DEVELOPMENT OF HIGH THERMAL BUILDING NANO-INSULATION MATERIAL USING PU NANOCOMPOSITES FOR ROOFING APPLICATION

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DEVELOPMENT OF HIGH THERMAL BUILDING NANO-INSULATION MATERIAL USING PU NANOCOMPOSITES FOR ROOFING APPLICATION

INTAN YUSNIZA MOHAMAD

Thesis submitted in partial fulfilment of the requirements
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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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Name of main supervisor : DR KAMAL YUSOH
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Date : 22 JANUARY 2014

STUDENT'S DECLARATION

I hereby declare that the work in this thesis 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.

Signature :
Name : INTAN YUSNIZA BT MOHAMAD
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DEDICATION

This work is dedicated to:

My parents,
who continuously provides loves and supports,
my brothers,
who has always understand me,
my supervisor,
whose guidance encourages and enlightens me,
my friends,
who always tend to my side in joy and sorrow

Thank you for everything.

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Last but not least, I dedicated this to my parents, my brothers and my friends, who became my source of motivation and strength. It was their presence and kind words that supported me throughout this research.

“In ordinary life we hardly realize that we receive a great deal more that we give, and that it is only with the gratitude that life becomes rich.” –Dietrich Bonhoeffer

ABSTRACT

Polyurethanes (PUs) are one of the most versatile classes of materials today and their demand as a high thermal insulator material continues to grow. The widespread application of PUs necessitates understanding the chemistry elements that improve the thermal stability and mechanical strength as these are crucial prerequisites to obtain the high performance of thermal insulator material for the structures and buildings. The first part of the experiment focuses on the modification of pristine clay with Transition Metal Ions (TMIs), Copper and Ferum using methanol solvent. The objectives of surface modification of pristine clay is due to the incompatibility between hydrophilic clay and hydrophobic polymer. After these modifications, the samples of organoclay are characterized using some sophisticated methods like Fourier Transform Infrared (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). FTIR and FESEM results illustrated modified nanoclays had smoother surfaces of pristine clay or montmorillonite (MMT) which proved that modification has taken place successfully. The samples then tested by Thermal Gravimetry Analysis (TGA) and Tensile Test to measure their thermal and mechanical properties respectively. Both the thermal stability and mechanical strength showed positive improvements. Thermal stability is hypothesized to have increased significantly, due to the transition metal ions hindering the pristine clay within the polymer matrices from decomposing easily. The stronger interfacial interaction causes to the increasing of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposite. Further research will be required to commercialize findings.

Keywords : Modification, Nanoclay, Montmorillonite, Organoclay, Transition Metal Ions (TMIs), Solution Intercalation, Thermoplastic Polyurethane (TPU), Thermal Stability, Mechanical.

ABSTRAK

Polyurethanes (PUs) adalah salah satu kelas yang paling serba boleh hari ini dan permintaan mereka sebagai bahan penebat haba yang tinggi terus berkembang. Permohonan meluas memerlukan unsur-unsur kimia yang meningkatkan kestabilan haba dan kekuatan mekanikal kerana ini adalah prasyarat penting untuk mendapatkan prestasi yang tinggi bahan penebat haba bagi struktur dan bangunan. Bahagian pertama eksperimen memberi tumpuan kepada pengubahsuaian dari tanah yang asli dengan Peralihan Logam Ion (TMIs), tembaga dan ferum menggunakan pelarut metanol. Objektif pengubahsuaian permukaan tanah liat yang bersih adalah disebabkan oleh ketidakserasian antara tanah liat hidrofilik dan polimer hidrofobik. Selepas pengubahsuaian ini, sampel organo dicirikan menggunakan beberapa kaedah yang canggih seperti Fourier (FTIR) dan Pelepasan Imbasan Elektron Mikroskop (FESEM). Nanoclays diubahsuai dan keputusan FTIR dan FESEM digambarkan mempunyai permukaan licin bagi tanah liat yang asli atau montmorilonit (MMT) yang membuktikan bahawa pengubahsuaian telah berlaku dengan jayanya. Sampel kemudiannya diuji oleh Analisis terma gravimetri (TGA) dan Tegangan Ujian untuk mengukur sifat haba dan mekanikal mereka masing-masing. Kedua-dua kestabilan haba dan kekuatan mekanikal menunjukkan peningkatan positif. Kestabilan terma hipotesis telah meningkat dengan ketara, disebabkan oleh ion logam peralihan menghalang tanah liat yang bersih di dalam matriks polimer daripada penguraian mudah. Interaksi antara muka yang lebih kukuh menyebabkan peningkatan tekanan dan kuasa-kuasa antara muka yang lemah boleh membawa kepada beberapa penurunan tekanan untuk nanocomposit. Penyelidikan selanjutnya diperlukan untuk mengkomersilkan penemuan.

Kata Kunci: Pengubahsuaian, Nanoclay, montmorilonit, organo, Peralihan Logam Ions (TMIs), Penyelesaian Interkalasi, Termoplastik Poliuretana (TPU), Kestabilan terma, Mekanikal.

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LIST OF ABBREVIATIONS

AAS	Atomic Adsorption Spectrometer
ABS	Acrylonitrile-butadiene-styrene
EDTA	Ethylenediaminetetraacetic acid
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform InfraRed
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IPDI	Isophoron diisocyanate
MDI	Diisocyanates 4,4'-methylene bis(phenyl isocyanate)
MMT	Montmorillonite
PNS	Polyurethane Nanocomposites
PTMEG	Polytetramethylene glycol
PU	Polyurethane
TDI	2,4-toluene diisocyanate
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
TMI	Transition Metal Ions
TPU	Thermoplastic Polyurethane
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Motivation and Statement of Problem

An ever increasing demand for energy saving in various areas coming to realize that there is a crucial need to reduce energy usage in buildings and it has to be done in an effective way. As buildings constitute a substantial part of the total energy consumption, savings within the building sector will be important, both for existing and new buildings. One of the key fields will be thermal building insulation materials and solutions. Recent studies (McKinsey, 2009) show that energy efficiency measures are the most cost-effective ones. As a result of increased energy cost and environmental concerns, insulation has become a priority in homes or public buildings to make important savings.

The traditional thermal building insulation materials have the drawback that they require rather thick building envelopes in order to meet the increasingly demanding thermal insulation requirements. Increasing the building envelope thickness up to between 400 and 500 mm, e.g., by use of mineral wool and similar insulation materials, forces new challenges both with respect to building physics and practice. In addition, such thick envelope structures are less cost-effective at locations where the area is restricted, i.e. by restrictions in physical dimensions or by high living area costs per square meter (Rehab & Salahuddin, 2005). Thus, with increasing thermal insulation, there is a strive to not increase the thickness of the building envelope substantially. For good work and comfortable life, human need buildings with a good indoor climate, which does not depend on weather conditions during the year. Thus, there should also be an aim to invent or develop new robust high performance thermal building insulation materials without the disadvantages.

Nowadays, type of insulating materials in use includes expanded and extruded polystyrene foams, rigid polyurethane foam, glass wool, or cellulosic fiber. However, their combination of performances and relatively low cost, polyurethane nanocomposites is ranked amongst the most popular choices for insulation. A polymer composite is made by the combination of a polymer and synthetic or natural inorganic filler. Fillers are incorporating to improve the desired properties of the polymer or simply reduce the cost. Nowadays, polymer composites have turned to a state of the art as engineering materials. Polymer composites with improved mechanical, thermal, and barrier properties are widely used in many applications. Even so, by the application of conventional fillers such as talc, fibers, calcium carbonate etc, it often requires to use a large amount of filler in the polymer matrix to have a good improvements in the composite properties which may result in some other undesired properties such as brittleness or loss of opacity (Zhang & Friedrich, 2003).

1.2 Objectives

The following are the objectives of this research:

I. To modify the surface of nanoclay to improve the interaction with thermoplastic polyurethane.
II. To fabricate polyurethane-modified clay nanocomposite.
III. To study the mechanical and thermal properties of polyurethane nanocomposite.

1.3 Scope of This Research

In order to achieve the objectives, the following scope of work are designated :

I. To modify clay using Catalytically Activated Metal Ion (TMI) and characterize using ICPMS and AAS.
II. To fabricate polyurethane-organoclay using solution mixing method.
III. To conduct mechanical and thermal test using Thermal Gravimetric Analysis (TGA) and Tensile Test.

1.4 Main Contribution of This Work

The main contribution of this research is roofing application. The properties of insulation materials depend on their structure, the raw materials used and the manufacturing process. In order to select a suitable thermal insulation material, thermal properties is the prime importance. High thermal stability and tensile strength is the main goal in order to achieve a great performance of high thermal building nano insulation materials for roofing application.

1.5 Organisation of This Thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 is literature review. In this section, it provides a description of the type of polymer chosen, type of nanofiller and also its structure. The other element is the method of preparation polymer nanocomposites, structural characterization and also testing of polymer nanocomposites as well as its properties.

Chapter 3 stated the methodology for modification of clay using an ion exchange method and also the fabrication of PU-Nanocomposites using solution mixing method. This chapter also discusses the methodology for characterization of organoclay and polymer nanocomposites by using AAS, ICPMS, FTIR and FESEM and then the sample were tested by using TGA and Tensile Test for thermal and mechanical properties respectively.

Chapter 4 mainly discusses about the result that collect from the characterization analysis of organoclay and testing of polymer nanocomposites. A detailed description of the analysis and previous research are also presented.

Chapter 5 is conclusion of the entire objectives in this research either it has been taken place successfully.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This paper presents the description of polymer nanocomposite (PNC) which have received much attention from the scientific research field in the past several years due to their improved properties at very low clay loading levels compared with conventional filler composites (Berta et al., 2006). Polymer nanocomposites has shown vast enhancement in modulus, toughness, and barrier properties as well as mechanical and thermal properties (Xiong et al., 2004). Interests in these materials stem from the fact that there is a unique physical state in the polymer of its silicate-polymer interface. Organoclays are one of the fillers that are commonly used in the polymer industry as a filler. Clay minerals such as montmorillonite (MMT) are ideal reinforcing fillers as it exhibits many interesting structural features such as exchangeable interlayer cations, hydroxyl groups on the edges of clay platelets and a high aspect ratio of the individual layers (Lagaly, 1999). However, as mentioned by Lucilene, (2008), it is important for proper organophilization to occur as it is the key step for successful exfoliation between the clay particles and the polymer matrix. With this exfoliation, a strong interfacial interaction between the polymer matrix and organoclays can be built whereby this interactions aids in improving the properties of the polymer matrix. Polyurethanes have widespread applications as coatings, adhesives, rubbers, foams and thermoplastic elastomers (Asim et al. 2005). Polyurethane can be designed as various applications as it has a wide range of physical and chemical properties. In recent years, polymer nanocomposites have attracted great interest among researchers because as it exhibits improved performance properties compared to pristine polymers because of their unique phase morphology by layer intercalation maximizes interfacial contact between the organoclay and its matrix (Byung et al., 2002). This chapter is focused on the review of the physical and thermal properties of polyurethane as well as the preparation and properties of polyurethane nanocomposites by using organoclay as the filler.

2.2 Polyurethane

Polyurethane was first developed in the year 1937 by Otto Bayer. It was developed by the polyisocyanate-polyaddition process. Polyurethane then started to become a material to be studied due to its unique properties. The properties of polyurethane can be adjusted via two approaches whereby the first is by changing the molecule structure if polyurethane by modification of its three basic building blocks and the second is by introducing inorganic fillers into the polyurethane matrix (Song et al., 2005). The structure of polyurethane is shown as below.

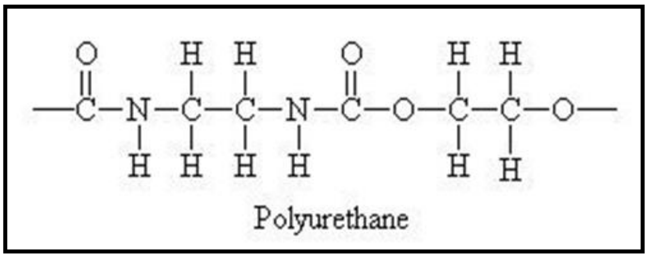

Figure 2.1: Structure of Polyurethane

Source: Otto Bayer (1937)

Polyurethanes find plenty of applications in a wide range of engineering works including in the biomedical field. Polyurethane is belongs to a class of polymer containing organic segments joined to each other by urethane linkages. Otto Bayer and coworkers have invented this polymer at the I.G. Farbenindustrie, Germany in 1937, however production in the industrial scale started only in 1940 when DuPont and ICI recognized its extraordinary elastic properties. The key components required for the synthesis of polyurethanes are:

a. Diisocyanate (aliphatic or aromatic)
b. Polyol (polyester or polyether)
c. Chain extender (low molecular weight diol or diamine).

The most commonly used diisocyanates are 4,4'-methylene bis(phenyl isocyanate) (MDI), 2,4-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate(HDI), isophoron diisocyanate (IPDI), etc. Although isocyanates play a vital role in the polyurethane synthesis (due to the differences in their reactivity depending on the presence of aromatic and aliphatic moieties) but the final property of the polyurethane are mostly determined by the type of polyol used. Function of the polyols may vary from 2 to 8 with an average molecular weight of 400 to 6000 grams per GM mole (Mn). In practice, polyol with molecular weight 1000 and 2000 grams per GM mole are most widely used (Pandey et al., 2005). Polyether polyol based polyurethanes are more resistant to hydrolysis, whereas, the polyester polyol based counterparts are thermally more stable. Polytetramethylene glycol (PTMEG) based polyurethane possess excellent hydrolytic stability and microbial resistance, outstanding dynamic properties including resilience and low temperature flexibility. The third most important component is the chain extender. The most widely used chain extender in preparing polyurethanes is 1,4-butane diol but methylene bis (O-chloro aniline) is normally used for the preparation of polyurethane urea (Hussain et al., 2006).

Catalysts play an important role in the synthesis of polyurethanes. Tertiary amines are mostly used in the synthesis of polyurethane foams (as it also promotes the reaction of the isocyanate with water). However, organometallic compounds especially dibutyl tin dilaurate is most widely used catalyst for the synthesis of thermoplastic polyurethanes (TPUs) (Giannelis, 1996).

In the synthesis of polyurethanes, chemistry of diisocyanate plays a important role. The isocyanate group contains a highly electrophilic carbon atom, which possess the resonating structures as shown in Figure 2.2.

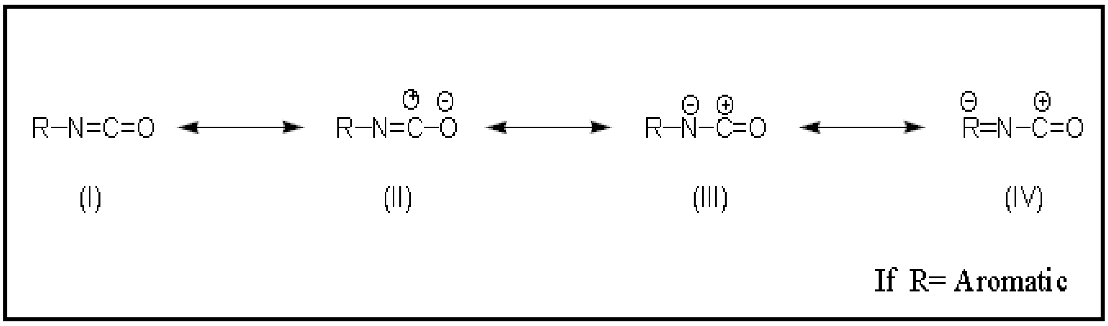

Figure 2.2: Resonating structures of isocyanate
Source: Giannelis (1996)

This electrophilic carbon present in the –NCO group plays a pivotal role in polyurethane chemistry. Three resonating structures (II, III and IV), out of the four, contain carbon atom having positive charge on it with the delocalization of negative charge on oxygen, nitrogen and R group (provided ‘R’ is aromatic). This is the only reason for the high reactivity of isocyanates towards nucleophiles and higher reactivity of aromatic isocyanates over aliphatic isocyanates. It is also found that the reactivity of aromatic isocyanate containing electron withdrawing group on the aromatic ring increases when present in another- and para- positions. Similarly, the reactivity diminishes significantly when the aromatic ring(s) contains electron donating substituents (Gilman, 1999).

2.2.1 Synthesis of Polyurethane

The methods of synthesis of polyurethanes can be differentiated according to the medium of preparation (bulk, solution, aqueous) and the addition sequence of the reactants (one shot process, two step pre-polymer process). Bulk polymerization (either one shot or two step prepolymer process) is generally preferred in industries as the process is cost effective and environmentally friendly because of solvent-free synthesis, whereas, solution polymerization is being used for laboratory synthesis (Fornes & Paul, 2003).However, reaction in aqueous media via the miniemulsion polymerization technique is mostly limited to the preparation of certain coatings and adhesives (Finnigan et ., 2004).

In one shot process, all the ingredients (polyol, diisocyanate, chain extender and catalyst) are mixed together. Even so, in the prepolymer process, polyol is first reacted with the diisocyanate to prepare the prepolymer, followed by chain extension reaction. In case of one shot process, high degree of shear is required to render homogeneous mixing (Cosoli,2008). Prepolymer process is the most widely used method as one can precisely control the morphology of the final product by this method. Figure 2.3 depicts the schematic representation of synthesis of polyurethanes by the propeller route.

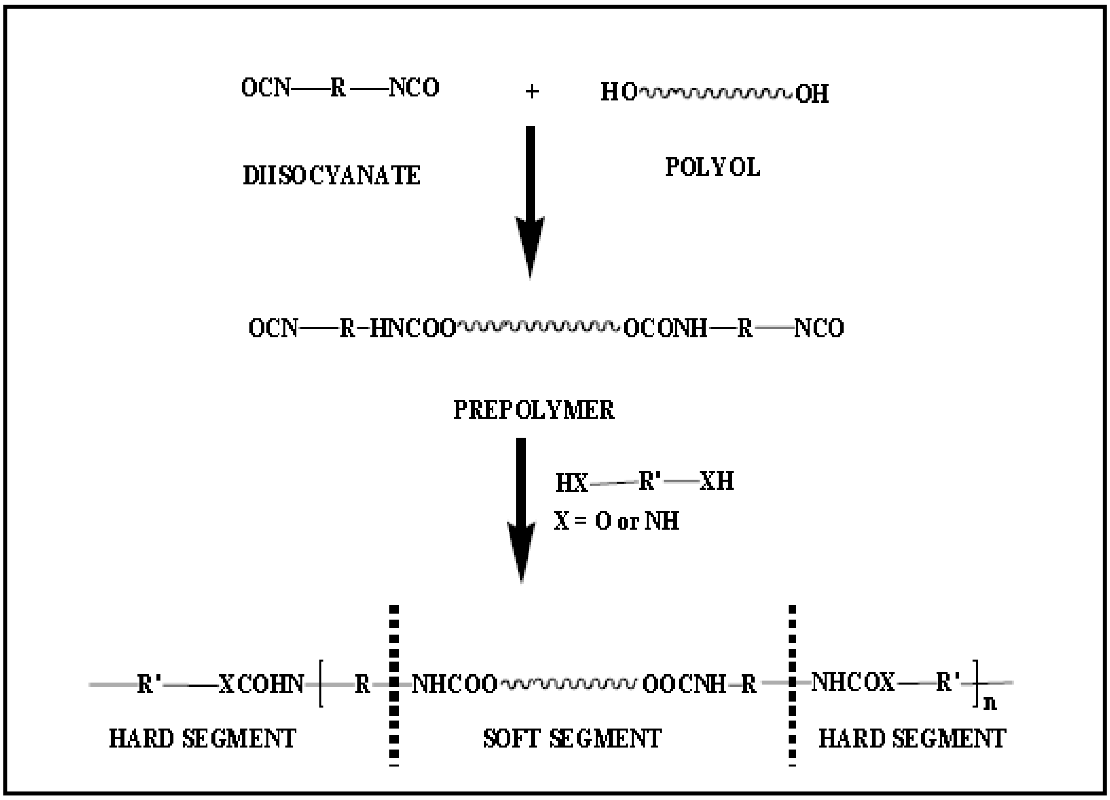

Figure 2.3: Preparation of polyurethane by prepolymer method

Source: Fornes & Paul (2003)

Polyurethanes can be classified into various categories depending on their properties and applications. Thermoplastic Polyurethane (Segmented polyurethane) – ranging from thermoplastic to thermoplastic elastomer

b. Castable Polyurethane

c. Millable Polyurethane

d. Polyurethane foams (Rigid and Soft)
e. Coatings
f. Adhesives.

2.2.2 Thermoplastic Polyurethane

Amongst all the grades of polyurethanes, TPU is the most widely used material. This is because of its higher mechanical strength, excellent abrasion resistance, ease in processing and bio-compatibility. TPU is a block copolymer composed of hard segments and soft segments arranged in a (A-B-A). The soft segment is prepared by the reaction between the poll and the discount, but hard segment is formed by the reaction between the discount and the chain extender. Phase separation (segregation) between the hard and soft segments occurs due to the difference in secondary forces (van der Waals, dipole-dipole, H-bonding interactions, etc.(Chingwada & Wildie, 2003). Thus, the degree of segregation between the hard and soft segments depend on the extent of interaction of the hard segments with each other and also with the soft segments (Krikorian & Pochan, 2003).

The phase segregation is less pronounced in polyester polyurethane than in polyester polyurethane and is most pronounced in polybutadiene based (e.g., HTPB) polyurethane. Also a drastic development in phase segregation and domain organization can be encountered due to the incorporation of urea moiety in the hard segment (Meneghetti & Qutubuddin, 2006), which causes improved mechanical strength such as higher mechanical properties, lower hysteresis, greater toughness and slower rate of stress relaxation (Sheng et al., 2004). Phase separation increases with increasing chain length of soft segment or with the increasing polarity leading to lesser hard-soft segment interactions . Bonart et al., (2006)reported the first direct evidence of the occurence of two-phase morphology from small angle X-ray scattering (SAXS) study.

Despite several advantages, TPU suffers from lower thermal stability and flame retardancy as compared to other engineering thermoplastics (polyester amides, polyester esters etc.) for similar applications (Lebaron et al., 1999).

2.2.3 Applications of Polyurethane

Polyurethane is one of the polymers that are highly ranked in the polymer field due to its unique properties that can be altered according to the application that is to be applied. Polyurethanes can be tailored to meet the highly diversified demands of modern technologies such as coatings, adhesives, fiber, foam and thermoplastic elastomers (Beyer, 2002).

According to Subrata et al. (2012) segmented polyurethanes are extensively used polymers in biomedical applications because of their bio-stability, biodegradability and tailorable backbone structure from a wide range of available precursors. Furthermore, their unique combination of biocompatibility, toughness and functionality has led to the widespread use in implantable devices such as vascular grafts, pacemaker leads, blood bags, bladders and artificial hearts that depend on elastomeric properties for interaction with, and mimicking of, soft tissue (Thostenson, 2005).

PU is also used widely in the coating area. According to Chigwada et al. (2006), the wide applicability of PU coatings is due to versatility in selection of monomeric materials from a huge list of macrodiols, discounts and chain extender (CE). PU coating are found on many materials such as on automobiles to improve the colour retention, in construction and as spray coating for durability against environmental deterioration.

With the increasing demand of polyurethane's usage, the development of polyurethane nanocomposites can be an added value for improvising and utilizing the full benefits of this polymer in its applications.

2.3 Nanofillers

2.3.1 Layered Silicate

The layered silicates are natural or synthetic minerals consisted of the regular stacks of aluminosilicate layers with a high aspect ratio and high surface area. Layered silicates are easily available and have low cost. The current most common layered silicates used in polymer nanocomposites preparation are clays. Clay is referred to a part of soil fraction with the particle size of less than 2 μm. The clay layers have a thickness of about 1 nm which is at the nanoscale. There are many members of clays with some difference in their formula, properties and structure including swelling and exfoliation (Yano et al., 1993). Those members who are able to be exfoliated by polymer chains or monomers and distributed as individual clay layers within a polymer matrix are suitable for the preparation of polymer nanocomposites. The individual clay layers can lead to the dramatic improvements in polymer properties due to their high aspect ratio and high interfacial interactions with polymer matrix (Zanetti et al., 2004).

2.3.2 Structure of Clays

Clays have layered structure. The layers are built from tetrahedral sheets in which a silicon atom is surrounded by four oxygen atoms and octahedral sheets in which a metal like aluminium or magnesium is surrounded by eight oxygen atoms. The tetrahedral (T) and octahedral (O) sheets are fused together by sharing the oxygen atoms. Unshared oxygen atoms are exhibit in hydroxyl form. Two main arrangements of octahedral and tetrahedral sheets bind together make the one layer structure of clay. One tetrahedral bound to one octahedral (1:1) is known as kaolin group with the general composition of $Al_2Si_2O_5(OH)_5$ and the layer thickness of ~ 0.7 nm. The crystal lattice consisted of one octahedral sheet sandwiched between two tetrahedral sheets (2:1) with the total thickness of 0.94 nm is well known as phyllosilicates. The 2:1 phyllosilicate layers might be electrostatically neutral with no inter layer ion present known as pyrophyllite. As no presence of inter layer ions, the layers do not expand in water. When silicon in tetrahedral sheets is altered by aluminium, the 2:1 structure is known as mica (Yao et al., 2004).

The negative charge generated by this substitution is balanced by the insertion of potassium cations between layers. Due to the equal size of potassium cation and the hole created by Si/Al tetrahedral sheets, the presence of potassium cation makes no inter layer spacing. Therefore, the 2:1 layers are held together strongly and the swelling or exfoliation of layers is not possible. When in neutral pyrophyllite, the aluminum cations in the octahedral layers are partially substituted by divalent magnesium or iron cations the smectite clay group is formed. The negative charge generated by this substitution is balanced by inter layer counter sodium or calcium ions. The charge created on the layers is not locally constant and varies from layer to layer (Yeh et al., 2008). An average charge value is evaluated for the layers which can be determined by cation exchange capacity (CEC) measurement. Due to the unequal size of inter layer cations with the holes of tetrahedral sheets, the presence of inter layer cations causes to an interlayer spacing. The layers stay near together with a regular gap between them. The gap is known as inter layer or gallery. The thickness of the repeated units in a regular multilayer structure contained of one layer and one inter layer space is called d-spacing (d001) or basal spacing . The basal spacing of clays can be measured or calculated from their X-ray diffraction patterns. The inter layer dimension is also depending on the clay nature and swelling or hydration degree of inter layer cations. The inter layer distance is around 1 nm for montmorillonite (Kornmann et al., 2003).

The van der waals and electrostatic forces stacked the layers together are relatively weak and inter layer distance varies depending on the charge density on the layers, its degree of hydration and inter layer cation radius. Because of the inter layer spacing and weak inter layer forces, the cations present between the layer might be hydrated in aqueous solutions known as clay swelling. The swelling cause increasing of inter layer space. The charge of density on the clay layers is differ in various clay groups with different clay structures (Mittal, 2007). Due to the inter layer spacing and weak forces between layers, especially in the hydrated form, other molecules also can be intercalated between layers, leads to the expanding of layered lattice and finally may be caused by the separation of individual layers. The unique exfoliation/intercalation behavior of smectite clay minerals which is responsible to the high aspect ratio of this clay type makes them very important and powerful as reinforcing filler for polymers.

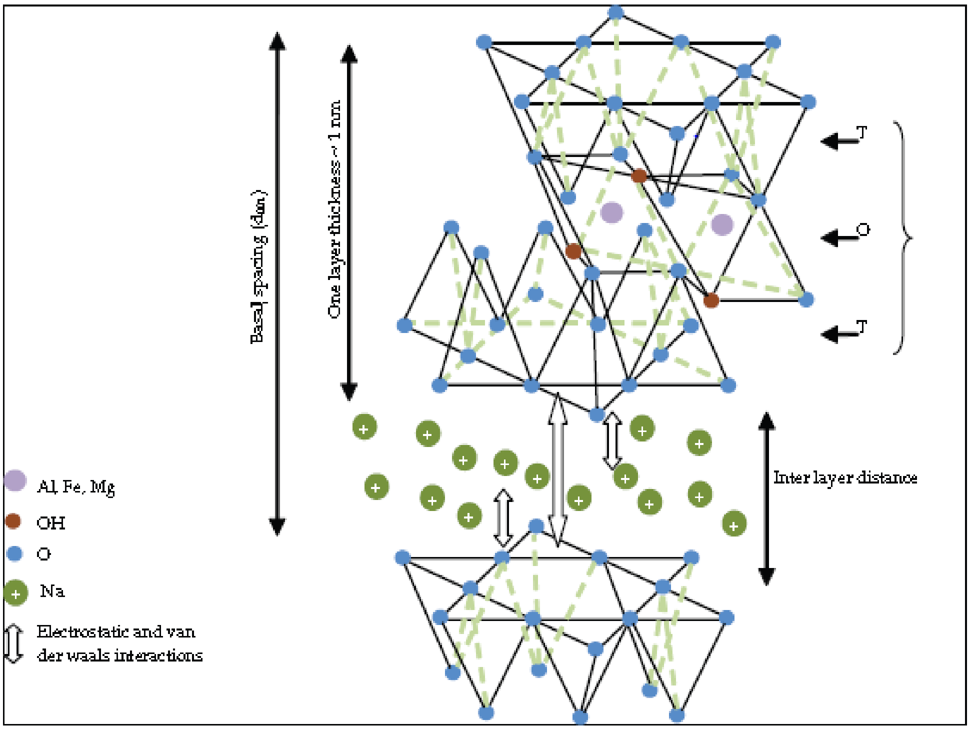

Figure 2.4: Smectite clay structure.

Source: Yao et al., (2004)

The dimension of 2:1 layer structures are around 1 nm in thickness and 30 nm to several microns in lateral depending on the source and preparation method of clay. The clay lateral dimensions and its ability to disperse into separated layers determine the aspect ratio of clay which is strongly important in polymer/clay interfacial interactions. Separation of individual clay layers having about 1 nm thickness display a perfect structure which strongly affects on the improvement of polymer properties. However due to the higher internal surface in high degrees of dispersed structures, the internal forces for agglomeration of individual layers is also increases. Therefore the layers have tendency to hold together or aggregate. Several layers formed parallel together with the total thickness of about 10 mm make primary clay particles. The primary particles are consequently joined together and make “micro aggregates”. “Aggregates” are formed by randomly joining of micro aggregates and primary particles, and finally the staying of aggregates close together makes “association” in the smectite structures. Clay minerals are belonging to the nanoplatelet structured filler particles in polymer composite technology. (Ma et al., 2006).

Montmorillonite, saponite and hectorite are the well known smectites which are most commonly used in the preparation of polymer nanocomposites (Table 2.1) (Pavlidou & Papaspyrides, 2008). Montmorillonite (MMT) has the widest acceptability for use in polymer nanocomposites because of its ease availability, well known intercalation/exfoliation chemistry, high surface area and high surface reactivity. The MMT layer aspect ratio might be in the range of 1000 in well dispersed state without breaking of layers and surface area of about 750 m2/g. Normally because of the breaking of clay layers in to small plates during preparation process of nanocomposite, the aspect ratio of MMT layers decreases to about 300-500.

Table 2.1: Chemical structure of commonly used smectite type clays, M: monovalent cation, x:degree of cations isomorphous substitution in octahedral sheets.

Smectites	Chemical Formula
Montmorillonite	$M_x(Al_{4x}Mg_x)Si_8O_{20}(OH)_4$
Hectorite	$M_x(Mg_{6x}Li_x)Si_8O_{20}(OH)_4$
Saponite	$M_xMg_{6x}(Si_{8x}Al_x)O_{20}(OH)_4$

Source: Pavlidou & Papaspyrides (2008)

Other clay materials such as mica, 1:1 structures and 2:1 pyrophillits are not commonly used in polymer nanocomposites because they have not useful intercalation/exfoliation characteristics or they are not easily separated into layers. Due to the higher charge density on the layers they are strongly stacked together and the hydration of inter layer cations or intercalation of polymer chains between layers are difficult or not possible (Pau et al., 2008).

2.3.3 Modification of Clay Layers

The development of polymerclay nanocomposites with good dispersion of clay layers within the polymer matrix is not possible by physical mixing of polymer and clay particles. It is difficult to disperse nanolayers in most polymers due to the high face to face stacking of layers in agglomerated tactoids and their intrinsic hydrophilisity which make them incompatible with hydrophobic polymers. Just a few hydrophilic polymers such as poly (ethylene oxide) and poly (vinyl alcohol) can be miscible with clay nanolayers (Pavildou & Papaspyrides, 2008). The intrinsic incompatibility of hydrophilic clay layers with hydrophobic polymer chains prevents the dispersion of clay nanolayers within polymer matrix and causes of the weak interface interactions. Weak and incompatibility interfacial interactions hinders the exfoliation and preparation of dispersed stable nanocomposite with improved properties. Modification of clay layers with hydrophobic agents is necessary in order to render the clay layers more compatible with polymer chains. That is a surface modification which causes to the reduction of surface energy of clay layers and match their surface polarity with polymer polarity. The organoclays with lowered surface energy are more compatible with polymers and polymer molecules are able to intercalate within their interlayer space or galleries below well defined experimental conditions (Phang et al., 2005).

The surface modification of clay layers can be achieved through a cation exchange process by the replacement of sodium and calcium cations present in the inter layer space or clay galleries by alkylammonium or alkylphosphonium (onium) cations (Ahmad et al., 2009). In addition to the surface modification and increasing the hydrophobisity of clay layers, the insertion of alkylammonium or alkylphosphonium cations into the galleries causes to some degree of increasing in the inter layer spacing which promotes the following intercalation of polymer chains into the galleries during nanocomposite preparation (Chigwada et al., 2006). Also the alkylammonium or alkylphosphonium cations can provide functional groups which interact with polymer chains or initiate the polymerization and therefore increase the interfacial interactions. Figure 2.5 shows the organically modification of clay layers using alkylammonium cations via the ion exchange process.

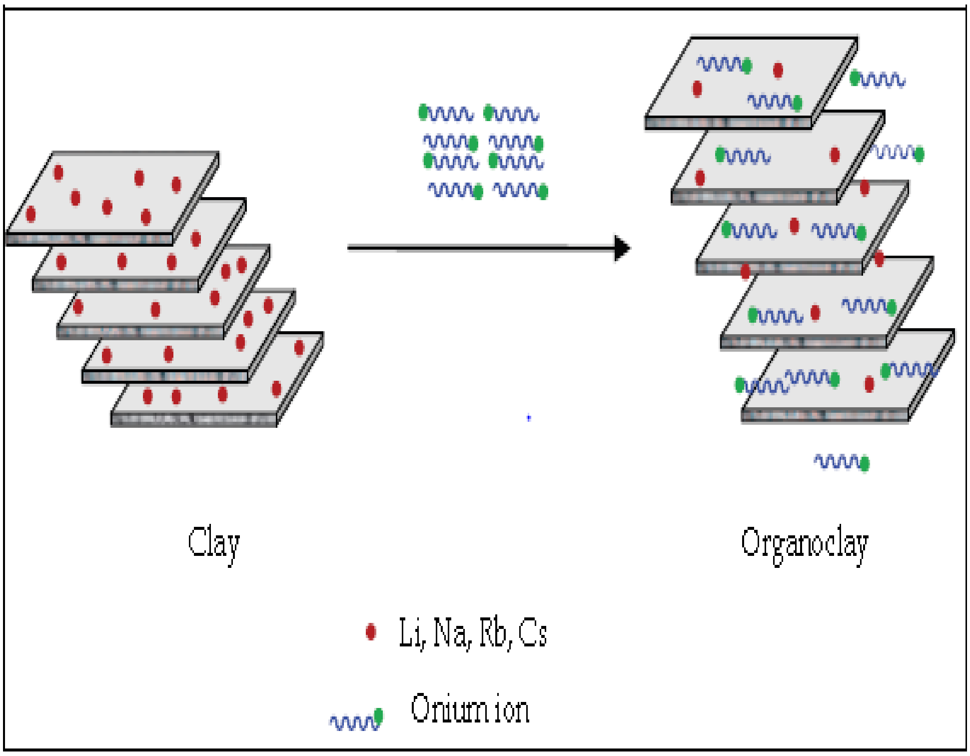

Figure 2.5: Scheme of the modification of clay layers by organic onium cations.
Source: Chigwada et al., (2006)

The ion exchange process is carried out in aqueous solution with the hydrated inter layer cations. The affinity of monovalent sodium cations to hydration promotes the ion exchange process and increases the efficiency of organic modification of clay layers. Clays containing divalent counter cations such as calcium cannot be easily hydrated and therefore their replacement by ion exchange process is not efficient. Hence, in these clays, the divalent cations should be ion exchanged with easily exchangeable sodium cations prior to modification by onium cations (Ray & Okamoto, 2003). The efficiency of organic modification by ion exchange process in the increasing of basal spacing and consequently the exfoliation of clay and formation of stable nanocomposite systems depends also on the surface charge of clay layers. The surface charge of density on clay layers depends on the clay nature and its preparation (growth) conditions. When the charge of density of clay layer is high such as about 1 equiv/mol for mica, so the electrostatic forces between layers is also increase.

Therefore the inter layer cations can not to hydrate or swollen and consequently the ion exchange process cannot be carried out. The medium charge densities (0.5–0.8

equiv/mol) such as in vermiculite, can make a strong potential for partial swelling and hydration of cations. However the divalent cations exist in the interlayer spacing of clays such as vermiculite make the swelling process difficult due to the lower affinity of divalent cations for hydration. The lower charge densities (0.25–0.5 equiv/mol) such as formed in montmorillonite causes to the weak electrostatic forces between layers. Also the presence of sodium cations, with strong affinity for hydration and exchanging, between the MMT layers make this kind of clays more suitable for organic modification, swelling and exfoliation (Ray et al., 2003).

The structure of the organoclays and their basal spacing also depends on the molecular size of organic onium and its configuration in the interlayer spacing after modification. Figure 2.6 schematically shows the various configurations of the organic modifiers inserted within the clay layers by ion exchange with sodium cations. It shows that the charge density of clay layers, the efficiency of ion exchange process and the spatial characteristics of onium cation are effective on the configuration of onium cations in the modified clays (Jordan et al., 2005).

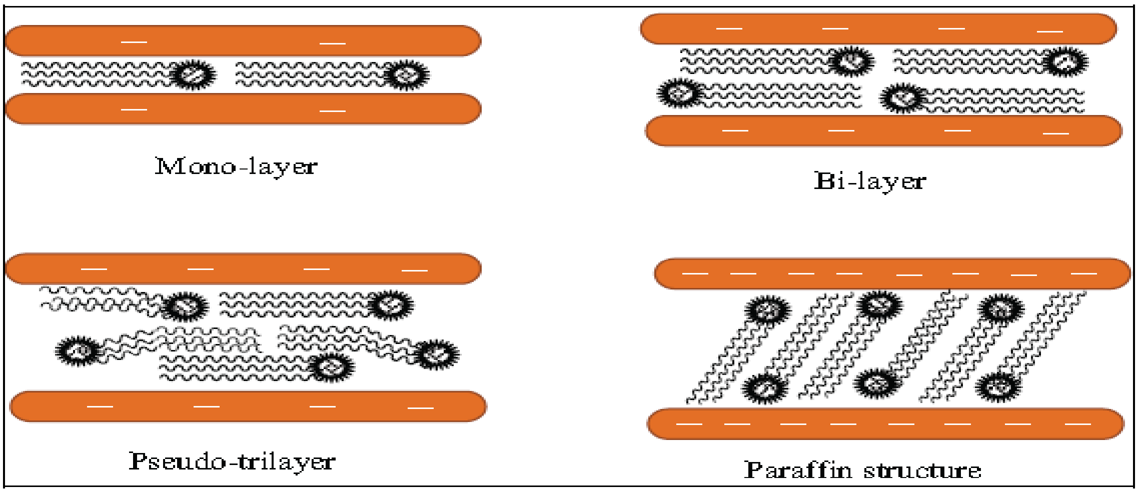

Figure 2.6: Various configurations of organic oniums into the clay galleries.

Source: Jordan et al., (2005)

The organic tail of onium laid up parallel to the clay layer can be obtained with lower charge densities. By increasing the charge density of clay layers, bilayer or trilayer structures with more increasing of inter layer spacing can be formed. Finally with the higher charge densities more inter layer spacing is obtained by the formation of paraffin structure. Also increasing of temperature can lead to the structures with more basal spacing by increasing the mobility of onium molecules into the galleries. However in a given temperature two parameters determine the equilibrium layer spacing, the charge density of layers, driving the packing and number of onium chains into the interlayer space, and the size or chain length of organic tail in onium compound (Jiang et al., 2005).

2.4 Nanocomposites Structure

In general, structures of polymerclay nanocomposites are classified according to the level of exfoliation and intercalation of polymer chains into galleries of clay. Various parameters including clay nature, polymer matrix, organic modifier and preparation method are affective on the intercalation and exfoliation level. Therefore depending on the nature and properties of clay and polymer as well as preparation methodology of nanocomposite, several composite micro-structures can be obtained.

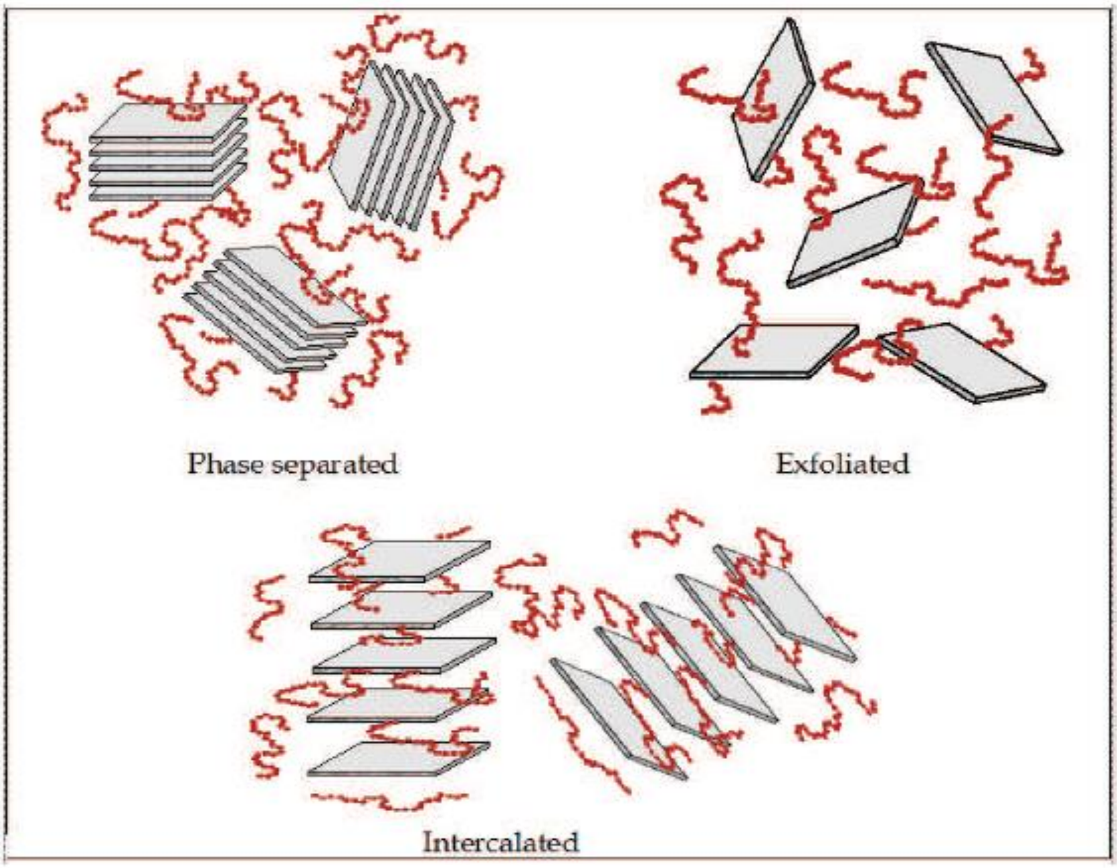

Figure 2.7: Various micro-structures of polymer/clay composites.

Source: Nam et al., (2001)

2.4.1 Phase Separated Structure

When the organic polymer is interacted with inorganic clay (unmodified clay), the polymer is unable to intercalate within the clay layers and the clay is dispersed as aggregates or particles with layers stacked together within the polymer matrix. The composite structure obtained is considered as "phase separated". The properties of phase separated polymer/clay composites are in the range of traditional micro composites.

2.4.2 Intercalated Structure

When there is one or more polymer chains are inserted into the inter layer space and cause to the increasing of the inter layer spacing, however the periodic array of the clay layer is still exist, the intercalated nanocomposite is represented. The polymer chains in the galleries causes to the low of electrostatic forces between the layers but it is not totally dissolved. A well-ordered multilayer hybrid morphology with a strong interference interactions consisted of clay layer and polymer chains is obtained in this configuration (Kojima et al., 2003).

2.4.3 Exfoliated Structure

Exfoliated or delaminated structure is obtained when the insertion of polymer chains into the clay galleries causes to the separation of the layers one another and individual layers are dispersed within the polymer matrix. Hence, when the polymer chains cause to the increasing of interlayer spacing more than 80-100 Å, the exfoliated structure is formed. Due to the good dispersion of individual clay layers, high aspect ratio is represent and lower clay content is needed for exfoliated nanocomposites (Okamoto, 2001). Also most significant improvement in polymer properties are obtained due to the large surface interactions between polymer and clay. Various polymer/clay structural configurations have been shown in Figure 2.7.

2.5 Preparation of Polymer Clay Nanocomposites

Many efforts have been made for the preparation of intercalated and exfoliated polymer/clay nanocomposites with improved properties. A variety of polymer characteristics including polarity, hydrophobicity, molecular weight reactive groups and also clay characteristics such as charge density and its modified structure and polarity are affective on the intercalation of polymer chains within the clay galleries. Therefore different synthetic approaches have been used for the preparation of polymer/clay nanocomposites. In general there are four preparation methods including in situ template synthesis, solution intercalation, in situ intercalative polymerization and melt intercalation (Wang et al., 2002).

2.5.1 In Situ Template Synthesis

In this method the clay layers are synthesized in situ in the presence of polymer chains. The polymer and clay primary materials dissolve in an aqueous solution. Typically silica, magnesium hydroxide and lithium fluoride as clay building blocks are mixed with polymer in a solvent. The gel or slurry is refluxed normally at high temperatures followed by washing then drying. The nucleation and growth of clay layers take place on the polymer chains and the polymer chains are trapped in the clay inter layers. Although the clay layers may be well dispersed within the polymer matrix without the modification of clay by onium cations, however this method has serious disadvantages. The high temperature applied for the synthesis of clay layers causes to the decomposition of polymers. Only hectorite clay is synthesized at the lower temperatures. Also the synthesized clay crystals, develop by the self-assembly process, have potential to aggregate. Therefore this method is not widely used and only a few nanocomposites using hectorite clay and poly (vinyl alcohol), polyaniline and polyacrylonitrile have been synthesized by this method (Alexandre, 2000).

2.5.2 Solution Intercalation

In this method the polymer or pre polymer is dissolved in a solvent and the clay is dispersed in the same solution. The clay is swollen in the solvent and the polymer chains intercalate between the layers. The intercalated nanocomposite is obtained by solvent removal through vaporization or precipitation. Clays can be swollen easily in solvents such as water, acetone, chloroform and toluene. The polymer chains are absorbed onto the delaminated sheets. During the solvent evaporation the entropy gained by the exit of solvent molecules from the interlayer spacing, allows the polymer chains to diffuse between the layers and sandwiching. Depending on the interactions between polymer and clay sheets, intercalated or exfoliated structures may be obtained in this method. This technique is used for the preparation of epoxy/clay nanocomposites. However due to the need for use solvent, this technique cannot be applied in industry. The nanocomposite preparation by emulsion polymerization, with the clays dispersed in the aqueous solution, is also categorized as solvent intercalation method (Rehab & Salahuddin, 2005). Toyota group has been used this technique to produce polyimide/clay nanocomposites (Yano et al., 1993). The emulsion and bulk polymerization methods have been used for the preparation of polystyrene/clay nanocomposites using the Na-MMT, cloisite 30B and cloisite 15A clay materials. The effect of clay swelling method and sonication on the inter layer spacing and intercalation have been investigated. Good dispersion of Na-MMT in the polystyrene (PS) matrix was observed when an emulsion polymerization was employed and good dispersion of cloisite 30B in the PS was observed during bulk polymerization. Cloisite 30B showed better dispersion when this clay was swollen with the monomer during emulsion polymerization. Sonication had good effect on dispersion of the clays in the PS matrix. PS/Cloisite 15A nanocomposites showed minor increase in d-spacing compared to the pure cloisite 15A. TGA analysis showed that the thermal stability of the nanocomposites has been improved compared to the pure polystyrene.

2.5.3 In Situ Intercalative Polymerization

This technique was the first method used for the preparation of polymer/clay nanocomposite by Toyota research group in the preparation of Nylon-6 nanocomposite from caprolactam monomer (Usuki et al., 1993). In this technique, the organoclay is swollen in monomer liquid or monomer solution. The monomers inserted into the interlayer spacing are polymerized by the heat or radiation, by the diffusion of the initiator or by the organic initiator present on the organic modifier of clay (Hussain et al., 2006). The polymerization is carried out within the clay galleries as well as extra galleries. The growth of polymer chains results to the exfoliation and formation of disordered structure. This method is suitable for the preparation of thermoset/clay nanocomposites and has been widely used for the epoxies and styrenic polymer nanocomposites (Lan et al., 1995). The polarity of monomer and clay layers determines the diffusion rate and equilibrium concentration of monomer within the clay galleries. Consequently the exfoliation and dispersion of clay layers can be tailored by the clay and monomer chemistry (Pavlidou, 2008). Polyaniline/MMT nanocomposites have been prepared by the insitu polymerization of aniline in the presence of MMT (Olad & Rashidzadeh, 2008). Both unmodified and organomodified MMT were used in the preparation of nanocomposites. Due to the using of acidic aqueous solutions for the polymerization of aniline, the polar organic anilinium cations can be interact with both unmodified and modified clays.

2.5.4 Melt Intercalation

Clay is mixed within the polymer matrix in molten temperature. The conventional methods such as injection molding and extrusion are used for dispersion of clay layers within the polymer matrix. This method is a good technique for the preparation of thermoplastic nanocomposites (Kornmann et al., 2001). The polymer chains are exfoliated or intercalated into the galleries. Thus, clays are organically modified and polymer chains are surface modified with more polar functional groups to enhance their compatibility and therefore promote the exfoliation. In melt intercalation method no solvent is required and it has many advantages for the preparation of nanocomposites and is a popular method for industry (Kiliaris et al.,2010).

2.6 Structural Characterization of Polymer Clay Nanocomposites

In the preparation of a polymer/clay nanocomposite it is important to know the degree of intercalation/exfoliation and its effect on the nanocomposite moderate properties. In other word there is need to analyze the micro structure of the prepared nanocomposite. Two common techniques including X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) are widely used to characterize the micro structure of nanocomposite as well as pure clay or pure organoclay. Clays as well as organoclays show a characteristic peak in XRD analysis due to their regular layered structures. The peak is indicative of the platelet separation or d-spacing in clay structure (Zhou et al., 2005). By using the peak width at half maximum height and peak position (2θ) in the XRD spectra the inter layer space can be calculated utilizing Bragg'slaw (eq. 1).

$$\sin \theta = n \lambda / 2d \qquad \text{(eq.1)}$$

Where λ is wave length of X-ray radiation used in the diffraction experiments, d is the space between layers in the clay lattice and θ is measured diffraction angle. Any change in the interlayer or d-spacing of a clay lattice by organic modification or polymer intercalation causes to the change in the, broadness, position and intensity of the characteristic peak in XRD spectra. According to the Bragg law, increasing of d-spacing results to the broadening and shifting of related XRD peak toward lower diffraction angles (2θ). By monitoring the position (2θ), shape and intensity of the characteristic peak for organoclay in nanocomposite structure it is possible to determine the degree of intercalation/exfoliation. For example Figure 2.8 shows the XRD patterns of pristine Na-MMT as well as polystyrene (PS)/Na-MMT nanocomposites prepared by emulsion polymerization method. The characteristic peak of MMT has been appeared at $2\theta = 7.13°$ corresponding to the inter layer space of 1.24 nm.

The XRD patterns of polystyrene/Na-MMT nanocomposites containing different clay percents (2-6 wt %) show diffraction peaks all shifted to lower 2θ degrees against the peak of pure Na-MMT, which indicates the increasing of layers spacing due to the intercalation or exfoliation. The experimental conditions, peak position (2θ) and related calculated clay layer spacing obtained from XRD spectra of pure clays and polystyrene/clay nanocomposites have been shown in table 2.2. The results indicate that the Na-MMT was efficiently dispersed in the polystyrene matrix during the emulsion polymerization due to the hydrophilicity of pure montmorillonite. Also the effect of sonication on the dispersion of Na-MMT layers in the polymer matrix was investigated. The results represented that the polystyrene/Na-MMT nanocomposite prepared by the application of sonication has no noticeable diffraction peak in the XRD spectrum at 2θ values of 2° to 10°. This indicates that the clay plates have been dispersed effectively and may be the exfoliated structure has been obtained (Zu et al., 2001)

Table 2.2: XRD data and inter layer space for MMT and PS/MMT nanocomposites.

Sample	Experimental Polymerization Condition	2θ (^{o})	d (Λ)
Pure Na-MMT	-	7.13	12.38
PS/ Na-MMT (2wt%)	Emulsion	2.58	34.16
PS/ Na-MMT (4wt%)	Emulsion	2.72	32.46
PS/ Na-MMT (6wt%)	Emulsion	2.58	34.16
PS/ Na-MMT (2wt%)	Bulk	6.00	14.72
Pure Clay 30B	-	4.68	18.86
PS/ Clay 30B (2wt%)	Emulsion, swelling with water	3.54	24.93
PS/ Clay 30B (2wt%)	Emulsion, swelling with water + sonification	3.02	29.27
PS/ Clay 30B (2wt%)	Emulsion, swelling with monomer	2.79	31.67
PS/ Clay 30B (4wt%)	Emulsion, swelling with monomer	2.99	29.51
PS/ Clay 30B (6wt%)	Emulsion, swelling with monomer	3.03	29.10
Pure Clay 15A	-	2.95	29.88
PS/ Clay 15A (2wt%)	Emulsion, swelling with monomer	2.75	32.16
PS/ Clay 15A (2wt%)	Bulk	2.69	32.76

Source: Zu et al., (2001)

It may be need to use wide-angle X-ray diffraction (WAXD) patterns in the range 1° < 2θ <10° to identify the fully exfoliated structures which is correspond to the d-spacing of at least 6 nm. The XRD technique offers a conventional method to determine the d-spacing in the pure clay as well as in nanocomposite structure, within 1-4 nm, using the position, broadness and intensity of characteristic peak in WAXD diffractogram. However the disappearance of such a peak is not a conclusive evidence for a highly exfoliated structure in nanocomposite (Hedayati & Arefazar, 2009). A direct way to visually observe the nanostructure of nanocomposites and clay d-spacing is to the use of transmission electron microscopy (TEM) technique.

TEM micrographs allow a qualitative understanding of the internal structure, spatial distribution or exfoliation of layers within the polymer matrix and their structural defects. In the TEM micrographs, the darker lines in the brighter matrix shows the clay layers because of the presence of heavier elements including Si, Al and O in the composition of clay sheets or layers compared the lighter atoms such as C, N, H and Na present in the polymer matrix or inter layer spacing of clay sheets. Therefore the distance between darker liner sections presented in the TEM micrographs can qualitatively show the d-spacing and dispersion status (Hedayati et al., 2009). Therefore the overall structure of the nanocomposite including intercalation, exfoliation, dispersion and defects of clay layer can be conclusively obtained using TEM technique.

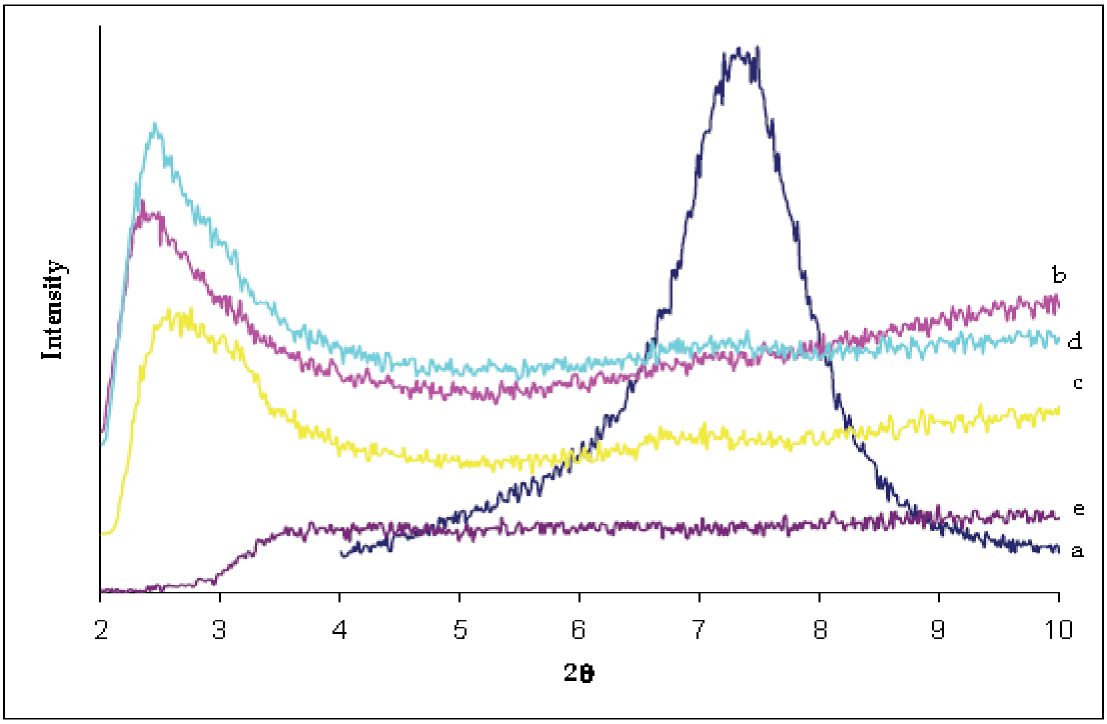

Figure 2.8: XRD patterns of pure Na-MMT (a) and PS/Na-MMT nanocomposites prepared by emulsion polymerization method with clay content of 2 wt % (b), 4 wt % (c) and 6 wt % (d) and PS/Na-MMT (2 wt %) with sonication (e).

Source: Hedayati & Arefazar, (2009).

However both TEM and XRD techniques are essential tools for evaluation of the nanocomposite structure and complementary show the structural features of polymer/clay nanocomposite microstructure. XRD gives almost quantitative and TEM provides qualitative informations about the exfoliation and d-spacing of clay layers in the polymer matrix compared to that of in pure clay material (Fornes et al., 2001). However, other techniques such as those based on thermal analysis, can be used to generate the interfacial interactions between clay layers and polymer chains.

2.7 Properties of Polymer Clay Nanocomposites

The aim for the addition of clay minerals to the polymers is to improve the polymer properties and to produce the polymer/clay nanocomposites with demand characteristics for desired applications. In short, it is wanted to obtain a nanocomposite with demand properties and characters or overcome the drawbacks of polymers while remaining the intrinsic advantages of primary polymer matrix (Gorrasi et al.,2003).

Because of the low price, availability, high aspect ratio and also desirable nanostructure and interfacial interactions, clays can provide adjustable dramatic improved properties at very lower loadings which help to the more remaining of polymer original useful properties. The nature and properties of components as well as preparation methodology and conditions affects on the final properties of polymer/clay nanocomposite (Ray, 2010). In this section the various improved properties of polymer/clay nanocomposites as well as the mechanism and effective parameters are discussed.

2.7.1 Mechanical Properties

The first and important goal in the application of fillers to the polymer is improvement in the mechanical properties and therefore fillers are commonly called as reinforcement agents (Jiang et al., 2005). The mechanism reinforcement is based on the higher resistance of rigid filler materials against straining due to their higher module. When a rigid filler is inserted to the soft polymer matrix, it will bring out the major portion of applied load to the polymer matrix under stress conditions, if interfacial interactions between filler and matrix is adequate (Tortora et al., 2003). Therefore the larger the interface between filler and matrix, and also more strong interfacial interactions, the outstanding the reinforcement effect will be. Also the modulus increases by increasing the filler ratio in the composite or nanocomposite composition. Because of the rigid structure of clay layers and their high aspect ratio, they have proven to be very effective in the increasing of modulus and stiffness of the polymer matrix in well dispersed condition. In fact due to the very higher aspect ratio of nano-clay fillers compared to that of regular fillers such as glass fibers, a dramatic improvements in the mechanical properties of nanocomposites are achieved even at very lower nanoclay additions (LeBaron, 1999).

In another approach, polymer chains, adhesived by great physisorption forces onto the rigid clay mono layers, become equally a portion of a rigid material and dramatically exhibit high modulus. By considering the very large interfacial area in well dispersed nanocomposite structures, significant improvement in the modulus can be expected. However any enhancement in the polymer-clay interfacial contact leads to the better stress transfer in the nanocomposite. It has been demonstrated that the enhancement in the interfacial adhesion properties between clay and polymer by surface modification of polymer chains using a suitable polar compatibilizer causes to the increasing in the mechanical properties of nanocomposite (Osman et al., 2005; Mittal, 2008). It should be detected that in higher loadings of compatibilzers, they will cause to the some degree of plasticization due to their lower molecular weight, which can be negatively affect on the modulus of nanocomposite (Mittal, 2008).

Also the using of organically modified clay filler increases both the modulus and stiffness of nanocomposite because of the more intercalation/exfoliation achieved. At all, any parameter which helps to the intercalation of polymer molecules within the clay galleries and consequently causes to the more exfoliation and interfacial interactions, results to the improvement in the modulus. However it is not easy to achieve the complete exfoliation of clay layers and there are variety of platelet structures with different thicknesses (depending on the number of layers stacked together) in polymer matrix. Fornes and Paul (2003) have analytically formulated the effect of incomplete exfoliation on the nanocomposite properties. Also it has been reported that the tensile modulus increases by increasing the filler volume fraction in nanocomposite (Mittal, 2007). However clay loading more than threshold limit value, causes to leveling-off in the increasing period of Young’s modulus, which is due to the formation of partially exfoliated/intercalated structure after that fully exfoliated structure formation (Ray & Okamoto, 2003; Alexandre & Dubois, 2000).

The incorporation of clay minerals also improves the tensile strength of polymers (Shelley et al., 2002). Even so, the tensile strength is influenced by the final morphology of nanocomposite. There are a number of reports on the reduction of tensile strength by the addition of clay minerals (Alexandre & Dubois, 2000; Finnigan et al., 2004). Similar to modulus, any factor affecting on the degree of intercalation/exfoliation has an impact on the tensile strength of nanocomposite. The effect of clay fillers on the stress at break values for polymer nanocomposites depends on the interfacial interactions between polymer and clay layers. The stronger interfacial, interaction causes to the increasing of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposite. The polymers with more polarity such as nylon and rubber based polymers have more strong interfacial interaction with polar clay layers and their nanocomposites represent improved stress at break values compared to that of pure polymer (Wang et al., 1998). Polyamide/clay nanocomposites have shown highly improved stress at break values, because of their high degree of exfoliated structures based on the presence of strong ionic bonds between polymer chains and clay layers (Alexandre, 2000). The nanocomposites of non-polar polymers like polyolefines with clays exhibit weak interfacial interactions and low degree of exfoliation and consequently show decreased or slightly improved stress at break values. On top of that the modification of polymer chains or clay layers may be causes to improved stress at break characteristics for non-polar polymers.

Elongation at break for polymer/clay nanocomposites is similarly dependent to the interfacial interactions of polymer/clay system. There are both decreasing and increasing reports of elongation at break for polymer/clay nanocomposites in literature (Finnigan et al., 2004; Yao et al., 2002). The impact strength of polymer/clay nanocomposites was also studied and compared with that of pure polymer systems. The reports are usually emphasis on the increasing of impact strength by the addition of very low fraction of clay loadings such as 0.1 wt% (Zhang et al., 2000; Oya et al., 2000). Then, in these studies, organic modified clay fillers were added to the compatibilized polyolefines. There are also reports on the decreasing of impact resistance by the addition of clay materials (Phang et al., 2005). Dynamic mechanical analysis studies on polymer/clay nanocomposites have shown that usually storage modulus and glass transition temperature (Tg) are improved by the addition of clay nanofillers (Nam et al., 2001; Laus et al., 1997; Krikorian & Pochan, 2003; Ray et al.,2002).

2.7.2 Thermal Properties

Thermal stability of polymer/clay nanocomposites have been analyzed and compared with that of pure polymer under various oxidative (air) or non-oxidative (inert gases) conditions. Thermogravimetric analysis (TGA) has been usually used to evaluate the thermal stability of polymer and their nanocomposites. In this method, the weight loss of the material due to the formation of volatile compounds under degradation because of the heating and temperature rising is monitored. In general, it has been reported that the polymer/clay nanocomposites are thermally more stable than pure polymers (Ray,2002). That is the incorporation of clay fillers into the polymer matrices results to the improvement of their thermal stability. The effect of clay layers has been detail explained as superior insulation and mass transport barrier against the volatile compounds generated during the decomposition of polymer under thermal conditions (Zhu et al., 2001). Also it has been reported that clays assist in the formation of layered carbonaceous char during degradation of polymer/clay nanocomposite (Ray et al., 2003).

Clay minerals are inorganic materials and are almost stable in the temperature ranges that organic polymers are degraded in to volatile compounds. Thus, in TGA experiments the clay content of nanocomposites is remain as residue after heating program (Gilman, 1999). Blumstein (1965) first reported the improved thermal stability of PMMA/MMT nanocomposite. TGA indicated that PMMA intercalated into the Na-MMT has 40-50 °C higher decomposition temperature. Vyazovkin (2004) reported the thermal stability of polystyrene/clay nano-composite compared to pure PS. They have showed that PS/clay nanocomposites have 30-40 °C higher degradation temperature compared to pure PS under nitrogen and air heating degradation conditions. Moreover, other studies have been showed that the nature of the clay modifier can affect on the thermal stability of modified clay and related nanocomposites (Mittal, 2007). In some other studies the thermal decomposition behavior of nanocomposites and pure polymers under air (oxidative decomposition) and inert gas (non-oxidative decomposition) have been compared (Beyer, 2002). Results showed that the formation of insulator layered char in oxidative degradation is achieved better than non-oxidative degradation heating program using some inert gases such as helium (Zhao et al., 2005; Beyer et al., 2002). Therefore under inert gas thermogravimetric experiments the nanocomposites may have the same degradation temperature as pure polymer.

Then, analyzed the thermal degradation behavior of PS/MMT nanocomposites as well as pure PS. According to the results, thermal stability of nanocomposite has been improved compared to the pure polystyrene. Thermogravimetric analysis (TGA) of neat PS and PS/clay nanocomposites was obtained by heating program of 10 °C /min. Figure 7 shows the TGA curves for PS and PS/MMT nanocomposites.

According to the results, the degradation temperature of the PS in nanocomposites has been shifted to higher temperatures compared to neat PS. The temperature of the 50% degradation of PS/clay nanocomposites has been increased compared to the pure PS. The 50% degradation temperature of pure PS was 411 °C, but that of the PS/Na-MMT nanocomposite was 422 °C and for PS/Cloisite 30B was 416 °C which is indicating respectively 11 °C and 5 °C improvement with 4 wt% of the clay loadings. For PS/Cloisite 30B nanocomposite two stages of weight loss under heating program took place. The first stage of weight loss at temperatures of about 220-312 °C represents the decomposition of modifying agent of Cloisite 30B. Then, the second stage of weight loss at temperatures of about 312-450 °C is related to the decomposition of PS. The TGA data obtain are summarized in table 3. The effect of polymer compatibilizer on the thermal degradation behavior of compatiblized polymer/clay nanocomposites has also been investigated. Results obtained shows that the incorporation of compatibilizers even with low molecular weight has not a significant unwanted effect on the thermal degradation of nanocomposites (Mittal, 2008).

2.7.3 Barrier Properties

One of the most considerable effects of clays in the polymer matrix properties is the dramatic improvement of barrier properties of polymers. Clay sheets are naturally impermeable. Clays increase the barriers properties of polymers by creating a maze or tortuous path that retards the diffusion of gas molecules through the polymer matrix (figure 9) (Pavlidou & Papaspyrides, 2008; Yano et al., 1993). The degree of enhancement in the barrier properties depends on the degree of tortuousity created by clay layers in the diffusion way of molecules trough the polymer film. The tortuous factor is determined by the ratio of actual distance which diffusive molecule is walked to the shortest distance to diffuse (polymer film thickness). This factor is affected by the aspect ratio of clay dispersed in the matrix. With increasing the lateral length of clay sheet as well as increasing of exfoliation or dispersion degree cause to the more barrier enhancement in the polymer matrix. Many studies have described the barrier properties of polymer/clay nanocomposites against the diffusion of gases and vapors (Tortora,2008).

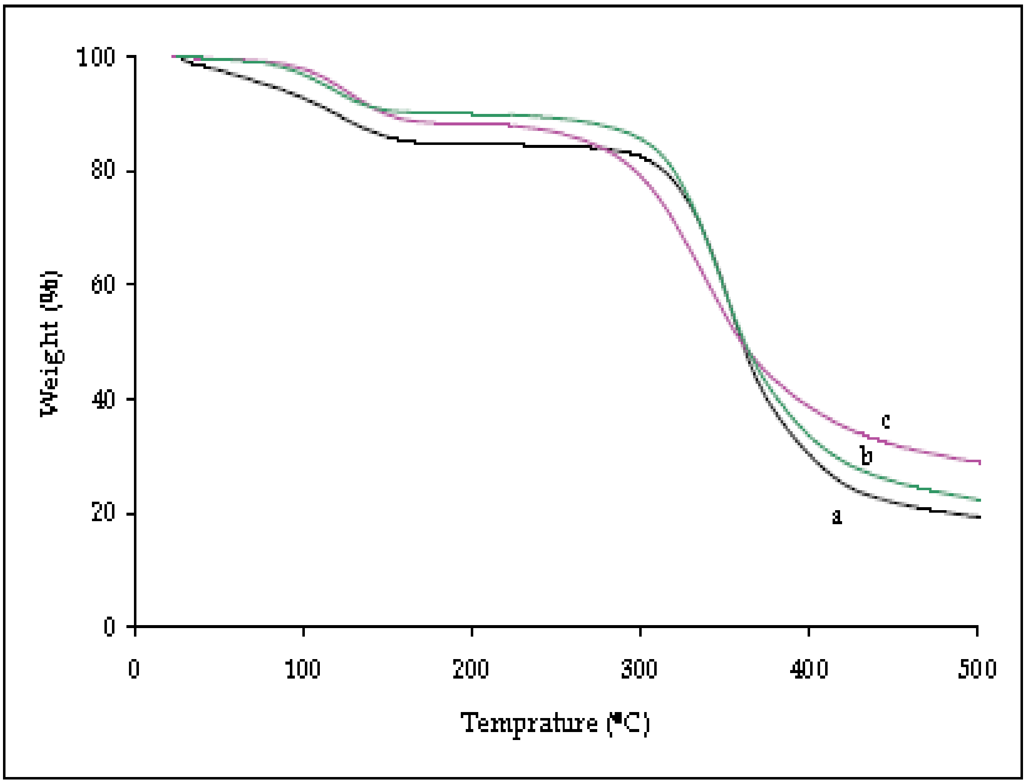

Figure 2.9: TGA thermograms of neat epoxy (a) and epoxy/cloisite 30B nanocomposites with 3 wt % (b) and 5 wt % (c) cloisite 30B contents.

Source: Pavlidou & Papaspyrides (2008)

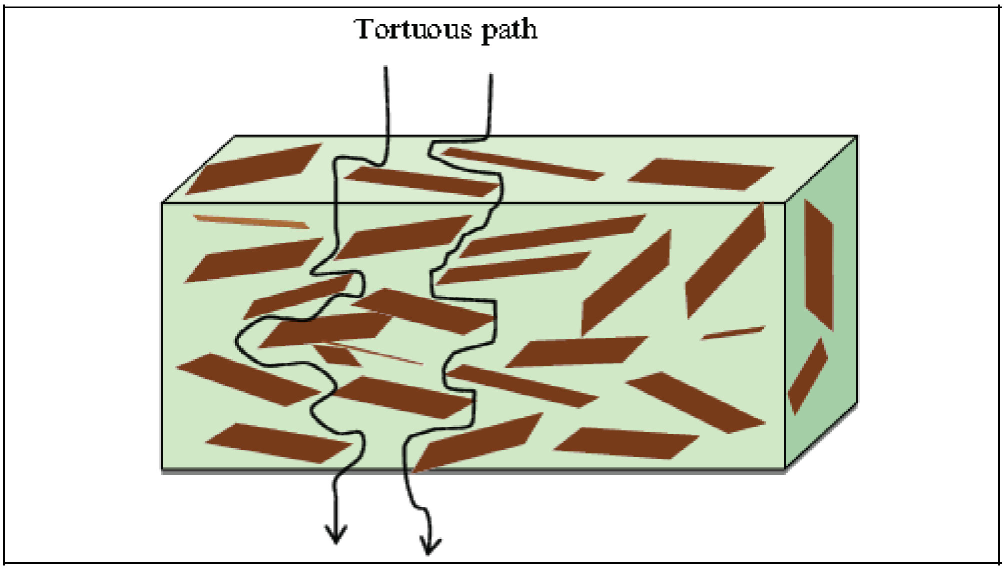

Figure 2.10: Scheme of the mechanism of barrier improvement by the addition of clay platelets.

Source: Tortora (2008).

2.7.4 Anticorrosive Properties

Polymers are widely used as anticorrosive coatings on metals to prevent the corrosion. Primarily polymeric coatings act as physical barrier against the diffusion of aggressive species to the metal surface. By then, most polymer coatings show some degree of permeations especially in long time period of contact with aggressive species. Various techniques have been applied to improve the barrier effect of polymeric coatings. One of the effective methods is based on the preparation of polymer based composite or nanocomposite coatings by the addition of proper fillers to the polymer coating matrix. It has been shown that the addition of platelet fillers like as layered silicates, effectively improves the anticorrosive barrier effect of polymer coatings by increasing the length of the diffusion pathways for aggressive species. Clay materials based on their platelet structure and high aspect ratio and in well dispersed state, decrease the permeability of polymer coating films by increasing the diffusion pathways such as shown in Figure 2-10 . The nanocomposite of various polymeric materials such as polystyrene, poly (styrene-coacrylonitrile), polyaniline, polypyrrole, polysulfone, polyacryltes, polyimide and epoxy with unmodified and organically modified clays have been investigated as anticorrosive coatings on metals (Yeh et al., 2008; Olad & Rashidzadeh, 2008).

2.8 Summary

PU nanocomposite is a Polymer nanocomposites (PNC) are a new class of materials which has promising potential future applications such as a 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. Other than that, solution intercalation method is implemented as it is widely used in industry and environmental friendly. The characterization of samples in this research is by using XRD and SEM for morphological analysis while DSC and TGA is use to characterize thermal analysis of the sample. Other than that, the tensile strength and Young’s modulus properties is observed from mechanical testing.

CHAPTER 3

MATERIALS AND METHODS

3.1 Overview

This paper presents the materials used and methodology in this experiment. The first part of the experiment focuses on the modification of pristine clay with Transition Metal Ions (TMIs), Copper and Ferum using methanol solvent. After these modifications, the samples of organoclay are characterized using some sophisticated methods like Fourier Transform Infrared (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). FTIR and FESEM results illustrated modified nanoclays had smoother surfaces of pristine clay or montmorillonite (MMT) which proved that modification has taken place successfully. The samples then tested by Thermal Gravimetry Analysis (TGA) and Tensile Test to measure their thermal and mechanical properties respectively.

3.2 Introduction

This research is about exploring the development of high thermal building nano-insulation material (NIMs) using PU nanocomposites. This research aims to prepare polyurethane nanocomposites using modified organoclay for roofing applications as a thermal insulator. Fabrication of polyurethane- organoclay nanocomposites is done by modification of organoclay (Na+) by using Catalytically Activated Metal Ions (TMI). After these modifications, the samples of organoclay are characterized using ICPMS and AAS to check whether the modification has taken place successfully. The successfully modified clay is then intercalated into polymer matrices and then tested again to determine its final properties.

3.3 Materials

3.3.1 Sodium Montmorillonite (MMT)

Sodium montmorillonite is a type of layered silicates that was used to improve the polymer properties such as mechanical and thermal properties. The combination of specific polymer with sodium montmorillonite will form a polymer nanocomposites that have more properties improvement compare to neat polymer. The Sodium Montmorillonite were obtained from Southern Clay, Texas, US and used as supplied. The properties of pure Sodium Montmorillonite is shown in the Table 3.1.

Table 3.1: Properties of Sodium Montmorillonite.

Physical Properties	
CAS Number	1302-78-9
Physical State	Solid
Molecular Weight (g/mol)	540.46
Bulk Density (lb/gal)	50-70 lb/cu.ft at 20^{o}C
pH	6-8 in 10% slurry
Color	Various
Odor	Odorless

3.3.2 Copper (II) Chloride

Based on this experiment, Copper (II) Chloride has been choose as the transition metal ion salts (TMI) in order to modify the pristine clay in ion exchange method. In this experiment, the pristine clay was modified by using Copper (II) Chloride as Cu atom acts as catalytically active TMI ion in modified clay. In details, the overall amount of absorbed Cu ions combined with residual surfactant seemed to exceed the overall ion exchange capacity. This Copper (II) Chloride was purchased from SIGMA-ALDRICH. The physical properties of Copper (II) Chloride are shown in Table 3.2.

Table 3.2: Properties of Copper (II) Chloride

Physical Properties	
CAS Number	7447-39-4
Molecular Formula	$CuCl_2$
Physical State	Powder
Molecular Weight (g/mol)	134.45
Relative Density (g/cm^3)	3,386 at at 20^{o}C
pH	3(50 g/L aq.sol at 20^{o}C)
Boiling Point	993^{o}C at 760mmHg (1819.40^{o}F)
Freezing/Melting Point	498^{o}C (928.40 ^{o}F)

3.3.3 Ferum (III) Chloride

Ferum (III) Chloride is also one of the transition metal ion used in modification of pristine clay. In this experiment, the pristine clay was modified using Ferum (III) Chloride and Ferum (Fe) atom acts as catalytically active TMI ion. The reason of this TMIs selection is Fe atom content in modified clay exceeds the CEC values. In details, the overall amount of absorbed Fe ions combined with residual surfactant seemed to exceed the overall ion exchange capacity. This Ferum (III) Chloride was purchased from SIGMA-ALDRICH. The physical properties of this Ferum (III) Chloride are shown in Table 3.3.

Table 3.3: Properties of Ferum (III) Chloride

Physical Properties	
CAS Number	7705-08-0
Molecular Formula	$FeCl_3$
Physical State	Powder
Molecular Weight (g/mol)	162.2
Relative Density (g/cm^3)	2.898
Boiling Point	306^{o}C at 760mmHg (1819.40^{o}F)
Freezing/Melting Point	315^{o}C

3.3.4 Methanol

The amount TMI salts absorbs into the interlayer gallery of pristine clay depend on the type of solvent. Methanol acts as solvent in this experiment as it can give a better overall contents of TMI in organically (Pranav et al., 2007). Methanol are acquired from Fisher Scientific. The physical properties of methanol are shown in Table 3.4.

Table 3.4: Properties of methanol

Physical Properties	
CAS Number	67-56-1
Molecular Formula	CH_4O
Color	Colorless
Odor	Weak odor
Physical State	Liquid
Vapor Pressure (mmHg)	128 at 20^oC
Viscosity (Cp)	0.55 at 20^oC
Solubility	Misicble
Molecular Weight (g/Mol)	32.04
Vapor Density (g/cm^3)	1.11 (air = 1)
Boiling Point	64.9^oC at 760mmHg
Melting Point	-98^oC

3.3.5 Thermoplastic Polyurethane (TPU)

Thermoplastic polyurethane (TPU) is a type of polymer and a reason of choosing TPU as a studied polymer is due to its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized and processed in most polymer processing equipment. Furthermore, TPU is not hazardous polymer. TPU was kindly provided by Bayer Materials Science Ltd., Chennai, India. It was developed from Poly tetramethylene glycol (PTMEG) with 4,4'-Methylenebis (phenyl isocyanate) (MDI) and 1,4- butanediol (BD). The properties of TPU are shown in the Table 3.5.

Table 3.5: Properties of Thermoplastic Polyurethane

Physical Properties	
CAS Number	26100-51-6
Molecular Formula	$C_{25}H_{42}N_2O_6$
Physical State	Solid
Molecular Weight (gms/gm mol)	60000
Color	White color
Specific Gravity (g/cm^3)	1.11

3.3.6 Chloroform

Chloroform is used as a solvent in a solution mixing method after finishing theclay modification. The properties of chloroform are shown in Table 3.6.

Table 3.6: Properties of Chloroform

Physical Properties	
CAS Number	67-66-3
Molecular Formula	$CHCl_3$
Color	Colorless
Physical State	Liquid
Vapor Pressure (kPa)	21.0861 at 20^{o}C
Solubility in water	0.8 g/100 mL at 20^{o}C
Molecular Weight (g/Mol)	119.38
Boiling Point	61.2^{o}C at 760mmHg
Melting Point	-63.5^{o}C

3.4 Modification of Sodium Montmorillonite

One of the main objectives of the research is to prepare polyurethane nanocomposite using modified nanoclay for roofing application as a thermal insulator. Following that, it is only appropriate if the experiment begins with the modification of the nanoclay. The purpose of surface modification of pristine clay is due to the incompatibility between hydrophilic clay and hydrophobic polymer. The different characteristic often causes agglomeration of clay mineral, its characteristic will change to hydrophobic and hence compatibility with the specific polymer.

3.4.1 Pre- Treatment Phase of Nanoclay for Ion Exchange Method

For 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 typical washing procedures were as follows.

10g of clay sample (Na^+ montmorillonite) were placed in 200 ml of solvent (methanol). Then, the suspension was vigorously stirred for 24 hours and upon stirring for a few hours, the suspension turned into viscous slurry due to swelling of the clay. The resulting slurry is kept in a 1 M. 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: Methanol and Nanoclay Slurry

3.4.2 Preparation of Metal Ion Solution and Surface Modification Phase

Once the clay has been dried, it is ready to be treated with 0.3 M of the desired metal ion salts. In this experiment, we will focus on two types of metal ions which are Copper^{2+} and Ferum^{3+}. Based on the molecular weight of each of the metal ion salts, the desired weight of material required to produce a 200ml, 0.3 M solution is determined and recorded in Table 3.7.

Table 3.7: Calculated mass of transition metal salt required.

Salt	Molecular weight (g/mol)	Weight required (g)
Copper (II) Chloride, $CuCl_2$	134.45	8.067
Ferum (III) Chloride, $FeCl_3$	162.20	9.732

The required amount of metal salt needed is first weighed and then dissolved in methanol (solvent). The solution is stirred for 1-2 hours prior to the addition of Na+ montmorillonite. For this experiment approximately 10g of pre-treated Na+ montmorillonite was used for every 250 ml of metal ion solution. Once the clay is added, the solution is stirred for 5-6 hours and 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 again in an oven for 12 hours at 80˚C (Nawani, 2007). The above procedure is repeated for the following combination of solvent-clay-metal ion as listed in Table 3.8.

Table 3.8: Prepared clay-solvent-metal ion combinations

Nanoclay	Solvent	Metal ions
Na- montmorillonite	Methanol	Copper
Na- montmorillonite	Methanol	Ferum

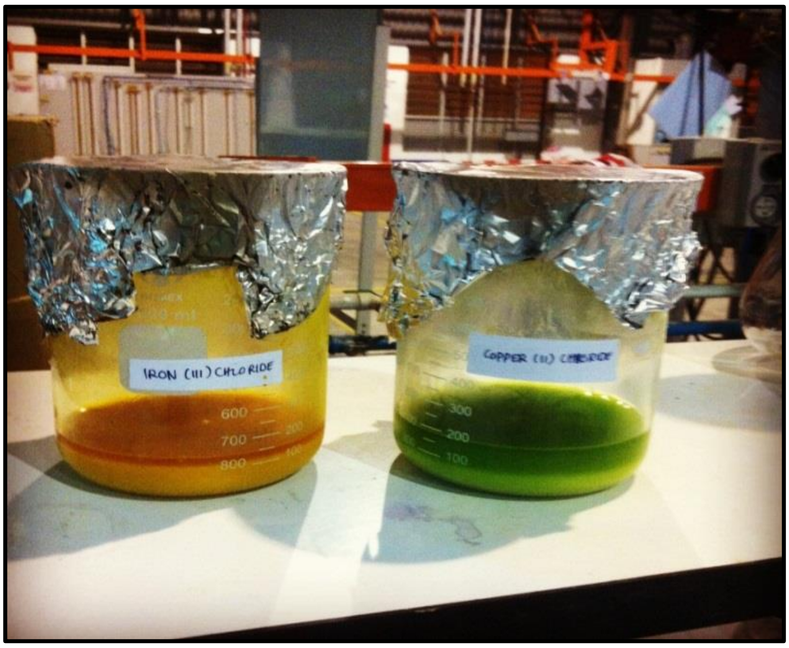

Figure 3.2: Transition Metal Ion Salt Solutions

3.5 Characterization

Characterization process is done to know the morphology of the sample and to prove that the modification of pristine clay has taken place successfully. There are two types of method used for characterization and shown below.

3.5.1 Inductively Coupled Plasma Mass Spectrometry (ICPMS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a one of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{12} (part per trillion). This process is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions. It allow multielemental detection, good precision and low limits of detection, ideal for the industrial routine analysis that, basically, require fast and highly sensitive techniques. Measurements of the elemental concentrations in the leachate samples were determined using inductively coupled plasma mass spectrometry (ICP-MS) (ThermoQuest/Finnigan Element 2), and the clay mixture samples were analyzed by ICP-MS and inductively coupled plasma – optical emission spectrometry (ICP-OES) (Perkin et al., 2000). The flow chart of ICPMS methods are shown below.

For Intermediate Stock (IS), pipette 5ml of stock solution into 50 ml solution volumetric flask giving 100 ppm. Pipette (0, 0.25, 0.5, 1.0, 2.5) from intermediate stock (100ppm) into respective volumetric flask. In addition, pipette 2.5ml from stock solution into 50 ml volumetric flask. Mark up with 2% HNO_3 GIVING (0, 0.5, 1.0, 2.0, 5.0 and 50.0 ppm) respectively. For digestion process, 0.5 g dried sample is weighed into digestion vessel. Introduce the vessel into the HTC safety shield and add 6ml of HNO3 and 2ml of H2O2 into vessel. Close the vessel, then tighten by using a machine and set microwave program and run. After digestion complete, transfer solution to 50ml volumetric flask and dilute to mark with 2% HNO_3. Analyse using Inductively Coupled Plasma Mass Spectrometer.

Figure 3.3: Sample of Clay Powder

3.5.2 Adsorption Intensity Testing Using Soil Leaching Procedure and Atomic Adsorption Spectometry (AAS)

The intensity of adsorption of the transition metal ions onto the surface of nanoclay due of utilization of different solvents are tested at this stage. Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state.

3.5.2.1 Soil Leaching Stage

In this step, first the soil leaching medium is prepared. The medium used is 0.05 M Ethylenediaminetetraacetic acid, EDTA which is prepared by first weighing 14.612 g of EDTA powder, with the molecular weight is 292.24 g/mol. Dissolve the EDTA powder weighted in the 500ml ultrapure water. Then, insert sodium hydroxide (NaOH) solid pellet until pH = 8 under stirring to make sure the solution is in an alkaline state. After that, add another ultrapure water until the solution reaches 1000ml. The recovery rate of heavy metals using this medium is approximately 0.98% (Hwang & Namkoong, 2007).

With the ratio of 1g : 10 ml, 5g of clay is placed in the schott bottle with the 50ml EDTA solution prepared. The bottles are then placed in an ultrasonic waterbath for 12 minutes at 60KW to leach the adsorbed metal ion back out of the surface of the nanoclay. 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 onto the surface of the nanoclay. Then, the solution is filtered once using vacuum pump with 1μm filter paper.

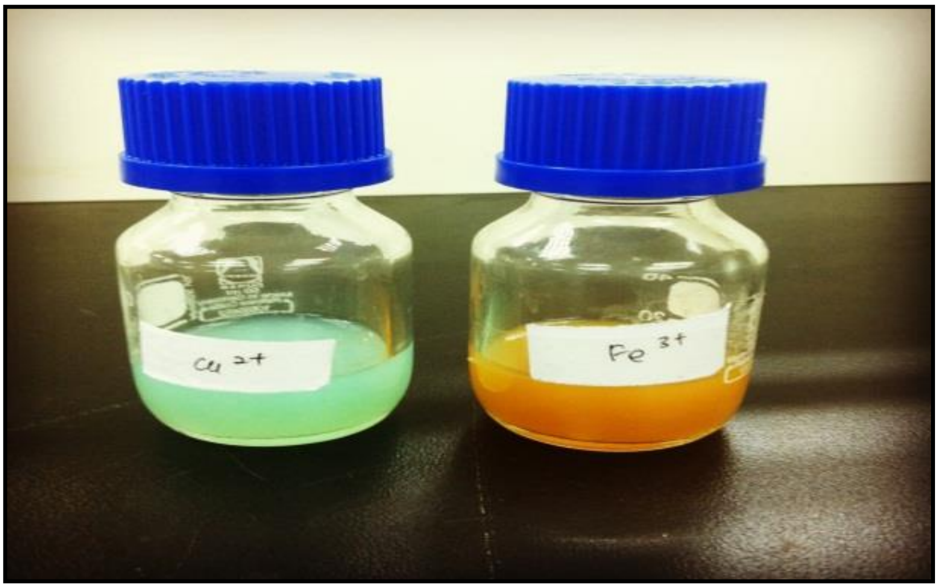

Figure 3.4: Solution after Soil Leaching Stage

3.5.2.2 Atomic Adsorption Spectometry (AAS)

Before running the sample in AAS, the sample clay leachate is filtered again using a vacuum pump with microfiber filter. Prepare the 10mg/L of stock solution with the volume of 1ml and add in ultrapure water until it reaches 100ml. Then, the standards for each metal ions to be tested is prepared at a concentration of 1mg/L using the following formula :

$M_1V_1 = M_2V_2$

M_1 = Concentration of stock solution (10mg/L)

M_2 = Concentration of first standard (1mg/L)

V_2 = Volume of standard needed (50ml)

Therefore, V_1, volume of stock solution needed = $\frac{\mathrm{M2V2}}{\mathrm{M1}}$

$$= \frac{\frac{1\mathrm{mg}}{\mathrm{L}} \mathrm{X}\ 50\mathrm{ml}}{10\mathrm{mg/L}}$$

= 5ml

Then, dilute with the ultrapure water until it reaches 50ml. This will provide for a 1mg/L standard solution. The subsequent standard prepared are 2mg/L, 4mg/L and blank.

The summary of standard and volume of stock volume needed is shown in Table 3.9

Table 3.9: Summary of Standard Solution

Transition Metal Ion	Standard concentration (mg/L)	Volume of stock solution needed (ml)
Fe	1	5
Fe	2	10
Fe	4	20
Cu	1	5
Cu	2	10
Cu	4	20
Blank	0	0

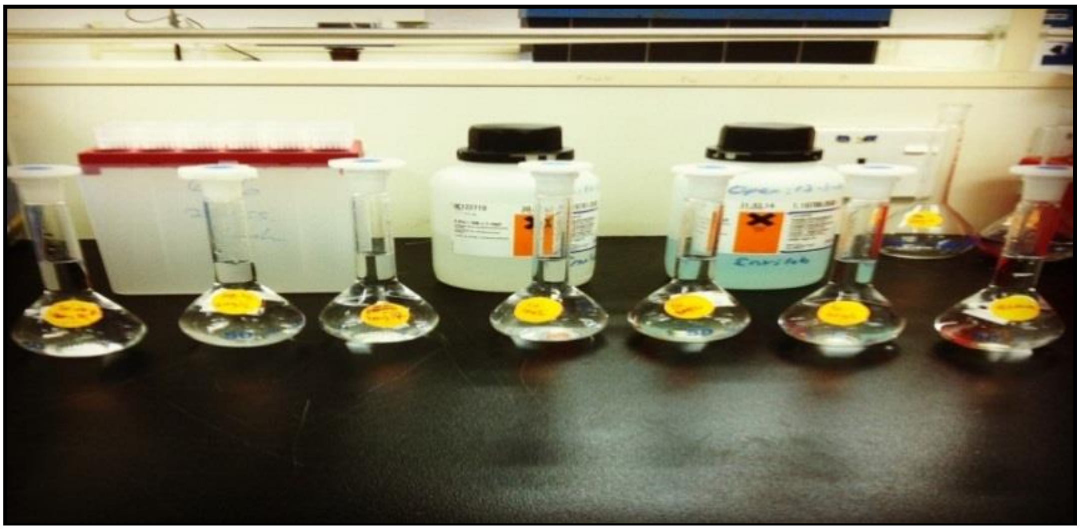

Figure 3.5: Standard Solution Prepared

After that, all the standard solution and sample prepared runs in Atomic Adsorption Spectometry (AAS). The method is shown in Figure 3.6.

Figure 3.6: Sample run in AAS

3.6 Fabrication of Polyurethane- Organoclay Nanocomposites using Solution Mixing Method

After finishing with the modification Na+ MMT, the experiment is continued with the process of intercalation of organoclay with polymer of thermoplastic polyurethane. The process flow of solution mixing method is shown below.

Table 3.10: Combination of sample

Num. of Sample	Type of Sample
1	Chloroform + Polyurethane (pure)
2	Chloroform + Polyurethane + Organoclay (1% fe)
3	Chloroform + Polyurethane + Organoclay (3% fe)
4	Chloroform + Polyurethane + Organoclay (5% fe)
5	Chloroform + Polyurethane + Organoclay (1% cu)
6	Chloroform + Polyurethane + Organoclay (3% cu)
7	Chloroform + Polyurethane + Organoclay (5% cu)

0.08 g of organoclay were placed in the beaker with 100ml chloroform while stirring under 80^{o}C for 90 minutes in a beaker A. On the other hand, 8g of polyurethane were dissolved in 200 ml chloroform under 80^{o}C while stirring for 4-5 hours (beaker B). After 90 minutes, poured a solution from beaker A into a beaker B and continue stirring until it reached 5 hours. After that, pour the suspension into clean Petrie dishes glass and left covered in a fume hood until the chloroform evaporated. Left the sample with covered for two days to make sure that the sample turned into a thin film.

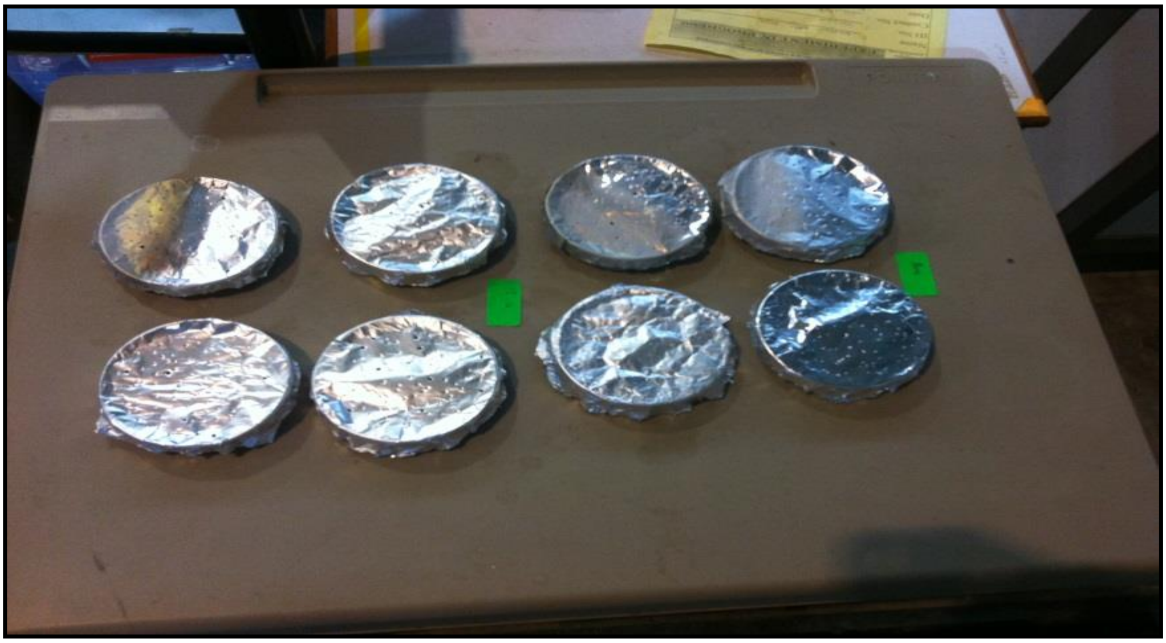

Figure 3.7: Drying the sample

3.7 Characterization

Characterization process has been done again to ensure that fabrication of polyurethane-organoclay nanocomposites using solution mixing method is achieved. Method used in characterization process is shown below.

3.7.1 Fourier Transform Infrared Spectroscopy (FTIR)

For FTIR, the test is run using SMART collector (Diffuse Reflection) head. The sample that been used is in thin film form. The backgrounds of the sample were all in kBr standard. The readings of the sample are taken after the background was complete. Thin film sample is making sure to be in line with the red beam to ensure accurate readings. The graph that generated shows the different level of absorbance between various peaks.

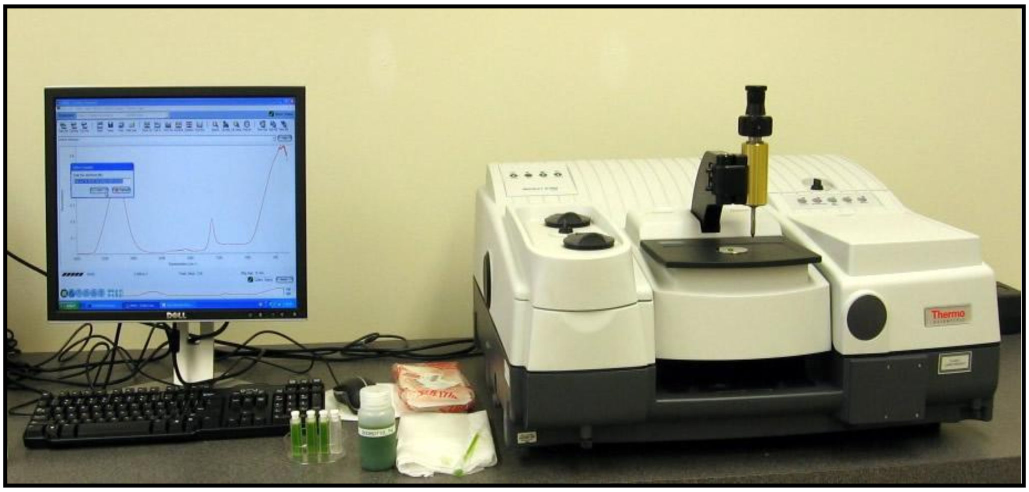

Figure 3.8: Nicolet 6700 FTIR-Spectrometer

3.7.2 Field Emission Scanning Electron Microscopy (FESEM)

The morphology structure of polyurethane nanocomposites with a domain size of less than 0.8 nm to 1.2 nm can be viewed by using a field emission scanning electron miscroscopy (FESEM). The FESEM is crucial for use in all fields that require characterization of solid materials such as polyurethane nanocomposites. FESEM in many cases mostly acquired a minute amount of sample and the data attainment is swift due to the higher analytical accuracy and stable electron probe.

During this research, it is very essential to use the FESEM for the purpose of visually studying the morphology structure of the obtained organoclay. The signal derived from the electron sample interactions would reveals information on the surface texture of polymer clay nanocomposites at the certain magnification range and hence, a clearer understanding of the surface structure can be establish.

The dispersion and distribution quality of polymer clay nanocomposites thin film were characterized by using JEOL FESEM JSM-7100F. The ‘Smart FESEM User Interface’ program was run on the computer and the coated samples were mounted on a universal sampler holder with the stub forceps. The contrast or brightness was adjusted to have a clearer view of the sample and would be later magnified. To make the image sharp and resolve as possible, the focus knob is turned. The best focus was determined by adjusting the stigmator knobs. The preferred image of polymer clay nanocomposites would be then saved. The usage procedure of FESEM is summarized below.

Run the 'Smart FESEM User Interface program. The sample was mounted on the universal holder with a stub forceps. Then, lid the filament and the working distance was adjusted. The contrast/brightness was optimally manipulated. The focus knob was turned to sharp the scanned image. The stigmator knobs woulb be slowly turned to obtain the best focus. Lastly, the FESEM image would be saved.

3.8 Testing

3.8.1 Thermo - Gravimetric Analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the physical and chemical properties of materials changes are measured in terms of temperature accession (consistent heating rate) or in terms of time (uniform temperature and/or uniform mass loss). It could provide information on physical and chemical phenomena.

The chemical phenomenon of thermal degradation of polymer nanocomposites is the focus in this research work. Therefore, TGA is necessary for the evaluation of thermal stability of the PU nanocomposites. Generally, TGA depends on high degree of precision in three parameters unit in which mass change, temperature and temperature change are measured. The basic requirement of a TGA device practically includes a pan loaded with a sample combined with precision balance and a programmable furnace. The sample environment is controlled by the gas that flows over the sample and is exhumed through the exhaust. The thermal stability of the material is determined from the TGA thermal curve obtained. The descending pattern of the TGA thermal curve indicates weight loss is occurring. However, if there is no mass change observed in the TGA thermogram for a certain range of temperature or duration of time, then the material is vindicated thermally stable in the respected temperature range.

For the thermal behavior determination of PU samples, a TGA characterization was performed on pelletized form of the samples with a TGA device (TGA/DSC-1 Mettler Toledo). The sample of 5 mg approximately had been purposely heated from 30-600 ºC at 10 ºC/min under the influence of nitrogen atmosphere. The evaluation of TGA curve was completed by using “STARe Excellence Software” of Mettler Toledo.

A minute amount of one sample (≈ 5mg) would be placed in a alumina pan. Next, continuosly heated under influence a nitrogen atmosphere from 30 to 600^{o}C at 5oC/min. Finally, obtained thermo gravimetric curves of samples and evaluate the TGA curves by using the "STARe Excellent Software".

3.8.2 Tensile Test

The most common type of test used to measure the mechanical properties of a material is the Tension Test. Tension test is widely used to provide a basic design information on the strength of materials and is an acceptance test for the specification of materials. The major parameters that describe the stress-strain curve obtained during the tension test are the tensile strength (UTS), yield strength or yield point (σy), elastic modulus (E), percent elongation (ΔL%) and the reduction in area (RA%). Toughness, Resilience, Poisson’s ratio (ν) can also be found by the use of this testing technique.

In this test, a specimen which is prepared suitable for gripping into the jaws of the testing machine type that will be used. The specimen used is approximately uniform over a gage length (the length within which elongation measurements are done). The process flow of tensile test are described below.

Put gage marks on the specimen and measure the initial gage length, width and thickness. Select a load scale to deform and fracture the specimen. Note that tensile strength of the material type used has to be known approximately. Then, record the maximum load. Conduct the test until fracture and measure the final gage length and diameter. The diameter should be measured from the neck.

3.9 Summary of Work Flow in Experimental Work

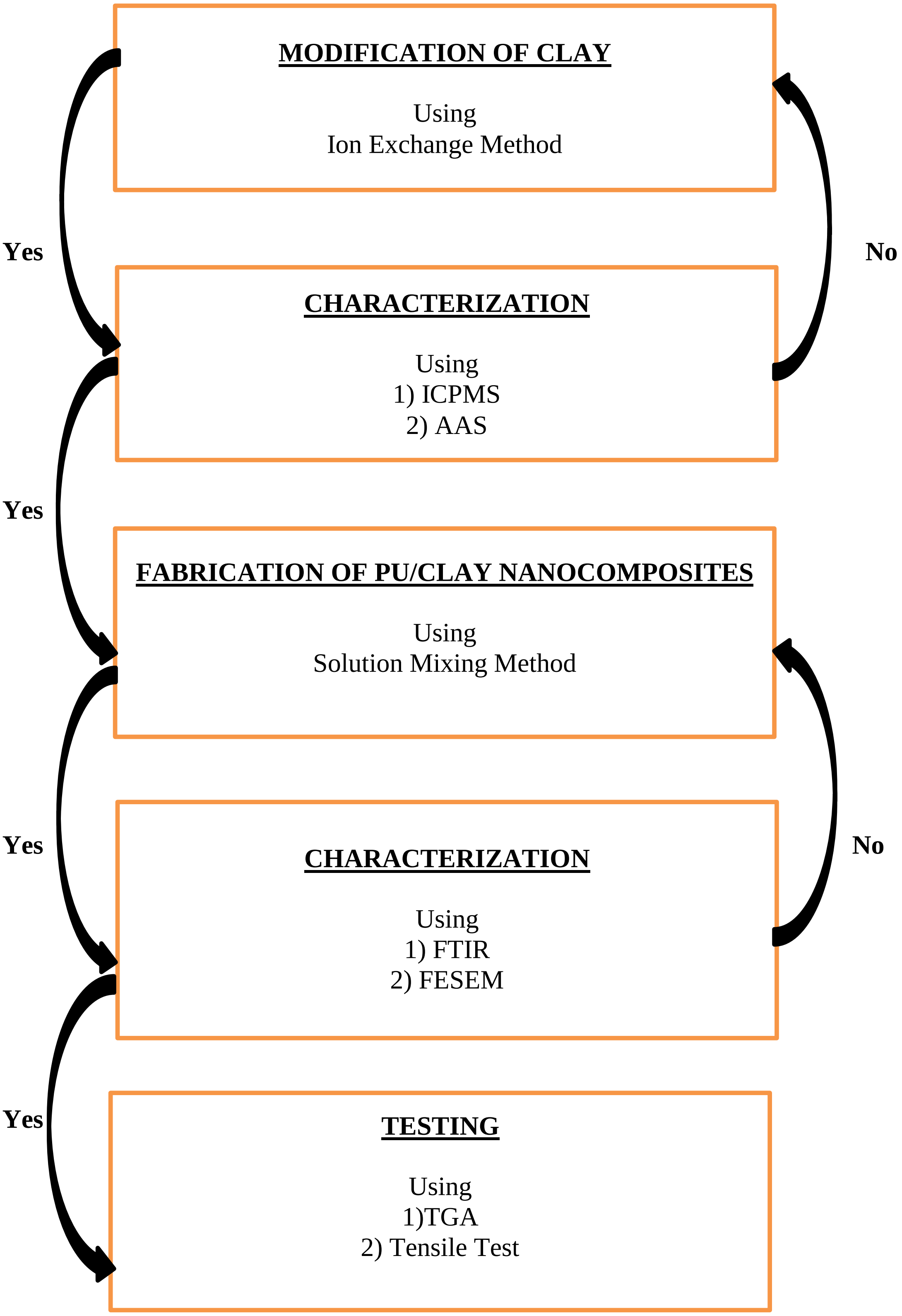

Figure 3.9 : Summary of Experimental Work

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter presents all the finding and data acquired throughout the course of this research. The effect of modification process before and after the preparation of polymer will be analyzed and discuss. The characterization by AAS, ICPMS, FTIR and FESEM after the modification and the polymer preparation take place will be discussed. Apart from that, the data of each sample are plot on the graph for better comparison and discussion. The effect of the fillers on thermal stability (TGA) and mechanical properties (Tensile Test) will be compared among different percentage of filler with and without existing of organoclay. The results are also discussed in detail, so that it may be used to support and prove the objectives and scope of this research.

4.2 Introduction

The first part of the experiment focuses on the modification of pristine clay with Transition Metal Ions (TMIs), Copper and Ferum using methanol solvent. The objectives of surface modification of pristine clay is due to the incompatibility between hydrophilic clay and hydrophobic polymer. After these modifications, the samples of organoclay are characterized using FTIR and FESEM. FTIR and FESEM results illustrated modified nanoclays had smoother surfaces of pristine clay or montmorillonite (MMT) which proved that modification has taken place successfully. The samples then tested by TGA and Tensile Test to measure their thermal and mechanical properties respectively. Both the thermal stability and mechanical strength showed positive improvements. Thermal stability is hypothesized to have increased significantly, due to the transition metal ions hindering the pristine clay within the polymer matrices from decomposing easily. The stronger interfacial interaction causes to the improvements of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposite.

4.3 Analysis of Atomic Adsorption Spectrometer (AAS)

Atomic Absorption Spectrometry (AAS) is a technique for measuring quantities of chemical element that present in environmental samples by measuring the absorbed radiation by the chemical element of interest. This is achieved by reading the spectra produced when the sample is excited by radiation. The atoms absorb visible light or ultraviolet and make transitions to higher energy levels. Atomic absorption methods identify the amount of energy in the form of photons of light that are absorbed by the sample. A detector in the element measures the wavelengths of light transmitted by the sample, and then compares them to the wavelengths which originally passed through the sample. A signal processor integrates the changes in the wavelength absorbed, which shows in the readout as peaks of energy absorption at discrete wavelengths. The energy needs for an electron to leave an atom is known as ionization energy and is prior to each chemical element. After all, when an electron moves from one energy level to another level within the atom, a photon is emitted to the energy E. Atoms of an element is then emit a characteristic spectral line. Every atom has its own different pattern of wavelengths at which it will absorb energy, due to their unique configuration of electrons in its outer shell. This process enables the qualitative analysis of a sample.

Table 4.1: Calibration data for Cu

ID	Mean Signal (Abs)	Entered Conc. mg/L	Calculated Conc. mg/L	Standard Deviation	%RSD
Blank	0.000	0	0.000	0.00	1.20
Calib std 1	0.154	1.0	1.087	0.00	1.10
Calib std 2	0.296	2.0	2.083	0.00	0.53
Calib std 3	0.558	4.0	3.932	0.00	0.35

Correlation coef. :0.997962

Slope : 0.41202

Table 4.2: Calibration data for Fe

ID	Mean Signal (Abs)	Entered Conc. mg/L	Calculated Conc. mg/L	Standard Deviation	%RSD
Blank	0.000	0	0.000	0.00	64.50
Calib std 1	0.094	1.0	1.035	0.00	4.47
Calib std 2	0.193	2.0	2.137	0.00	0.59
Calib std 3	0.354	4.0	3.916	0.00	0.16

Correlation coef. :0.997116

Slope : 0.09044

The concentration of the sample is calculated based on the Beer-Lambert law. The absorbance measured is directly proportional to the concentration of the analyte absorbed for the existing set of conditions.

The concentration is usually determined from a calibration curve, obtained using standards of known concentration.

Table 4.3: Calibration Curve of Copper in Clay Leachate

Mean Signal (Abs)	Concentration (mg/L)
0.000	0.0
0.154	1.0
0.296	2.0
0.558	4.0

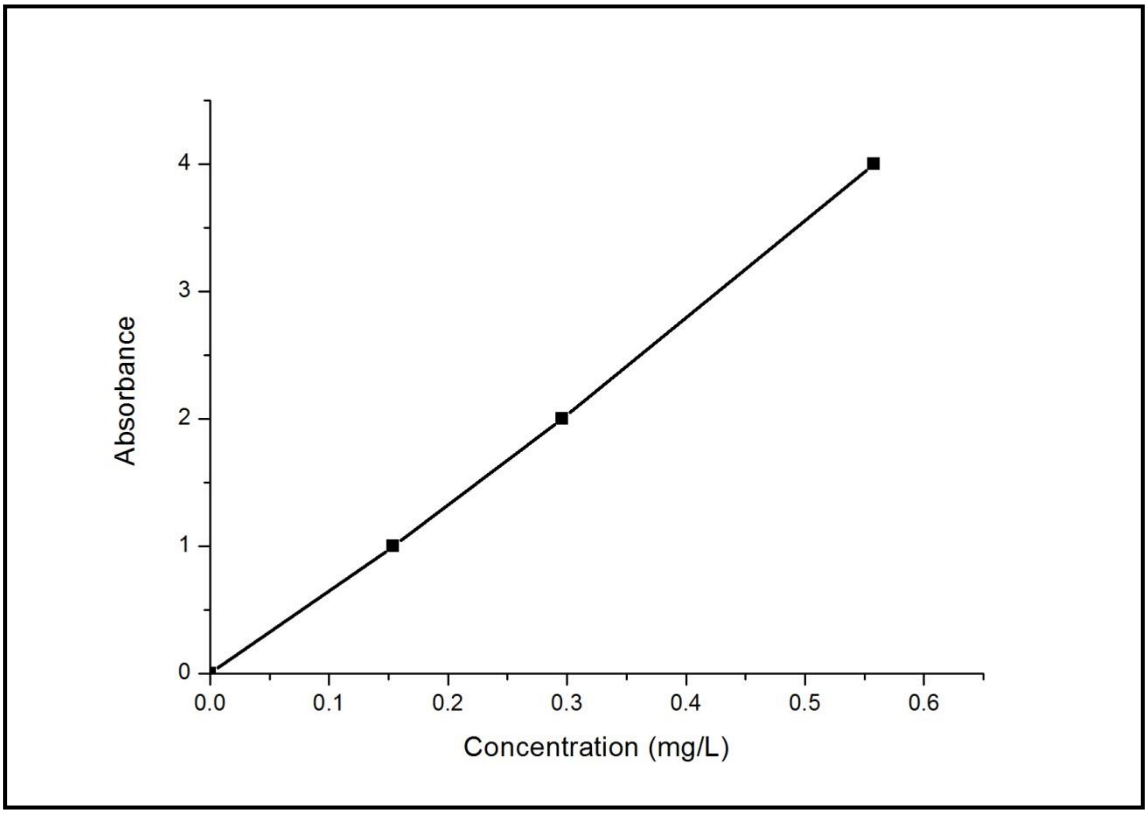

Figure 4.1: Calibration Curve of Cu in Clay Leachate

Table 4.4: Calibration Curve of Ferum in Clay Leachate

Mean Signal (Abs)	Concentration (mg/L)
0.000	0.0
0.094	1.0
0.193	2.0
0.354	4.0

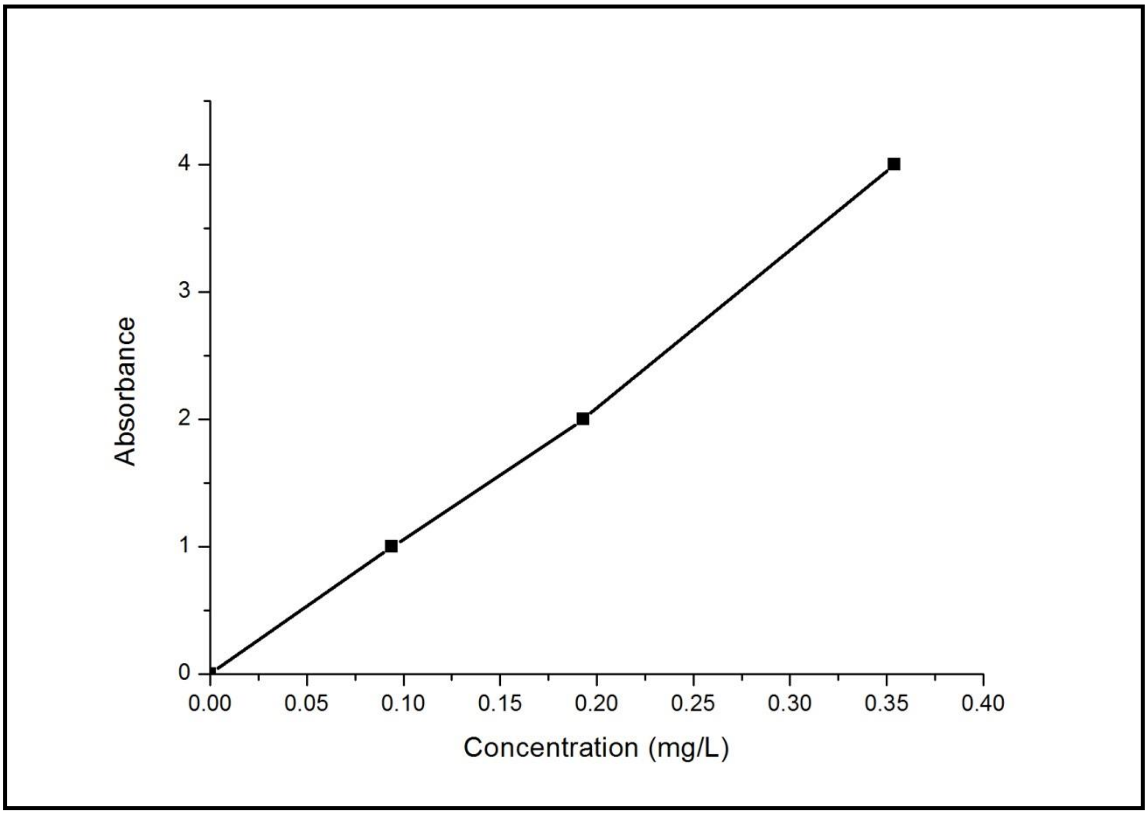

Figure 4.2: Calibration Curve of Ferum in Clay Leachate

For the first group, absorbance of Cu in clay leachate solution is plotted against the concentration of Cu in clay leachate. The plot is shown in Figure 4-1 and in the appendix for Set 1. The plots shown above suggest that Cu enhances absorbance. As concentration of Cu increases, the absorbance also increases. Similarly, a more concentrated solution yields greater absorbance. Same goes to the absorbance of Fe in clay leachate solution. The second plot (Figure 4.2) shows the increasing trend in the absorbance as the concentration increases.

In the Atomic Adsorption Spectrometer test, the concentration and amount of transition metal ions that have been attached itself to the surface of the nanoclay are tested. Each sample was prepared using different transition metal ion (Fe^{3+} and Cu^{2+}).

The concentration values acquired through AAS are summarized in Table 4.5.

Table 4.5: AAS Result for Mean Concentration Soil Leachate

Transition Metal Ion	**Soil Leachate Mean Concentration (mg/L)**
Cu^{2+}	15.29
Fe^{3+}	11.30

For all following tests, the sample leachates were diluted with 1:10 V/V ratio. Thus, actual concentration sample is calculated using the following formulae :

$$\text{Actual concentration} = \frac{\text{AAS Reading x Dilution Factor}}{\text{Recovery Rate}}$$

Given : Dilution Factor = 10

Recovery Rate = 0.98

Table 4.6: Actual Concentration Metal Ion

Transition Metal Ion	**Actual Concentration of Transition Metal Ion (mg/L)**
Cu^{2+}	156.02
Fe^{3+}	115.31

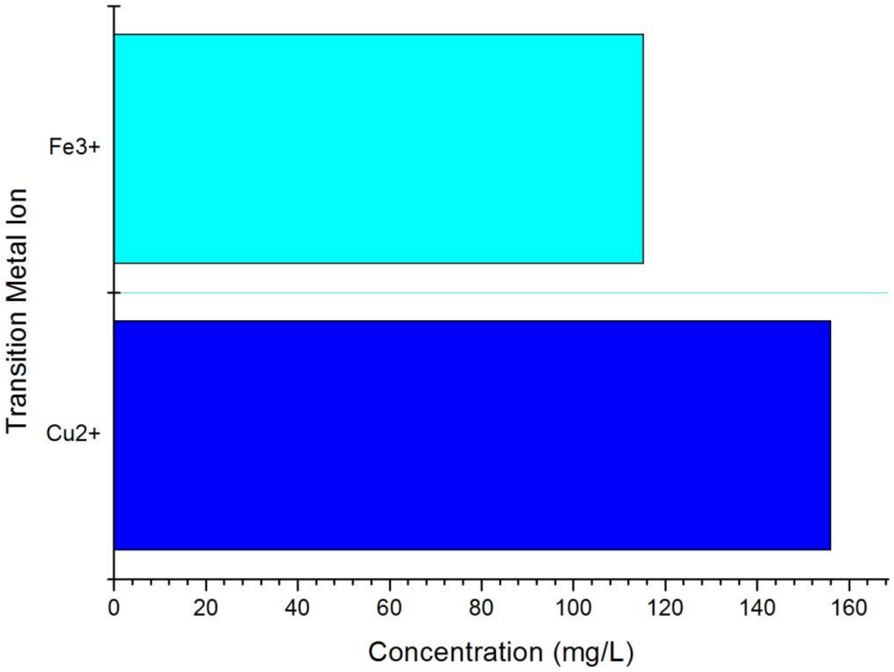

Figure 4.3: Actual Concentration of Metal Ion in Clay Leachate

From the graph, concentration of Copper is higher compare to the concentration of Ferum. The linearity of the calibration for Copper and Ferum measurements was defined with the AAS methods. With both metals, the correlation coefficient was the best possible in all three measured standard series, which indicates a good linearity. The correlation coefficient obtained directly from AAS equipment was slightly deviant, but being 0.997, it was still very good. Following the very good and constant results from correlation and residuals, the linearity can be said to be valid in both methods.

In the Copper and Ferum measurements with the initial method, some validation factors seemed to be on quite good and valid levels. Such were the correlation of the standard curve, which was nearly 1, and the limits of detection and quantitation which were on relatively good levels.

Recovery rate for this sample is 0.98. A literature survey showed that the recovery of nearly 100% is possible to reach with both studied metals in clay samples as presented in the results of Willis' (1961) studies. The system's repeatability in the Copper measurements stated in quite similar values after the modifications were executed, which proves that the equipment was working evenly all the time. The (%) RSD value lowered from 1.20 to a level around 0.35, which is already a notable improvement. On the other hand, for the Ferum, it showed a dramatically decreased in (%) RSD value which started from 64.50 to 0.16. The differential partitioning of cations between the clay and oxide particles cannot be attributed to differences in the sorption capacities of each mineral, but must have resulted from different metal ion-mineral bonding energies.

Murray et al., 1968 implying that attractive forces other than coulombic interactions are responsible for sorption of these ions. Cation sorption by expanding montmorillonite clay is considered to be primarily due to coulombic attraction of the metal ions by permanent, negative charges on the mineral structure. For this reason, cation sorption by montmorillonite should be strongly influenced by the concentrations of all cations present in solution. The greater sorption of the metals by the montmorillonite particles was most likely due to the above-mentioned differences in the sorption mechanisms of clays and oxides. These differences resulted in differing degrees of competition between Na and the other metal ions for the available sorption sites on each mineral. The presence of 0.05 M Na provided strong competition for heavy metal sorption by the montmorillonite but had little effect on the sorption of these ions. Thus Cu, and Fe were strongly attracted to the montmorillonite particles resulting in the marked fractionation of these metals onto the oxide.

The reasearch proved the need of some modifications to the clay sample, especially with the amounts of $CuCl_2$ and $FeCl_3$ solution added into the samples. The results of this study prove that the transition metal ion traced in clay sample are reliable and can be reported forward. Overall, modification of clay has taken place successfully as concentration of transition metal ion present in clay leachate has been detected.

4.4 Analysis of Inductively Coupled Plasma Mass Spectrometry (ICPMS)

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10^{12} (part per trillion). This is attained by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions. For "dry" plasma, the elemental material that is contributed to the plasma from air entrainment becomes significant. Gray has reported the use of a flared torch bonnet, which fits over the ICP torch in a manner similar to traditional bonnets. This bonnet was flared to match the angle of the sampler and had an outer diameter equal to that of the sampler cone. Ince et al. showed that a significant reduction in ICP-MS signal noise was obtained when using this bonnet. The noise reduction was related to a decrease in the interaction of the plasma with atmospheric gases, i.e., the reduction of air entrainment into the plasma. Use of the flared bonnet reduces air entrainment and results in lower polyatomic backgrounds and enhanced sensitivity for the lighter elements.

Rege et al., used a similar flared bonnet in an ongoing effort to reduce the effect of the air entrainment. They introduced externally Kr gas into the torch box at an approximate rate of 1.2 L/min. Kr was chosen as it is easy to detect, is not a major component of air, and the background levels are low. Kr levels were measured using both a conventional bonnet and a flared bonnet. It was figure out the Kr gas entrainment was reduced with the flared (4.4×106 signal cps for 83Kr using the normal bonnet, 0.64×106 signal cps for 83Kr using the flared bonnet). In the present study, normal bonnet is used because the analyte ions concentrated in the central channel of plasma (Hoffman e al., 2000) (~3mm wide when plasma depth about 5 mm), meanwhile, on the torch axis, the cooler central gas stream shows a relatively low Ar+ population, but at each side of the centre, the higher degree of ionization of Ar in the hotter induction region (14 mm).

In order to study different sampling methods, the laser beam was rastered over the sample surface during laser ablation and moreover, an ablation at a single point was investigated. It is found that single point measurements lead to high relative standard deviations of ion intensities (>50%) because of a loss of ion intensities with time. As the laser beam is defocused during a single point measurement, laser power density changes with time and for that reason a loss of ion intensities was observed. Therefore, ion intensities are a factor of 50 lower during a single point measurement compared to the sampling method where the laser beam was rastered over the sample surface. For these reasons, the analytical signals are greatly affected by the sample mass ablated by the laser beam. The efficiency of the ablation (E) defined as (Gray et al., 1996) the ratio of the ablated mass to the incident energy depends on the coupling condition between the laser beam and the sample surface. Measurements are performed with a focused laser beam rastered over the sample surface because better precision and higher sensitivity were observed in this case.

A comparison of the determined element concentration in clay samples obtained using calibration curves (with 13C as internal standard element) and relative sensitivity coefficients is given in Table 4.7. Most values agree within the analytical precision.

Table 4.7: Concentration (ppm) of heavy metal in clay samples

Sample : Copper (II) Chloride

No	Parameter	Results	Unit
1	Copper (Cu)	43809.33	ppm

Sample : Ferum (III) Chloride

No	Parameter	Results	Unit
1	Ferum (Fe)	6012.83	ppm

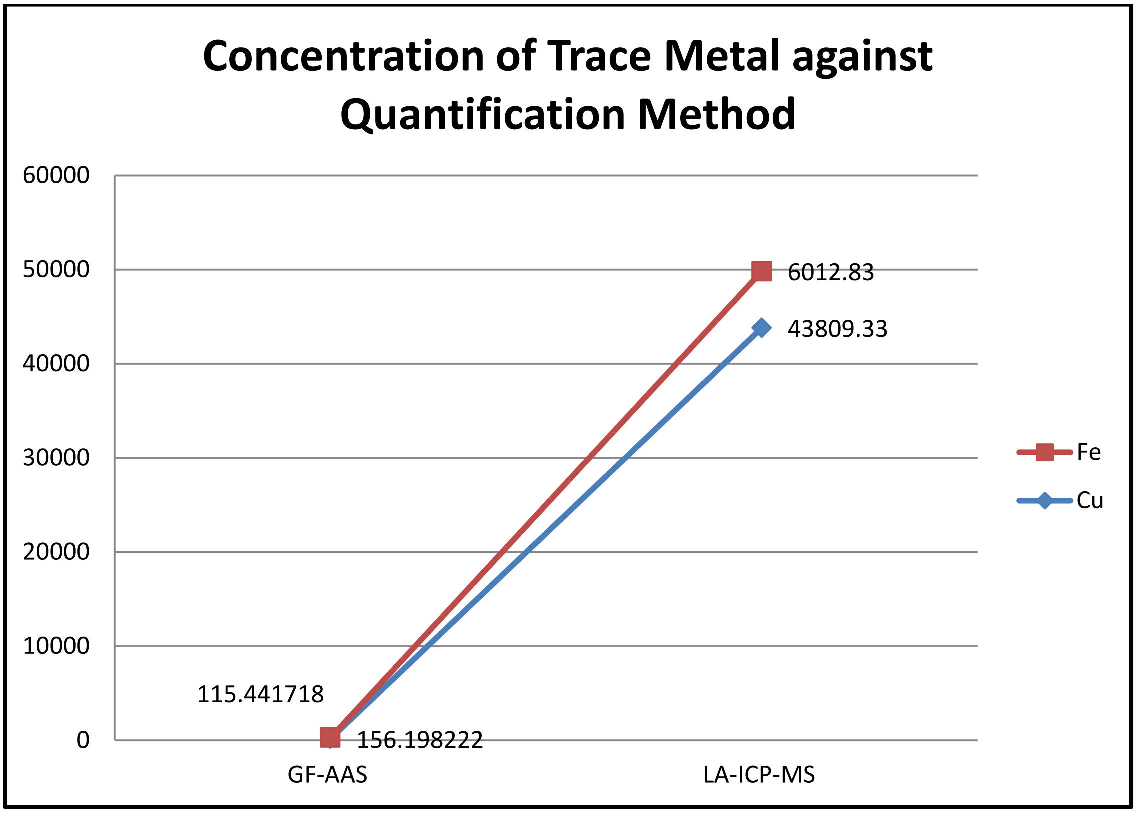

Figure 4.4: Concentration of Trace Metal against Quantification Methods (ICPMS & AAS)

Both quantification methods lead to different results in the case of Copper and Ferum. The Copper concentration determined in clay sample. However, the latter value is in good agreement with the atomic absorption spectrometry (GF-AAS) result of156.19822 ppm. The Copper concentration in clay samples are out of the calibration curve range (3424-13699 ppm) of the measured calibration curve. For that reason, a high Cu concentration was determined. So, for the quantification via calibration curves the element concentration must be in the calibration range and at least three reference materials are needed. Alternatively, dilute matrix matched and the samples by ultrapure graphite and measure at the same conditions.

Rege et al., also used a similar technique in the trace analysis of clay. Figure 4.5 shows comparison between the analytical results obtained by calibration curves in LA-ICP-MS and GF-AAS.

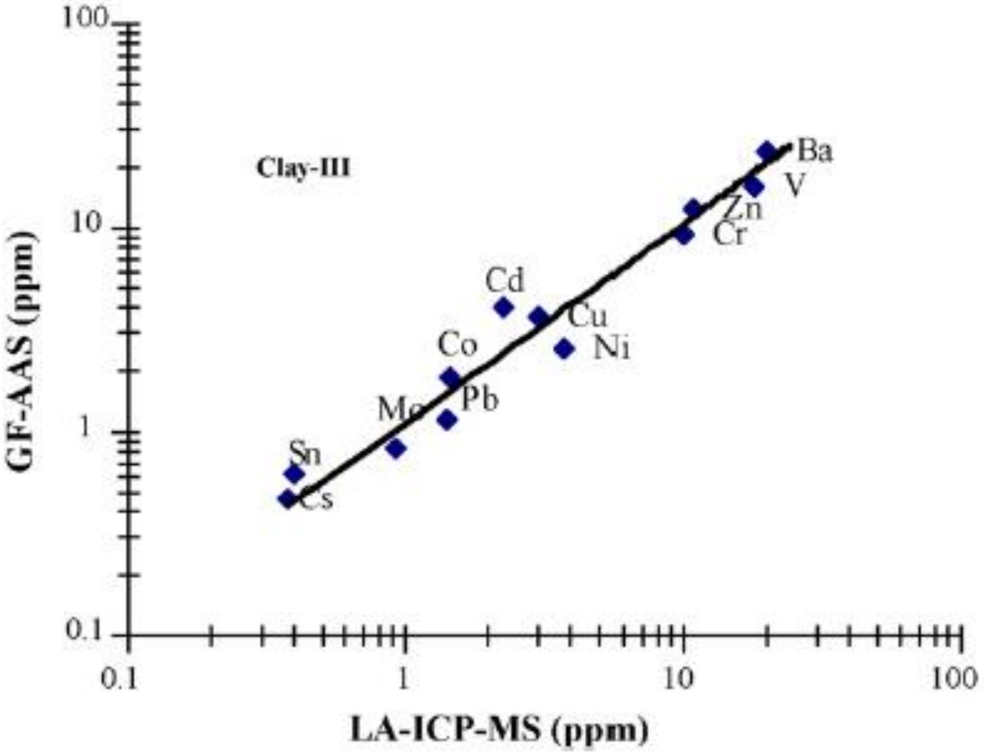

Figure 4.5: LA-ICP-MS values obtained by calibrations curves plotted against values obtained by GF-AAS.

Source: Rege et al., (2005)

The results of this characterization proved that there have transition metal ion traced in clay sample. In short, modification of clay has taken place successfully as concentration of transition metal ion present in clay sample has been detected.

4.5 Analysis of Fourier Transform Infrared Transform (FTIR)

After modification process to the structure of pristine clay by using the ion exchange method, the Fourier Transform Infrared Spectrometry (FTIR) analysis need to be done in order to justify the surface modification of pristine clay is achieved. FTIR is an analytical technique used to identify mainly organic materials. FTIR result which is in absorption spectra will provide information about the chemical bonds and molecular structure of a material. FTIR also used to obtain an infrared spectrum of emission, absorption, photoconductivity or Raman scattering of a solid, liquid or gas. Apart from that, an FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This is significantly give advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. Every sample had been analyse after intercalated with pure polyurethane by solution mixing method. The FTIR pattern is discussed below.

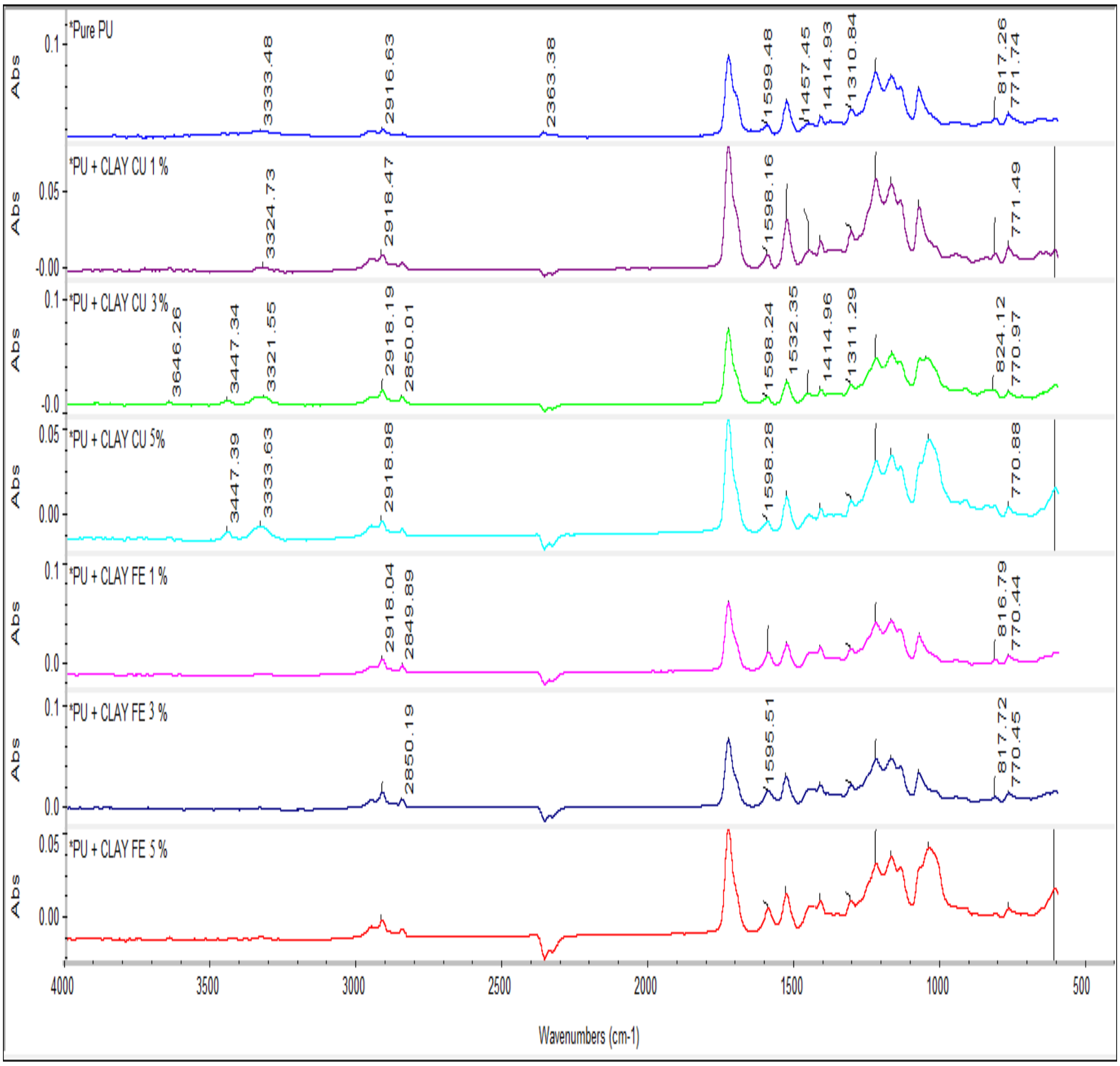

Figure 4.6: FTIR pattern for pure polyurethane and modified nanoclay (Cu and Fe) /PU nanocomposite with different clay loading.

The FTIR spectra of the polyurethane exhibited the typical bonds for polyurethanes: -NH, (free and bonded) at 3300-3400 cm-1 , CH2 at 2850-2970 cm-1 , C=O in bonded urethane group at 1680-1720 cm-1 and -C-O-C- in ester group at 1053 cm-1. Almost all the infrared studies on polyurethanes were focused on two principal vibration regions: the N-H stretching vibration (3200-3400 cm-1) and the carbonyl C=O stretching vibration in the amide I region (1680-1720 cm-1). Polyurethanes are capable of forming several kinds of hydrogen bonds due to the presence of a donor N-H group and a C=O acceptor group in the urethane linkage. This is why that hard segment-hard segment or hard segment-soft segment hydrogen bonding can exist. In the case of -polyurethane elastomers, the appearance of a single N–H band at 3310 cm–1 which is growing bigger with the nature of cross-linking of the hard segment suggested that most of its N–H groups were hydrogen bonded.

FTIR spectra of PUs (and polyol-based polyurethanes) are well known to be sensitive to hard domain organization and the urea and urethane hydrogen bonding. Consequently, to understand the possible reactions that may occur among the reactants (PU and nanoclay), the FTIR spectra of PU nanocomposites containing 1 wt%, 3% and 5% modified clay for different metal ion (Cu and Fe) are recorded . then, the characteristic absorptions peaks of the pure PU are observed at 3333.48 cm-1 (N–H stretching frequency), 2916.63–2363.38 cm-1 (–CH2– and –CH3 stretching frequencies), 1731.66 cm-1 (carbonyl urethane stretching), 1599.48 cm-1 (CHN vibration), 1457.45 cm-1 (coupled C–N and C–O stretching), and 1310.84 cm-1 (C–O stretching). Comparison of neat PU with the nanocomposite indicates that all the characteristic absorptions of PU remain unchanged in the modified nanoclay (Fe and Cu) /PU nanocomposite with different clay loading. But the urethane characteristic peaks at 1731.79 and 11732.02 cm-1 for 1% clay loading of Cu and Fe respectively are enhanced due to the formation of more number of urethane linkages during the course of the curing reaction. Some polymer chain ends with –NCO groups come closer to the vicinity of the clay galleries during nanocomposites preparation and react with CH2CH2OH group of the quaternary ammonium ions to produce urethane linkage, –CO–NH–, contribute to a fine dispersion of the clay particles.

4.6 Analysis of Field Emission Scanning Electron Miscoscope (FESEM)

A field emission scanning electron microscope (FESEM) is a type of electron microscope that developed images of a sample by scanning it with a focused beam of electrons. The electrons contacted with atoms in the sample, creating various signals that can be detected and that provide information about the sample's surface topography and composition. The electron beam is basically scanned in a raster scan pattern, while the beam's position is combined with the detected signal to produce an image. In general, a quality of dispersion and distribution of delaminated platelets in the polymer matrix were relatively correlated to the amount of clay content used as proved by FESEM (10000 view magnification) micrographs in the Figure 4.7. The samples of polymer nanoclay that was compounded at shear intensity of 100 rpm were selected for this FESEM characterization. In the micrograph, the grey coloured regions indicate the bulk of polymer matrix and the brighter spots indicate the distribution of clay particles. The number and size of aggregation nanoclays could be clearly pointed out from the micrograph of modified nanoclay (Cu) /PU nanocomposite with 1wt %, 3 wt % and 5 wt % as well as for modified nanoclay (Fe) /PU nanocomposite.

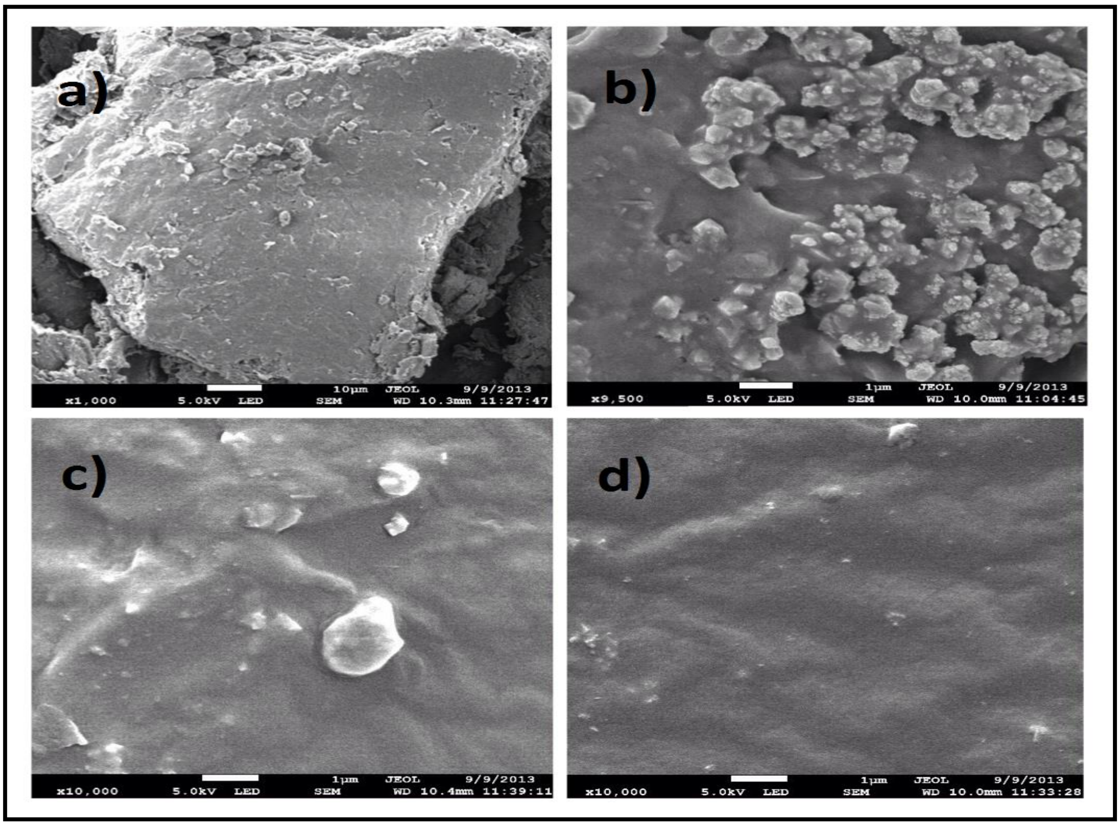

Figure 4.7: FESEM micrograph (10kx view magnification) of a) pure clay b) PU/clay nanocomposites (Cu) with loading of b) 1wt% and c) 3wt% d) 5wt%, respectively.

Figure 4.7 a) features the highest amount and the biggest agglomeration for the unmodified clay while b) and c) shows that agglomeration had medium and small amount of agglomerates and had been smaller in size with the modification of clay with Cu and Fe respectively. No obvious particle agglomeration was observed in the polymer-matrix in higher clay loading indicating that PU favors forming high quality nanocomposites. Somewhat surprisingly, in the literature most of the researcher have often utilized that higher particle loading in the polymer matrix lead to the poor dispersion as it features a high amount of agglomerates as well as the size were bigger. Razak et al., illustrated that higher clay loading in acrylonitrile-butadiene-styrene (ABS) shows an increasing in amount of agglomerates. At higher clay concentrations (eg >3wt%), clay agglomeration is usually very difficult to avoid to some extent. The co-existence of exfoliated and intercalated nanostructures is frequently observed in a number of thermoplastic and thermoset polymer/claynano-systems. This complexity of organoclay morphologies among the polymer matrices might be definitely reflected by the changes in the properties of the final products. The result is in agreement with previous research reported by Fu and Qutubuddin, where non-treated MMT tends to agglomerate and has poor dispersion.

4.7 Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is basically carried out in air or in an inert atmosphere, such as Argon or Helium, and the weight is recorded as a function of increase in temperature.

The thermal degradation of polyurethane occurs in two stages: the first stage is mainly governed by the degradation of the hard segment and the second stage correlates well with the degradation of the soft segment. Generally, clay particles can enhance the thermal stability of polymer by acting as thermal insulator and mass transport barrier to the volatile products generated during decomposition. The performance of clay as thermal insulator and mass transport barrier on thermal stability can be increased with improving the dispersibility of organoclay. The thermo-gravimetric analysis curve for pure polyurethane and modified organoclay is depicted in Figure 4.8 and 4.9.

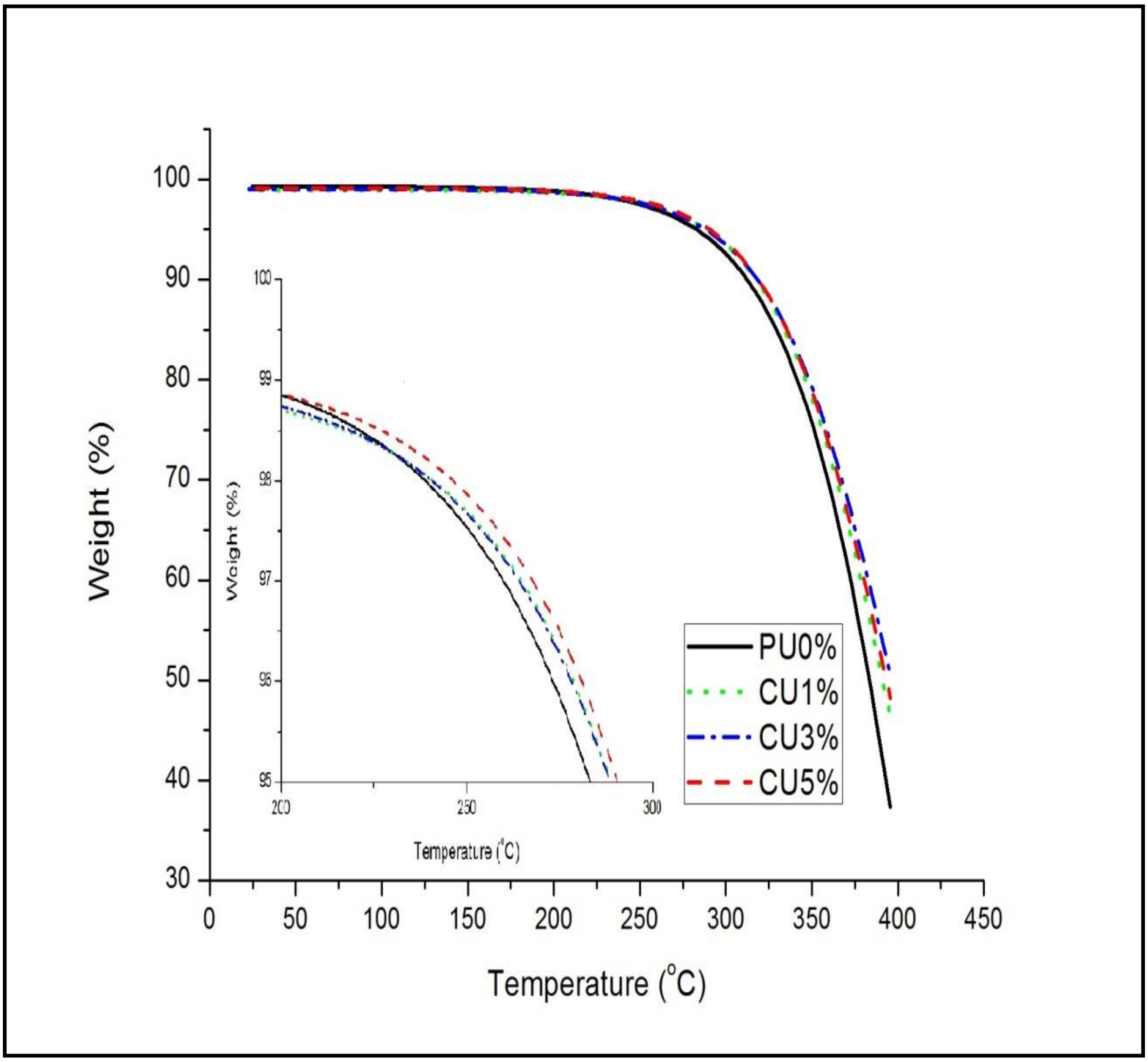

Figure 4.8: TGA curve of modified nanoclay (Cu) /PU nanocomposite with different clay loading.

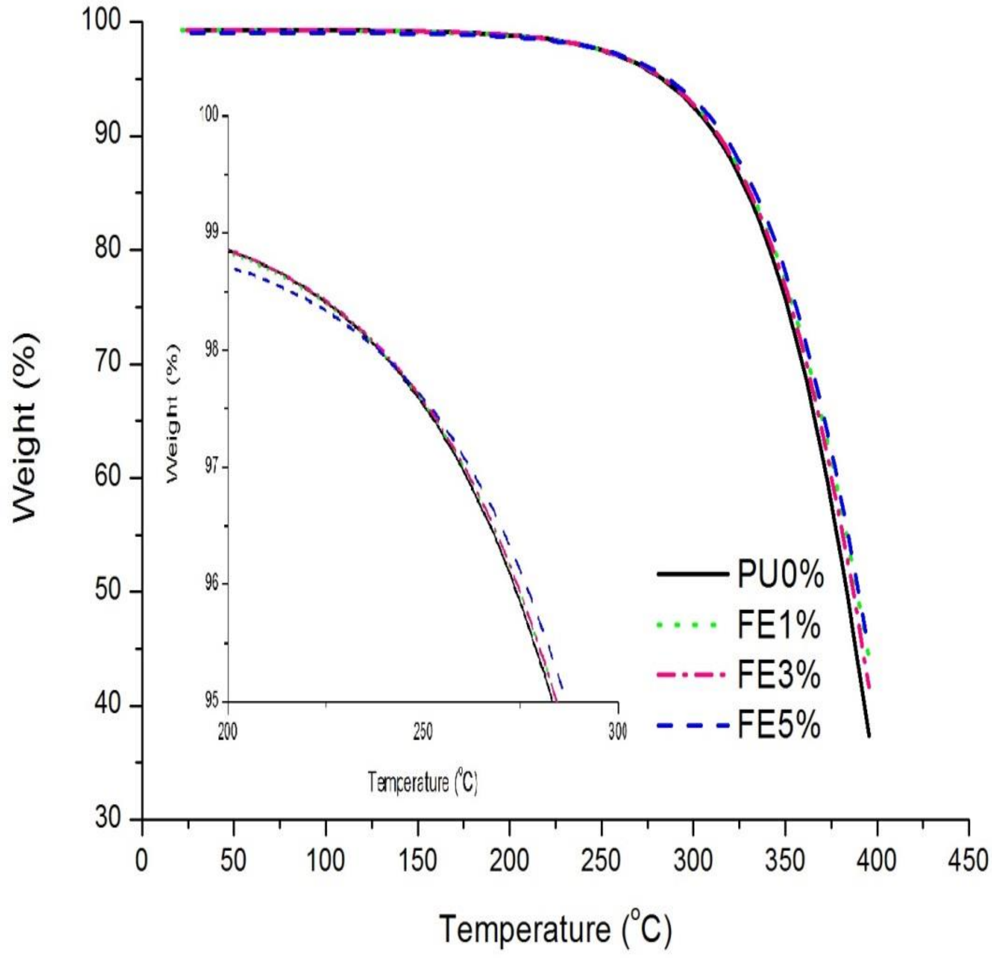

Figure 4.9: TGA curve of modified nanoclay (Fe) /PU nanocomposite with different clay loading.

In general, it has been reported that the polymer/clay nanocomposites are thermally more stable than pure polymers (Ray & Bousima, 2005; Becker et al., 2004;Wang et al., 2002; Zanetti et al., 2004). That is the incorporation of clay fillers into the polymer matrices results to the improvement of their thermal stability. The existing of clay layers has been more explained as superior insulation and mass transport barrier against the volatile compounds generated during the decomposition of polymer under thermal conditions (Zhu et al., 2001). Also it has been reported that clays assist in the formation of layered carbonaceous char during degradation of polymer/clay nanocomposite (Ray et al., 2003). Clay minerals are inorganic materials and are almost stable in the temperature ranges that organic polymers are degraded in to volatile compounds. Hence in TGA experiments the clay content of nanocomposites is remain as residue after heating program (Gilman, 1999). Table 4.8 and 4.9 indicated the thermal degradation data of PU and PU/clay nanocomposites based on the TGA results.

Table 4.8: Thermal Degradation Data of modified nanoclay (Cu) /PU nanocomposites : 50% Degradation Temperature ($T_{0.50}$) and 75% Degradation Temperature ($T_{0.75}$).

Percent Clay Loading (%)	$T_{0.50}$ (°C)	$T_{0.75}$ (°C)	End Degradation Temperature (°C)
Pure (0%)	383.79	350.71	395.52
1	390.69	355.11	395.46
3	392.19	356.29	395.63
5	393.81	357.12	395.65

Table 4.9: Thermal Degradation Data of modified nanoclay (Fe) /PU nanocomposites : 50% Degradation Temperature ($T_{0.50}$) and 75% Degradation Temperature ($T_{0.75}$).

Percent Clay Loading (%)	$T_{0.50}$ (°C)	$T_{0.75}$ (°C)	End Degradation Temperature (°C)
Pure (0%)	383.79	350.71	395.52
1	387.15	350.52	395.60
3	387.15	352.06	395.62
5	389.16	354.17	395.69

According to the results, thermal stability of nanocomposites has been improved compared to the pure polyurethane. Thermogravimetric analysis (TGA) of neat PU and PU/clay nanocomposites was obtained by heating program 10 °C/min**.** Figure 4.8 and 4.9 shows the TGA curves of PU and PU/modified nanoclay. Based on the results, the degradation temperature on PU in nanocomposites has been shifted to the higher temperature compared to pristine PU. The 50% degradationof PU/clay nanocomposites has been increased compared to pure PU. The 50% degradation of pure PU was 383.79°C, but that of the PU/clay nanocomposite with Cu and for PU/clay nanocomposite with Fe was 387.15°C which is indicating respectively 6.9°C and 3.36°C improvement with 1% of the clay loading. Thermal stability had been increased significantly, due to the transition metal ions hindering the pristine clay within the polymer matrices from decomposing easily. This enhancement of PU/clay nanocomposites with Cu is might be due to its concentration which is higher that Fe based on the characterization process using AAS and ICPMS.

Blumstein (1965) first reported the improved thermal stability of PMMA/MMT nanocomposite. TGA illustrated that PMMA intercalated into the Na-MMT has 40-50 °C higher decomposition temperature. Vyazovkin et al. (2004) has been reported the thermal stability of polystyrene/clay nano-composite compared to pure PS. They have showed that PS/clay nanocomposites have 30-40 °C higher degradation temperature compared to pure PS under nitrogen and air heating degradation conditions. Other studies have been proved that the nature of the clay modifier can affect on the thermal stability of modified clay and related nanocomposites (Mittal, 2007). Figure 4.10 shows the TGA curve for pure PS and PS/clay nanocomposites.

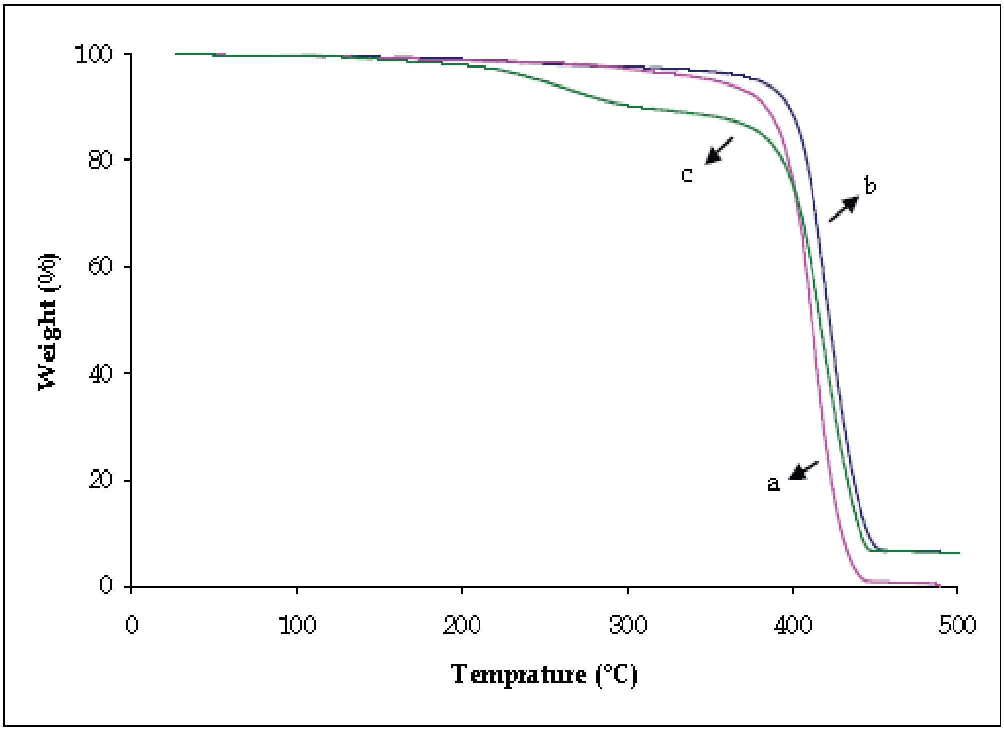

Figure 4.10: TGA curves for PS (a), PS/Na-MMT (b) and PS/Cloisite 30B (c).

Source: Mittal (2007)

Derivative thermal gravimetric (DTG) was further used to study the thermal stability of the nanocomposites as compared to the pure polyurethane (see Figure 4.11)

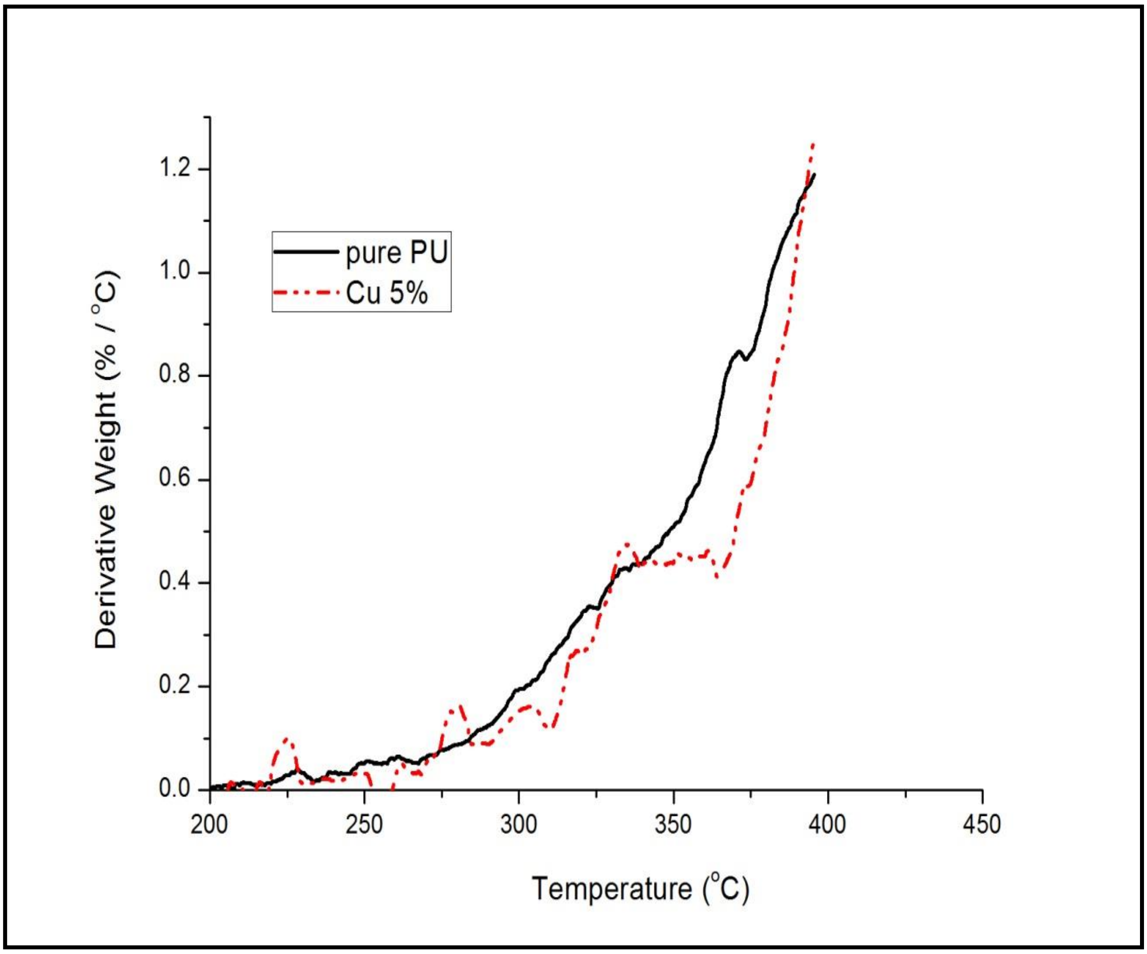

Figure 4.11: Derivative Weight vs Temperature based on pure and cu 5%

Different thermal behavior was observed with the addition of transition metal ion into the polyurethane nanocomposites. As compared with the peak presented in the pure polyurethane, polyurethane with 5% Cu loading was observed to have more peaks as shown in the inset of Figure 4.11. The first peak is attributed to the bulk polyurethane matrix while the other peak at higher temperature is due to the nanoparticle surface. This phenomenon indicates a strong chemical bonding between the nanoparticles and the polyurethane matrix.

4.8 Tensile Test Analysis

In order to study the effect of the interfacial interaction on the mechanical properties of polymer nanocomposites, this research used tensile testing to determine the ultimate strength (MPa), elastic modulus (MPa) and elongation (%) for the specimen. The testing was carried out using seven samples for each of the PU and Pu nanocomposites. The average result is shown in Figure 4.12 and Figure 4.13.

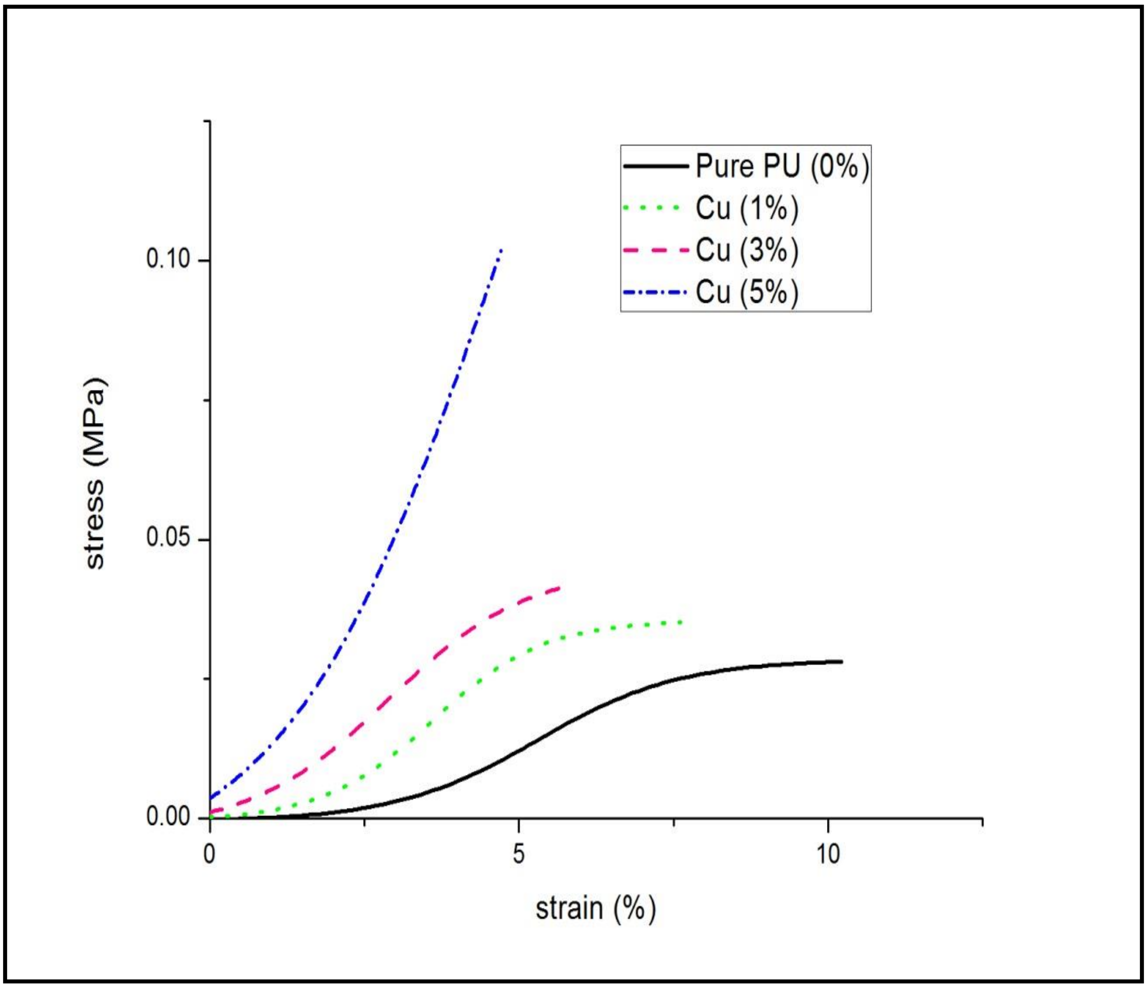

Figure 4.12: Tensile stress versus strain curves of nanocomposites at different modified clay (Cu) loadings.

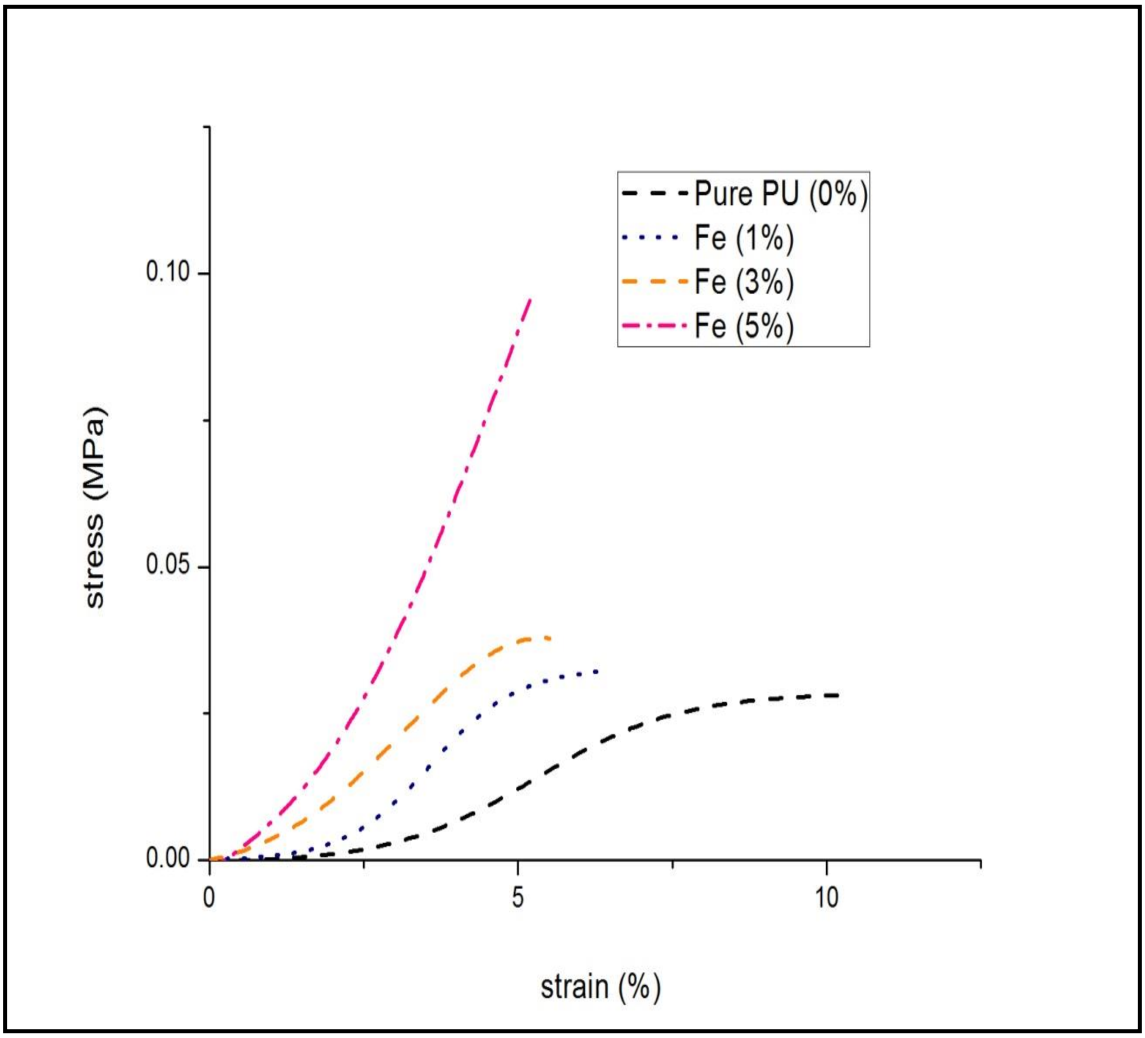

Figure 4.13: Tensile stress versus strain curves of nanocomposites at different modified clay (Fe) loadings.

Based on Figure 4.12 and Figure 4.13, the addition of modified clay (Cu and Fe) nanoparticles is seen to increase both the strength and the modulus together with enhancement of toughness. 5% clay loading for both Fe and Cu shows the great increasing of strength followed by 3% clay loading, 1% clay loading and the lowest one which is pure PU. The mechanical properties of pure polyurethane and nanocomposites with different loading are summarized in Table 4.10.

Table 4.10: Mechanical properties of the pure polyurethane and nanocomposites with different loadings

Sample Designation	Modulus Elasticity (MPa)	Strength (MPa)	Elongation (%)
Pure Polyurethane	19.5×10^{-4}	28.6×10^{-3}	10.2191
PU / modified nanoclay (Cu) 1%	45.5×10^{-4}	34.6×10^{-3}	7.6098
PU / modified nanoclay (Cu) 3%	71.2×10^{-4}	40.4×10^{-3}	5.6750
PU / modified nanoclay (Cu) 5%	204.0×10^{-4}	95.5×10^{-3}	4.7080
PU / modified nanoclay (Fe) 1%	49.5×10^{-4}	31.7×10^{-3}	6.3978
PU / modified nanoclay (Fe) 3%	68.6×10^{-4}	37.8×10^{-3}	5.5184
PU / modified nanoclay (Fe) 5%	179×10^{-4}	92.8×10^{-3}	5.1908

As compared with the pure polyurethane, the addition of 1% modified clay (Cu) increase the Young's modulus and strength by a factor of 133% and 21%, respectively. The sacrificing loss of elongation is about 25%. On the other hand, with the addition of 1% modified clay (Fe) shows the increasing trend for the Young's modulus and strength by a factor of 153% and 11%, respectively. An increase of about 10.46 times and 3.3 times in the modulus and strength, respectively, was observed in the composites reinforced with 5% modified clay (Cu) as compared with the pure polyurethane. The Young's modulus and strength for 5% modified clay (Fe) also indicated an increment with 8.72 times and 3.2 times respectively compared to the pure polyurethane but decrease in elongation about 49% due to the constraint effect of clay on mobility of polymer chains. The effect of clay fillers on the stress at break values for polymer nanocomposites depends on the interfacial interactions between polymer and clay layers. The stronger interfacial interaction causes to the increasing of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposite.

The polymers with more polarity such as nylon and rubber based polymers have more strong interfacial interactions with polar clay layers and their nanocomposites represent an improved stress at break values compared to that of pure polymer (Wang et al., 1998). Even so, the modification of polymer chains or clay layers may be causes to improved stress at break characteristics for non-polar polymers. Elongation at break for polymer/clay nanocomposites is similarly dependent to the interfacial interactions of polymer/clay system. There are increasing and decreasing results of elongation at break for polymer/clay nanocomposites in literature (Finnigan et al., 2004; Yao et al., 2002). The impact strength of polymer/clay nanocomposites was also studied and compared with that of pure polymer systems. The reports are usually emphasis on the increasing of impact strength by the addition of very low fraction of clay loadings such as 0.1 wt% (Zhang & Oya, 2000).

4.9 Summary

The first part of the experiment focuses on the modification of pristine clay with Transition Metal Ions (TMIs), Copper and Ferum. After these modifications, the samples of organoclay are characterized using Fourier Transform Infrared (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). FTIR and FESEM results illustrated modified nanoclays had smoother surfaces of pristine clay or montmorillonite (MMT) which proved that modification has taken place successfully. The samples then tested by Thermal Gravimetry Analysis (TGA) and Tensile Test to measure their thermal and mechanical properties respectively. Both the thermal stability and mechanical strength showed positive improvements. Thermal stability is hypothesized to have increased significantly, due to the transition metal ions hindering the pristine clay within the polymer matrices from decomposing easily. The stronger interfacial interaction causes to the increasing of stress at break and the weak interfacial forces may lead to some decreasing of stress at break for nanocomposite.

CHAPTER 5

CONCLUSION

5.1 Conclusion

Polyurethane nanocomposites reinforced with modified nanoclay were synthesis using solution intercalation method. For the first part of the research, FTIR and FESEM results illustrated modified nanoclays had smoother surfaces of pristine clay or montmorillonite (MMT) which proved that modification was successful. As point out with the pure PU, PU nanocomposites with modified clay are significantly strengthened and have improved thermal stability. The tensile test had been revealed a strengthened structural nanomaterial and a tensile strength was observed to increase by 3.2 times (for Cu 5%) higher than the pure polyurethane. The most essential is PU nanocomposites with this improved performances was able to develop new robust high performance thermal building insulation materials for roofing application.

5.2 Future Work

This research carried in this project (modification of clay) is currently being expanded for high thermal nano insulation building material by Shamini A/P Gunaseelan (MSc student). Modification with the addition of zinc in polyurethane has been analyze for further study in permeability analysis. The samples was characterized using various analysis which are AAS, ICPMS, SEM, TEM, FESEM, FTIR, XRD, DSC, TGA, Gas Permeation, and Water Permeation. This high thermal nano insulation building material has highly potential around the world as well as in Malaysia.

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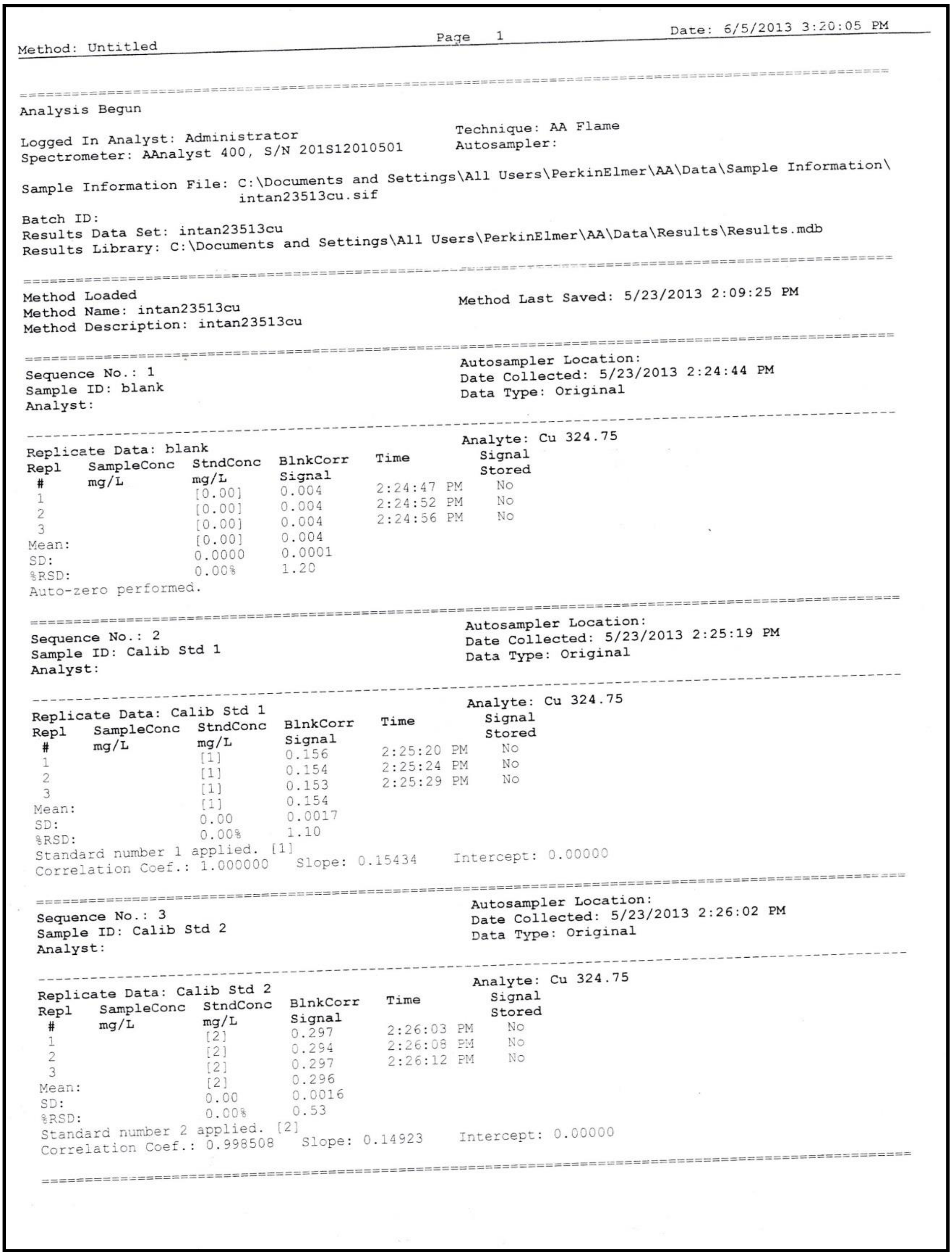
APPENDIX A1



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Method: Untitled                          Page   1                Date: 6/5/2013 3:20:05 PM
=========================================================================================
Analysis Begun

Logged In Analyst: Administrator                   Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501       Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         intan23513cu.sif

Batch ID:
Results Data Set: intan23513cu
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

=========================================================================================
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Method Description: intan23513cu

=========================================================================================
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Sample ID: blank                                   Data Type: Original
Analyst:
-----------------------------------------------------------------------------------------
                                                   Analyte: Cu 324.75
Replicate Data: blank
Repl    SampleConc   StndConc    BlnkCorr     Time         Signal
 #      mg/L         mg/L        Signal                    Stored
 1                   [0.00]      0.004        2:24:47 PM    No
 2                   [0.00]      0.004        2:24:52 PM    No
 3                   [0.00]      0.004        2:24:56 PM    No
Mean:                [0.00]      0.004
SD:                  0.0000      0.0001
%RSD:                0.00%       1.20
Auto-zero performed.
=========================================================================================
                                                   Autosampler Location:
Sequence No.: 2                                    Date Collected: 5/23/2013 2:25:19 PM
Sample ID: Calib Std 1                             Data Type: Original
Analyst:
-----------------------------------------------------------------------------------------
                                                   Analyte: Cu 324.75
Replicate Data: Calib Std 1
Repl    SampleConc   StndConc    BlnkCorr     Time         Signal
 #      mg/L         mg/L        Signal                    Stored
 1                   [1]         0.156        2:25:20 PM    No
 2                   [1]         0.154        2:25:24 PM    No
 3                   [1]         0.153        2:25:29 PM    No
Mean:                [1]         0.154
SD:                  0.00        0.0017
%RSD:                0.00%       1.10
Standard number 1 applied. [1]
Correlation Coef.: 1.000000    Slope: 0.15434     Intercept: 0.00000
=========================================================================================
                                                   Autosampler Location:
Sequence No.: 3                                    Date Collected: 5/23/2013 2:26:02 PM
Sample ID: Calib Std 2                             Data Type: Original
Analyst:
-----------------------------------------------------------------------------------------
                                                   Analyte: Cu 324.75
Replicate Data: Calib Std 2
Repl    SampleConc   StndConc    BlnkCorr     Time         Signal
 #      mg/L         mg/L        Signal                    Stored
 1                   [2]         0.297        2:26:03 PM    No
 2                   [2]         0.294        2:26:08 PM    No
 3                   [2]         0.297        2:26:12 PM    No
Mean:                [2]         0.296
SD:                  0.00        0.0016
%RSD:                0.00%       0.53
Standard number 2 applied. [2]
Correlation Coef.: 0.998508    Slope: 0.14923     Intercept: 0.00000
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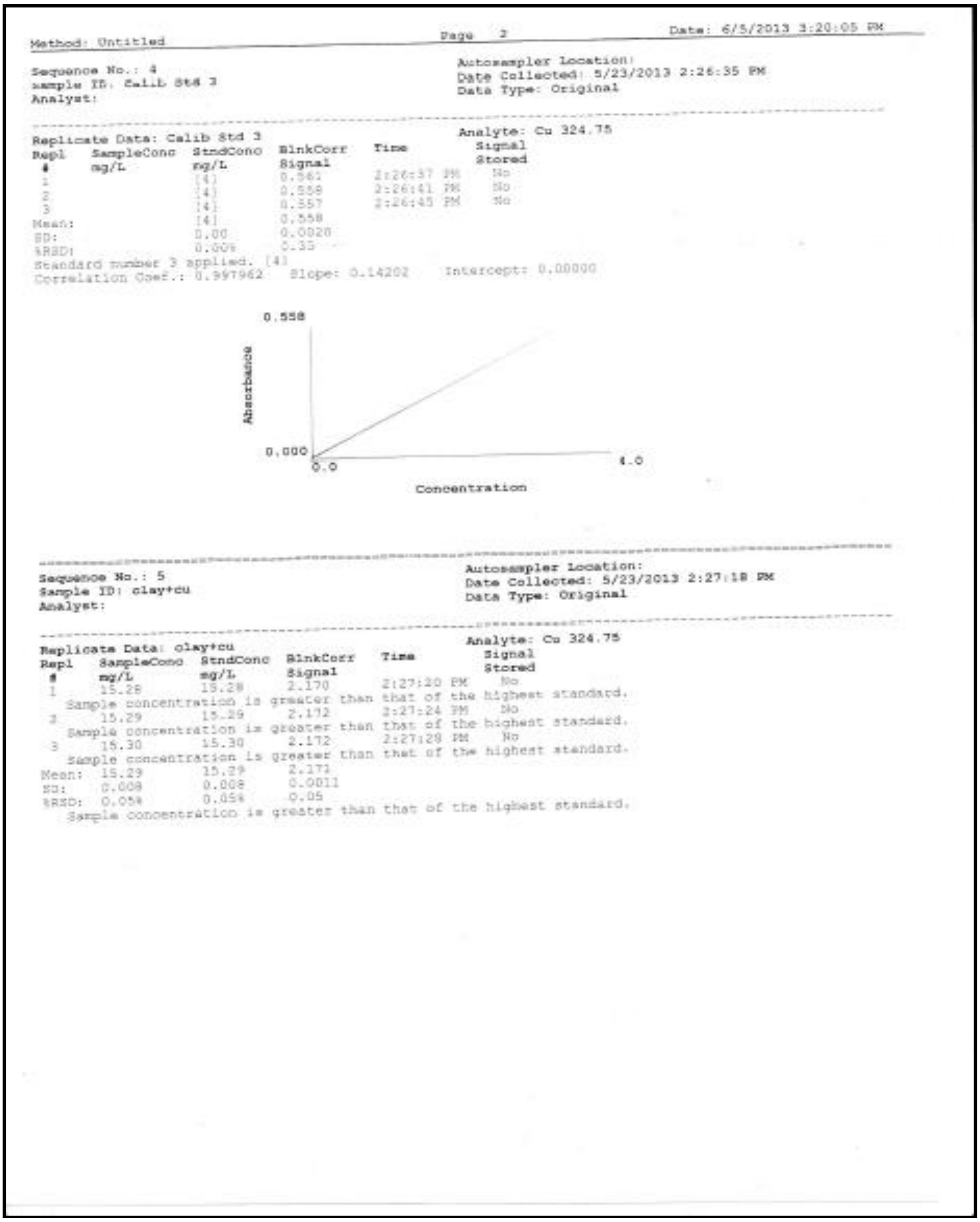
APPENDIX A2



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Sequence No.: 4                          Autosampler Location:
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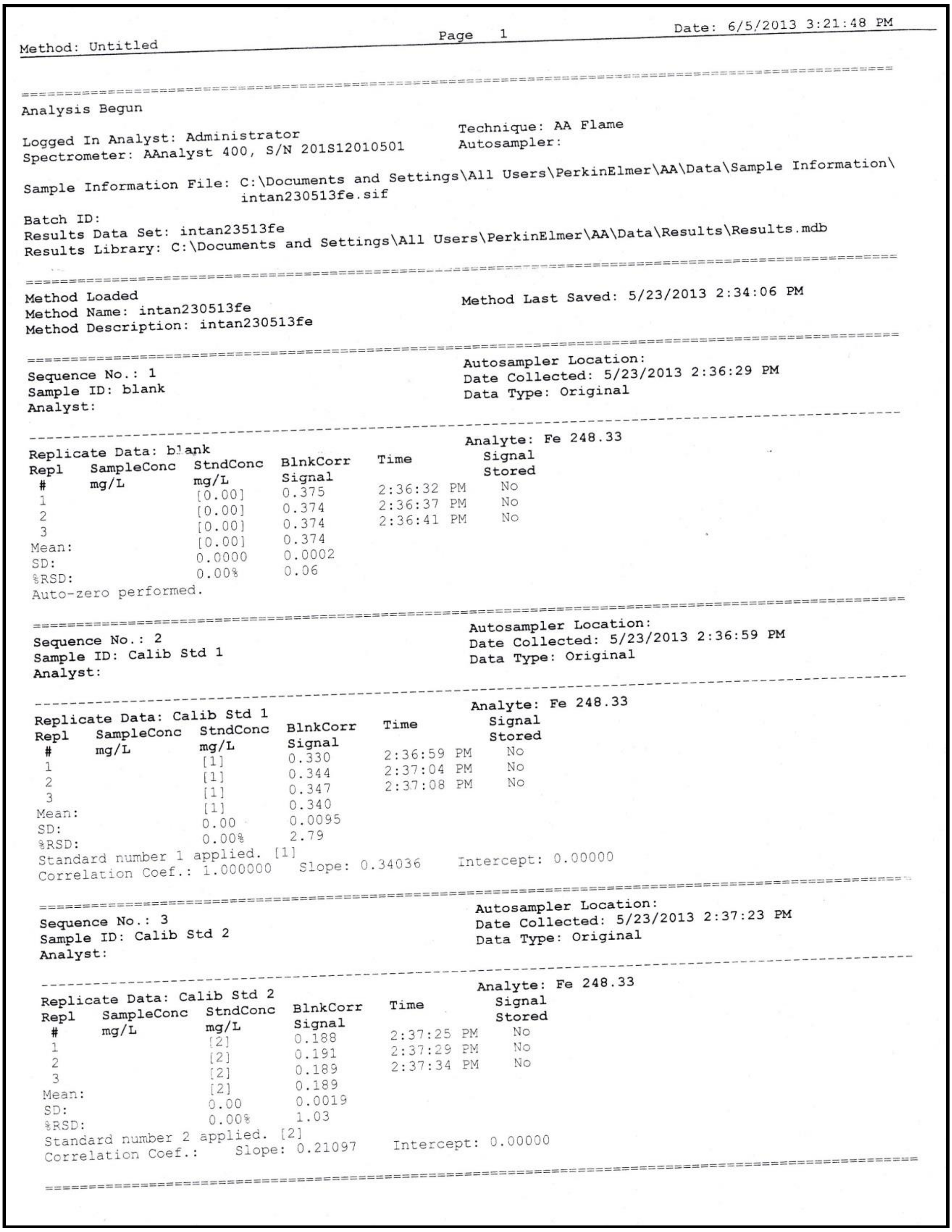
Analyst:                                 Data Type: Original
--------------------------------------------------------------------------------------
                                         Analyte: Cu 324.75
Replicate Data: Calib Std 3
Repl   SampleConc  StndConc  BlnkCorr   Time          Signal
 #     mg/L        mg/L      Signal                   Stored
 1                 [4]       0.561      2:26:37 PM     No
 2                 [4]       0.558      2:26:41 PM     No
 3                 [4]       0.557      2:26:45 PM     No
Mean:              [4]       0.558
SD:                0.00      0.0020
%RSD:              0.00%     0.35
Standard number 3 applied. [4]
Correlation Coef.: 0.997962   Slope: 0.14202    Intercept: 0.00000

--------------------------------------------------------------------------------------
Sequence No.: 5                          Autosampler Location:
Sample ID: clay+cu                       Date Collected: 5/23/2013 2:27:18 PM
Analyst:                                 Data Type: Original
--------------------------------------------------------------------------------------
                                         Analyte: Cu 324.75
Replicate Data: clay+cu
Repl   SampleConc  StndConc  BlnkCorr   Time          Signal
 #     mg/L        mg/L      Signal                   Stored
 1     15.28       15.28     2.170      2:27:20 PM     No
   Sample concentration is greater than that of the highest standard.
 2     15.29       15.29     2.172      2:27:24 PM     No
   Sample concentration is greater than that of the highest standard.
 3     15.30       15.30     2.172      2:27:28 PM     No
   Sample concentration is greater than that of the highest standard.
Mean:  15.29       15.29     2.171
SD:    0.008       0.008     0.0011
%RSD:  0.05%       0.05%     0.05
   Sample concentration is greater than that of the highest standard.
```

APPENDIX A3



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Analyst:
------------------------------------------------------------------------------------------
                                                   Analyte: Fe 248.33
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Repl   SampleConc  StndConc  BlnkCorr   Time          Signal
 #     mg/L        mg/L      Signal                   Stored
 1                 [0.00]    0.375      2:36:32 PM    No
 2                 [0.00]    0.374      2:36:37 PM    No
 3                 [0.00]    0.374      2:36:41 PM    No
Mean:              [0.00]    0.374
SD:                0.0000    0.0002
%RSD:              0.00%     0.06
Auto-zero performed.
==========================================================================================
                                                   Autosampler Location:
Sequence No.: 2                                    Date Collected: 5/23/2013 2:36:59 PM
Sample ID: Calib Std 1                             Data Type: Original
Analyst:
------------------------------------------------------------------------------------------
                                                   Analyte: Fe 248.33
Replicate Data: Calib Std 1
Repl   SampleConc  StndConc  BlnkCorr   Time          Signal
 #     mg/L        mg/L      Signal                   Stored
 1                 [1]       0.330      2:36:59 PM    No
 2                 [1]       0.344      2:37:04 PM    No
 3                 [1]       0.347      2:37:08 PM    No
Mean:              [1]       0.340
SD:                0.00      0.0095
%RSD:              0.00%     2.79
Standard number 1 applied. [1]
Correlation Coef.: 1.000000   Slope: 0.34036     Intercept: 0.00000
==========================================================================================
                                                   Autosampler Location:
Sequence No.: 3                                    Date Collected: 5/23/2013 2:37:23 PM
Sample ID: Calib Std 2                             Data Type: Original
Analyst:
------------------------------------------------------------------------------------------
                                                   Analyte: Fe 248.33
Replicate Data: Calib Std 2
Repl   SampleConc  StndConc  BlnkCorr   Time          Signal
 #     mg/L        mg/L      Signal                   Stored
 1                 [2]       0.188      2:37:25 PM    No
 2                 [2]       0.191      2:37:29 PM    No
 3                 [2]       0.189      2:37:34 PM    No
Mean:              [2]       0.189
SD:                0.00      0.0019
%RSD:              0.00%     1.03
Standard number 2 applied. [2]
Correlation Coef.:     Slope: 0.21097     Intercept: 0.00000
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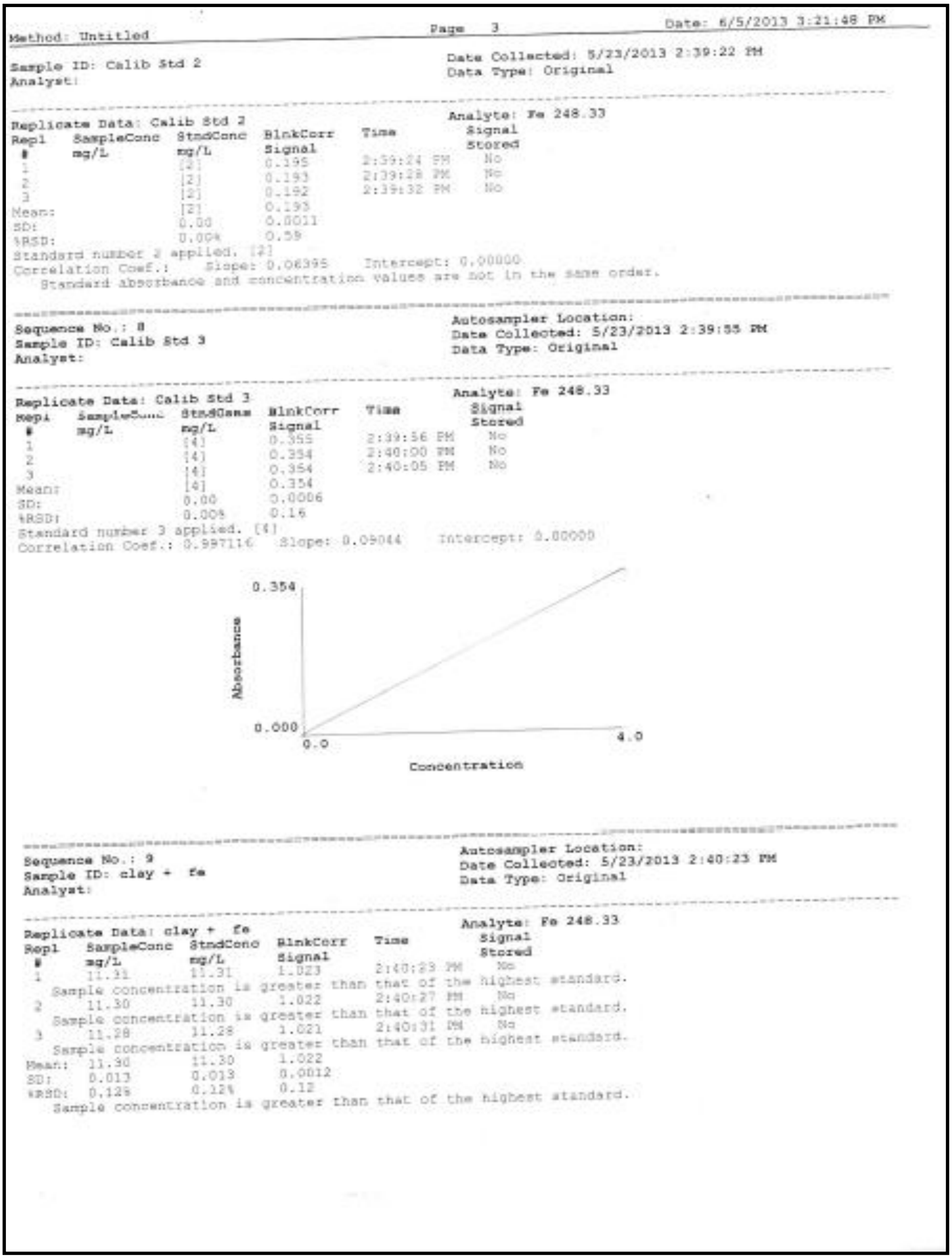
APPENDIX A4



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---------------------------------------------------------------------------------------------------
                                                             Analyte: Fe 248.33
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 #      mg/L        mg/L      Signal                     Stored
 1                  [2]       0.195       2:39:24 PM     No
 2                  [2]       0.193       2:39:28 PM     No
 3                  [2]       0.192       2:39:32 PM     No
Mean:               [2]       0.193
SD:                 0.00      0.0011
%RSD:               0.00%     0.59
Standard number 2 applied. [2]
Correlation Coef.:     Slope: 0.06395     Intercept: 0.00000
   Standard absorbance and concentration values are not in the same order.
===================================================================================================
Sequence No.: 8                                              Autosampler Location:
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Analyst:                                                     Data Type: Original
---------------------------------------------------------------------------------------------------
                                                             Analyte: Fe 248.33
Replicate Data: Calib Std 3
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 #      mg/L        mg/L      Signal                     Stored
 1                  [4]       0.355       2:39:56 PM     No
 2                  [4]       0.354       2:40:00 PM     No
 3                  [4]       0.354       2:40:05 PM     No
Mean:               [4]       0.354
SD:                 0.00      0.0006
%RSD:               0.00%     0.16
Standard number 3 applied. [4]
Correlation Coef.: 0.997116   Slope: 0.09044     Intercept: 0.00000
```

```
===================================================================================================
Sequence No.: 9                                              Autosampler Location:
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Analyst:                                                     Data Type: Original
---------------------------------------------------------------------------------------------------
                                                             Analyte: Fe 248.33
Replicate Data: clay +  fe
Repl    SampleConc  StndConc  BlnkCorr    Time           Signal
 #      mg/L        mg/L      Signal                     Stored
 1      11.31       11.31     1.023       2:40:23 PM     No
   Sample concentration is greater than that of the highest standard.
 2      11.30       11.30     1.022       2:40:27 PM     No
   Sample concentration is greater than that of the highest standard.
 3      11.28       11.28     1.021       2:40:31 PM     No
   Sample concentration is greater than that of the highest standard.
Mean:   11.30       11.30     1.022
SD:     0.013       0.013     0.0012
%RSD:   0.12%       0.12%     0.12
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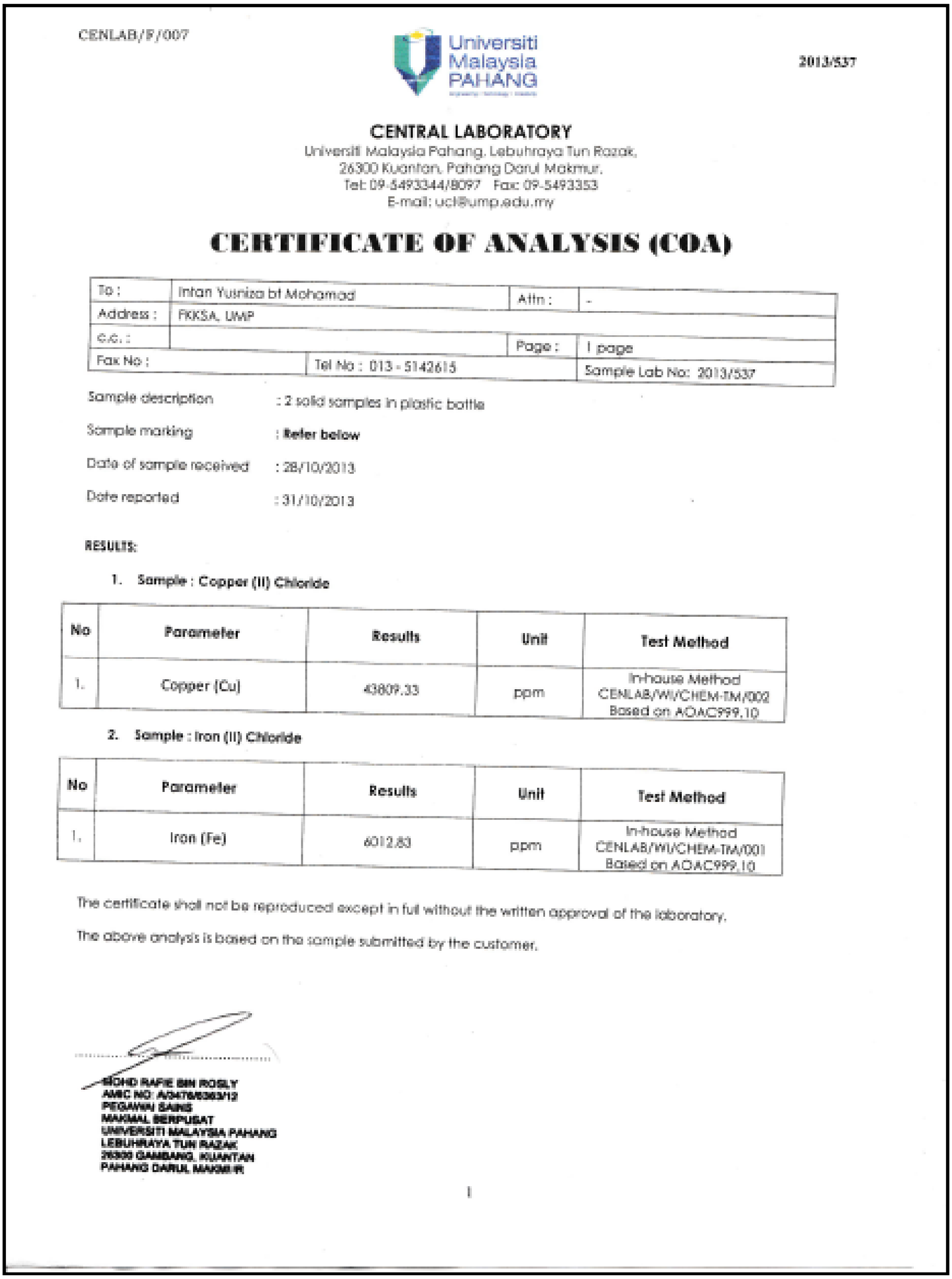
APPENDIX B1



CENLAB/F/007

2013/537

CENTRAL LABORATORY

Universiti Malaysia Pahang, Lebuhraya Tun Razak,
26300 Kuantan, Pahang Darul Makmur.
Tel: 09-5493344/8097 Fax: 09-5493353
E-mail: ucl@ump.edu.my

CERTIFICATE OF ANALYSIS (COA)

To :	Intan Yusniza bt Mohamad	Attn :	-
Address :	FKKSA, UMP		
c.c. :		Page :	1 page
Fax No :	Tel No : 013 - 5142615		Sample Lab No: 2013/537

Sample description : 2 solid samples in plastic bottle

Sample marking : **Refer below**

Date of sample received : 28/10/2013

Date reported : 31/10/2013

RESULTS:

1. Sample : Copper (II) Chloride

No	Parameter	Results	Unit	Test Method
1.	Copper (Cu)	43809.33	ppm	In-house Method CENLAB/WI/CHEM-TM/002 Based on AOAC999.10

2. Sample : Iron (II) Chloride

No	Parameter	Results	Unit	Test Method
1.	Iron (Fe)	6012.83	ppm	In-house Method CENLAB/WI/CHEM-TM/001 Based on AOAC999.10

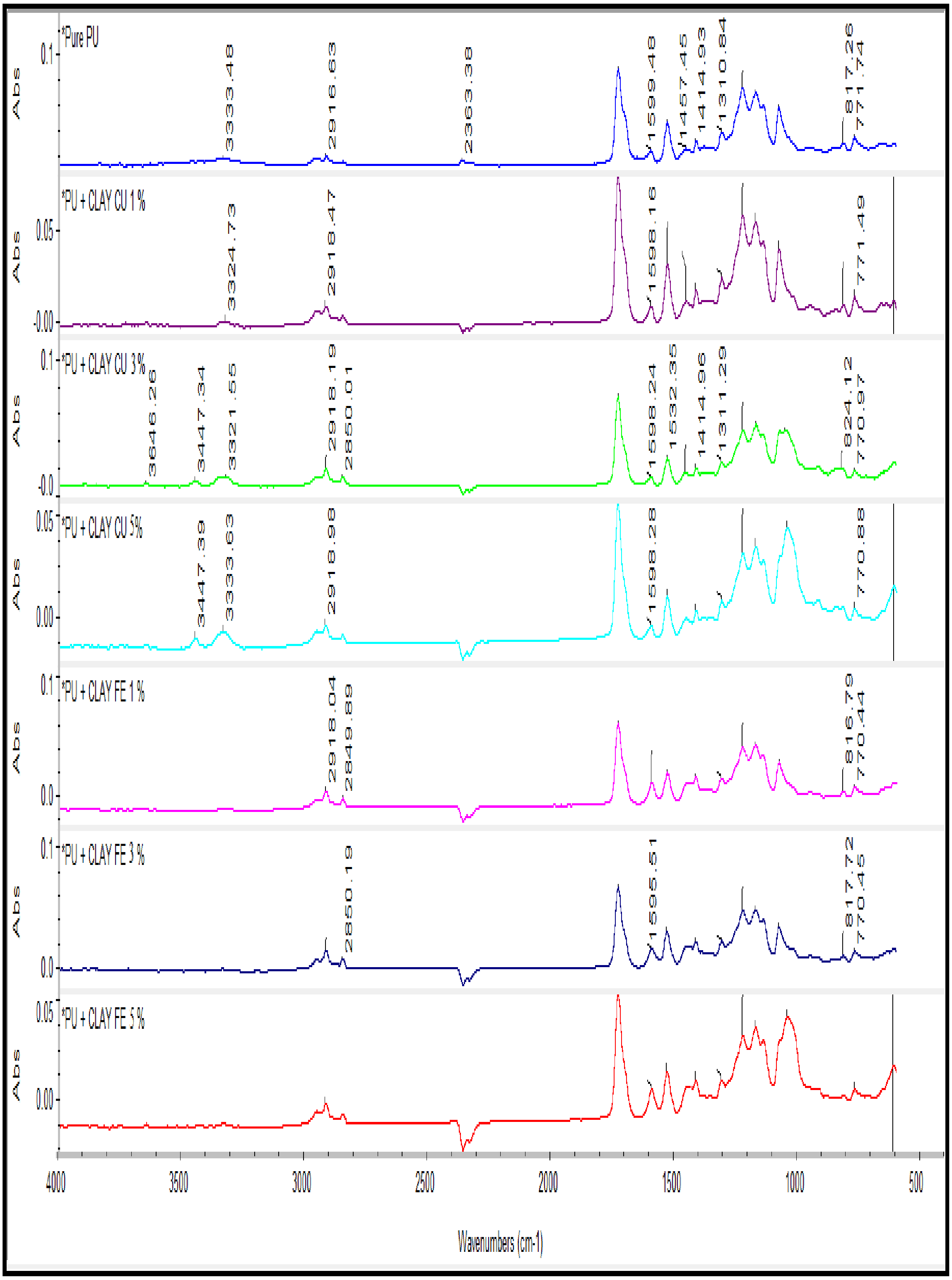
The certificate shall not be reproduced except in full without the written approval of the laboratory.

The above analysis is based on the sample submitted by the customer.

MOHD RAFIE BIN ROSLY
AMIC NO: A/0476/6363/12
PEGAWAI SAINS
MAKMAL BERPUSAT
UNIVERSITI MALAYSIA PAHANG
LEBUHRAYA TUN RAZAK
26300 GAMBANG, KUANTAN
PAHANG DARUL MAKMUR

1

APPENDIX C1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3333.48
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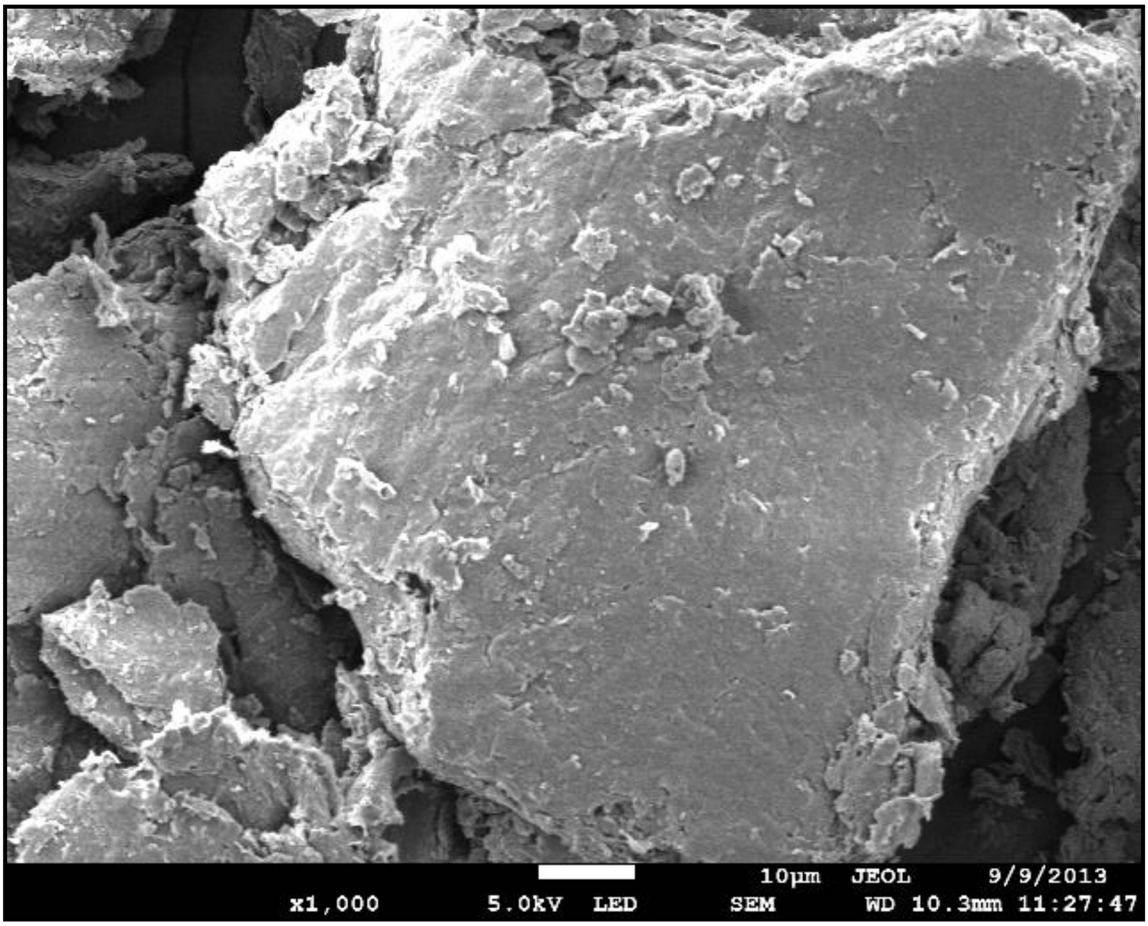
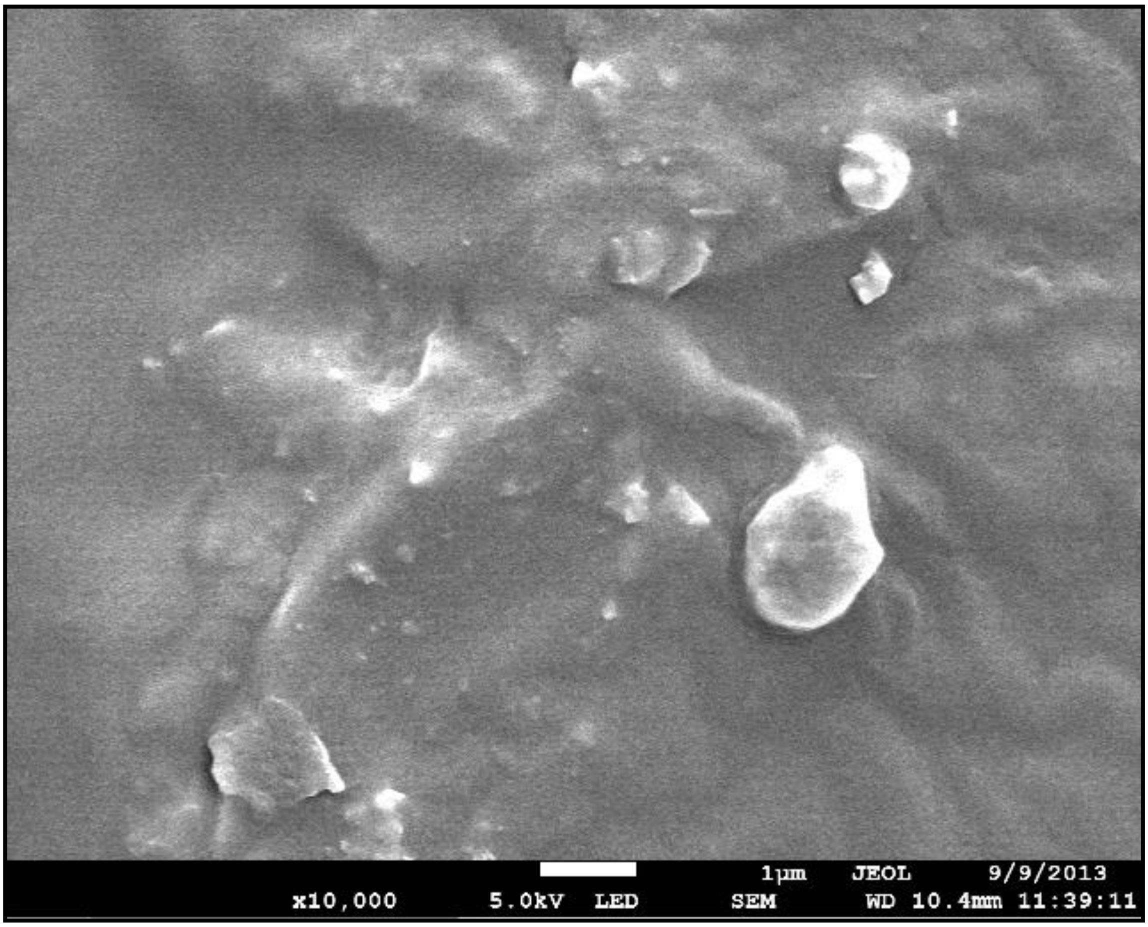
2363.38
1599.48
1457.45
1414.93
1310.84
817.26
771.74
Abs
0.05
-0.00
*PU + CLAY CU 1 %
3324.73
2918.47
1598.16
771.49
Abs
0.1
-0.0
*PU + CLAY CU 3%
3646.26
3447.34
3321.55
2918.19
2850.01
1598.24
1532.35
1414.96
1311.29
824.12
770.97
Abs
0.05
0.00
*PU + CLAY CU 5%
3447.39
3333.63
2918.98
1598.28
770.88
Abs
0.1
0.0
*PU + CLAY FE 1 %
2918.04
2849.89
816.79
770.44
Abs
0.1
0.0
*PU + CLAY FE 3 %
2850.19
1595.51
817.72
770.45
Abs
0.05
0.00
*PU + CLAY FE 5 %
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

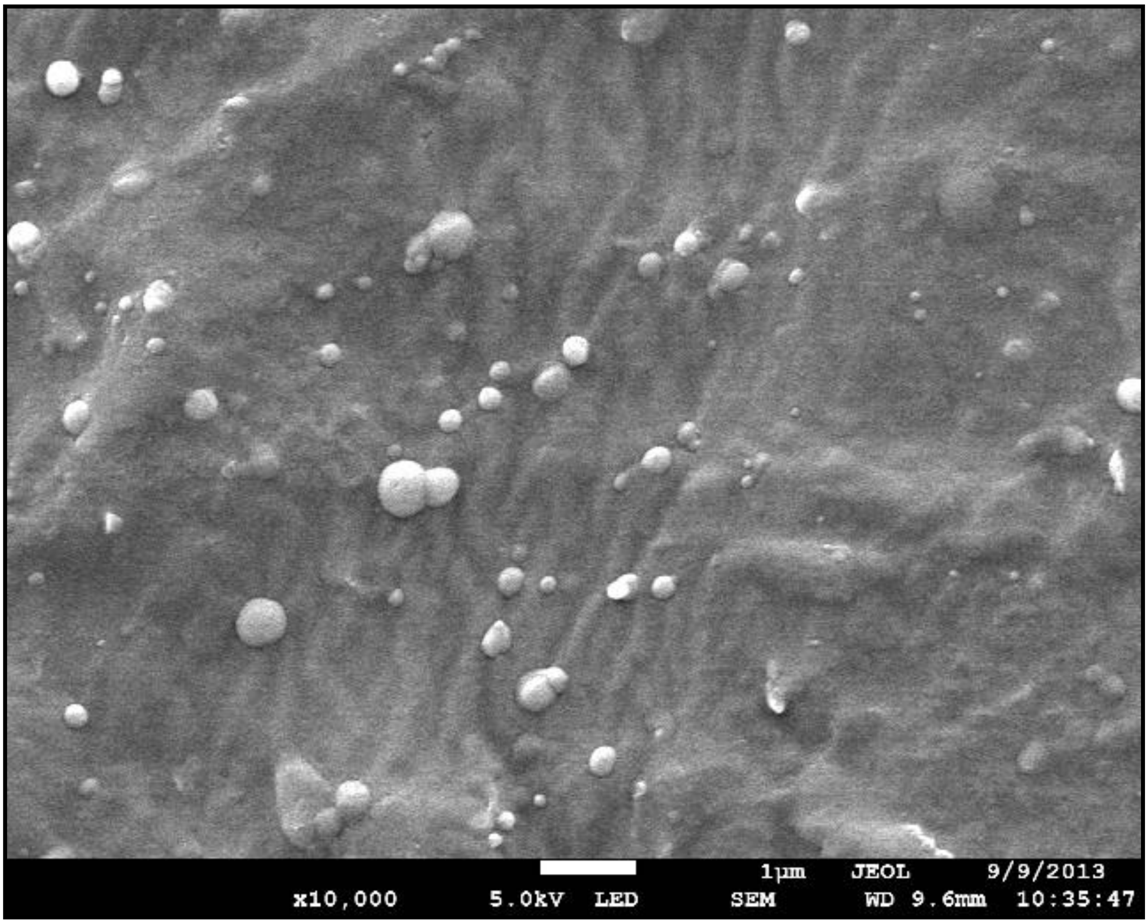
APPENDIX D1



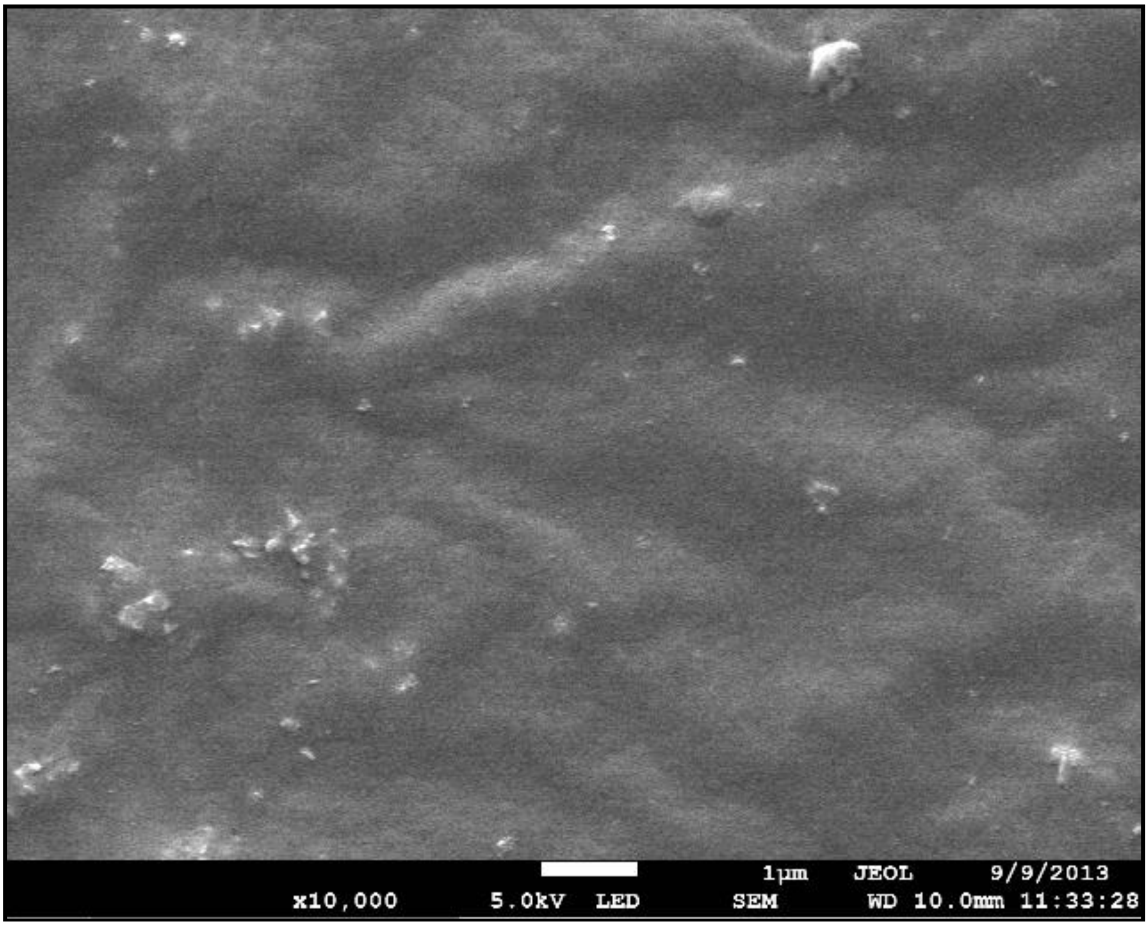
APPENDIX D2



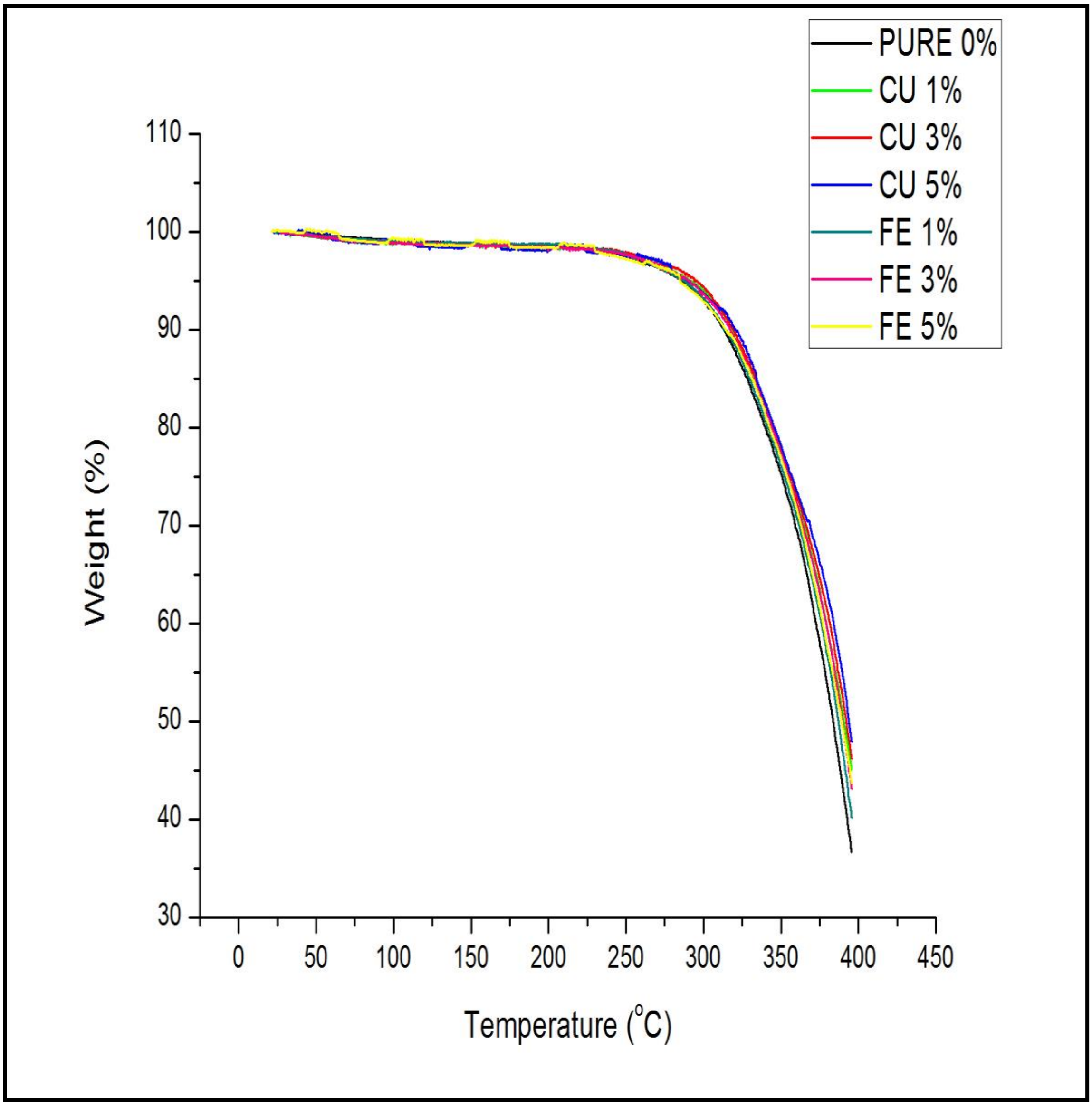
APPENDIX D3



APPENDIX D4



APPENDIX E1


PURE 0%
CU 1%
CU 3%
CU 5%
FE 1%
FE 3%
FE 5%
Weight (%)
110
100
90
80
70
60
50
40
30
0
50
100
150
200
250
300
350
400
450
Temperature (°C)