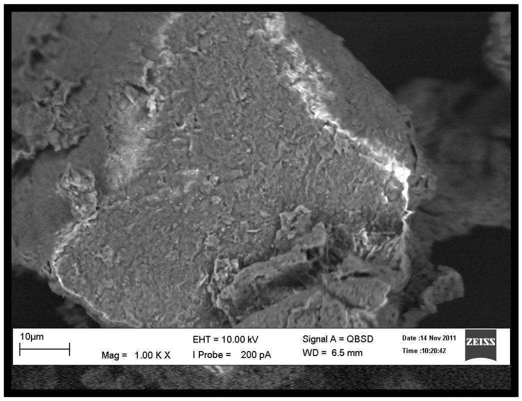


Figure 4.8: Modified Cloisite Na^+ with Ferum 1000x

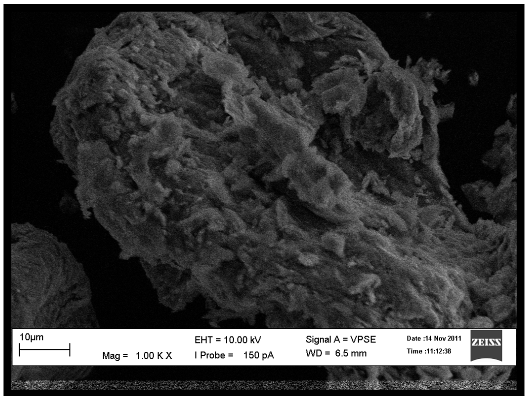


Figure 4.9: Unmodified Cloisite Na^+ 1000x

From the visual inspection of the above three images, it is found that the Cloisite Na^+ modified with Ferum has a smoothest surface with the smallest surface area. This is followed by Cloisite Na^+ modified with Nickel which shows a mediocre quality of surface smoothness. The modification with Copper ions brought forth the poorest surface quality when visualized under a 1000x magnification SEM image.

4.2.2 Modified Cloisite Na^+ (400x magnification)

The Figures 4.7 till Figure 4.13 show the SEM images that were taken at 400x magnification for modified and unmodified Cloisite Na^+.

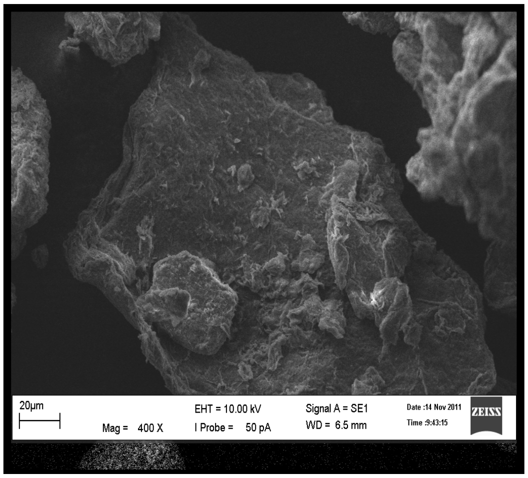


Figure 4.10: Modified Cloisite Na^+ with Nickel 400x

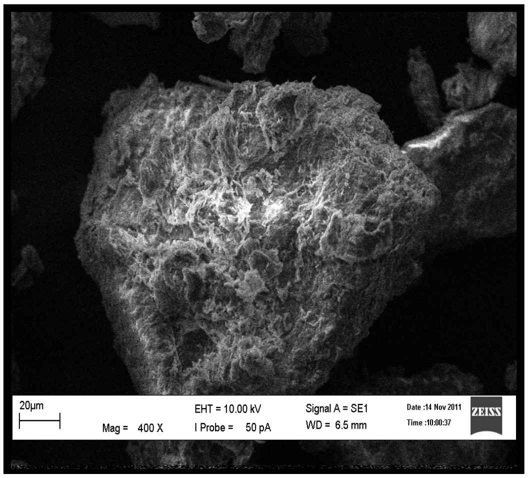


Figure 4.11: Modified Cloisite Na^+ with Copper 400x

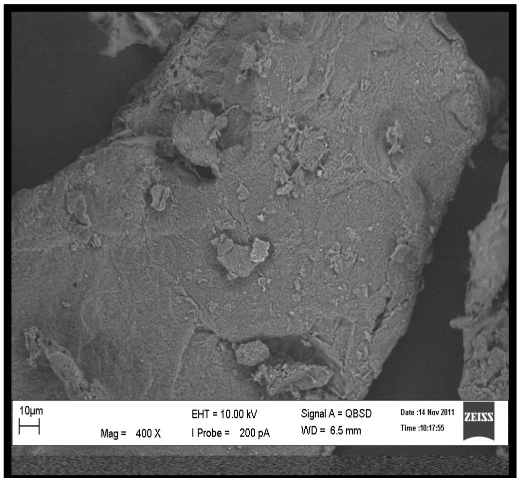


Figure 4.12: Modified Cloisite Na$^+$ with Ferum 400x

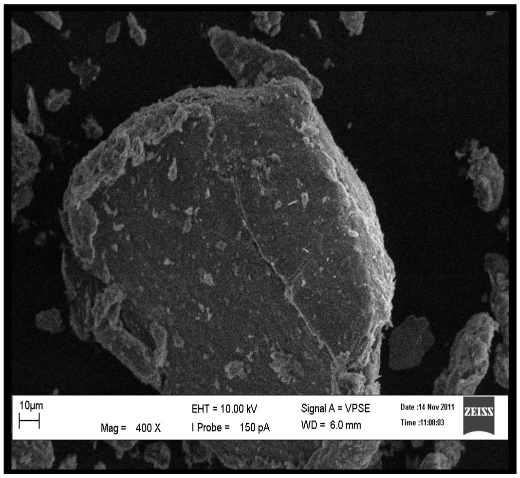


Figure 4.13: Unmodified Closite Na$^+$ 400x

In terms of particle size, the unmodified nanoclay has the smallest particle size. From Figure 4.13, it is apparent that there are a higher number of individual particles per frame at 400x which indicates a smaller particle size. The second highest number of particles per frame can be seen in Figure 4.11 which shows images captured of modified Cloisite Na$^+$ with Copper. This indicates a slightly larger particles size in comparison to unmodified Closite Na$^+$. Based on the number of particles per frame in Figure 4.10 and Figure 4.12, it can be concluded that the paticle size of modified Closite Na$^+$ with Ferum is the largest followed by Cloisite Na$^+$ modified with Nickel. It is probable that a larger particle size is due to a higher degree of transition metal ion attachment.

4.2.3 Modified Cloisite C20 (x1000 magnification)

The Figures 4.14 till Figure 4.16 show the SEM images that were taken at 1000x magnification for modified and unmodified Cloisite C20.

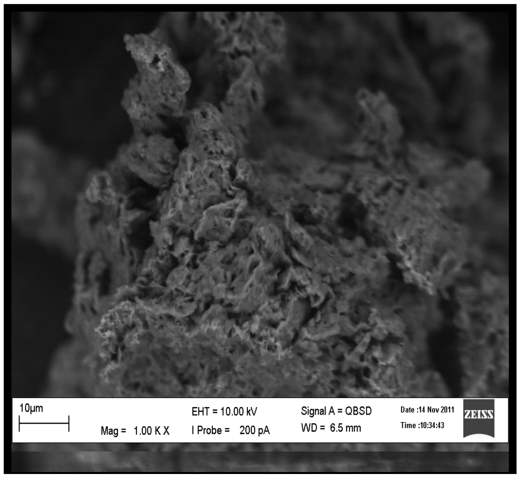


Figure 4.14: Modified Cloisite C20 with Nickel 1000x

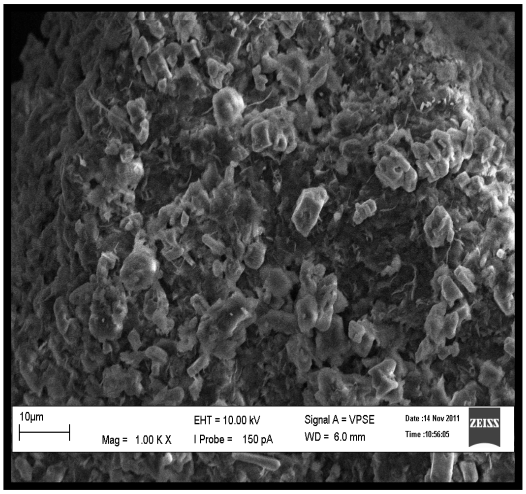


Figure 4.15: Modified Cloisite C20 with Copper 1000x

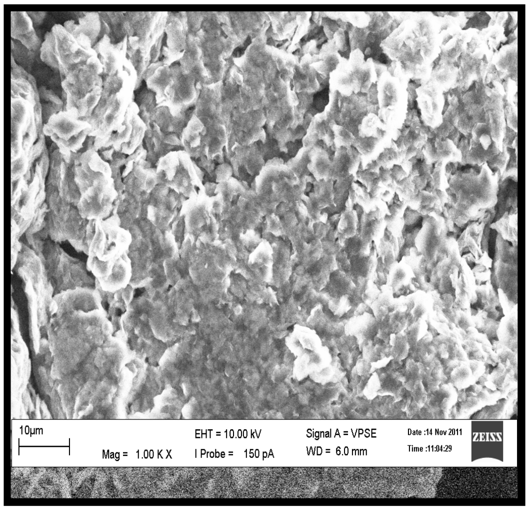


Figure 4.16: Modified Cloisite C20 with Ferum 1000x

From the visual inspection of the above three images, it is found that the Ferum-modified Cloisite C20 has the smoothest overall surface;- as large flat surfaces can be noticed. This is followed by Nickel-modified Cloisite C20 which shows an average quality of surface smoothness. The modification with Copper ions brought forth the poorest surface quality with many small protuberances that caused irregularities when visualized under a 1000x magnification SEM image.

4.2.4 Modified Cloisite C20 (x 400 magnifications)

The Figures 4.17 till Figure 4.20 show the SEM images that were taken at 400x magnification for modified and unmodified Cloisite C20.

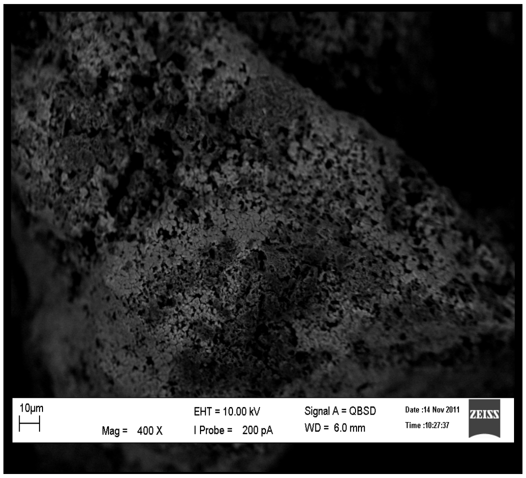


Figure 4.17: Modified Cloisite C20 with Nickel 400x

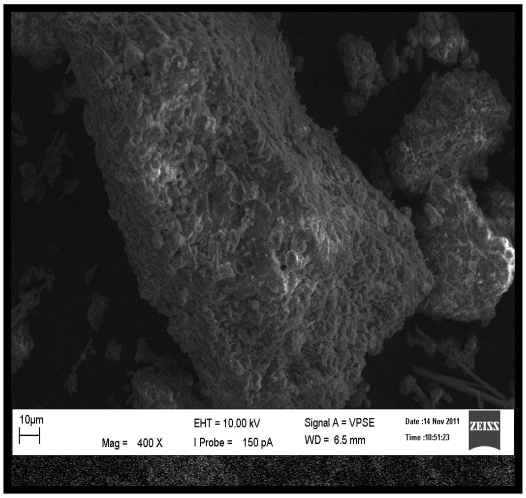


Figure 4.18: Modified Cloisite C20 with Copper 400x

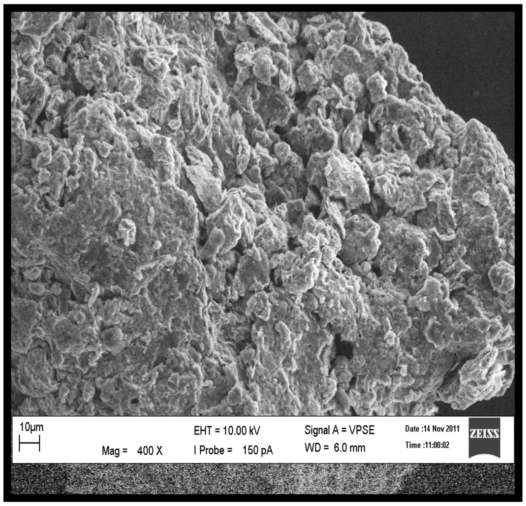


Figure 4.19: Modified Cloisite C20 with Ferum 400x

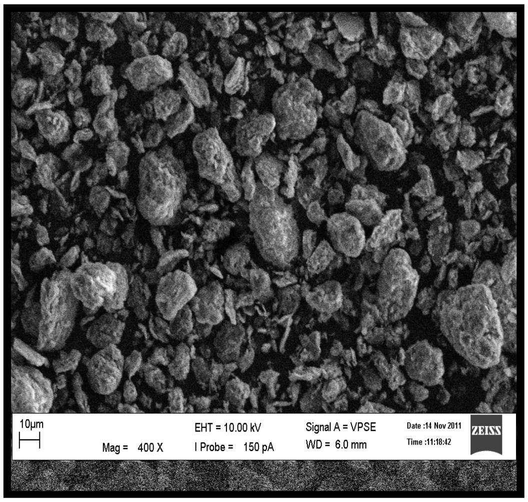


Figure 4.20: Unmodified Cloisite C20 400x

In terms of particle size, the unmodified nanoclay has the smallest particle size. From Figure 4 20, it is apparent that there are a higher number of individual particles per frame at 400x which indicates a much smaller particle size. The second highest number of particles per frame can be seen in Figure 4 18 which shows images captured of Copper modified Cloisite C20. This indicates a slightly larger particles size in comparison to unmodified Closite C20. Based on the number of particles per frame in

Figure 4.17 and Figure 4.19, it can be concluded that the paticle size of Ferum modified Closite C20 is the largest followed by Nickel modified Cloisite C20. It is theorized that a larger particle size eludes to a higher degree of attachment of transition metal ions.

4.2.5 Comparison between Surface Area of Specific TMIs

When comparing between the two clays, Cloisite C20 and Cloisite Na^+ in terms of surface condition after treatment with transition metal ions, a general observation that Cloisite Na^+ showed a cleaner attachment of ions. The surface area as well as the particle size of the Modified Cloisite Na^+ showed little variance when compared the original form of Cloisite Na^+. This is as theorized in a journal by Pawani which concludes that the majority of the transition metal ions are intercalated into the silicate layers rather than being deposited on the surface.(2007)

Table 4.3: Summary of Modified Nanoclay Surface Description

No.	Sample	Description
1	Mmt + Ni	Average particle size and surface smoothness
2	Mmt + Cu	Smallest particle size, surface is least smooth
3	Mmt + Fe	Largest particle size, surface is most smooth
4	C20 + Ni	Surface is the least smooth
5	C20 + Cu	Showed average surface smoothness
6	C20 + Fe	Surface Is Most Smooth

4.3 FOURIER TRANSFORM INFRARED (FTIR) RESULTS AND DISCUSSION

From the comparison spectra of the modified and unmodified Cloisite Na^+, it can be seen that the structure.

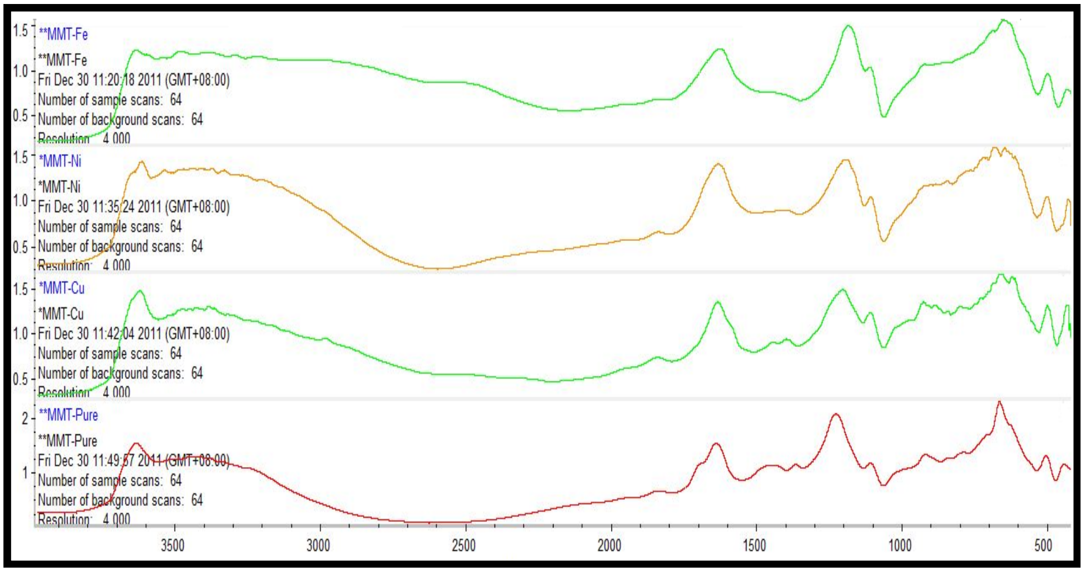


Figure 4.21: Comparison Spectra of Modified and Pure Cloisite Na^+ (MMT)

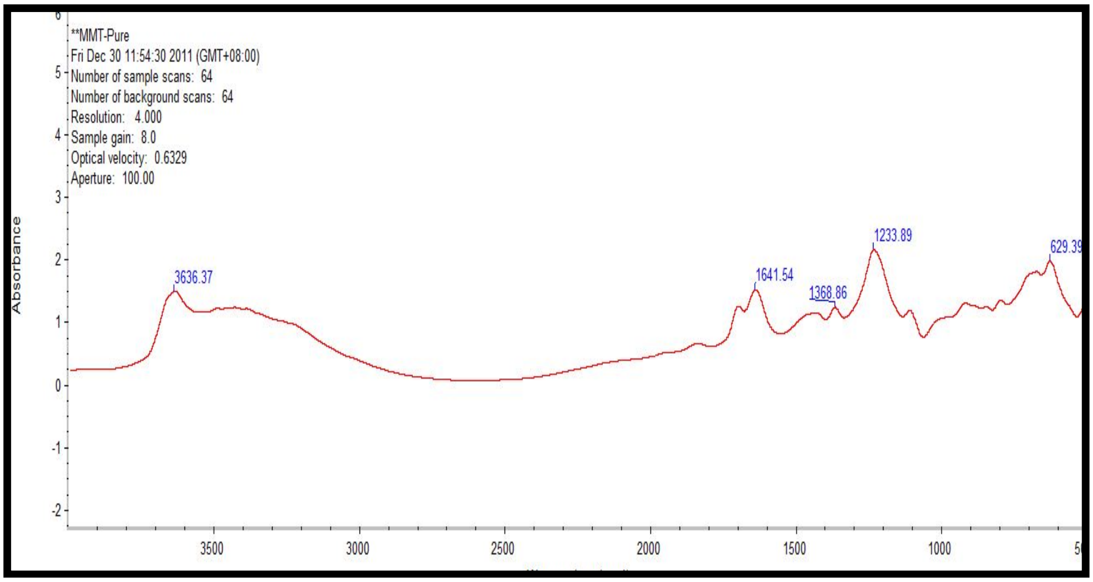


Figure 4.22: Spectra of Pure Cloisite Na^+ (MMT)

From the above spectra, it can be seen that the modification does not alter a lot of the bondings, as most of the peaks remains relatively the same with the exceptions being on the level or intensity of adsorption. This means that the amount of metal ions that have intercalated within the structure have homogenized enough for it to retain the essential or core structure of the clay. This proves that the modification has been done successfully.

4.4 BIODEGRADABILITY (HYDROLYTIC DEGRADATION) RESULTS AND DISCUSSION

Table 4.4 below shows the weight change that was recorded once the samples were immersed in a Phosphate Buffer for 10 days. The weight loss that happens is illustrated in Figures 4.23, 4.24, and 4.25

Table 4.4: Recorded Weight Before and After Immersion

Sample	Before (mg)	After (mg)		Average Final Weight (mg)	Average Weight Loss (mg)
		1st Run	2nd Run		
PLA/Cloisite Na$^+$	0.300	0.293	0.295	0.2940	0.0060
PLA/Cloisite Na$^+$/Ferum	0.300	0.278	0.273	0.2755	0.0245
PLA/Cloisite Na$^+$/Nickel	0.300	0.287	0.286	0.2865	0.0135
PLA/Cloisite Na$^+$/Copper	0.300	0.294	0.290	0.2920	0.0080

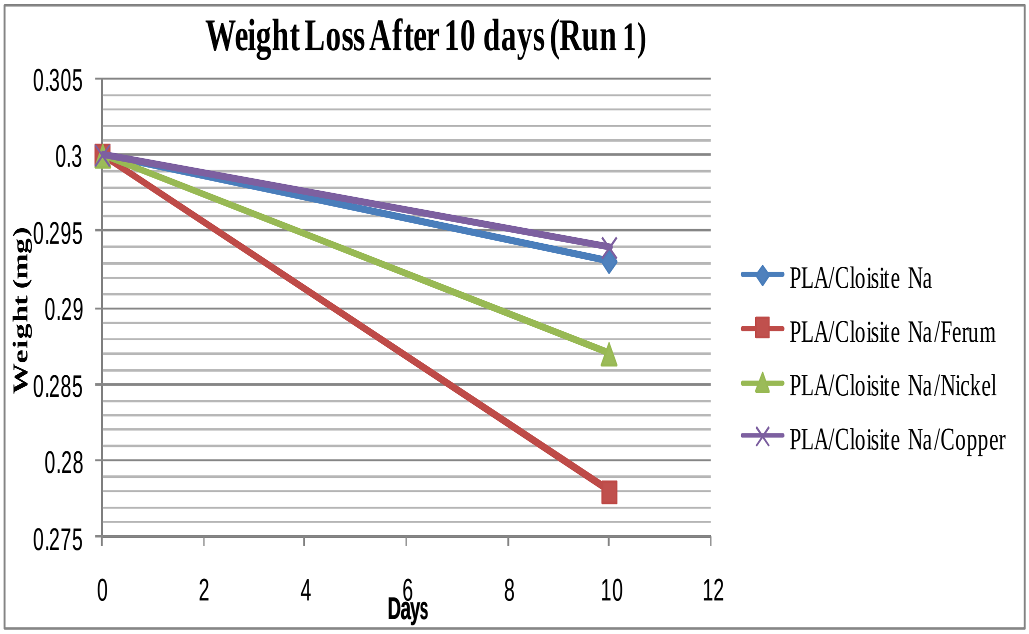


Figure 4.23: Weight Loss after 10 days (Run 1)

Figure 4.24: Weight Loss after 10 days (Run 2)

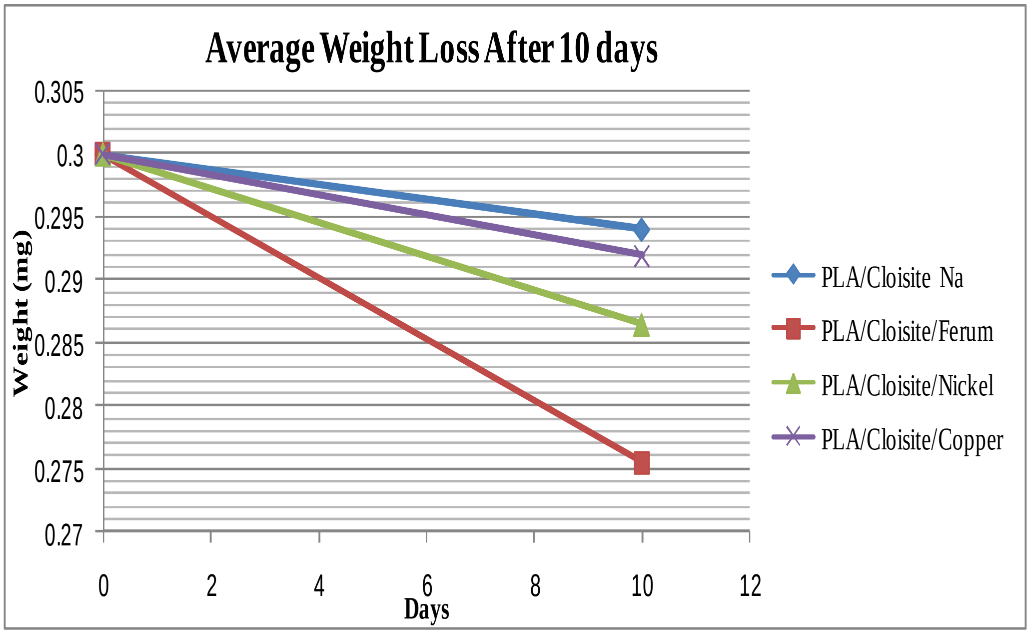


Figure 4.25: Average weight loss after 10 days

From, the plotted graph and data, we can see that the weight loss of the polymer nanocomposite with modified organoclay is larger. The highest weight loss was found in the Ferum-modified organoclay sample. This was followed by Nickel and finally Copper. Though the copper modified sample showed improvement in terms of degradability, this improvement was the least, with a 33% increase in weight loss. The ferum modified sample on the other hand, showed a 300% increment in weight loss. Whereas, the Copper modification demonstrated a spike of 125% in weight loss. The biodegradability (hydrolytic degradation) of a polymer should be evaluated together with the thermal stability, when choosing the most function polymer nanocomposite. According to Nawani (2009), the addition of Copper and other equivalent transition metal ions acts as a catalyst that accelerates the decomposition of PLA. Amongst the three transition metal ions tested, Nickel showed an average level of efficiency in aiding the decomposition of PLA. From the above results, we can conclude that Ferum acts as a better catalysts in the decomposition of PLA. This mayb due to Ferum being more easily oxidized. Once Ferum begins to undergo oxidation it starts losing dissipating its charge (electrons) which causes surrounding bonds to lose strength. The effectiveness of the metal ions as a decomposition aiding material has been found to be opposite to the value of its electronegativity;- with, Copper having the highest electronegativity, followed by Nickel and subsequently Ferum. This further substatiates this theory, however, further tests need to be run in order to fully prove this hypothesis.

4.5 THERMAL GRAVIMETRY ANALYSIS (TGA) RESULTS AND DISCUSSION

The thermal stability of the PLA/modified-Cloisite Na^+ nanocomposites are tested using a Thermalgravimetric Analyzer. The decomposition and degradation graph achieved for all four samples including that of PLA/non-modified graph are plotted and discussed. Figure 4.26 and 4.27 shows the overall decomposition curve for all samples whereas Figures 4.28 till 4.31 are plotted to acquire the rate of thermal degradation once the degradation temperature has been reached.

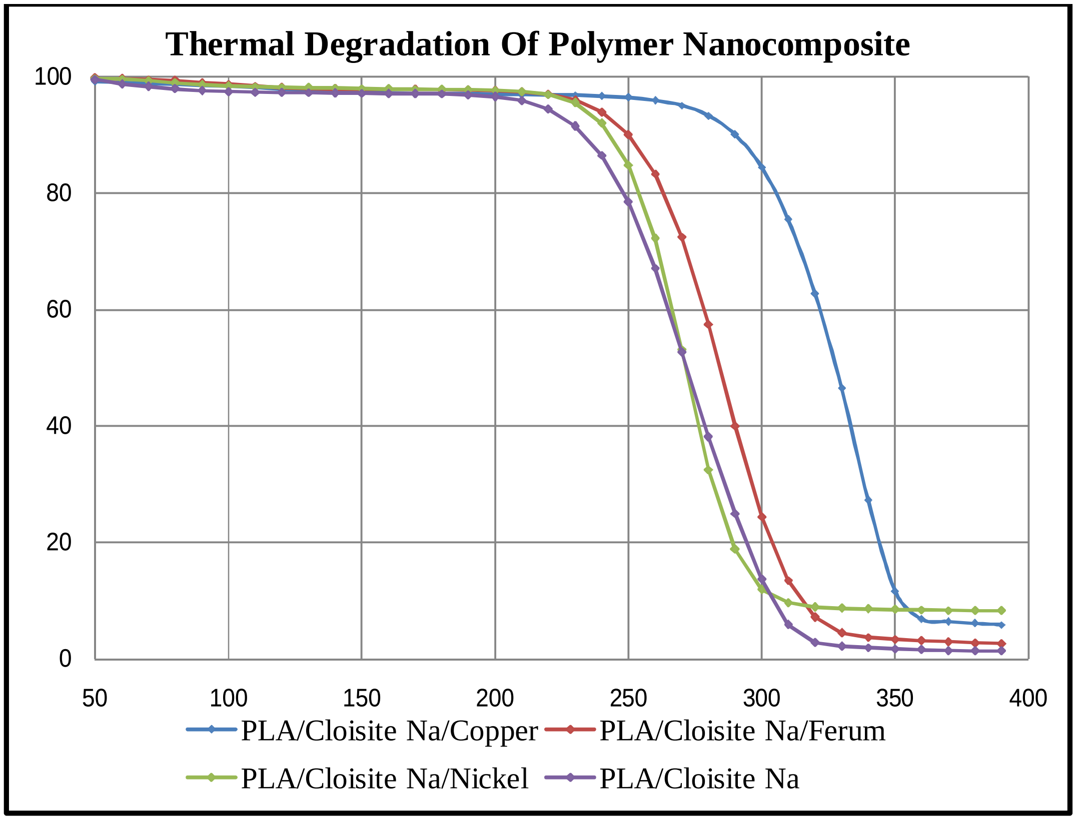


Figure 4.26: Thermal Degradation of Polymer Nanocomposite

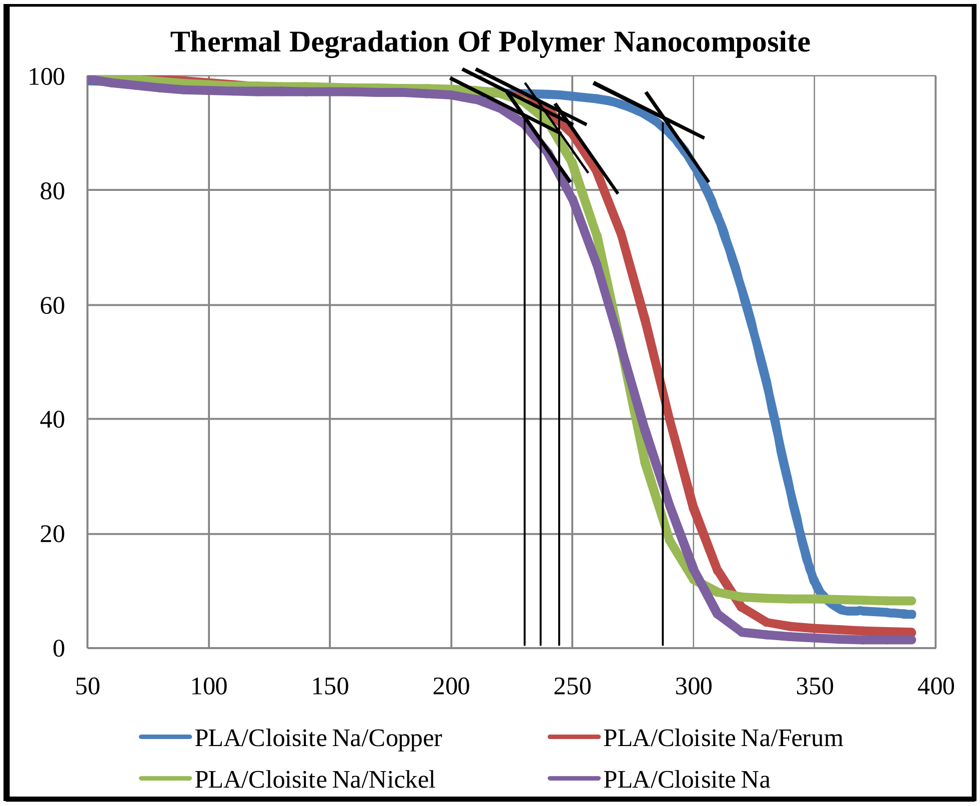


Figure 4.27: Thermal Gravimetry Analysis Temperature Profile

Table 4.1 gives degradation temperature of the clays as estimated from Figure 4.27. from the values it is noticeacle that inclusion of copper into the silicate layers improves thermal stability the most.

Table 4.5: Thermal Degradation Temperature Profile

Sample	Temperature (°C)
PLA/Cloisite Na/Copper	282
PLA/Cloisite Na/Nickel	242
PLA/Cloisite Na/ Ferum	246
PLA/ Cloisite Na	230

From Figure 4.26 and 4.27, it can be seen that the onset of thermal degradation occurs later for the nanocomposites which were made of modified nanoclay. The offset of thermal degradation when compared to un-modified nanoclay nanocomposite was most pronounced in Copper, Ferum and finally Nickel. Also, the char value which relates the correlates with the amount of residue polymer nanocomposite which were unable to be degraded were higher in samples that contained the transition metal ions. These results are comparable to the results acquired by Pawani (2009) in his research which proved addition of transition-metal ions on Cloisite C20 increases its thermal stability. These hypothesis can be said to generally hold true for all organoclays;- in this case Cloisite Na^+. Figures 4.28 till 4.31 shows the rate of degradation of PNC.

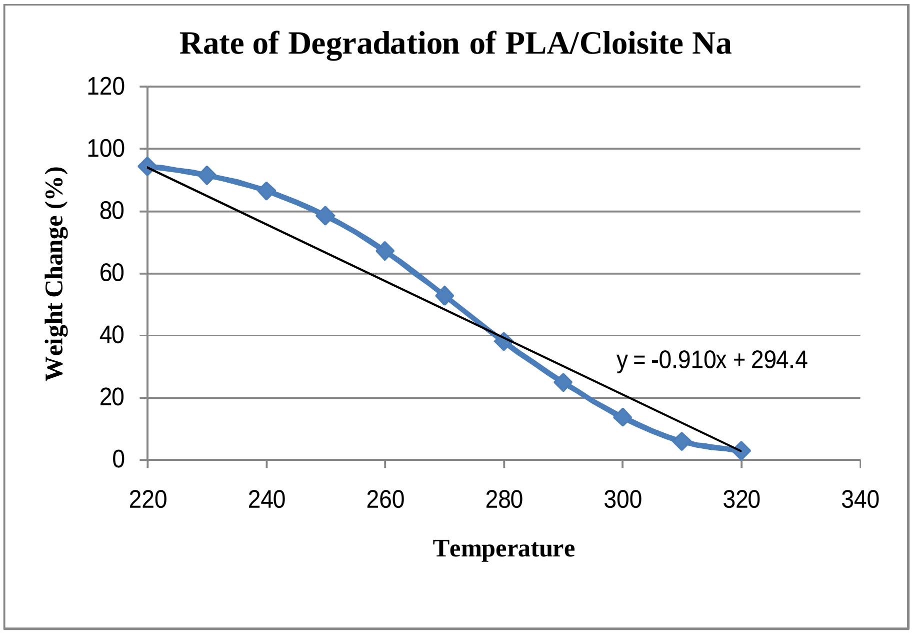


Figure 4.28: Rate of Thermal Decomposition of Pure Organoclay PNC

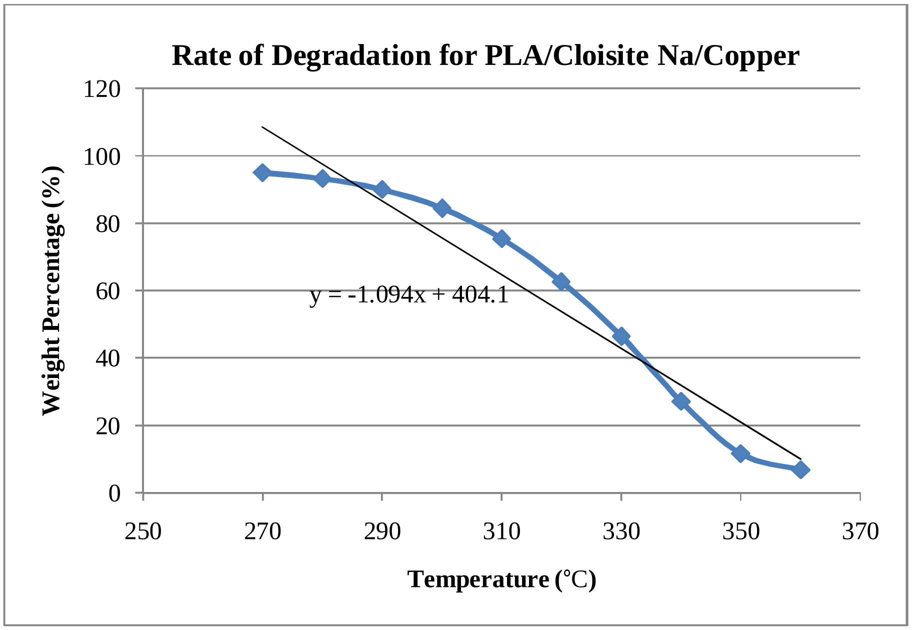


Figure 4.29: Rate of Thermal Decomposition of Copper-Modified PNC

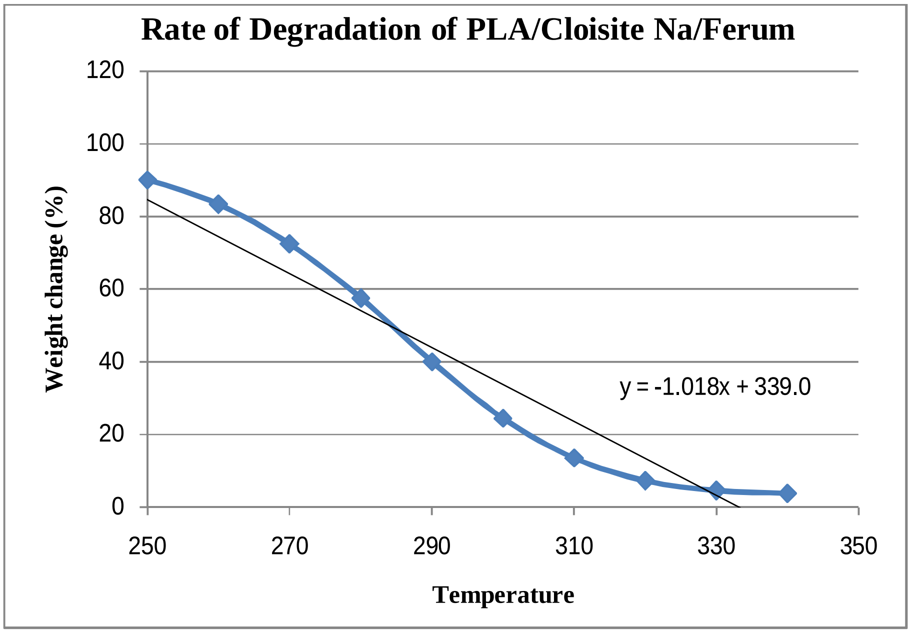


Figure 4.30: Rate of Thermal Decomposition of Ferum Modified PNC

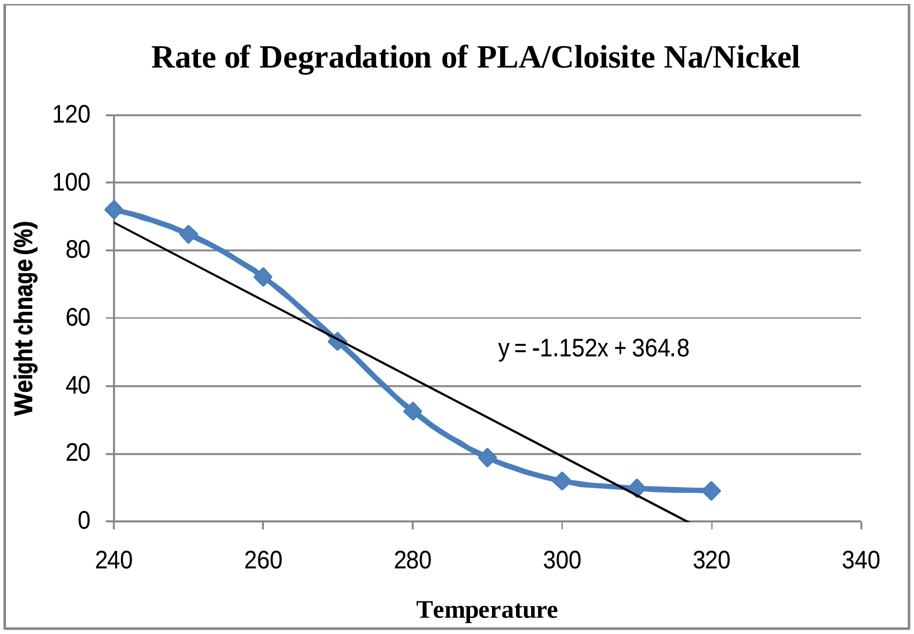


Figure 4.31: Rate of Thermal Degradation of Nickel Modified PNC

When comparing between Figures 4.28 till Figure 4.31, we note that once the onset thermal degradation temperature has been reached, polymer nanocoposites that contain modified organoclays seems to decompose at a faster rate. The fastest degradation took place for nickel-modified organoclay, followed by copper and finally Ferum. The decomposition rate of pure Cloisite Na intercalated polymers is 0.91%/min^{-1}. This can be explained by looking at the structure of the modified organoclay. The modifications which happen only happen at the surface and some parts of within the structure. Therefore initially, in order to break these bonds, the thermal degradation temperature is pushed back as it requires more energy. On another hand, once these bonds are broken, what is left is the original structure of organoclay which has already been weakened by the prior modifications. This causes the decomposition rate of the modified organoclay intercalated polymers to be faster once the onset thermal degradation temperature is reached.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.0 INTRODUCTION

In this chapter, the conclusion of the study has been discussed where the overall research is summarized. It includes general significance of the research to the industry and the approach on whether the research carried out met the objectives.

5.1 CONCLUSION

The objectives of this study have been successfully achieved. This is because; the surface modification was able to be done using ethanol as a solvent. Also the biodegradability and thermal stability of the polymers using the modified nanoclay were able to be improved when comparing against pure organoclay intercalated polymers.

From the research, the two most viable options in terms of commercial production would be Cloisite Na^+ modified with either Ferum or Copper. This is because the Ferum-modified organoclay can be seen to be highly degradable which suitable feature when looking at environmentally friendly polymers. Unfortunately, this modification does not drastically increase the thermal stability unlike the modification with Copper. The Copper modification increases the onset of thermal degradation by about 70°C. However, in terms of biodegradability it only manages to improve the weight loss by 33%. Therefore, the modification which is deemed to be the best will ultimately fall back on the requirement of particular industries. It is hoped that this research has helped further develop industrial polymeric technologies.

5.3 RECOMMENDATION

In order to improve the quality of the results, it is highly recommended that the polymer nanocomposite used for the testing is made through extrusion. For this a larger quantity of modified clay will be required. This is to guarantee a more homogenized mixing of the clay and polymer. Also, the quality of dispersion should be checked using X-Ray Diffraction and Nuclear Magnetic Resonance (NMR), this is to make sure the samples that are tested are of almost similar quality and standards. The readings should also be triplicated in order to guarantee its accuracy. The standard deviation and mean values of readings will help lend support to proposed theories and hypothesis.

From the research, it is shown that the amount of extract is influenced by temperature, power, extraction time, and amount of lemongrass. Temperature, extraction time and amount of lemongrass give positive effects to the amount of extract, the amount of extract increases when these variables increase. On the other hand, power gives negative effect on the amount of extract, the amount of extract decreases as power increases.

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APPENDIX A

AAS Analysis: Copper

```
Table of Each Element        12/23/2011 2:19 PM

Analysis Mode        Flame/Manual
Analysis Name        Standard Analysis
Comment
Description    ABSORTION OF METAL ION ON SURFACE OF NANOCLAY
                USING VARIOUS SOLVENTS



Meas. Date      12/23/2011 2:16 PM
Element         Cu        STD Unit       ppm     UNK Unit

Sample ID                     Conc.          RSD(%)       ABS           REF
STD1                           0.00          0.00         0.0009        -0.0062
STD2                           2.50          0.00         0.0739         0.0657
STD3                           5.00          0.00         0.1676         0.1371
STD4                           10.00         0.00         0.3281         0.2770
Coefficient     K1=3.271428E-002   K0=2.000001E-002
Corr.Coef.      0.9999

Sample Name
UNK-001         C20-DX        1.78           0.00         0.2726        0.0031
UNK-002         MMT-DX        0.91           0.00         0.1590        -0.0046
UNK-003         C20-E         1.98           0.00         0.2163        -0.0011
UNK-004         MMT-E         1.05           0.00         0.1761        -0.0035
UNK-005         C20-M         2.52           0.00         0.2084         0.0000
UNK-006         MMT-M         1.99           0.00         0.1234        -0.0093
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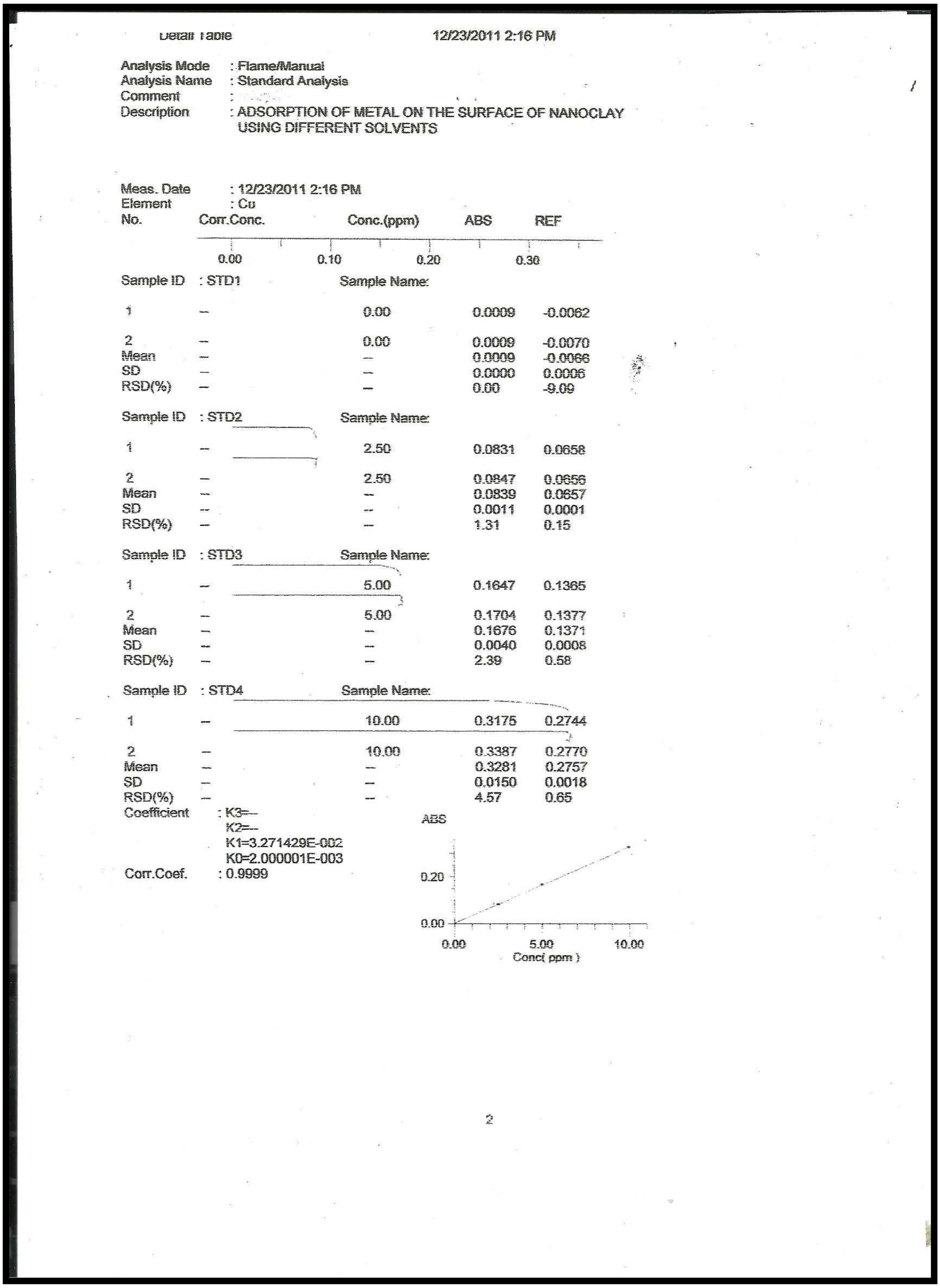

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Detail Table                          12/23/2011 2:16 PM

Analysis Mode    : Flame/Manual
Analysis Name    : Standard Analysis
Comment          :
Description      : ADSORPTION OF METAL ON THE SURFACE OF NANOCLAY
                   USING DIFFERENT SOLVENTS


Meas. Date       : 12/23/2011 2:16 PM
Element          : Cu
No.        Corr.Conc.          Conc.(ppm)      ABS        REF

           0.00       0.10        0.20        0.30

Sample ID  : STD1              Sample Name:

 1          --                   0.00         0.0009     -0.0062

 2          --                   0.00         0.0009     -0.0070
Mean        --                   --           0.0009     -0.0066
SD          --                   --           0.0000      0.0006
RSD(%)      --                   --           0.00       -9.09

Sample ID  : STD2              Sample Name:

 1          --                   2.50         0.0831      0.0658

 2          --                   2.50         0.0847      0.0656
Mean        --                   --           0.0839      0.0657
SD          --                   --           0.0011      0.0001
RSD(%)      --                   --           1.31        0.15

Sample ID  : STD3              Sample Name:

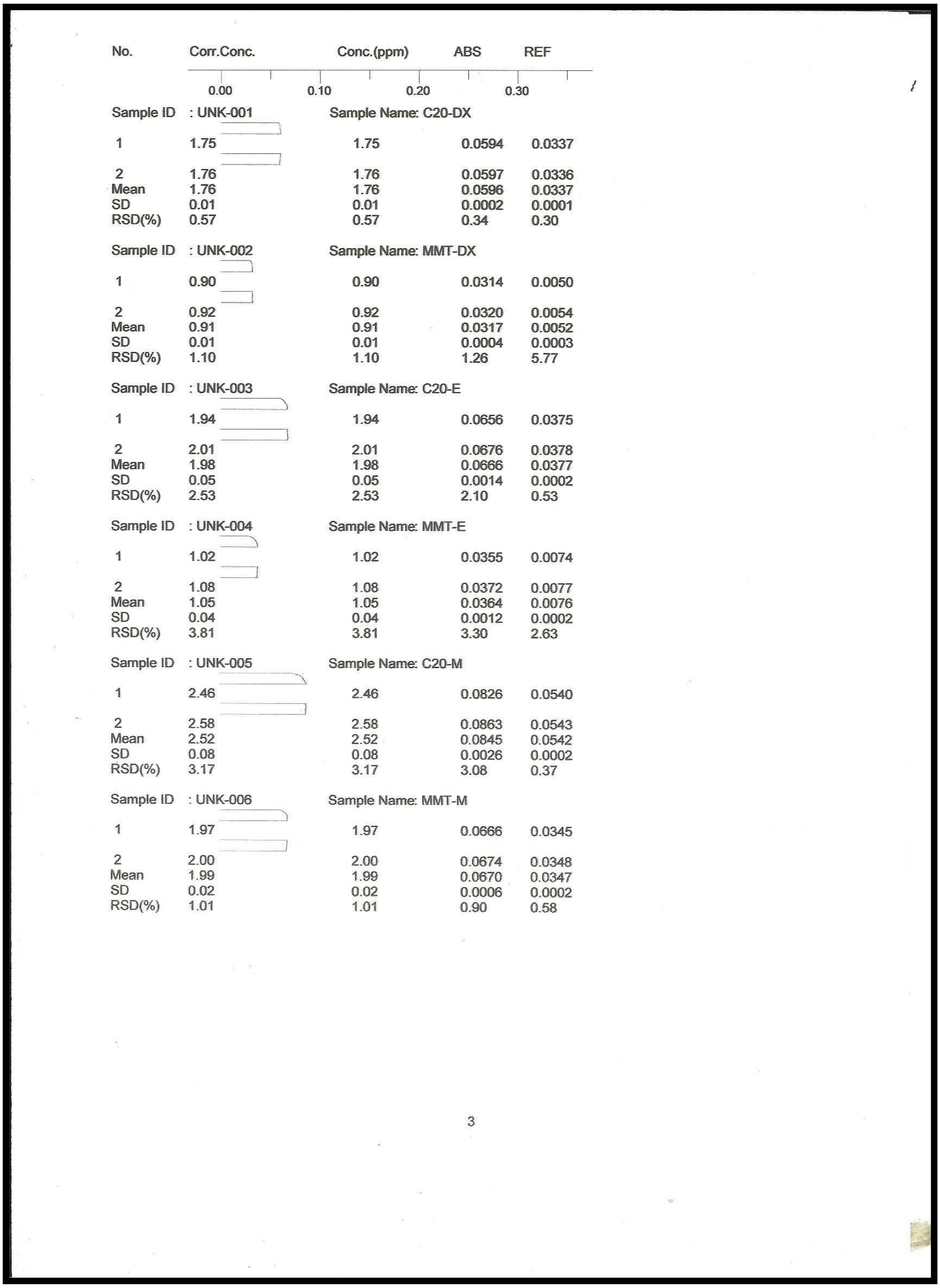
 1          --                   5.00         0.1647      0.1365

 2          --                   5.00         0.1704      0.1377
Mean        --                   --           0.1676      0.1371
SD          --                   --           0.0040      0.0008
RSD(%)      --                   --           2.39        0.58

Sample ID  : STD4              Sample Name:

 1          --                   10.00        0.3175      0.2744

 2          --                   10.00        0.3387      0.2770
Mean        --                   --           0.3281      0.2757
SD          --                   --           0.0150      0.0018
RSD(%)      --                   --           4.57        0.65
Coefficient     : K3=--
                  K2=--
                  K1=3.271429E-002
                  K0=2.000001E-003
Corr.Coef.      : 0.9999
```



```
No.          Corr.Conc.         Conc.(ppm)     ABS        REF
                 |    |    |    |    |    |    |
               0.00      0.10      0.20      0.30
Sample ID    : UNK-001          Sample Name: C20-DX

 1           1.75                1.75          0.0594     0.0337

 2           1.76                1.76          0.0597     0.0336
Mean         1.76                1.76          0.0596     0.0337
SD           0.01                0.01          0.0002     0.0001
RSD(%)       0.57                0.57          0.34       0.30

Sample ID    : UNK-002          Sample Name: MMT-DX

 1           0.90                0.90          0.0314     0.0050

 2           0.92                0.92          0.0320     0.0054
Mean         0.91                0.91          0.0317     0.0052
SD           0.01                0.01          0.0004     0.0003
RSD(%)       1.10                1.10          1.26       5.77

Sample ID    : UNK-003          Sample Name: C20-E

 1           1.94                1.94          0.0656     0.0375

 2           2.01                2.01          0.0676     0.0378
Mean         1.98                1.98          0.0666     0.0377
SD           0.05                0.05          0.0014     0.0002
RSD(%)       2.53                2.53          2.10       0.53

Sample ID    : UNK-004          Sample Name: MMT-E

 1           1.02                1.02          0.0355     0.0074

 2           1.08                1.08          0.0372     0.0077
Mean         1.05                1.05          0.0364     0.0076
SD           0.04                0.04          0.0012     0.0002
RSD(%)       3.81                3.81          3.30       2.63

Sample ID    : UNK-005          Sample Name: C20-M

 1           2.46                2.46          0.0826     0.0540

 2           2.58                2.58          0.0863     0.0543
Mean         2.52                2.52          0.0845     0.0542
SD           0.08                0.08          0.0026     0.0002
RSD(%)       3.17                3.17          3.08       0.37

Sample ID    : UNK-006          Sample Name: MMT-M

 1           1.97                1.97          0.0666     0.0345

 2           2.00                2.00          0.0674     0.0348
Mean         1.99                1.99          0.0670     0.0347
SD           0.02                0.02          0.0006     0.0002
RSD(%)       1.01                1.01          0.90       0.58




                                       3
```

APPENDIX B

AAS Analysis: Ferum

Table of Each Element 12/27/2011 3:15 PM

Analysis Mode Flame/Manual
Analysis Name Standard Analysis
Comment
Description ABSORTION OF METAL ION ON SURFACE OF NANOCLAY USING VARIOUS SOLVENTS

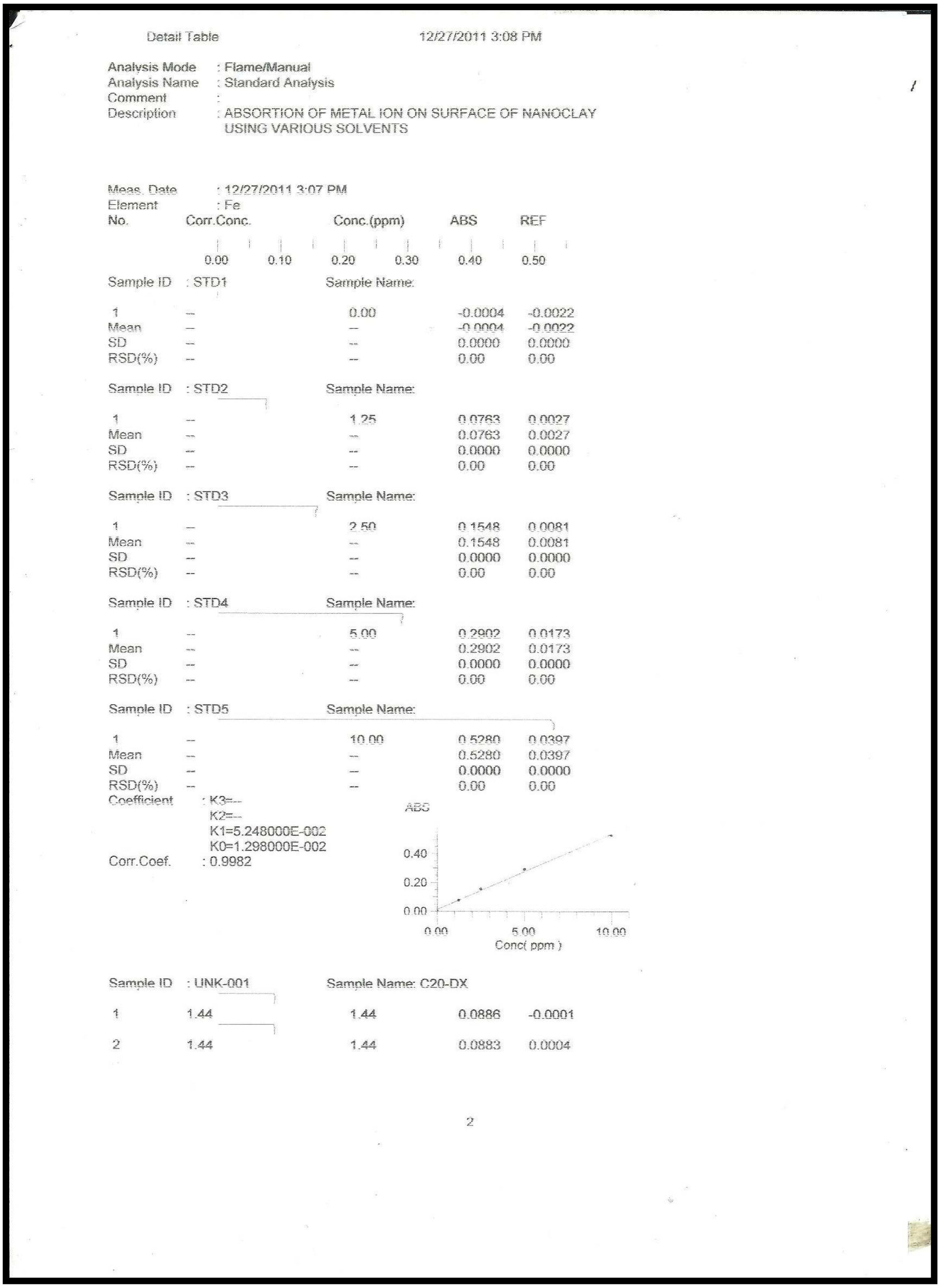
Meas. Date 12/27/2011 3:07 PM
Element Fe STD Unit ppm UNK Unit

Sample ID	Conc.	RSD(%)	ABS	REF
STD1	0.00	0.00	-0.0004	-0.0022
STD2	1.25	0.00	0.0763	0.0027
STD3	2.50	0.00	0.1548	0.0081
STD4	5.00	0.00	0.2902	0.0173
STD5	10.00	0.00	0.5280	0.0397

Coefficient K1=5.248000E-002 K0=1.298000E-002
Corr.Coef. 0.9982

Sample Name

UNK-001	C20-DX	1.44	0.00	0.0885	0.0002
UNK-002	MMT-DX	1.23	0.81	0.0774	-0.0013
UNK-003	C20-E	2.55	0.78	0.1466	0.0033
UNK-004	MMT-E	1.35	0.74	0.0837	-0.0020
UNK-005	C20-M	0.76	0.00	0.0530	-0.0047
UNK-006	MMT-M	0.52	0.00	0.0401	-0.0064



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     Detail Table                                   12/27/2011 3:08 PM

Analysis Mode     : Flame/Manual
Analysis Name     : Standard Analysis
Comment           :
Description       : ABSORTION OF METAL ION ON SURFACE OF NANOCLAY
                    USING VARIOUS SOLVENTS


Meas. Date        : 12/27/2011 3:07 PM
Element           : Fe
No.         Corr.Conc.                Conc.(ppm)        ABS         REF

                 0.00      0.10      0.20      0.30      0.40      0.50

Sample ID   : STD1                  Sample Name:

 1          --                       0.00            -0.0004     -0.0022
Mean        --                       --              -0.0004     -0.0022
SD          --                       --               0.0000      0.0000
RSD(%)      --                       --               0.00        0.00

Sample ID   : STD2                  Sample Name:

 1          --                       1.25             0.0763      0.0027
Mean        --                       --               0.0763      0.0027
SD          --                       --               0.0000      0.0000
RSD(%)      --                       --               0.00        0.00

Sample ID   : STD3                  Sample Name:

 1          --                       2.50             0.1548      0.0081
Mean        --                       --               0.1548      0.0081
SD          --                       --               0.0000      0.0000
RSD(%)      --                       --               0.00        0.00

Sample ID   : STD4                  Sample Name:

 1          --                       5.00             0.2902      0.0173
Mean        --                       --               0.2902      0.0173
SD          --                       --               0.0000      0.0000
RSD(%)      --                       --               0.00        0.00

Sample ID   : STD5                  Sample Name:

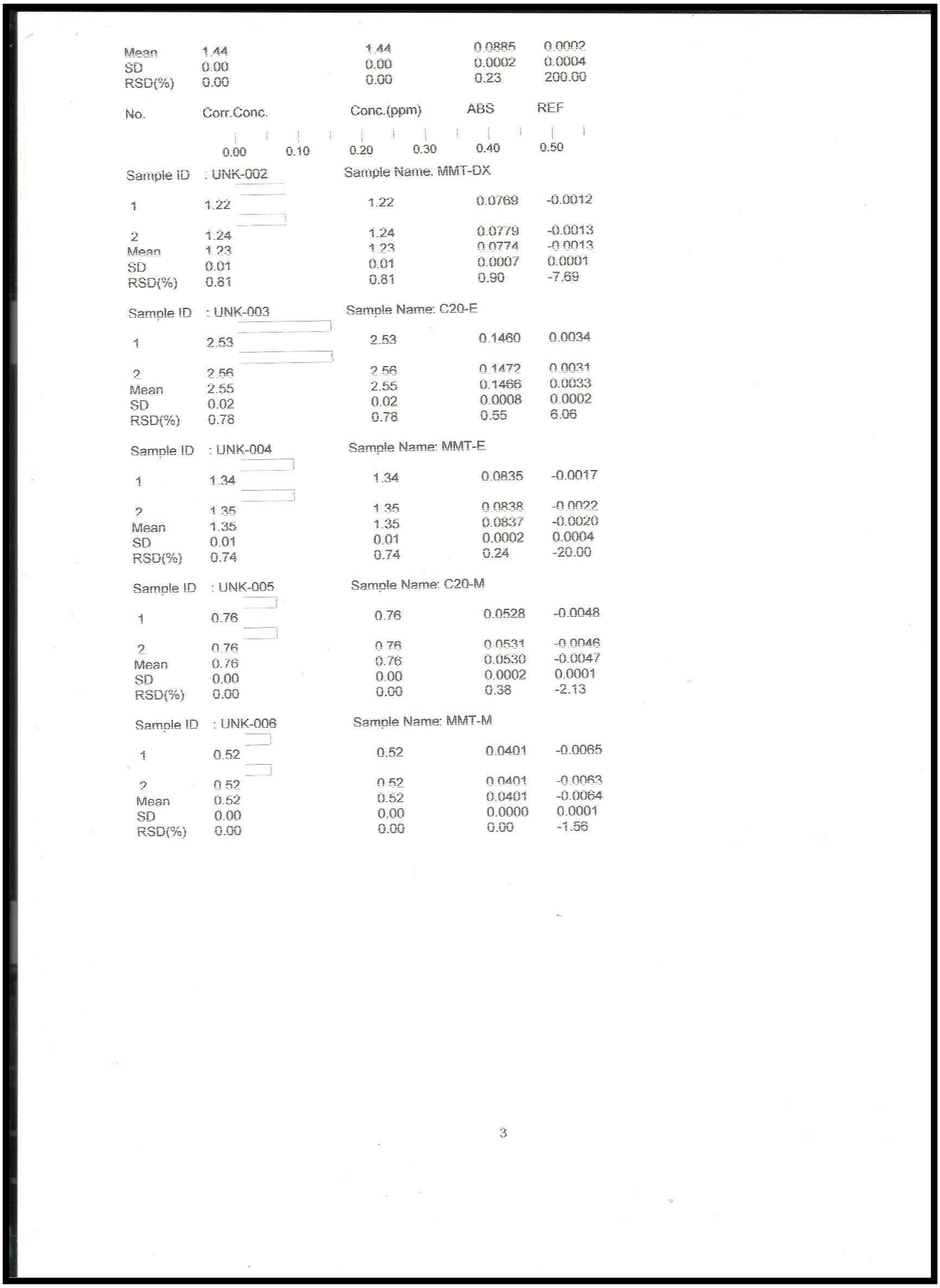
 1          --                       10.00            0.5280      0.0397
Mean        --                       --               0.5280      0.0397
SD          --                       --               0.0000      0.0000
RSD(%)      --                       --               0.00        0.00
Coefficient    : K3=--
                 K2=--
                 K1=5.248000E-002
                 K0=1.298000E-002
Corr.Coef.     : 0.9982


Sample ID   : UNK-001               Sample Name: C20-DX

 1          1.44                     1.44             0.0886     -0.0001

 2          1.44                     1.44             0.0883      0.0004


                                     2
```



```
Mean        1.44                 1.44         0.0885     0.0002
SD          0.00                 0.00         0.0002     0.0004
RSD(%)      0.00                 0.00         0.23       200.00

No.         Corr.Conc.           Conc.(ppm)   ABS        REF

              0.00      0.10      0.20      0.30      0.40      0.50
Sample ID   : UNK-002            Sample Name: MMT-DX
1           1.22                 1.22         0.0769     -0.0012

2           1.24                 1.24         0.0779     -0.0013
Mean        1.23                 1.23         0.0774     -0.0013
SD          0.01                 0.01         0.0007     0.0001
RSD(%)      0.81                 0.81         0.90       -7.69

Sample ID   : UNK-003            Sample Name: C20-E
1           2.53                 2.53         0.1460     0.0034

2           2.56                 2.56         0.1472     0.0031
Mean        2.55                 2.55         0.1466     0.0033
SD          0.02                 0.02         0.0008     0.0002
RSD(%)      0.78                 0.78         0.55       6.06

Sample ID   : UNK-004            Sample Name: MMT-E
1           1.34                 1.34         0.0835     -0.0017

2           1.35                 1.35         0.0838     -0.0022
Mean        1.35                 1.35         0.0837     -0.0020
SD          0.01                 0.01         0.0002     0.0004
RSD(%)      0.74                 0.74         0.24       -20.00

Sample ID   : UNK-005            Sample Name: C20-M
1           0.76                 0.76         0.0528     -0.0048

2           0.76                 0.76         0.0531     -0.0046
Mean        0.76                 0.76         0.0530     -0.0047
SD          0.00                 0.00         0.0002     0.0001
RSD(%)      0.00                 0.00         0.38       -2.13

Sample ID   : UNK-006            Sample Name: MMT-M
1           0.52                 0.52         0.0401     -0.0065

2           0.52                 0.52         0.0401     -0.0063
Mean        0.52                 0.52         0.0401     -0.0064
SD          0.00                 0.00         0.0000     0.0001
RSD(%)      0.00                 0.00         0.00       -1.56


                                 3
```

APPENDIX C

AAS Analysis: Nickel

Table of Each Element 12/27/2011 3:01 PM

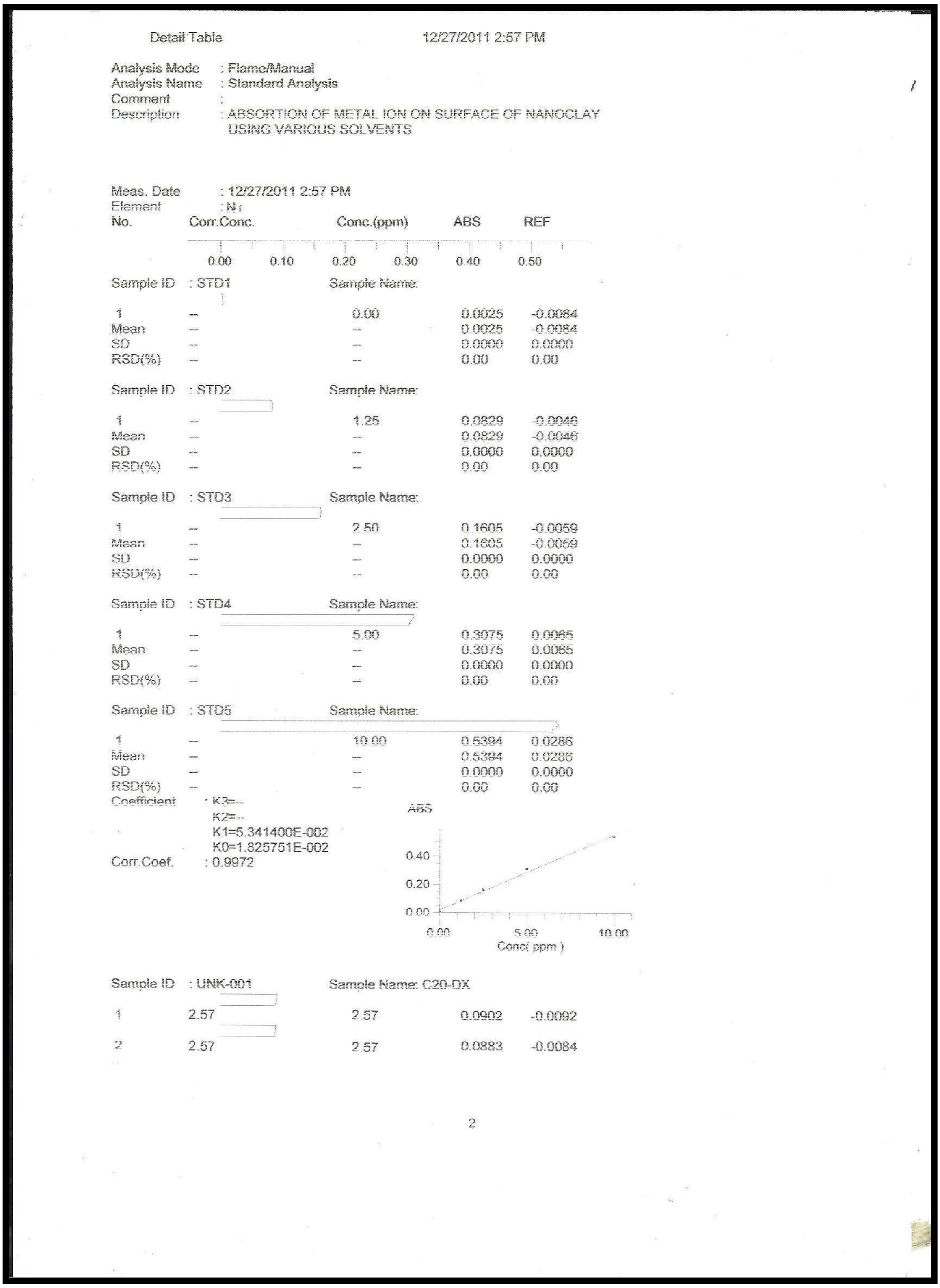
Analysis Mode Flame/Manual
Analysis Name Standard Analysis
Comment
Description ABSORTION OF METAL ION ON SURFACE OF NANOCLAY USING VARIOUS SOLVENTS

Meas. Date 12/27/2011 2:57 PM
Element Ni STD Unit ppm UNK Unit

Sample ID	Conc.	RSD(%)	ABS	REF
STD1	0.00	0.00	0.0023	-0.0073
STD2	2.50	0.00	0.1284	-0.0045
STD3	5.00	0.00	0.2340	0.0062
STD4	10.00	0.00	0.3460	0.0162

Coefficient K1=3.367657E-002 K0=3.034000E-002
Corr.Coef. 0.9972

Sample Name					
UNK-001	C20-DX	2.57	0.00	0.2726	0.0031
UNK-002	MMT-DX	1.67	0.00	0.1590	-0.0046
UNK-003	C20-E	2.14	0.00	0.2163	-0.0011
UNK-004	MMT-E	1.21	0.00	0.1761	-0.0035
UNK-005	C20-M	2.01	0.00	0.2084	0.0000
UNK-006	MMT-M	0.79	0.00	0.1234	-0.0093



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        Detail Table                                12/27/2011 2:57 PM

Analysis Mode    : Flame/Manual
Analysis Name    : Standard Analysis
Comment          :
Description      : ABSORTION OF METAL ION ON SURFACE OF NANOCLAY
                   USING VARIOUS SOLVENTS


Meas. Date       : 12/27/2011 2:57 PM
Element          : Ni
No.          Corr.Conc.          Conc.(ppm)       ABS        REF

               0.00      0.10      0.20      0.30      0.40      0.50

Sample ID    : STD1              Sample Name:

 1           --                    0.00           0.0025     -0.0084
Mean         --                    --             0.0025     -0.0084
SD           --                    --             0.0000     0.0000
RSD(%)       --                    --             0.00       0.00

Sample ID    : STD2              Sample Name:

 1           --                    1.25           0.0829     -0.0046
Mean         --                    --             0.0829     -0.0046
SD           --                    --             0.0000     0.0000
RSD(%)       --                    --             0.00       0.00

Sample ID    : STD3              Sample Name:

 1           --                    2.50           0.1605     -0.0059
Mean         --                    --             0.1605     -0.0059
SD           --                    --             0.0000     0.0000
RSD(%)       --                    --             0.00       0.00

Sample ID    : STD4              Sample Name:

 1           --                    5.00           0.3075     0.0065
Mean         --                    --             0.3075     0.0065
SD           --                    --             0.0000     0.0000
RSD(%)       --                    --             0.00       0.00

Sample ID    : STD5              Sample Name:

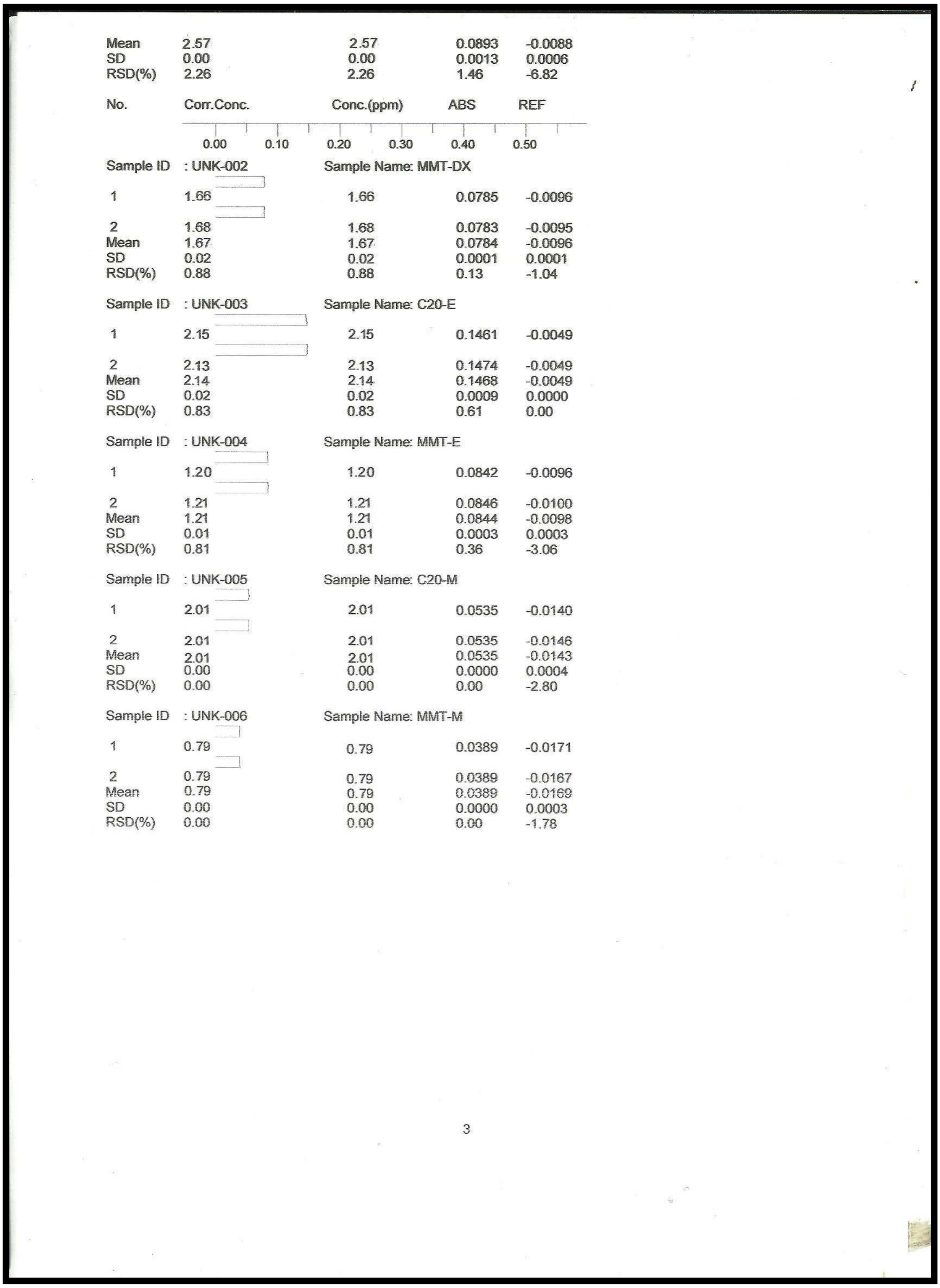
 1           --                    10.00          0.5394     0.0286
Mean         --                    --             0.5394     0.0286
SD           --                    --             0.0000     0.0000
RSD(%)       --                    --             0.00       0.00
Coefficient    : K3=--
                 K2=--
                 K1=5.341400E-002
                 K0=1.825751E-002
Corr.Coef.     : 0.9972


Sample ID    : UNK-001           Sample Name: C20-DX

 1           2.57                  2.57           0.0902     -0.0092

 2           2.57                  2.57           0.0883     -0.0084

                                    2
```



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Mean        2.57                 2.57          0.0893     -0.0088
SD          0.00                 0.00          0.0013      0.0006
RSD(%)      2.26                 2.26          1.46       -6.82

No.         Corr.Conc.         Conc.(ppm)      ABS        REF

              0.00       0.10       0.20       0.30       0.40       0.50
Sample ID   : UNK-002          Sample Name: MMT-DX

 1          1.66                 1.66          0.0785     -0.0096

 2          1.68                 1.68          0.0783     -0.0095
Mean        1.67                 1.67          0.0784     -0.0096
SD          0.02                 0.02          0.0001      0.0001
RSD(%)      0.88                 0.88          0.13       -1.04

Sample ID   : UNK-003          Sample Name: C20-E

 1          2.15                 2.15          0.1461     -0.0049

 2          2.13                 2.13          0.1474     -0.0049
Mean        2.14                 2.14          0.1468     -0.0049
SD          0.02                 0.02          0.0009      0.0000
RSD(%)      0.83                 0.83          0.61        0.00

Sample ID   : UNK-004          Sample Name: MMT-E

 1          1.20                 1.20          0.0842     -0.0096

 2          1.21                 1.21          0.0846     -0.0100
Mean        1.21                 1.21          0.0844     -0.0098
SD          0.01                 0.01          0.0003      0.0003
RSD(%)      0.81                 0.81          0.36       -3.06

Sample ID   : UNK-005          Sample Name: C20-M

 1          2.01                 2.01          0.0535     -0.0140

 2          2.01                 2.01          0.0535     -0.0146
Mean        2.01                 2.01          0.0535     -0.0143
SD          0.00                 0.00          0.0000      0.0004
RSD(%)      0.00                 0.00          0.00       -2.80

Sample ID   : UNK-006          Sample Name: MMT-M

 1          0.79                 0.79          0.0389     -0.0171

 2          0.79                 0.79          0.0389     -0.0167
Mean        0.79                 0.79          0.0389     -0.0169
SD          0.00                 0.00          0.0000      0.0003
RSD(%)      0.00                 0.00          0.00       -1.78

                                      3
```

APPENDIX D

TGA Analysis: Excel Data

Nickel modified Nanoclay PNC

Time Min	Temperature °C	Weight %	Deriv. Weight %/°C
	0		
	10		
	20		
	30		
	40		
1.61	50	99.76	0.02937
2.87	60	99.61	0.02741
3.92	70	99.33	0.04483
4.94	80	98.98	0.04623
5.95	90	98.66	0.04242
6.95	100	98.42	0.0348
7.95	110	98.27	0.02365
8.95	120	98.19	0.01331
9.95	130	98.13	0.007452
10.95	140	98.07	0.006146
11.95	150	98.00	0.006129
12.95	160	97.94	0.004522
13.95	170	97.90	0.00279
14.95	180	97.84	0.003543
15.95	190	97.77	0.005026
16.95	200	97.67	0.009092
17.95	210	97.46	0.01895
18.95	220	96.95	0.0454
19.95	230	95.53	0.1029
20.95	240	92.04	0.2082
21.95	250	84.86	0.3793
22.95	260	72.20	0.644
23.95	270	53.18	0.9566
24.95	280	32.54	1.325
25.95	290	18.84	1.489
26.95	300	11.90	1.401
27.95	310	9.717	1.227
28.95	320	8.940	1.007
29.94	330	8.724	0.5181
30.95	340	8.616	0.1441
31.94	350	8.532	0.02899
32.94	360	8.448	0.02285
33.94	370	8.369	0.0203
34.95	380	8.299	0.01622
35.95	390	8.313	0.0114

Copper modified Nanoclay PNC

Time Min	Temperature °C	Weight %	Deriv. Weight %/°C
	0		
	10		
	20		
	30		
	40		
2.21	50	99.16	0.0151
3.24	60	99.02	0.02281
4.26	70	98.85	0.02756
5.26	80	98.70	0.02353
6.26	90	98.56	0.02208
7.26	100	98.40	0.02417
8.26	110	98.18	0.02519
9.26	120	97.93	0.02401
10.26	130	97.71	0.01857
11.26	140	97.51	0.01251
12.26	150	97.36	0.008283
13.26	160	97.24	0.005112
14.26	170	97.18	0.003958
15.26	180	97.12	0.004233
16.26	190	97.07	0.002972
17.27	200	97.02	0.002657
18.27	210	96.97	0.003687
19.27	220	96.91	0.003876
20.27	230	96.84	0.006167
21.27	240	96.71	0.009889
22.27	250	96.46	0.01625
23.27	260	95.98	0.02848
24.27	270	95.07	0.04837
25.27	280	93.33	0.08453
26.27	290	90.07	0.1512
27.26	300	84.45	0.2528
28.26	310	75.50	0.4156
29.26	320	62.70	0.6915
30.26	330	46.50	1.100
31.26	340	27.29	1.700
32.27	350	11.65	2.429
33.26	360	6.88	2.211
34.25	370	6.45	0.1534
35.27	380	6.11	0.02218
36.26	390	5.87	0.01743

Ferum modified Nanoclay PNC

Time Min	Temperature °C	Weight %	Deriv. Weight %/°C
	0		
	10		
	20		
	30		
	40		
2.33	50	99.79	0.01473
3.36	60	99.70	0.0183
4.37	70	99.55	0.02455
5.37	80	99.35	0.0324
6.38	90	99.03	0.03953
7.37	100	98.71	0.04346
8.37	110	98.38	0.04169
9.37	120	98.13	0.03254
10.37	130	98.00	0.02082
11.37	140	97.92	0.01172
12.37	150	97.87	0.007331
13.35	160	97.84	0.00578
14.38	170	97.81	0.002406
15.38	180	97.77	0.001719
16.38	190	97.72	0.003008
17.38	200	97.63	0.004596
18.38	210	97.43	0.007362
19.38	220	97.02	0.01159
20.38	230	96.03	0.02078
21.38	240	93.94	0.04154
22.38	250	90.06	0.08875
23.38	260	83.30	0.1862
24.38	270	72.50	0.3688
25.38	280	57.48	0.6131
26.38	290	40.04	0.8662
27.38	300	24.47	1.064
28.38	310	13.50	1.300
29.38	320	7.152	1.429
30.38	330	4.481	1.607
31.38	340	3.706	1.379
32.38	350	3.399	0.1766
33.38	360	3.168	0.026
34.37	370	2.968	0.02091
35.37	380	2.797	0.01767
36.37	390	2.658	0.01356

Unmodified/Pure Nanoclay PNC

Time Min	Temperature °C	Weight %	Deriv. Weight %/°C
	0		
	10		
	20		
	30		
	40		
1.72	50	99.51	0.01116
2.77	60	98.77	0.02223
3.8	70	98.33	0.03308
4.8	80	97.94	0.03445
5.8	90	97.64	0.02797
6.8	100	97.46	0.01938
7.8	110	97.36	0.01117
8.8	120	97.30	0.006886
9.8	130	97.24	0.005662
10.8	140	97.19	0.006465
11.8	150	97.15	0.006895
12.8	160	97.12	0.003881
13.8	170	97.08	0.00518
14.8	180	97.03	0.00586
15.8	190	96.88	0.00795
16.8	200	96.60	0.01401
17.8	210	95.90	0.03133
18.8	220	94.40	0.08469
19.8	230	91.55	0.2244
20.8	240	86.54	0.5084
21.8	250	78.53	0.9694
22.8	260	67.09	1.598
23.8	270	52.76	2.132
24.81	280	38.12	1.730
25.8	290	24.99	1.068
26.8	300	13.69	0.3609
27.8	310	5.936	0.1341
28.8	320	2.835	0.04057
29.8	330	2.226	0.01276
30.8	340	1.979	0.0094
31.8	350	1.769	0.008597
32.79	360	1.585	0.008167
33.8	370	1.449	0.00755
34.8	380	1.401	0.006385
35.8	390	1.387	0.007448