CHPTER ONE

INTRODUCTION

CHAPTER ONE

1-Introduction

1-1 Background

Natural rubber (NR) is an significant organic material used in a wide variety of engineering applications. Natural rubber is a high molecular weight polymer of isoprene, C_5H_8 [1,2] .

The expression enhancement in tensile properties or strengthening refers to an improvement in end use performance of the rubber compound connected with an increase in modulus and in the so called end properties counting tensile strength and elongation at break [3] .

Most polymer in thermodynamically incompatible gives reduced tensile properties . However, modified fillers are incorporated in order to transform certain properties to a suitable level. Clay is one of the most widely used fillers for rubber . Clay is an inexpensive natural mineral and has been an important part of the rubber industry , where it is used as economical filler to modify processing and performance of natural and synthetic rubbers [4,5] . Montmorillonite clay (MMT) has attracted a lot of attention due to it's features such as high cation exchange capacity, swelling ability and the high platelet aspect ratio. Therefore , it represents the most commonly used non-black filler in polymers and rubber [6-8] . MMT is considered an economical filler to modify processing and performance of natural and synthetic rubbers, it has been well known that particle size, structure and surface characteristics of reinforcing materials are the three factors that influence and help decide their reinforcing ability, and of these factors particle size of the filler has the most important influence [9-11].

However, it’s reinforcing ability is poor because it has a large particle size and low surface activity [12]. MMT is hydrophilic (organophobic) in nature because it contains inorganic cations on the basal planar. So, the clay particles can only be dispersed on the micro-scale in the polymer matrix even though the clay is comprised of silicate layers. Modification of MMT is required to improve it’s reinforcing ability. Arecent way of enhancing this ability is by changing MMT from hydrophilic to organophilic material via ion exchange of the clay interlayer cations with organic cations, such as alkylamidioumion or alkyl- ammonium to produce organoclay[13,14]. Mixed natural rubber (NR) with organoclay modified by dodecyl ammoniuom chloride (DDA) or octadecyl amine ammonium chloride (ODA) synthesized from petroleum oil or fatty hydrazide (FH) synthesized from vegetable oil forming natural rubber nanocomposites have good engineering properties oil , this process leads to an expansion in the basal spacing of the clay layers [15,17] .

The incorporation of organoclay in the polymers and rubber can offer an attractive method to create nanocomposites. The enhancement in thermal stability &tensile properties can be achieved by the addition of 1–5 phr of organoclays in comparison to the neat rubber [18, 19] .

In this study, fatty amides (FAs) synthesized from vegetable oil were used for modification of the MMT. The presence of long-chain fatty acids (mainly 16 and 18 carbon (C) atoms) in FAs containing Oxygen (O) and Nitrogen (N)donor sets suggests they should be very useful as surfactants for clay modification [20, 21] . The use of FAs will reduce the dependence on petroleum-based surfactants. Modified MMT was used to prepare new rubber/clay nanocomposite, and comparative results of dodecyl ammonium chloride (DDA) petroleum based surfactants for clay modification [22] .

1-2 Justification of the Study

Montmorillonite is naturally hydrophilic, this makes it poorly suite to mixing and interacting with natural rubber or polypropylene matrices. Moreover, the stacks of clay platelets are held tightly together by electrostatic forces. Counter ions are attracted to the net negative charge within the clay platelets that are held tightly together. For these reasons, the clay must be treated before it can be used to produce a nano-composite. After all, these stacks of the clay platelets are much larger than one nanometer in every dimension. Making a composite out of untreated clay would not be a very effective use of material, because the clay would be stuck inside, unable to interact with the polymer matrix .

A popular and relatively easy method of modifying the clay surfaces, making it more compatible with an organic matrix, is cation exchange. The cations are not strongly bound to the clay surface so the small molecule cations can replace the cations present on the clay.

The role of a compatibilizing agent such as alkylammonium ions in the organoclay is to lower the surface energy of the inorganic host and improve it’s wetting characteristics with the polymer. In this study, organically modified montmorillonite was prepared for the first time by using fatty amides as one of organic compounds to alter the surface of the dispersed clay. The organic cation are intercalated into the clay interlayer through an ion exchange reaction. The method employed offers several advantages such as renewable and abundant of raw materials, simple reaction procedure, mild reaction condition, environmentally friendly process, and high yield of the product. The use of FAs, which can be synthesized from palm oil , reduces the dependent on petroleum based surfactants.

1-3 Objectives of the Study

This study aims to produce new nanocomposites (nano-NR) having higher enhanced thermal and tensile properties, this introduced by the steps below respectively :

1-To prepare modified clay (FAs- MMT) from Na -MMT and fatty amides (FAs) synthesized from palm oil.

2-To characterize FAs-MMT by X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

3-To compare FAs-MMT with unmodified clay (Na- MMT).

4-To prepare NR /FAs-MMT from NR with FAs-MMT.

5-To characterize NR /FAs-MMT using XRD, TGA ,transmission electron microscopy (TEM) and tensile properties measurements.

6- To compare NR /FAs-MMT nano-NR with NR/Na-MMT micro-NR.

7-Compartive results of different surfactants FAs-MMT and DDA-MMT for clay modification .

CHAPTER TWO

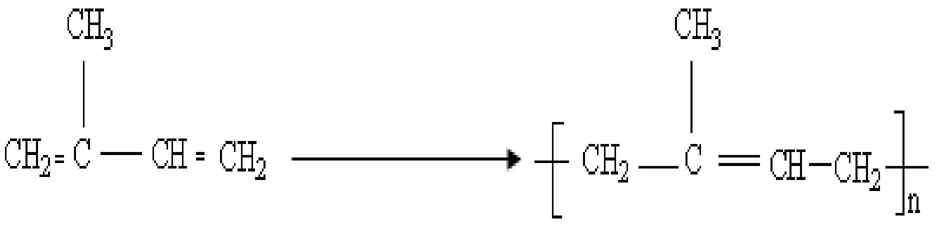
LITERAURE REVIEW

CHAPTER TWO

2- LITERATURE REVIEW

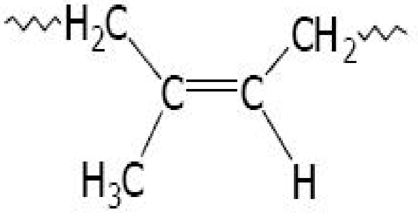
2-1 Natural rubber

Today more than 80% of the total world production of natural rubber comes from southeast Asia. Malaysia is the largest producer, followed by Indonesia. Thailand accounts for much of the remainder in this area [23]. Rubber is collected in the form of latex that exudes from the bark of the tree when it is cut. The average rubber content of latex may range between 30-45%. This fresh latex is not utilized in it's original form due to it's high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate the latex , so that the end product is stable and contains 60 % or more of rubber. Latex concentrates are differentiated by the method of concentration, and type of preservative used. Concentration is achieved by centrifugation(most common), or by evaporation. Currently, about 50% of all latex concentrate is consumed by the dipped goods industry , gloves. Other uses of latex are in carpet backing, thread and adhesives. Natural rubber is a high molecular weight polymer of isoprene , C_5H_8 . The repeating unit is = $- CH_2 - C(CH_3) CH – CH_2-$. Hevea rubber, is the major naturally occur in form of 1,4-polyisoprene. This type of rubber contains more than 98% of it’s double bonds are in the cis configuration which is essential for elasticity in polyisoprene. Over 90% of all cis 1,4-polyisoprene used industrially is natural Hevea rubber [1]. 1,4 polymerization of the conjugated diene system of isoprene leads to a polymer structure with a repeating alkene double bond in the polymer chain (I).



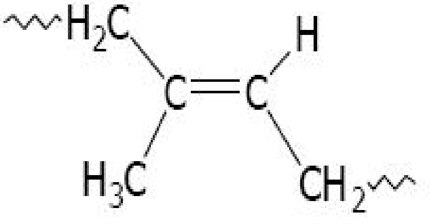
$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CH{=}CH_2 \longrightarrow \left[CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2 \right]_n \qquad (I)$$

The double bond in each repeating unit in the polymer chain is a site of stereo isomerism since it can have either a cis or a trans configuration. The polymer chain segments on each carbon atom of the double are located on the same sides of the double bond in the cis configuration (II) and on the opposite sides in the trans configuration (III).



Cis

(II)



Trans

(III)

Stereo isomerism in 1,4-polyisoprene results in significant differences in the properties of the cis and trans polymers. The trans isomer has a higher molecular symmetry crystallizes to a greater extent and therefore has higher melting point (T_m) and glass transition point (T_g) values. Cis- 1,4-polyisoprene has very low crystallinity, low T_m and T_g values, and is an excellent elastomer over a temperature range. Trans-1,4-polyisoprene is a much harder with a much less rubbery polymer since it has relatively high T_m and T_g values and a significant

crystallinity. It is less an elastomer and more like a thermoplastic. 1,4-polyisoprene is found in nature in both the cis and trans forms [24,25] .

2-2 Clay mineral fillers

Clays represent the largest volume non-black filler used in rubber. They are second to carbon black in this respect. Clay minerals are widely used in rubber because of their cost efficiency in terms of providing beneficial reinforcing and processing properties at a modest cost. The main clay mineral of importance is kaolinite and the derivative produced by chemical treatment and heating .

Clay is classified as hard clay (smaller particulate clay) if it reinforces rubber and also imparts high modulus, tensile strength, and resistance to scratch.

Clay is considered soft if it produced compound with lower physical properties. Several profitable clays have been treated with silane coupling agents to develop their performance in rubber. Since the silane coupling agent provides a means to bond the clay particles to the rubber, increased modulus and tensile strength are obtained.

Clay can be form ulated to rather high loadings in most elastomers. The main factor to consider in adding clay to most form ulations is it’s reduction of cure rate. This decrease will require the addition of an activator and increase in accelerator system [26,27].

Obtain from above a minerals to have sum property:

-Naturally occurring.

-Inorganic.

-Having known chemical compositions.

-Have definite physical properties.

-They are usually crystalline.

Minerals are classified based on chemical composition and crystal structure. This structure depend on sizes and charges on ions, most common mineral group is the silicates. All silicate minerals contain silicon and oxygen :

Mafic silicate minerals contain iron or magnesium and are dark in color .

Felsic silicates don't contain magnesium or iron , and are light in color, (Figure 2.1) Clarify Mafic and Felsic silicates.

Figure 2.1 a- Clarify Mafic Silicate b- Felsic Silicate [28,29] .

The origin clay minerals consist of rocks and water produces clays, either at or near the surface of the earth.

Rock +Water → Clay

For example :

The CO_2 gas can dissolve in water and form carbonic acid, which will become hydrogen ions and bicarbonate ions, and make water slightly acidic.

$CO_2+H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$

The acidic water will react with the rock surfaces and tend to dissolve the K ion and silica from the feldspar. Finally, the feldspar is transformed into kaolinite.

Feldspar + hydrogen ions+water → clay (kaolinite) + cations, dissolved silica

$2KAlSi_3O_8+2H$ ion + $H_2O \rightarrow Al_2Si_2O_5(OH)_4$ + 2K ion + $4SiO_2$

Note that the hydrogen ion displaces the cations. The alternation of feldspar into kaolinite is very common in the decomposed granite [29,30] .

2-2-1 Clay minerals are made of two distinct structural units :

1) Silicon Tetrahedron : Simplicity , let’s represent silica (Si)

2) Aluminum Octahedron : Simplicity , let’s represent alumina(Al), (Figure 2.2) clarify clay minerals units .

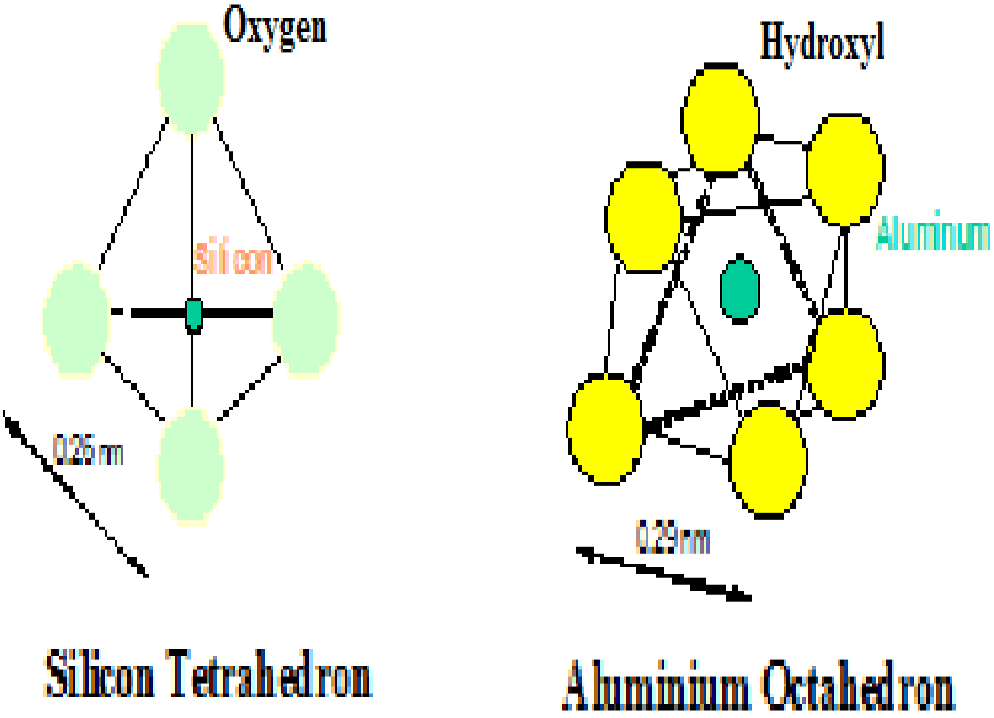


Figure 2.2 Clarify Silicon Tetrahedron & Aluminum Octahedron unit [28,29] .

2-2-2 Clay minerals are made of two distinct structural sheets

1) Tetrahedral Sheet: This sheet represent several tetrahedrons units joined together, (Figure 2.3) clarify this clay mineral tetrahedral sheet.

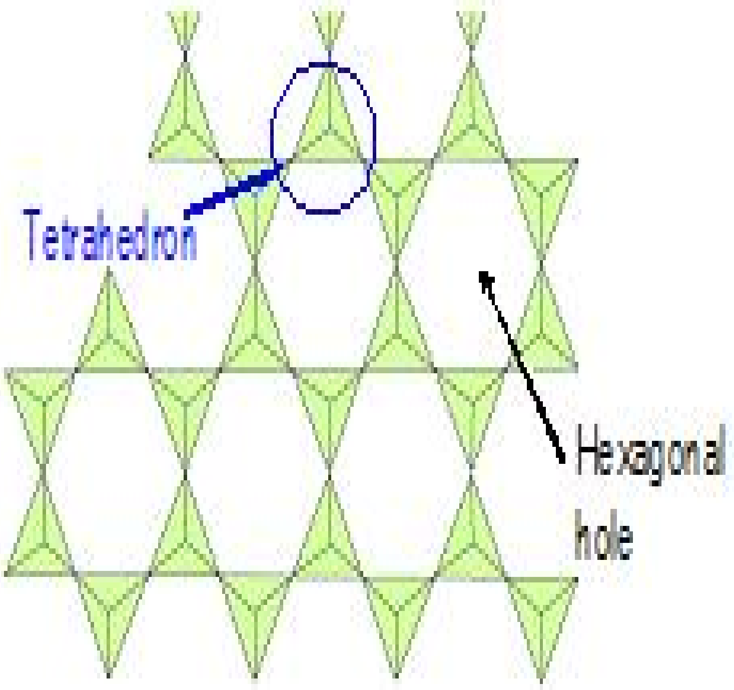


Figure 2.3 Clarify Tetrahedral sheet [29] .

2) Octahedral sheet : This sheet represent several octahedrons units joined together , (Figure 2.4) clarify this clay mineral Octahedral sheet.

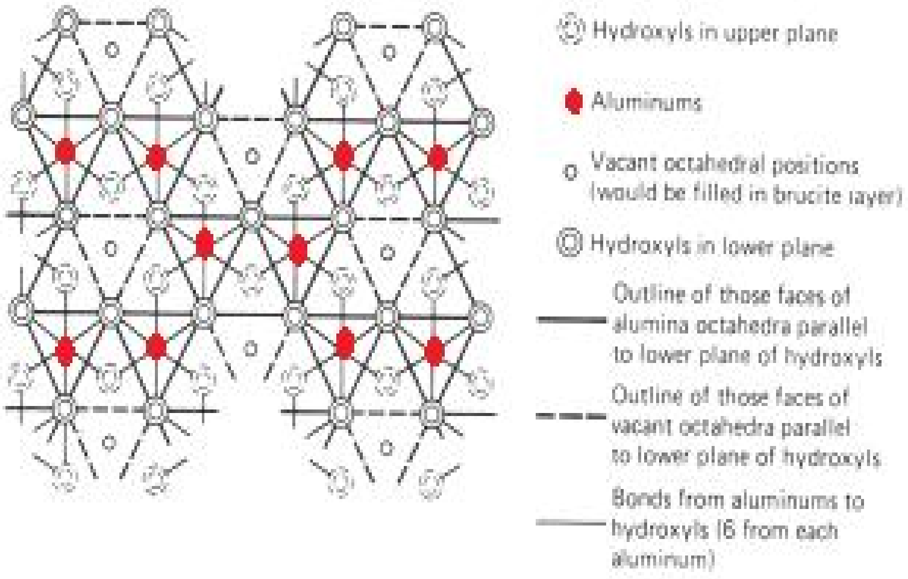


Figure 2.4 Clarify Octahedral sheet [27,30] .

2-3 Clay mineral fillers primary characteristics

As before noted the reinforcing ability of filler is influenced by three primary characteristics: particle size, structure and surface activity (polymer–filler bonding).

2-3-1 Particle size

Development in the physical properties is directly related to filler particle size. The increase of modulus and tensile strength is very much dependent on the particle size of the filler, smaller particulate fillers imparting greater strengthening to the rubber compound than the common ones. Since particle size is directly related to the reciprocal of surface area per gram of filler, it is the increase in surface area that is in contact with the rubber phase which probably leads to the increase in strengthening. Reducing particle size also simply results in a greater influence of polymer-filler contact.

In adding up to average particle size, the particle-size distribution also has an important effect on reinforcement. Particulate fillers with a broad particle-size distribution have better packing in the rubber matrix, which results in a lower viscosity than that provided by an equal volume of filler with a narrow particle-size distribution. Another important concern in strengthening is the presence of large particles or agglomerates in the rubber. These agglomerates not only reduce the contact between filler and matrix but function as failure initiation sites which would lead to premature breakdown of materials [24,31] .

2-3-2 Particle Structure

In addition to the surface area, the shape of the filler particle is an important factor that affects the performance of a rubber compound. Inorganic and mineral fillers posse's significant differences in particle geometry, depending on the crystal form of the mineral. The minimum anisometry is found with materials that form crystals with about equal dimension in the three directions, i.e. isometric particles. More an isometric are particles in which one dimension is much smaller than the two others, i.e. platelets. The most isometric particles which have two dimensions much smaller than the third, so that they are rod–shaped. In compounds containing fillers with identical surface area and chemical nature but different shape, modulus increases with increasing anisomery [24,32]. Particles with a high aspect ratio, such as platelets or fibrous particles have a higher surface-to volume ratio, which results in higher strengthening of the rubber compound . The greatest rigidity is also provided by rod-shaped or plate-like particles, which can line up parallel to one another during processing, compared to spherical particles of similar diameter. Particle shape has a more pronounced effect on processing behavior than on strengthening and provides important benefits in this area. It can also considerably increase modulus due to occlusion or shielding of some of the rubber phase in highly structured fillers such as structural aggregates of carbon black or silica [24,33] .

2-3-3 Surface activity

The particle size of the filler as discussed earlier may be considered as a physical contribution to strengthening, while filler surface activity provides the chemical payment. The ability of the filler to react with the polymer results in bonding, which increases strength significantly. In the absence of strong coupling bonds, the polymer is physically absorbed on the surface of the filler, resulting in a reduced mobility of the rubber molecules near the surface of the filler. Polymer-filler bonding, particularly in the case of carbon black, develops through active sites on the filler surface resulting in bound rubber attached to the filler surface.

The effect of these surface interactions has been established by comparing the effect of using carbon black before and after graphitization .

Through this treatment the activity of the sites is lost and the amount of bound rubber (rubber inextricable from the unvulcanized mix.) drops radically. The disappearance of active sites for physical absorption has the most profound effect on the mechanical properties of the compound made with this black. Bound rubber is regarded as the result of rubber to filler interactions which can be considered as a measure of the surface activity of the black or white filler and therefore, is reflected in the rubber properties related to surface activity such as modulus, abrasion and tear resistance [24,34].

Adhesion between polymer and filler may also be induced by a coupling agent, which participates in the vulcanization reaction to form polymer-filler cross-links. This mechanism of increasing strength is well established with both mineral fillers and carbon blacks [35]. Both mechanisms lead to the formation of high modulus compounds, which is very clear indicator that polymer-filler bonding has taken place. The increased modulus occurs as a direct result of attachment of the rubber to the filler, which has the effect of reducing polymer mobility. Organo silane coupling agents have been successfully utilized to further increase the physical properties of a number of non-black fillers including calcium silicate, clay, mica, silica, and talc [24,26] .

2-4 Types clay minerals fillers

Different combinations of tetrahedral and octahedral sheets form , this types it's :

2-4-1 1:1 Clay mineral e.g. Kaolinite

2-4-2 2:1 Clay mineral e.g. Montmorillonite

2-4-1 1:1 Clay minerals (e.g . Kaolinite)

Reviously,consider Kaolinite very impartment from this type in industry 1:1 clay minerals contain tetrahedral (Silica) and octahedral (Alumina) sheets , chemical structure to Kaolinite ($Si_2Al_2O_5(OH)_4$), (Figures 2. 5 & 2.6) explain layer unit and layer structure sheet in kaolinite type respectively.

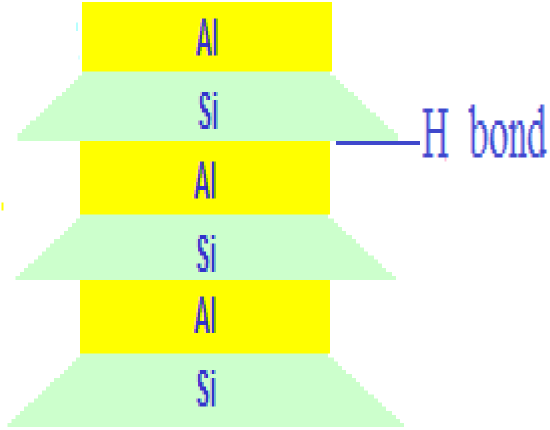


Figure 2.5 Layers unit of Kaolinite

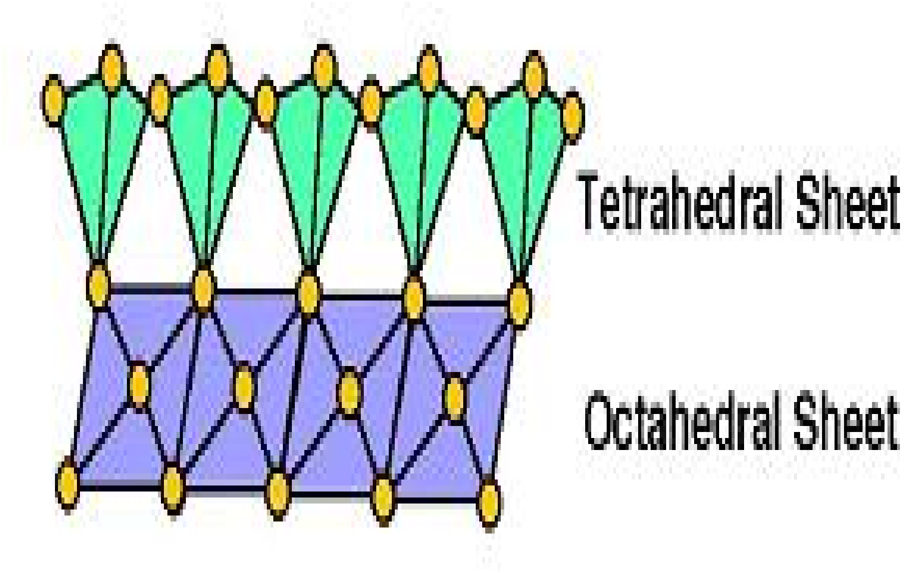


Figure 2.6 Layers structure sheet of Kaolinite [24,30] .

Kaolinite depending on particle size, it can be used as a very little size reinforcing filler (hard clay) or a non-reinforcing filler (soft clay) in which they produce harder and softer rubber compounds, respectively. Application includes chemical liners, bicycle tires, conveyor belts, shoe soles, gasket and flooring where good reinforcement, moderate cost, and good process ability are desired. Clays are commonly added to rubber compounds at levels to 150 phr. Pure kaolinite has the idealized chemical composition $Si_2Al_2O_5(OH)_4$. It is a crystalline material with a triclinic form found in microscopic pseudo-hexagonal plates [18]. The inability of kaolinite crystals to show interlayer (intracrystalline) expansion or swelling is indicative of strong interlayer bonding. The forces holding the layers together have been attributed to O-H---O hydrogen bonding, shown in (Figure 2.5) [36] , (Figure 2.6) illustrates the layer structure of kaolinite clay assembled as a 1:1 layer silicate. It's structure can be regarded as a gibbsite $Al(OH)_3$ layer bonded to a siloxane (Si_2O_5) layer. The Si atom in the siloxane layer is tetrahedrally bound to four oxygen atoms and the Al atom in the gibbsite grouping completes its favored octahedral environment by coordinating to two oxygen atoms in the siloxane group. Therefore, one face of this structure is comprised of oxygen's and hydroxyl and the other hydroxyl groups. These will interact through hydrogen bonding giving a layered kaolinite crystals, which has a pseudo-hexagonal platy shape. These thin, hexagonal plates have aspect ratios in the range of 5:1 to 50:1, which are dependent on particle size. In the natural rubber industry, kaolinite clays are commonly incorporated in natural rubber compounds. They are added dry to a well-stabilized natural rubber or dispersed in water with the aid of small amounts of dispersing agents.

The products at those levels are very hard and show virtually no rubbery characteristics. In low proportion (up to 30 parts per 100 parts of rubber), soft vulcanizates are obtained which have an increased tension set . It has been argued that the reinforcing effect of inorganic fillers in dry rubber is not analogous to the reinforcement observed when the same fillers are incorporated in natural rubber. Therefore carbon black and fine-particle kaolinite clays do not enhance the tensile strength and tear strength of vulcanized natural rubber deposits as they do for products made from dry rubber. This difference is believed to be associated with the absence of mastication, step in natural rubber products. Mastication is a rigorous mechanical process that can cleave polymer molecules so that polymeric free radicals are produced. These radicals are able to interact with reactive sites on the surface of filler particles and hence improve adhesion, and increase strength considerably.

1:1 Type clay minerals to have other type e.g. Halloysite this type from kaolinite family , but this type hydrated and tubular structure, chemical structure to halloysite : $Si_2Al_2O_5(OH)_4.2H_2O$ [37] .

2-4-2 2:1 Clay minerals e.g. Montmorillonite

The montmorillonte can modify and additive to the natural rubber by certain percentages we get the nanocomposites being have swells on contact with water and high affinity to water and control viscosity or impart theory to verity of liquid polymers based on unsaturated polyesters(polyvinyl chloride) ,pvc .

The montmorillonite group comprises a number of clay minerals within the dioctahedral smectite group, montmorillonite to have chemical stricture: $Al_2Si_4O_{10}(OH)_4.nH_2O$.

The startling property of montmorillonite is it's ability to expand and contract it's interlayer structure while maintaining two-dimensional crystallographic integrity. By this means, a large active surface area (700-800 m^2 /g) is potentially exposed, allowing an enormous range of guest molecules to be intercalated [36]. Expansion takes place as water or some polar organic compound, such as ethylene glycol, enters the interlayer space. When montmorillonite expands, the interlayer cation may be replaced by other cations, therefore the cation-exchange capacities (CEC) of montmorillonite groups are high compared to other clay minerals that do not expand. Montmorillonite belongs to the 2:1 type phyllosilicates, or layer silicates [38].

All layer silicates are basically composed of two modular units, a sheet of corner-linked silica tetrahedra and a sheet of edge-linked octahedra. These are joined together in varying proportions and stacked on top of each other.

The 2:1 clay minerals can be assembled is shown in(Figure 2.7). Two tetrahedral sheets to one octahedral sheet is formed by inverting a tetrahedral sheet, bring it down on top of the 1:1 layer (the lower plane of an octahedral sheet and a tetrahedral sheet) and replacing two third of the hydroxyls with apical oxygen ions.

This assemblage makes a tetrahedral- octahedral- tetrahedral (TOT) sandwich. Montmorillonite has the origin of it's layer charge primarily in the octahedral sheet. Substitution by ions of lesser charge, notably Si^{4+} by Al^{3+} in tetrahedral positions and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral positions, results in negative charges on the interlayer space which are balanced by interlayer cations, commonly Na^{+}, Ca^{2+} and Mg^{2+} but a wide range of other cations, including organic ions, can be introduced by exchanged reactions , (Figure 2.7) shows the idealized layer of montmorillonite and the occupancy of the interlayer space by exchange able cations as monovalent ions. Consider Bentonite and Illite from same montmorillonite (MMT) family , but this type of clay note use with natural rubber because illite contain K ions between two sheet of Si and Bentonite used as drilling mud in slurry trench walls stopping leaks .

Figure 2.7 Layers unit structure of Montmorillonite [35]

2-5 Structure and Properties of Layered Silicates for 2:1 phyllosilicates e.g. MMT

Clay minerals are hydrous aluminum silicates which are classified either as phyllosilicates, or as layer silicates. The silicates commonly used in nanocomposites belong to the structural family of 2:1 phyllosilicates. All layer silicates can be imagined as constructed from two modular units [39], a sheet of corner-linked tetrahedra and a sheet of edges hared octahedra. The 2:1 type layer structure is made up of two tetrahedral sheets of silica fused to an octahedral sheet of either aluminum (gibbsite) or magnesium (brucite) hydroxide as illustrated in (Figure2**.**8). The layer thickness is approximately 1 nm and the lateral dimension of these layers may vary from 300 ºA to several microns and even larger depending on the particular silicate.

These layers organize themselves to form stacks with a regular electrostatic and van der Waals bonded gap between them is called the interlayer or gallery. Various layer silicates are classified either as dioctahedral or trioctahedral. In clay minerals, the smallest structural unit contains three octahedral sites. If all three octahedral sites are occupied, i.e. have octahedral cations at their centers, the sheet is classified as trioctahedral. If only two octahedral sites are occupied and the third octahedron is vacant, the sheet is classified as dioctahedral. The

2:1 type layer silicates have various cation substitutions in both the tetrahedral and octahedral positions. Substitutions within the layers by ions of lesser charge, notably Si^{4+} by Al^{3+} in tetrahedral positions and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral positions, result in negative charges on the layers. These are normally interlayer counterbalanced by alkali or alkali earth cations situated in the interlayer space. In pristine layer silicates the interlayer cations are usually hydrated Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} ions, but a wide range of other cations, including organic ions, can be introduced by exchange reactions [40].The substitute of inorganic exchange cations in the galleries of the native clay by cationic surfactants such as alkylamidioumion ions is known to help compatibilize the surface chemistry of the clay and the hydrophobic polymer matrix. Montmorillonite, hectorite and saponite are the most commonly used layered silicates. Their structure of 2:1 phyllosilicates is given in (Figure 2.8).

The replacement of inorganic exchange cations in the galleries of the native clay by cationic surfactants such as alkylamidioumion ions is known to help compatibilize the surface chemistry of the clay and the hydrophobic polymer matrix. Montmorillonite, hectorite and saponite are the most commonly used layered silicates. Their structure is given in (Figure 2.8) and their chemical formula $Al_2Si_4O_{10}(OH)_4.nH_2O$.

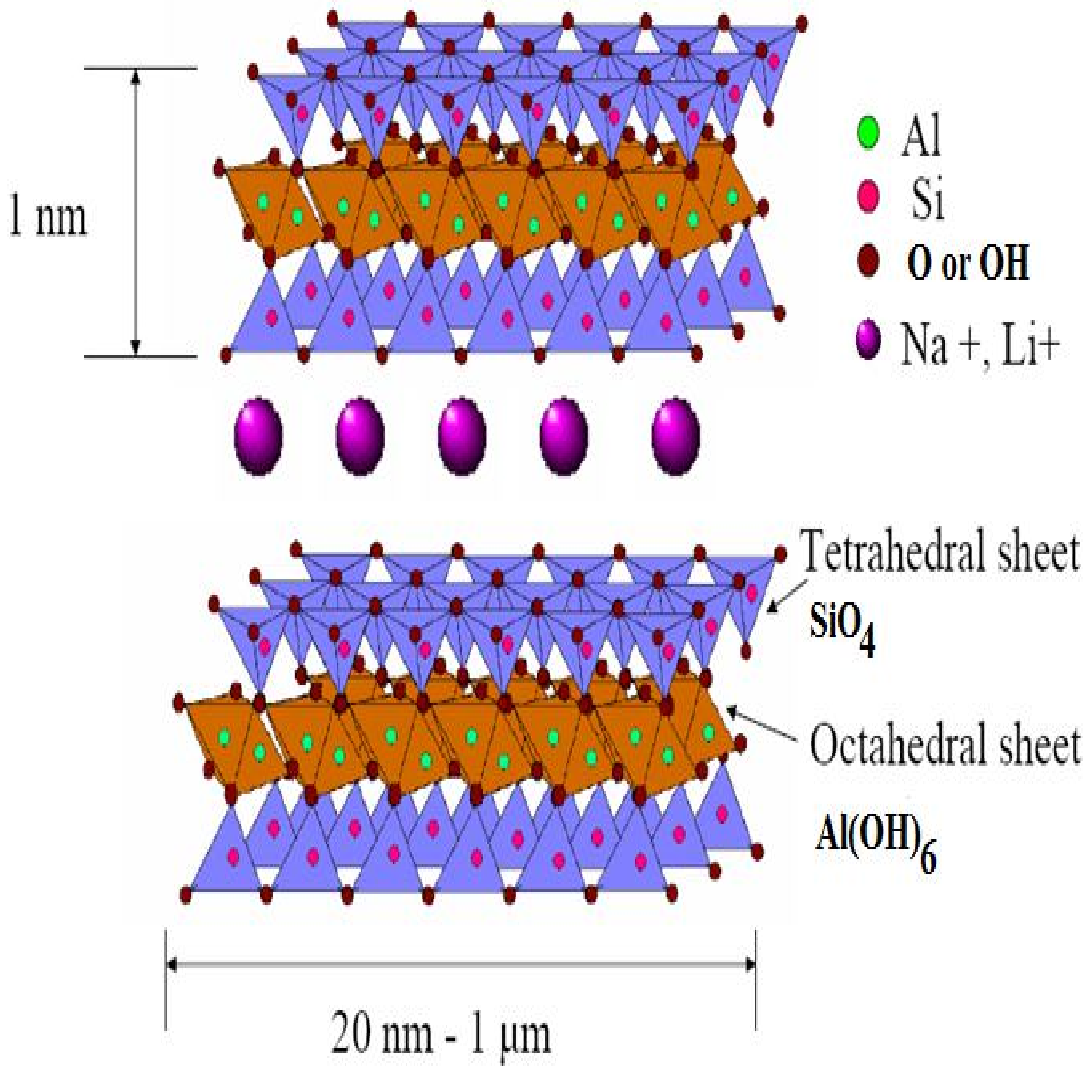


Figure 2.8 Structure of 2:1 phyllosilicates [24,41]

A number of factors are of interest in filler composite system using clay minerals :

- Low loading levels.
- Transparency.
- Incorporation flexibility.
- Safety.
- Synergies with other additives.
- Low cost.
- Nanocomposites typically contain 2-10% loadings on a weight basis, yet Property improvements can equal and may exceed conventional composites containing 20 – 35 % mineral or glass . Machine wear is reduced and process ability is increased .
- Nanoclay particles have a dimension below the visible light wavelength
- The particles are tough. They can withstand solvents, polymerization temperatures and compounding shear. They can be processed without concern about degradation.
- Clays are generally innocuous materials which have been used safely in end user products for decades.
- A wealth of experience demonstrates that they act synergistically with other minerals [27,29] .

2-6 Structure and Properties of Organocaly (Modified Layered Silicate)

The physical mixture of a polymer and layered silicate may not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation into discrete phases takes place. In immiscible systems, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the layered silicate in polymer layered silicate (PLS) nanocomposites lead to the organic and inorganic phases being dispersed at the nanometer level.

As a result, nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers. Pristine layered silicates usually contain hydrated Na^+ or K^+ ion [38,42]. Obviously, in this pristine state, layered silicates are only miscible with hydrophilic polymers, such as polyethylene oxide (PEO) or polyvinyl alcohol (PVA) [43]. To render layered silicates miscible with other polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one, making the intercalation of many engineering polymers possible . Generally, this can be done by ion exchange reactions with cationic surfactants including primary , secondary ,tertiary & quaternary alkylammonium, alkylamidioumion or alkylphosphonium cations. cationic surfactants in the organosilicates lower the surface energy of the inorganic host and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing. Additionally, the cationic surfactants can provide functional groups that can react with the polymer matrix, or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix [44].

Traditional structural characterization to determine the orientation and arrangement of the alkyl chain was performed using wide angle X-ray diffraction (WAXD). Depending on the packing density, temperature and alkyl chain length; the chains were thought to lay either parallel to the silicate layers forming mono or bilayers, or radiate away from the silicate layers forming mono or bimolecular arrangements (Figure 2.9).

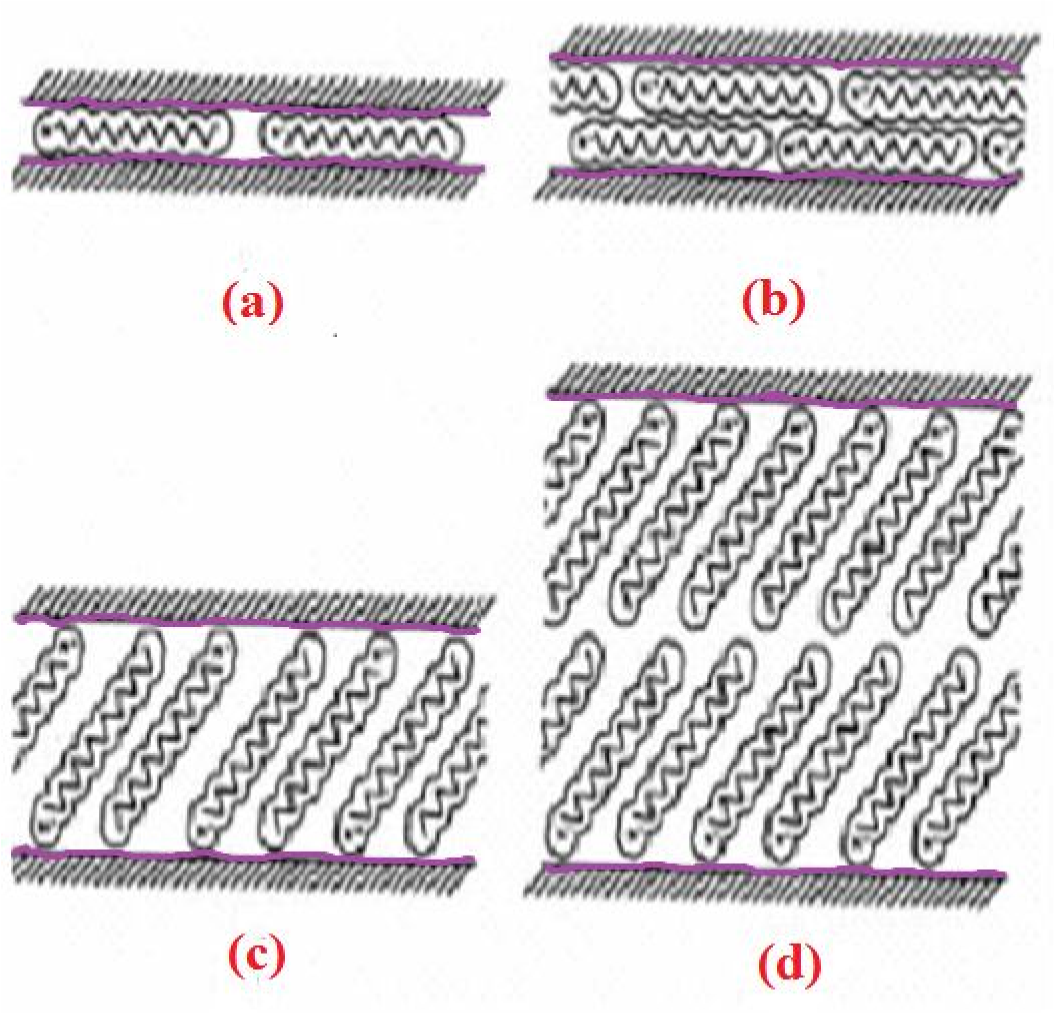


Figure2.9 Alkyl chain aggregation in mica-type Silicates:

(a) lateral monolayer b) Lateral bilayer
(c) paraffin-type monolayer d) Paraffin-type bilayer [25,45].

2-7 Nanocomposites

Layered silicates dispersed as a reinforcing phase is an engineering polymer matrix are emerging as a relatively new form of useful materials .These composites exhibit a change in composition and structure over a nanometer length scale and posses remarkable property enhancements relative to pure polymer. Owing to the nanometer size particles obtained by dispersion, these nanocomposites exhibit superior properties such as mechanical, thermal, optical and physico-chemical properties at a lower level loading compared with either the pure polymer or conventional micron sized composites.Their unique properties stem from a combination of factors: the platelet structure of nanolayer clay, the high aspect ratio (width to thickness) of the platelets with thicknesses on the order of a nanometer and widths or lengths on the order of 500:1 - 2000:1, and the molecular bonds formed between the platelets and the polymer during compounding that may modify polymer properties. It has been demonstrated that the complete dispersion of clay nanolayers in a polymer optimizes the number of available reinforcing elements carrying tremendous surface area of the clay in the platelet and applied load and deflecting cracks [46]. Coupling between the form (750 m^2/g) and polymer molecules that constitute the matrix, facilitates stress transfer to the reinforcement phase, allowing for improvements in tensile and toughness properties. Conventional polymer-clay composites containing aggregated nanolayer tactoids (micron sized particles) ordinarily improve rigidity, but they often sacrifice strength, elongation and toughness. The high aspect ratio characteristic of silicate nanolayers in exfoliated nanocomposites has also been found to greatly reduce gas and water permeability by imposing a tortuous path way that a permeant has to travel in order to path impermeable clay layers. Enhanced barrier characteristics, chemical resistance, reduced solvent uptake and flame retardance of clay-polymer nanocomposites all benefit from the hindered diffusion path way through the nanocomposite [47,48] .

2-8 Nanocomposites structure

Three main types of composites may be obtained when a layered clay is associated with a polymer. These primarily depend on the method of preparation and the nature of components used (layered silicates, organic cation and polymer matrix) [3,47] . When the polymer is unable to intercalate between the silicate layers, a phase separated polymer/ silicate composite is obtained (Figure 2.10a). This conventional composite contains clay tactoids of stacked layers in a coplanar orientation, that are associated in aggregates and agglomerates dispersed as a segregated phase. Their properties stay in the same range as those seen for traditional microcomposites. Beyond this classical family of composites, two types of nanocomposites are possible.

Intercalated structures in which typically more extended polymer chains are pictured as occupying the interlayer space between silicate layers resulting in a well ordered multilayer morphology of alternating polymeric and inorganic layers (Figure 2.10b). When the silicate layers (1nm thick) are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained (Figure2.10c). The structure of polymer layered silicate (PLS) nanocomposites has traditionally been elucidated using x-ray (XRD) and transmission electron microscopy (TEM) . XRD is the most commonly used technique to identify intercalated structures due to the periodic arrangement of the silicate layers both in the pristine and the intercalated states. The repetitive multilayer structure is well preserved in intercalated structures, allowing the interlayer spacing to be determined. Intercalation of polymer chains usually increases the interlayer spacing, in comparison to the spacing of the original silicate, resulting in a shift of the X-ray diffraction (XRD) peak toward lower angles. The diffraction angle is related to the layer spacing through the well known Bragg's relation $n\lambda = 2d\sin\theta$.In the case of exfoliated structures, extensive layer separation associated with delamination of the original silicate structure in the polymer matrix leads to the disappearance of any coherent x-ray scattering from the layers. Loss of coherent scattering may be due to either the presence of an extremely large regular ordered spacing between the layers, too large to be detected in the angular range of XRD normally operated, or the nanocomposite no longer has an ordered layer structure. TEM is therefore used to determine nanocomposite morphology. In addition to these two defined structures, both intercalation and partial exfoliation result in a broadening of the diffraction peak.

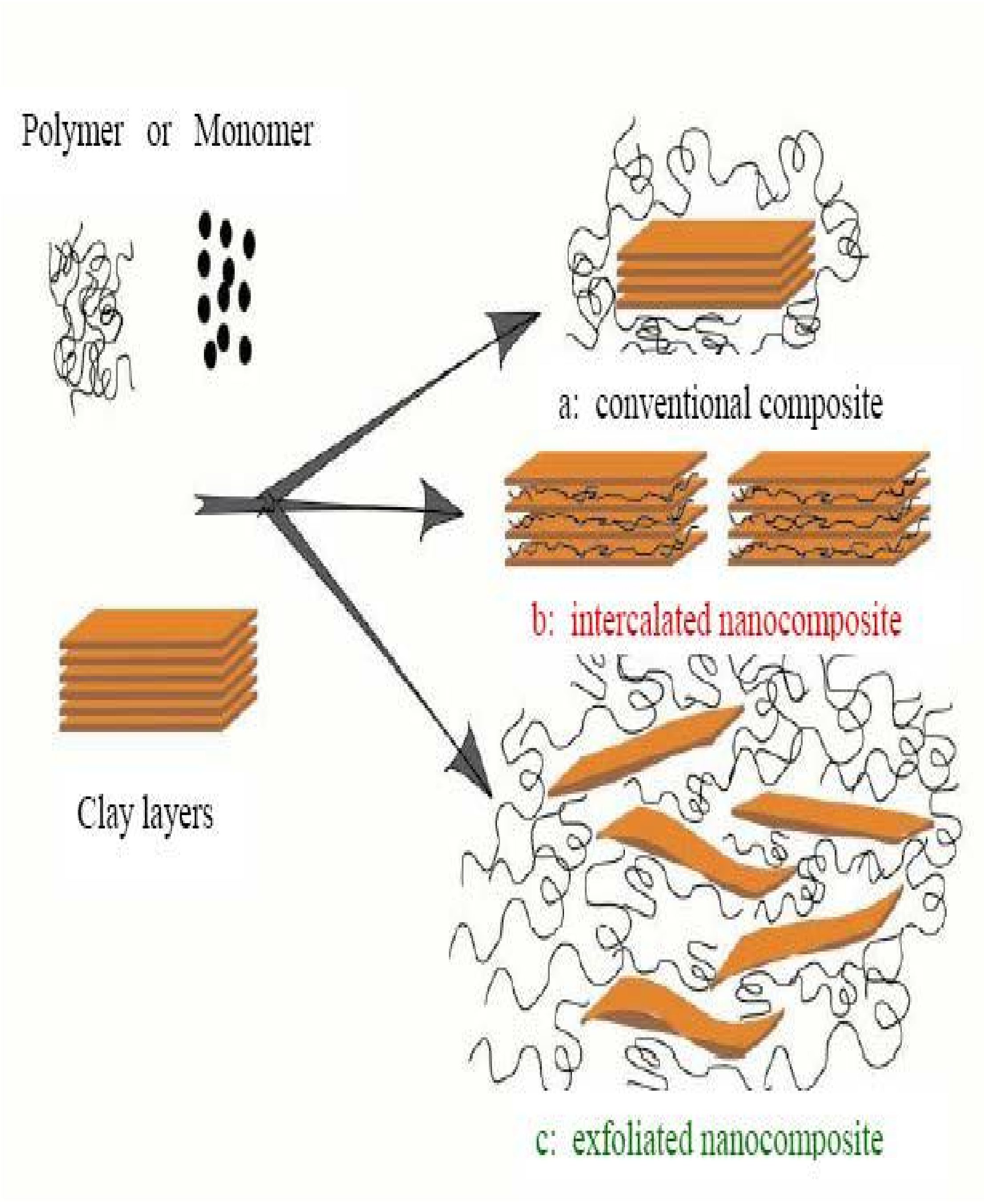


Figure 2.10 Schematic illustration of three types of polymer/clay layers (micro & nano) composites [25,49].

2-9 Effect clay and organoclay on engineering properties in natural rubber

2-9-1 Effect montmorillonite and modified montmorillonite (organoclay) on thermal stability in natural rubber

Most of the thermoanalytical studies reveal new insights into the structure of intercalated clays.Thermogravimetric analysis (TGA) gives information on the montmorillonite structure of the intercalating molecules by the weight loss steps(200 -500 ^{o}C) and organoclay weight loss steps it's higher range . Thermal degradation of montmorillonite shows two steps [40,50]. The first one is before 200 ^{o}C because of the volatilization of water adsorbed on the external surfaces of the montmorillonit and water inside the interlayer space. The second step is in the range from 500 to 1000 ^{o}C due to the loss of hydroxyl groups of the montmorillonite structure [51] .

2-9-2 Effect montmorillonite& modified montmorillonite on tensile properties in natural rubber

Layered silicates are potentially well - suited for use as reinforcing materials . They have chemically stable siloxane surfaces and a high surface area . They also posses high in - plane strength , stiffness , and a high aspect ratio . Moreover, the rich intercalation chemistry of clay silicate can be used to facilitate exfoliation of silicate nanolayers into the polymer network. Layer exfoliation maximizes interfacial contact between the organic and inorganic phases. Tensile (tensile strength , elongation at break and young's modulus) properties have been proved to be greatly improved by the reinforcing effect of silicate nanolayers The tensile properties were measured by using an Instron Universal Testing Machine ,also the tensile properties can be calculated in law methods :

- **Tensile Strength**:

Tensile strength is calculated by dividing the load at break by the original minimum cross sectional area. The result is expressed in megapascals (MPa):

$$\text{tensile strength} = \frac{(\text{Load of break})}{(\text{original width})\,(\text{original thickness})}$$

- **Percent Elongation at break** :

Percent elongation is calculated by diving the elongation at the moment of rupture by the initial gauge length and multiplying by 100 . When gauge marks or extensometers are used to define a specific test section , only this length is used in the calculation , otherwise the distance between the grips is used as the initial gauge length . The result is expressed in percent :

$$\text{Percent elongation} = \frac{(\text{elongation at rupture})*100}{(\text{initial gauge length})}$$

- Young's modulus :

Young's modulus is calculated by drawing a tangent to the initial linear portion of the stress-strain curve , selecting any point on the this tangent , and dividing the tensile stress by the corresponding strain . For purposes of this calculation , the tensile stress shall be calculated by dividing the load by the average original cross sectional of the test specimen . The result is expressed in gigapascals (GPa) [37,52] :

$$\text{Young's modulus} = \frac{(\text{load at point on tangent})/(\text{original width})(\text{original thickness})}{(\text{elongation at point on tangent})/(\text{initial gage length})}$$

CHAPTER THREE

MATERIALS & METHODS

CHAPTER THREE

3-Materials and methods

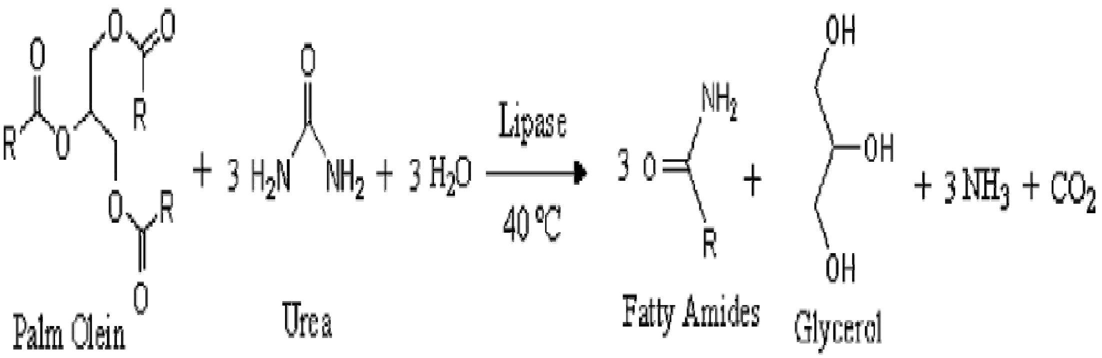
3-1 Materials

Montmorillonite clay (Kunipia F) with a cation exchange capacity (CEC) was obtained from Kunimine , Japan. Palm olein was obtained from Ngo Chew Hong Oils and Fats (NCHOF),Malaysia .The immobilized lipase used was the product from Novo Nordisk, Denmark. Urea, sodium hydroxide, concentrated hydrochloric acid and hexane were purchased through local suppliers from Merck, Germany. Natural rubber (NR) of SMR (CV60) grade was kindly provided by the Malaysian Rubber Board (MRB), Malaysia .

3-1-1 Synthesis of fatty amides (FAs)

The lack of ready-made fatty amides in the laboratory, are prepared from raw materials constituent, using the steps involved from the user reference and be prepared as follows, synthesized by reacting 3.84 g of commercial palm olein in 17 mL of hot hexane as a solvent with 4.20 g of urea and water. The pH was adjusted to 7 by adding of about 5 mL of

0.5 M NaOH. The reaction was carried out in the presence of lipase catalyst in a 100 mL Stopper flask. The mixture was incubated in water shaker (125 rpm) at 40 °C for 36 h. Hot hexane was added to the reaction to dissolve the product. The organic phase was then separated from water phase using a separation funnel. To obtain the solid fatty amides, the hexane fraction was cooled in a refrigerator at 5 °C for 5 h, filtered and then reprecipitated by hexane. The product was then dried in an oven at 50 °C. The preparation reaction is shown in the Scheme below [21] .



R = C12: 0, C14: 0, C16: 0, C16:1, C18: 0, C18: 2, or C18: 3

3-1-2 Preparation of organoclay(modification of Montmorillonite)

Organoclay was prepared with a cationic exchange process where Na^+ in the MMT was exchanged with the alkylamidioumion from FAs synthesized from vegetable oil (palm olein), in an aqueous solution. Sodium montmorillonite (Na- MMT) (4.00 g) was stirred vigorously in 600 mL of hot distilled water for 1 h to form a clay suspension. Subsequently, FAs (4.50 g), which had been dissolved in 400 mL of hot water and concentrated hydrochloric acid (16.00 mL) was added into the clay suspension. After being stirred vigorously for 1 h at 80 °C, the organoclay suspension was filtered and washed with distilled water until no chloride was detected with a 1.0 M silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay (FAs-MMT) was ground until the particle size was less than 100 µm before the preparation of the nanocomoposite (nano-NR).

3-1-3 Preparation of natural rubber/organoclay nanocomposite

The designed amount of NR was prepared by an internal mixer(Haake Polydrive). The NR was first softened for 1 min and mixed with a required amount of the modified clay in the second and third minutes until 12 minutes at 185°C and 50 rpm [53], and the amount of NR and the modified clay used in this study are listed in (Table A2-1) .

3-1-4 Initiating specimens of natural rubber/clay anocomposite

The tensile specimens were prepared as shown in (Figure 3.1)

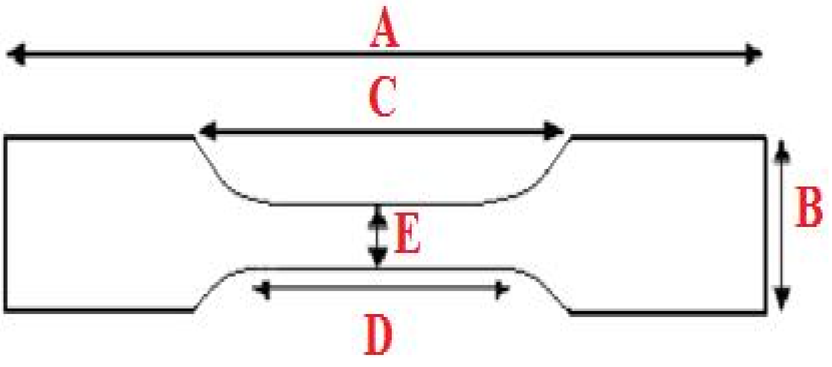


Figure 3.1 Dumbbell dimension diagram for tensile test:

(A) length of test specimen (75 mm)

(B) width of test specimen (12.5 mm)

(C) length (25 mm)

(D) length of bench marker (20 mm)

(E) width of bench marker(4 mm) and thickness (1mm)

The specimens of natural rubber/clay nanocomposites were then moulded in an electrically heated hydraulic press at 130 °C for 10 minutes and a pressure of 150 kg cm^{-2}. At the end of the molding time, the compounds were immediately cooled for 5 minutes to obtain the sheet (1 mm thickness) used in this study [52] .

3-2 Major Techniques of Characterization Methods

3-2-1 X-Ray diffraction (XRD) analysis

X-Ray diffraction study was carried out using Shimadzu diffractometer model 6000,this method is very common techniques to analyze the composition of the materials. X-rays are the electromagnetic radiation, according to quantum theory, which have wave-particle duality. The diffrctogram was scanned in the ranges from 2 to 10° at a scan rate of 1°/min. and their energy ranges from 100eV to 10MeV. X-rays were discovered by German physicist Wilhelm Conrad Rontgen in 1895 [54,55]. Afterwards, the idea that a crystal can be the diffraction grating was proposed by Paul Peter Ewald and Max von Laue. Since the order of magnitude of wavelength is larger than the spacing in crystals, visible light as the diffraction source cannot reflect from crystal. On the contrary, Laue successfully used X-Ray for the diffraction which has the same order of magnitude of wavelength with spacing in crystals. In 1912, William Lawrence Bragg and his father William Henry Bragg formulated Bragg's law $n\lambda=2d\sin\theta$ which is the significant equation to build the relation of diffraction. When the wavelength of radiation is close to the spacing between the atoms, the atoms can be considered as the diffraction grating and have the constructive and destructive interference of the scattering which is shown in (Figure A1- 1) . The incident beam a and b have the same incident angle and travel distance which causes the constructive interference.The incident beam c moves in phase with a and b if the extra travel distance 2dsinθ is equal to the integral number of wavelength , or it results in destructive interference when out of phase [56,57].

The constituents of an X-Ray diffractometer are the source, sample, mono-chromater, detector and output device. In the hot cathode tube, the electrons are emitted from tungsten filament when heated, and travel through the electron field to impinge anode. There are two phenomena that happen when the impingement occurs. One is the inelastic collision when the partial kinetic energy of electron transfers into the continuous spectrum which is also called white radiation. Another is the characteristic spectrum which is caused by the excitation of the inner-shell electron with collision and meanwhile, the outer-shell electron fills the inner-shell and releases energy between the energy levels in X-Ray form. The source of the X-Ray diffractometer has a characteristic radiation, usually using Cu Kα and filtered by nickel as the mono-chromater, the wavelength of which is (λ= 0.15406 nm) [54].

The sample is mounted for the measurement and held in the x-ray beam passage and rotated. The detector is working as the film or charge-coupled device to record the pattern of spots or reflection. Afterwards, the output device assesses the collected data [55].

3-2-2 Tensile properties measurements

The tensile strength, tensile modulus and elongation at the break were measured by using an Instron Universal Testing Machine Model 4301 at 5 mm/ min of crosshead speed in accordance with ASTMD638,shown in (Figure 3.2) .

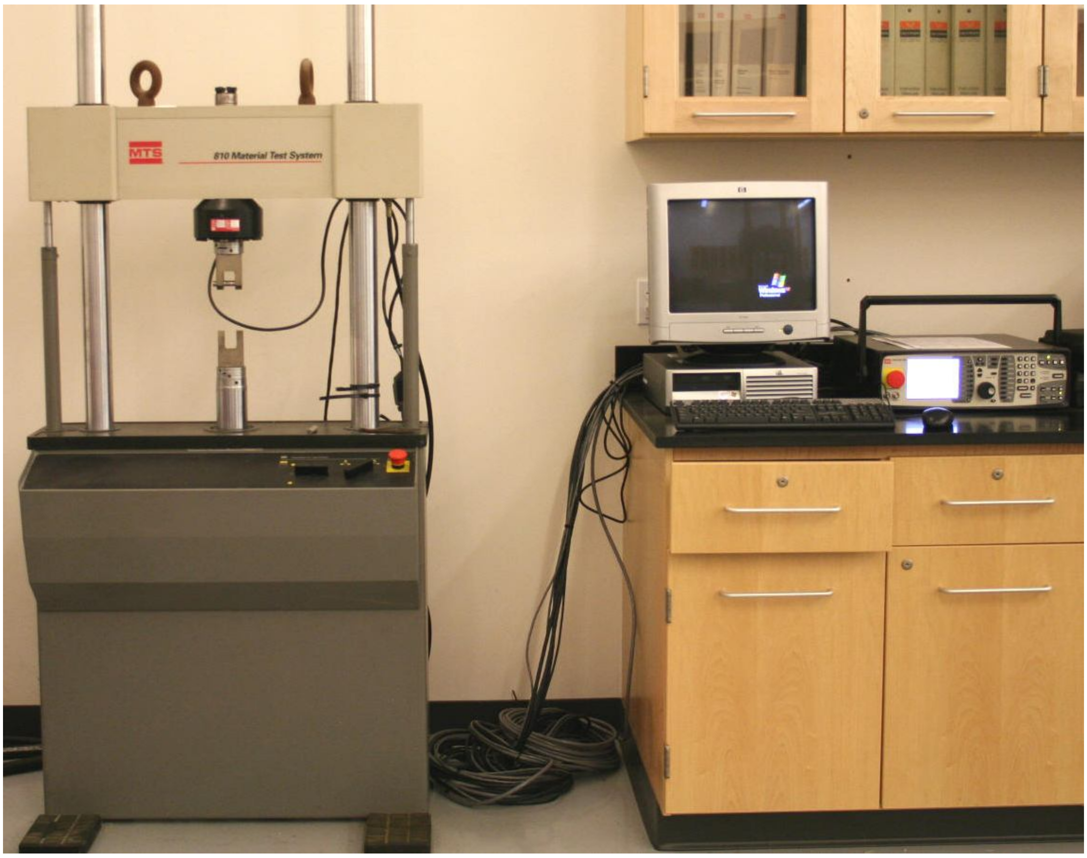


Figure 3.2 Instorn universal tasting machine model 4301[52].

Seven samples were used for the tensile test and an average of five results was taken as the resultants value, samples have a gauge length of bench marker 20 mm ,a width of bench marker 4 mm and thickness of 1mm . Thickness was taken at three different places on the specimen and averaged for modulus calculation, (Figure 3.3)shows the specimen before and after applied stress .

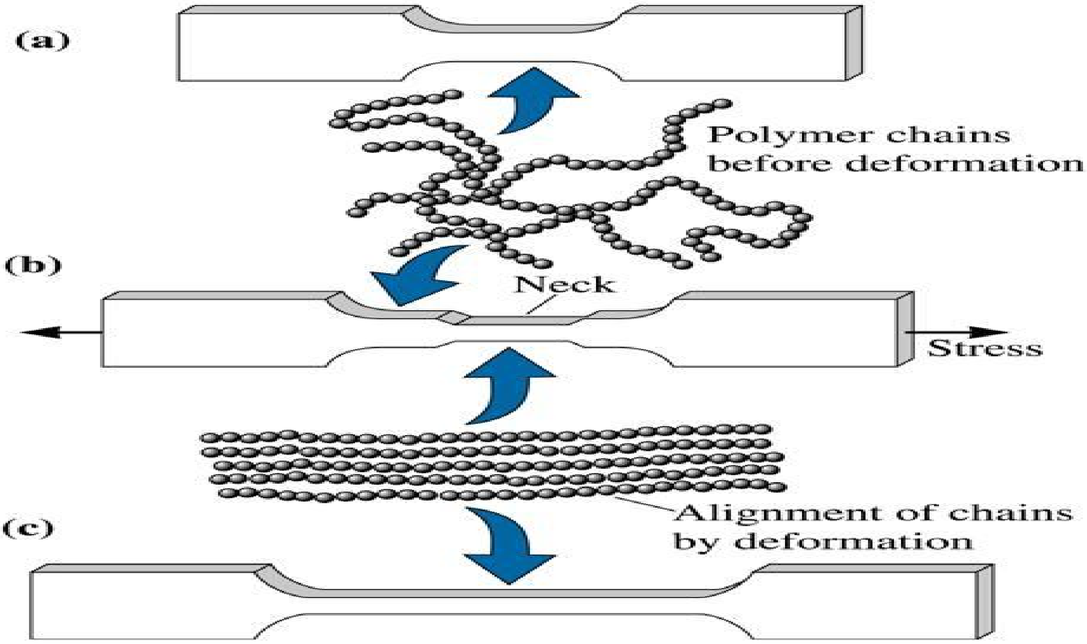


Figure 3.3 In an undeformed thermoplastic polymer tensile sample :

a) The polymer chains are randomly oriented .

b) When a stress is applied , neck develops as chains become locally aligned . The neck continues to grow until gage chains in the entire gage length have aligned .

c) The strength of the polymer is increased .

Young’s modulus was reported as the slope of the initial linear region of the stress-strain curve . The actual experimental values were reported as load- deformation curves .

Therefore the experimental curves require scale transformation to obtain the desired stress-strain curves , tensile strength (TS) and region between M and E to polymer (nano-NR) occurs when polymer backbones are aligned and about to break ,shown in (Figure 3.4) .

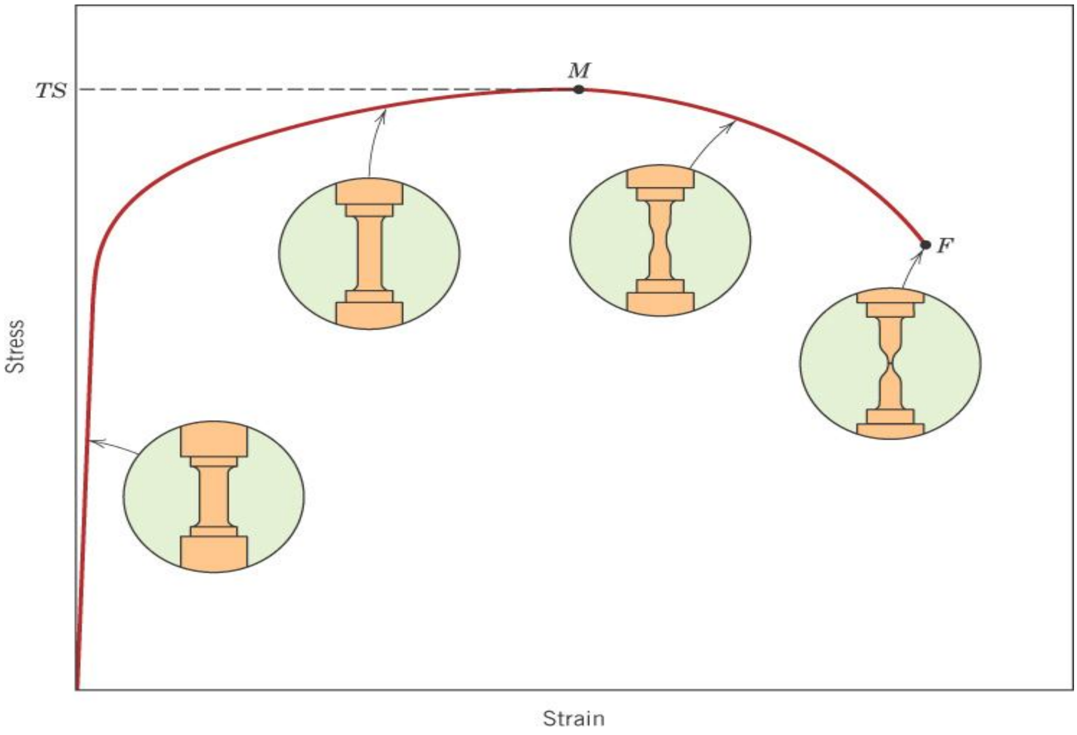


Figure 3.4 Stress-strain curves of specimen NR /organoclay nano-composite (nano-NR) [37,52] .

This can be accomplished by the following definitions, (Figure A1-2) shown on a stress-strain diagram of NR/organoclay nano- composite, from this figure obtain same point explain as follows :

. Elastic region (point 1-2)

In this region, the material will return to it's original shape after the material is unloaded (like a rubber band) . And stress is linearly proportional to the strain in this region .

Stress= Force or load (F) / Cross sectional area (A)

Strain $= (L- L_0) / L_0$

L_0 is the original, unstretched length of the specimen

L is the stretched length of the specimen

Thus Young's modulus in a tensile test is given by

(Young's modulus) E = d(Stress) / d(Strain)

.Yield strength (point 2)

A point where permanent deformation occurs . If it is passed , the material will no larger return to it's original length .

. Tensile strength (point 3)

The largest value of stress on the diagram is called tensile strength(TS) or ultimate tensile strength (UTS) . It is the maximum stress which the material can support without breaking .

. Strain hardening

If the material is loaded again from point 4, the curve will follow back to point 3 with the same elastic modulus (slope) .The material now has a higher yield strength of point 4 .Raising the yield strength by permanently straining the material is called strain hardening .

. Fracture (point 5)

If the material is stretched beyond point 3 , the stress decreases as necking and non-uniform deformation occur . Fracture will finally occur at point 5 .

The end data of the stress-strain curve denotes the rupture or failure of the material obtained from personal computer with Instron model 4301 ,which is characterized by the tensile strength and the ultimate strain or elongation to break [52,58] .

3-2-3 Thermogravimetric analysis (TGA)

Observation of the response of the materials when heated is dated back to ancient times. However, the serious measurement is based on the invention of thermocouple at the end of 19th century. The development of thermal analysis applied to geosciences is from the experiment of La Chatelier in 1887 when he classified the different samples of clay by their dehydration point. In the1930, it became a simple and inexpensive technology in the field of mineralogy, compared to X-ray diffraction (XRD) which was expensive during that time [59]. Thermogravimetric analysis (TGA) is a common thermal analysis technique involving measuring the sample weight as a function of temperature or time while the sample is loaded on a precise thermobalance and subjected to a heating program in a controlled atmosphere ,the thermal stability of the samples was studied by using Perkin Elmer model TGA thermogravimetry analyzer.

The samples are heated from 35 to 800 ^{o}C with the heating rate of 10 ^{o}C /min under nitrogen atmosphere with a nitrogen flow rate of 20 ml/min[60]. The components of the instrument are microbalance, furnace, programmer controller and a computer (Figure A1-3). The balance should be in a suitably enclosed system so that the nature and pressure of the atmosphere surrounding the sample can be controlled[61]

Thermogravimetric curves are plotted with the weight change on the vertical axis and temperature on the horizontal axis. However, this curve is difficult to interpret. Therefore, the first derivative of the weight loss curves are plotted to assist in the interpretation and reveal the inflection points [59] . Generally, TGA can provide information on physical and chemical properties. The physical properties include melting, evaporation, sublimation and adsorption while the chemical properties include dehydration, dissociation, oxidation and reduction. Specifically, TGA characterizes the decomposition and thermal stability of materials under various conditions including the specific temperature ranges and heating rates and to examine the kinetics of the physicochemical processes occurring in the sample [62]. For polymer nanocomposites, TGA is beneficial in quantifying the amount of the organic matter exchanged on the surface of the filler particles, thus generating an idea of the success or extent of the ion exchange process [63]. For clay minerals, the endothermic reactions occur with adesorption of surface H_2O, dehydration of interlayer H_2O at low temperature ($<100\ ^oC$), dehydroxylation at high temperature and melting. Exothermic reactions are related to recrystallization which are concurrent or after dehydroxylation and melting [64].

3-2-4 Transmission electron microscopy (TEM)

The transmission electron microscopy (TEM) is an essential instrument to diagnose materials. The historical development of TEM is from the discovery of the electron by J. J. Thomson in 1897 and the fact that electron beams could be deflected and concentrated through electrostatic and magnetic fields. In 1924, Louis de Broglie revealed the hypothesis that the electrons travel in a waveform pattern and derived the formula ($\lambda=h/mv$) where h is Planck's constant, m is the mass of a particle and v is the velocity of a particle. Afterwards, Ernst E. Ruska developed the magnetic lens and built the first TEM in 1931 [65].

The TEM can provide information on several properties of the material studied including morphology, structure, lattice imaging and chemical composition [66]. The TEM can be divided into three components: the illumination system, the objective lens/specimen stage, and the imaging system. The illumination system, consisting of the gun and the condenser lenses, emit the electrons from the heated filament. They are a ccelerated by a potential difference and passed through a set of condenser lenses to limit the desired diameter. The illumination system can be operated in two principal modes: parallel beam and convergent beam. The objective lens and the sample stage system is the heart of the

TEM where the electron beams penetrate the ultra thin specimen and cause all the interactions (Figure A1-4) .

The lenses of the imaging system magnify the electron intensity distribution and focus on a fluorescent screen. The image can be recorded by direct exposure of a photographic emulsion or an image plate inside the vacuum or digitally via a fluorescent screen coupled by a fiber-optic to a charge-coupled device (CCD) [67, 68].

The dispersion of clay was studied by using Energy Filtering Transmission Electron Microscopy (EFTEM) .TEM pictures were taken in a LEO 912 AB Energy Filtering Transmission Electron Microscope with an acceleration voltage of 120 Ke V. The specimens were prepared using a Ultracut E (Reichert and Jung) cryomicro tome. Thin sections of about 100nm were cut with a diamond knife at -120 ^{o}C [57,67] .

CHAPTER FOUR

RUSULTS AND DISCUSSION

CHAPTER FOUR

4-Results and discussion

4-1 Effect of clay and organoclay content in natural rubber

4-1-1 X-ray diffraction analysis

X-ray diffraction technique was used to measure the interlayer distance of the silicate layers of the clay and modified clay with alkyl-amidioumion cation (FAs-MMT). It was also used to measure the silicate layers interlayer distance of natural clay (Na-MMT) and modified clay (FAs-MMT) [36]. The interlayer distance of Na-MMT was expanded from 1.21nm to about 2.65nm for FAs-MMT obtained from XRD analysis, shown in (Table 4.1) .

Table 4.1 XRD analysis of natural clay (Na-MMT) and modified clay (FAs-MMT)

Type of clay	Exchange cation	2θ (degree)	d-spacing (nm)
Na-MMT	Na^+	7.28	1.21
FA_s-MMT	$RCO\text{-}NH_3^+$	3.47	2.65

The summary of the intercalated silicate layer in NR/ unmodified MMT and NR/modified MMT (FAs-MMT) used in this study, obtained from the XRD analysis is given in (Table 4.2) .

Table 4.2 XRD analysis of NR/unmodified clay (Na-MMT) and NR/modified clay(FAs-MMT)

NR/Type of clay	d-Spacing (nm)				
	1 phr	2 phr	3 phr	4 phr	5 phr
NR/Na-MMT	1.37	1.38	1.33	1.31	1.30
NR/FA$_S$-MMT	2.05	2.78	3.14	2.15	1.90

4-1-2 Tensile properties measurements

The (Figure 4.1) shows the effect of clay content on the tensile strength properties of NR/ Na-MMT microcomposites (micro-NR) and NR/FAs-MMT nanocomposites (nano-NR) . The reinforcing effect of unmodified MMT in the NR matrix was increased with a low rate of increment. The maximum tensile strength was obtained when the clay content was 2 % of the weight.

Further increasing the clay content decreases the tensile strength .Na-MMT acts as conventional particulate filler in the NR matrix. Low tensile strength is obtained for NR/Na-MMT because the clay–clay interactions are stronger than those NR–clay interactions. A poor compatibility between the clay and the NR matrix is expected as the mixing is at micro-level [69] .A similar behavior of the clay content affects the modulus and elongation at the break of NR/ Na-MMT is observed (Figures 4.2 & 4.3). The increment of tensile strength, modulus, and elongation at the break for the nanocomposite with FAs-MMT loadings are similar to that of microcomposite. However, the rate of the increment of tensile properties for the nanocomposite increases. The highest tensile strength, modulus, and elongation at the break of the FAs-MMT nanocomposite is obtained when 3 % of FAs-MMT loadings are used (Figures 4.1 , 4.2 & 4.3).

He is due to the increase of the amount of the incorporated NR chains enhancing effect of the FAs-MMT on the mechanical properties is probably in the clay layers. The rubber–clay interactions include the interactions of the intercalated NR chains with surface layers of the silicates. However, the tensile strength, modulus and elongation at the break decrease when the FAs-MMT loadings are increased to more than 3 %. The decrease of tensile strength, modulus, and elongation at the break is due to the decrease of the NR chains interaction with the clay as the clay coagglomerates.

The clay galleries were changed from the originally hydrophilic to organophilic silicate resulting in increases in the layer-to-layer spacing of Na-MMT due to the presence of FAs chain in the clay galleries. Based on Bragg's law ($n\lambda = 2d\sin\theta$) , the d refers to the distance of two consecutive clay layers, and λ is the wavelength of the intercept X-rays at the incident angle θ [56]. By using the XRD test, Na-MMT assigns to d the diffraction peak at $2\theta = 7.28^{o}$. This value indicates an interlayer distance of the Na-MMT with a basal spacing of 1.21 nm. The Na-MMT surface was treated by FAs as an intercalation agent through a cation exchange process. The maximum basal spacing of FAs-MMT increases from 1.21 to 2.65 nm . The (Table 4.1), indicating that these FAs were successfully intercalated into the Na-MMT galleries .

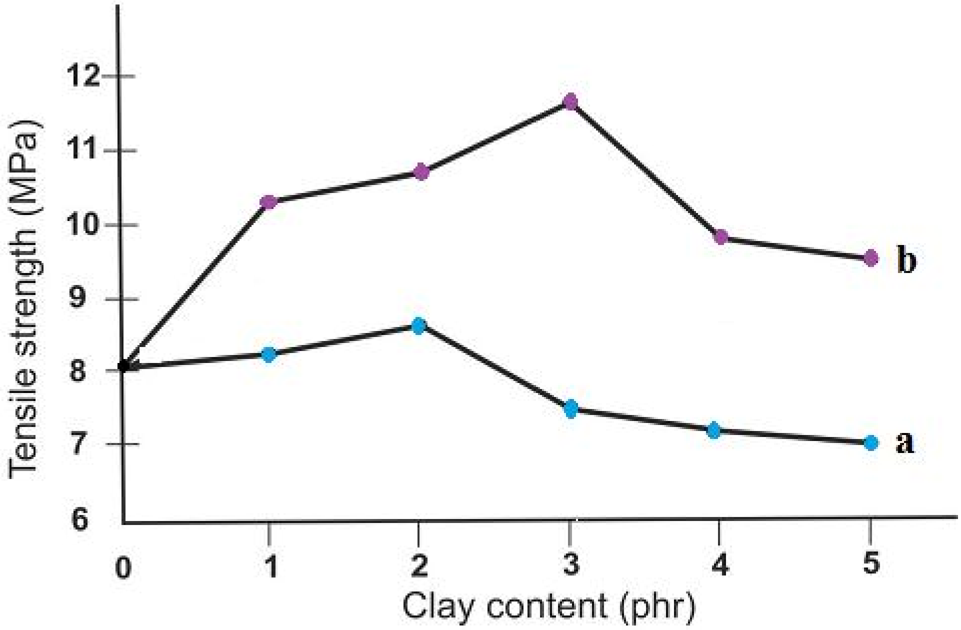


Figure 4.1 Tensile strength of a- NR/Na-MMT microcomposites (micro-NR) & b- NR/FAs-MMT nanocomposites (nano-NR)

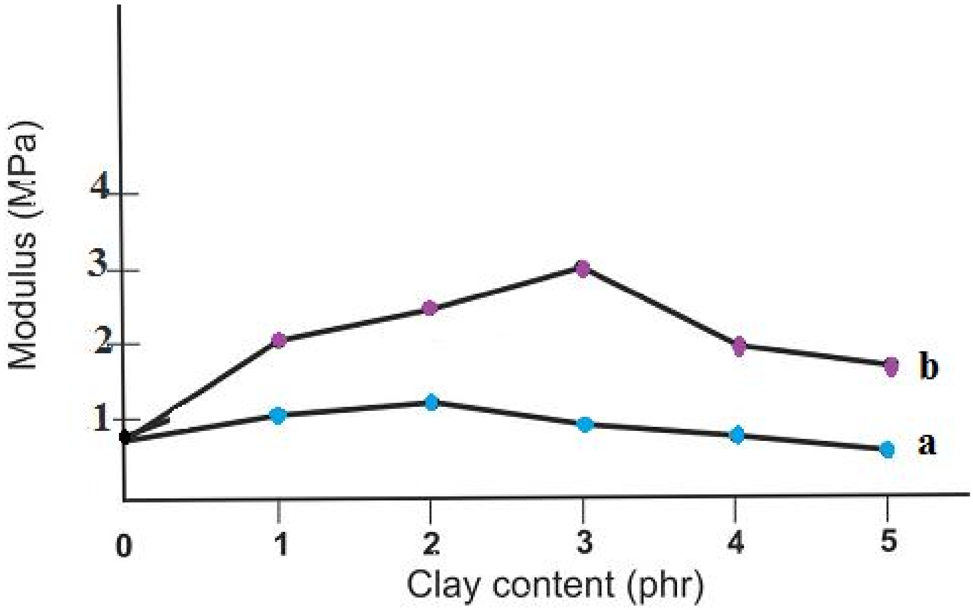


Figure 4.2 Modulus of a- NR/Na-MMT microcomposites and b- NR/FAs-MMT nanocomposites

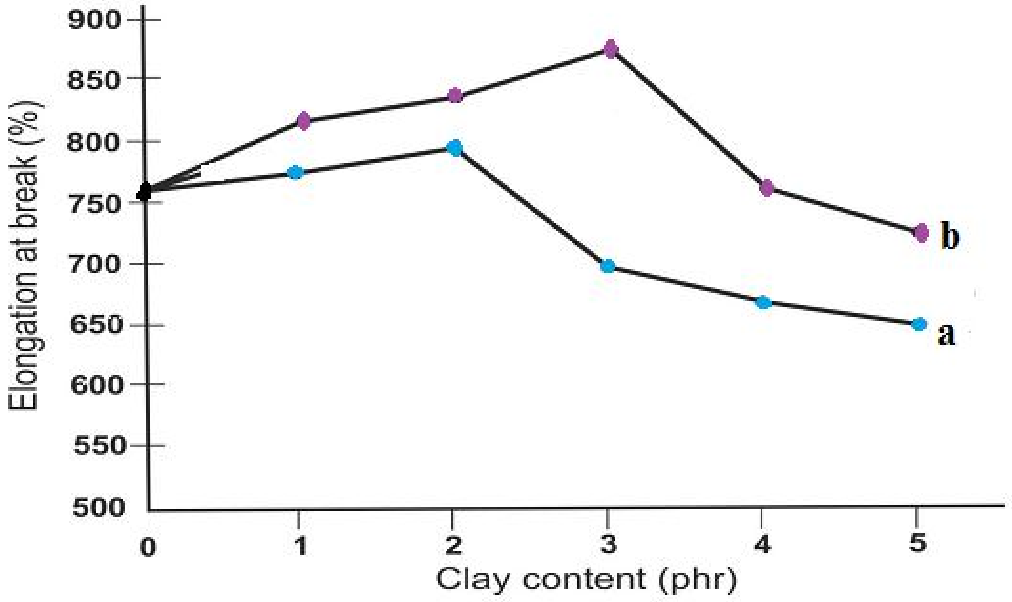


Figure 4.3 Elongation at break of a- NR/Na-MMT microcomposites and b- NR/FAs-MMT nanocomposites

4-1-3 Thermogravimetric analysis (TGA)

The (Figure 4.4) shows the weight loss curves of Na-MMT, FAs, FAs-MMT, NR, NR/Na-MMT microcomposites and NR/FAs-MMT nanocomposites. Na-MMT contains water due to hydrated sodium (Na^+) cations intercalated inside the clay layers. The presence of alkylamidioumion groups within the MMT interlayer spacing lowers the surface energy of the inorganic structure and will transform organophobic (hydrophilic) to organophilic materials.

The major difference between the thermogram of the unmodified clay and that of the organoclay is that the organic constituents in the organoclay decompose in the range from 200 to 500 °C, as the organic constituent in the organoclay decomposes in this range .

The FAs decomposed as the temperature is increased from 155 to 600 °C, decomposition process ends at around 310 °C (Figure 4.4b) .It can be observed that the decomposition temperatures of the FAs-MMT (Figure 4.4c) are higher than those of the pure FAs and Na-MMT. The increase in the decomposition temperatures of the FAs in the organoclays implies that there is a strong intermolecular interaction between the alkylamidioumion cations and the clay. In other words, after the ion of the FAs is intercalated and attached to the silicate layers of the clay, their decomposition temperature increases. Thermogravimetric analyses were also done on the NR/Na-MMT microcomposite and the NR/FAs-MMT nanocomposite in order to determine the effect of unmodified and modified clay content in the rubber matrix on thermal properties. The results of the TGA are shown in (Figure 4.4e,f). The onset of the degradation of the nanocomposite is higher, at 365 ^{o}C , for NR containing FAs-MMT, compared to that of the pure NR (Figure 4.4d) and NR/Na-MMT microcomposite, which are 264 and 285 ^{o}C , respectively. The FAs presence of silicate layers dispersed homogeneously in the polymer sheet hinders the permeability of volatile degradation products out from the material and helps delay the degradation of the nanocomposite.

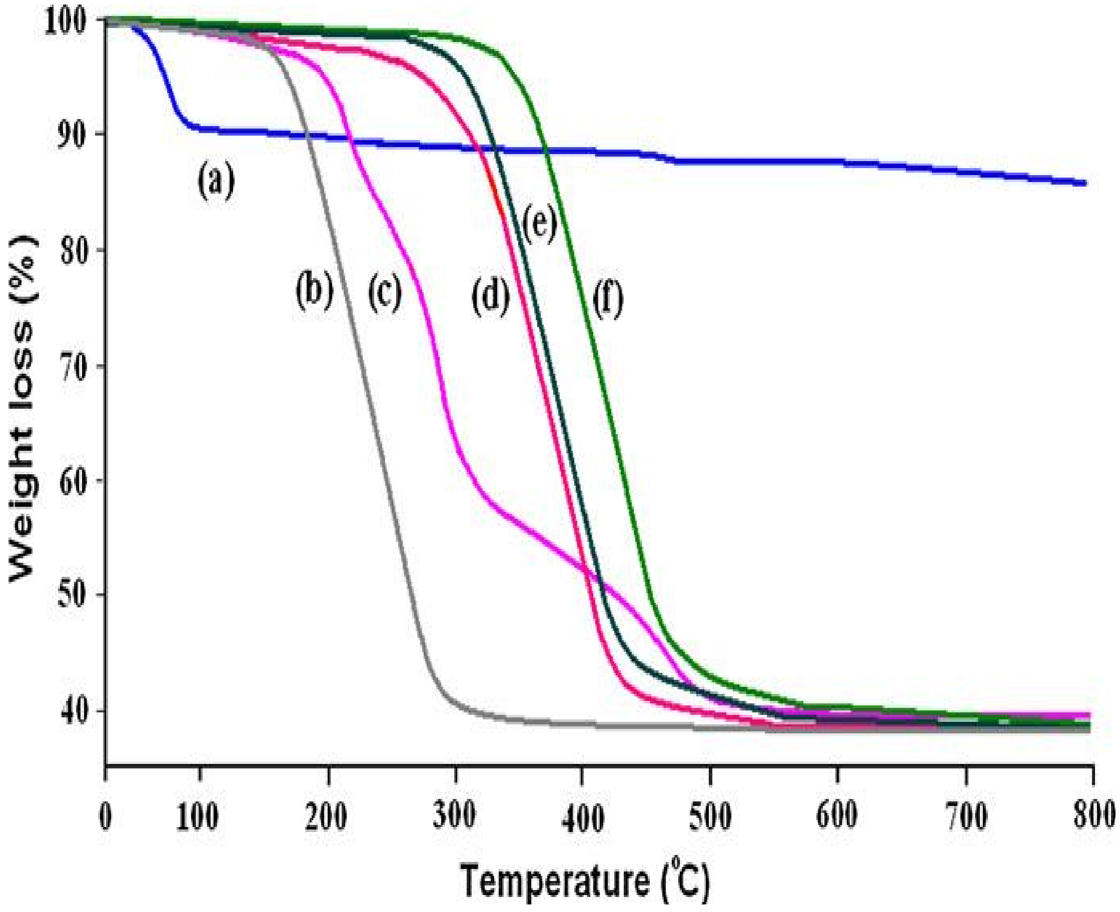


Figure 4.4 TGA thermograms of a- Na-MMT, b- FA_S , c- FAs-MMT, d- NR, e- NR/2phr Na-MMT microcomposite & f- NR/3phr FAs- MMT nanocomposite

4-1-4 Transmission electron microscopy (TEM)

Transmission electron microscopy micrographs of the NR composites reinforced with Na-MMT and FAs-MMT are illustrated in (Figure 4.5). The NR/2phr Na-MMT image shows that the original Na-MMT stack morphology is fully preserved in the NR matrix due to the incompatible nature of both constituents (Figure 4.5a). Dark bundles represent the thickness of the individual clay layers or agglomerates. The (Figure 4.5b) exhibits the TEM images of NR/3 phr FAs-MMT nanocomposites, which modified clay are dispersed in the NR matrix with an intercalated state, which can be observed clearly in the images. Previous results have been published the first scientific paper in high – impact factor is a global journal , Res. Chem. Intermed., shown in (Appendix A3).

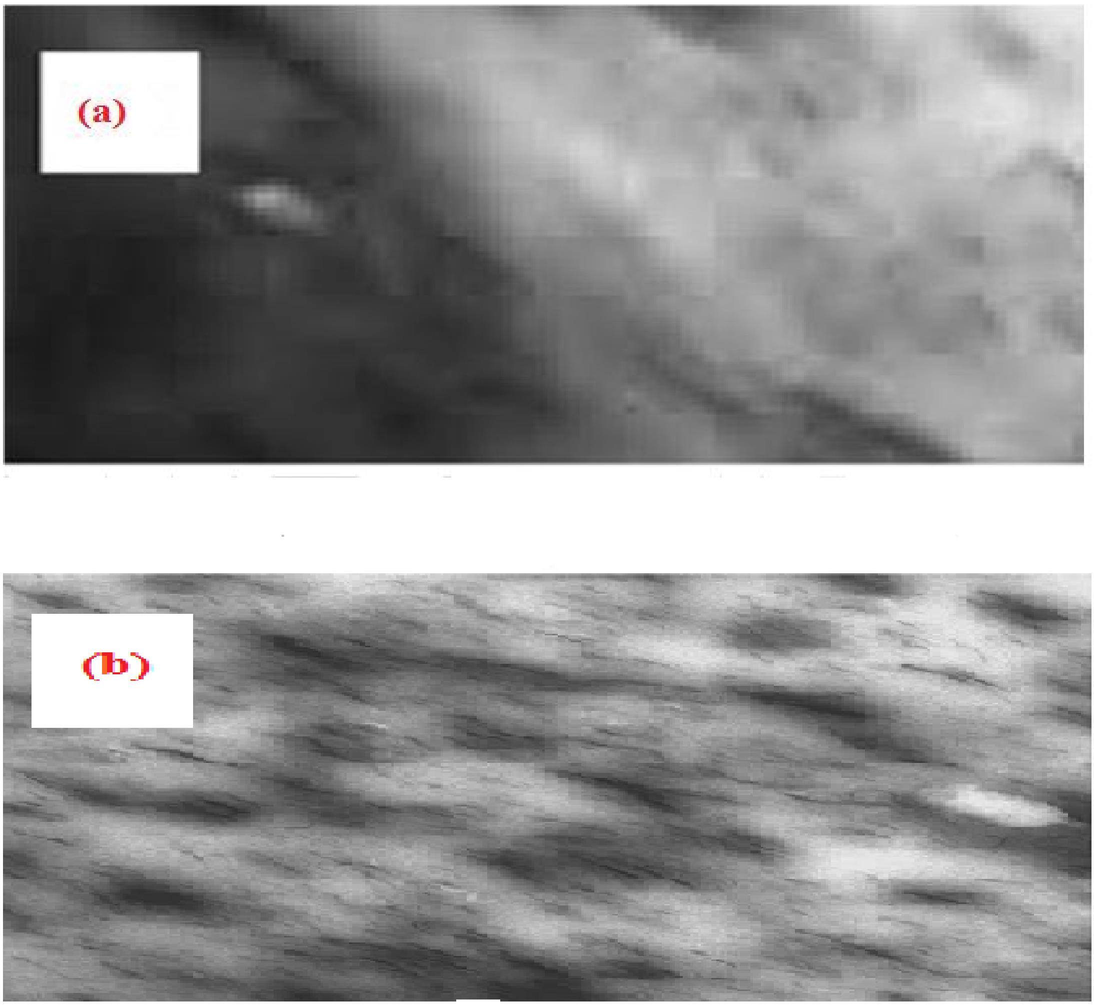


Figure 4.5 TEM image at of a- NR/2 Phr Na-MMT microcomposite and b- NR/3 Phr FAs-MMT nanocomposite

4-2 Comparative results of different surfactants for clay modification

4-2-1 X-ray diffraction (XRD) analysis

X-ray diffraction technique was used to measure the interlayer distance of the silicate layers of the clay and modified clay with alkylammonium or alkylamidioumion cations. It was also used to measure the silicate layers distribution of modified clays in the NR matrix, a (Table 4.3) shows the interlayer distance of natural clay (Na-MMT) and modified clays (DDA-MMT and FAs-MMT) [34,36]. The interlayer distance of Na-MMT was expanded from 1.21 nm to about 1.67 and 2.65 nm for Na-MMT, DDA-MMT and FAs-MMT respectively.

Table 4.3 Unmodified and different modified MMT characterized by XRD

Type of clay	Exchange cation	2θ (degree)	d-Spacing (nm)
Na-MMT	Na^+	7.28	1.21
DDA-MMT	$C_{12}H_{25}NH_3^+$	5.26	1.67
FAs-MMT	$RCO\text{-}NH_3^+$	3.47	2.65

The summary of the intercalated silicate layer in NR / unmodified MMT and NR/modified MMT nanocomposites used in this study, obtained from the XRD analysis is given in (Table 4.4) .

Table 4.4 XRD analysis of NR/unmodified MMT and NR/modified MMT composites

NR/Type of clay	d-Spacing (nm)				
	1 phr	2 phr	3 phr	4 phr	5 phr
NR/Na-MMT	1.37	1.38	1.33	1.31	1.30
NR/DDA-MMT	1.83	2.85	2.73	2.03	1.69
NR/FAs-MMT	2.05	2.78	3.14	2.15	1.90

4-2-2 Tensile properties measurements

The (Figure 4.6) shows a tensile strength of NR/Na-MMT micro-composite and organoclays (NR/FAs-MMT and NR/ DDA-MMT) nano-composites. As expected, the silicate reinforced system prepared by melt mixing NR with various amounts of organoclay has superior tensile strength relative to pristine NR. The maximum tensile strength was obtained when clay content (Na-MMT) was 2 phr of the weight. Further increasing the clay content decreases the tensile strength. A poor compatibility between the clay and the NR matrix is at micro-level [69]. A similar behavior of the clay content affects the modulus and elongation at the break of NR / Na-MMT is observed (Figures 4.7 & 4.8) .

The (Figures 4.6 , 4.7 & 4.8) also show that organoclay of FAs-MMT and DDA-MMT reinforced nanocomposites have higher tensile properties (tensile strength, modulus and elongation %) compared to unmodified montmorillonite because the clay galleries were changed from the originally hydrophilic to organophilic silicate resulting in increases in the layer to layer spacing of Na-MMT due to the presence of FAs or DDA chain in the clay galleries [70- 72] .

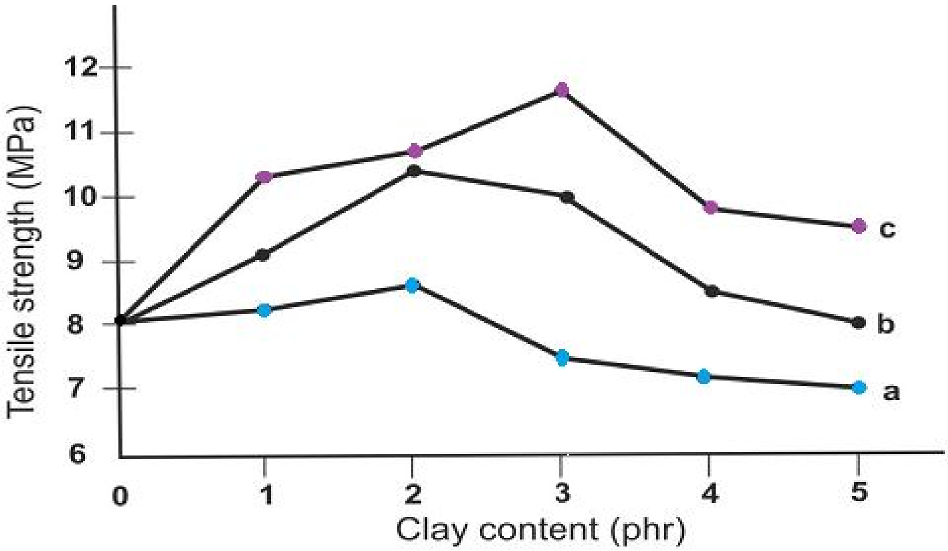


Figure 4.6 Tensile strength of a- NR/Na-MMT microcomposites and b- NR/DDA-MMT ,c- NR/FAs-MMT nanocomposites

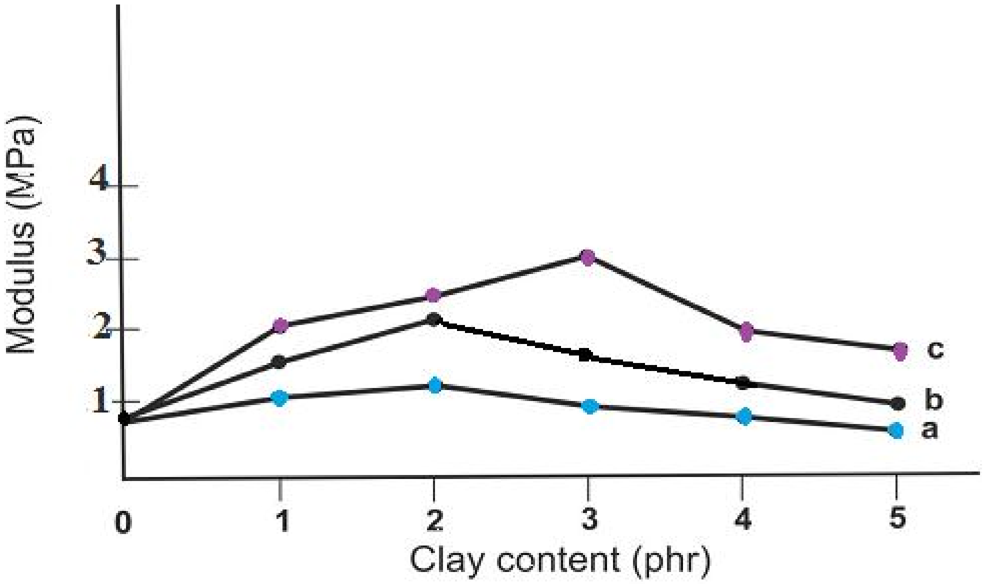


Figure 4.7 Modulus of a- NR/Na-MMT microcomposites and b- NR/DDA- MMT , c- NR/FAs-MMT nanocomposi

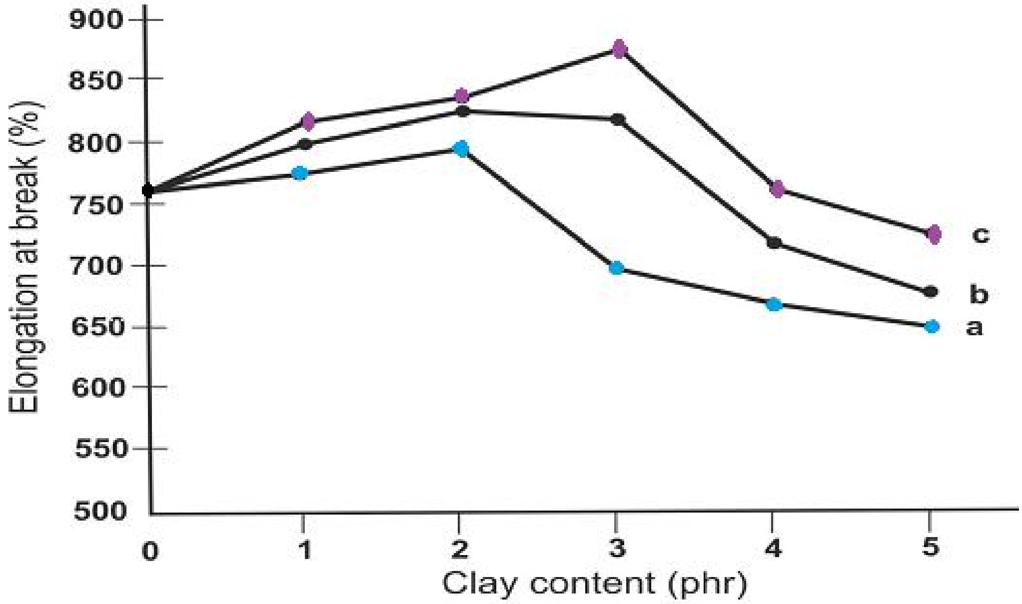


Figure 4.8 Elongation at break of a- NR/Na-MMT microcomposites and b- NR/DDA-MMT , c- NR/FAs-MMT nanocomposites

The highest tensile properties of NR/2phr DDA-MMT and NR/3phr FAs-MMT nanocomposites obtained are shown in (Figures 4.6 , 4.7 & 4.8). However, at higher clay content b and c (2 phr and 3 phr) for DDA-MMT and FAs-MMT, respectively, tensile properties start to decrease and remain constant with increasing clay content up to 5 phr. From the above testing, it was shown that the mechanical properties (tensile properties) of NR/FAs-MMT are superior to those of NR/DDA- MMT.

4-2-3 Thermogravimetric analysis (TGA)

The (Figure 4.9) shows a weight loss curves for increasing temperatures of Na-MMT, DDA, FAs, DDA-MMT, FAs- MMT, NR and NR/2 phr Na-MMT (micro-NR) and NR/2 phr DDA-MMT, NR/3 phr FAs-MMT (nano-NR), Na-MMT contains water due to hydrated sodium (Na^+) cation intercalated inside the clay layers.

The presence of alkylamidioumion cations or alkylammonium cations groups from vegetable or petroleum-based surfactants within the MMT interlayer spacing lowers the surface energy of the inorganic structure and will transform organophobic to organophilic materials. The major difference between the thermogram of the unmodified clay and that of the organoclay is that the organic constituents in the organoclay decompose in the range 200–500 ^oC . The DDA and FAs decomposed as the temperature is increased from 120 to 580 ^oC and 155 to 600 ^oC , respectively. The decomposition process of DDA and FAs ends at around 295 and 310 ^oC, respectively as shown in (Figures 4.9b,c). It can be observed that the decomposition temperature of the FAs-MMT (Figure 4.9e) is higher than those of DDA-MMT and pure FAs, DDA and Na-MMT. The increase in the decomposition temperatures of DDA or FAs in the organoclays implies that there is a strong intermolecular interaction between the surfactants cations and the clay.

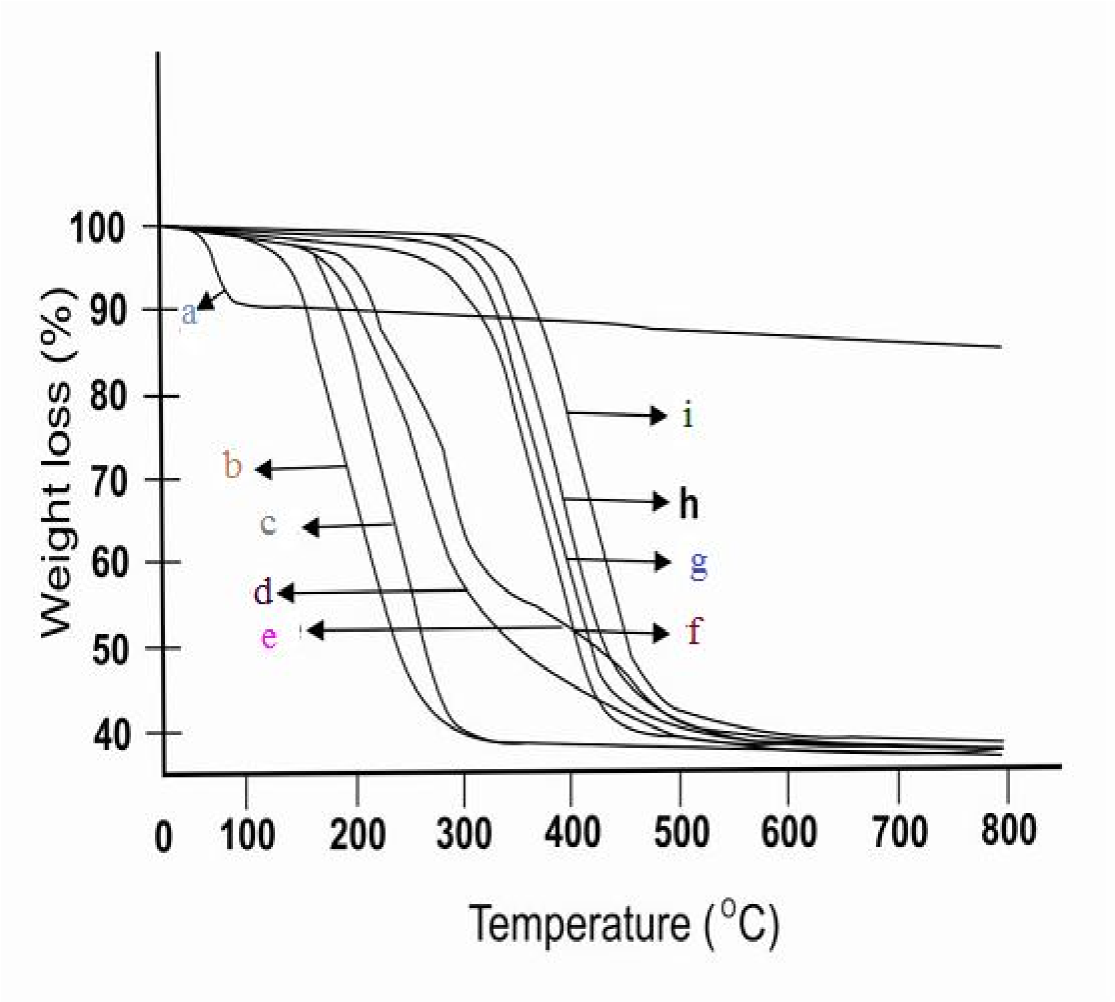


Figure 4.9 TGA thermograms of a-Na-MMT, b- DDA, c-FAs, d- DDA-MMT, e- FAs-MMT , f- NR , g - NR/2 phr Na-MMT micro - composite and h- NR/2 phr DDA-MMT , i- NR/3 phr FAs-MMT nanocomposite

In other words, after the ion of the DDA or FAs is intercalated and attached to the silicate layers of the clay, their decomposition temperature increases. Thermogravimetric analysis (TGA) was also done on the NR/Na-MMT microcomposites and two types of nanocomposites (NR/DDA- MMT and NR/FAs-MMT) in the order to determine the effect of unmodified and modified by vegetable oil or petroleum oil clay content in the rubber matrix on thermal properties.

The results of the TGA are shown in (Figures 4-9g-i). The onset of the degradation of the nanocomposites (NR/ 2 phr DDA-MMT and NR/3 phr FAs-MMT) is higher at (320–365 ^{o}C), respectively, compared to that of NR/2 phr Na-MMT microcomposites.

The results from (Figure 4.9) showed that the NR with modified clay nanocomposites based on FAs shows higher thermal stability in comparison with those of the NR with modified clay nanocomposites based on DDA surfactant because NA/FAs-MMT has more homogeneous distribution of silicate layer without clay aggregates and higher (d-spacing).The results also show that thermal stability increases with the increase of DDA-MMT and FAs-MMT loading up to 2–3 phr, respectively and increase above this percentage does not improve the thermal stability. On the other hand, NR/Na-MMT shows only slight improvement in the thermal stability compared to the nanocomposites because the hydrophilic clay sheets are not well dispersed, and the latest was greater than NR/Na-MMT [73- 75] .

4-2-4 Transmission electron microscopy (TEM)

Transmission electron microscopy micrograph observations are shown in (Figures 4.10a,b). NR/2 % DDA-MMT illustrates exfoliated lamellae and aggregates of tactoide . However, the NR/3 % FAs-MMT show more homogeneous distribution of silicate layer without clay aggregates. Also the XRD pattern of both NR/DDA-MMT and NR/FAs-MMT clearly show that interlayer distance reduces with high increase of organoclay contents. The extent of intercalation depends on several factors such as the polymer transport process through the agglomerate micropores, agglomerate size, diffusion elastomer chain within the silicate layer and the nature of the elastomer itself [54]. The (Table 4.4) shows the interlayer silicate distance of the clay layer obtained from the XRD analysis. Previous results have been published the second scientific paper in high – impact factor is a global journal , Rend. Fis. Acc. Lincei.& Conference, shown in (Appendix A3).

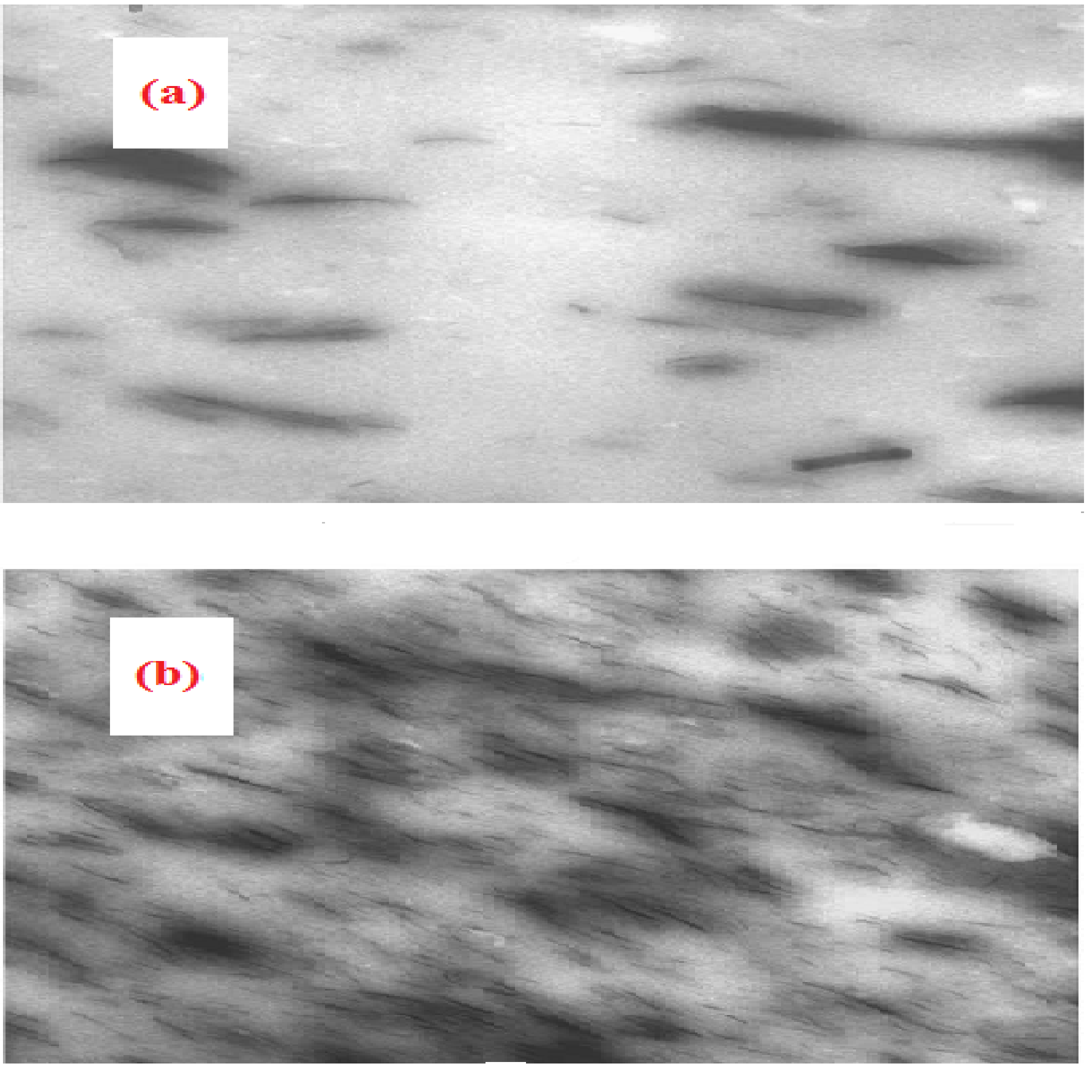


Figure 4.10 TEM image at of a- NR/2 phr DDA-MMT and b- NR/3 phr FAs-MMT nanocomposites

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER FIVE

5- Conclusions and recommendations

5-1 Conclusions

Fatty amides (FAs) synthesized from vegetable oil were used for modification of the MMT. The presence of long-chain fatty acids (mainly16 and 18 carbon atoms) in FAs suggests they should be very useful as surfactants for clay modification.. Modified MMT was used to prepare new rubber/clay nanocomposites (nano-NR) . Another type of rubber nanocomposite properties were investigated using dodecyl ammonium chloride (DDA) as a clay modifier. Production of rubber nanocomposites using FAs as a modifier showed more thermal stability and improvement tensile properties compared with microcomposites and nanocomposites produced based on DDA as surfactant shown in (Figure A1-5) and (Table A2-2). The use of FAs will reduce the dependence on petroleum-based surfactants. In addition to renewable resources, these nanocomposites are considered as environmentally friendly.

5-2 Recommendations

Recommendation for further work are :

1- Add FAs-MMT to synthetic rubber and get a nanocomposites and compare their properties with nanocomposites that have been reached them through research .

2- The use of other vegetable oils (vegetable oils for non-food) to for modification natural and synthetic rubber respectively into nanocomposites and comparil the results of the two types .

3- Add a mixture of surfactants (FAs & other surfactants) in different proportions to NR for get the best enhancement in the engineering properties.

REFERENCES

References

1- Odian , G . principles of polymerization .John Wiley & Sons :PP, 749 , (1991) .

2- Morton .Rubber Technology .3ed , van Nostrand Reinhlod co, NewYork :PP, 631 , (1987) .

3- Alexandre ,M. &Dubois . Polymer – layered silicate Nano-composities preparation Properties , sci, Eng ,PP,1-63, (2000) .

4- Blackley . High polymer Lattices . Their science and Technology Co, New York, (1966) .

5- Winspear . The Vanderbit latex Handbook . R.T. Vanderbit , (1954).

6- Varghese,S. &Karger-Kocsis,J. J. Appl. Polym. Sci.:PP, 91, 813, (2004).

7- Al-Mulla, E.A.J., Suhall, A.H., &Aowda, S.A. New biopolymer Nano composites based on epoxidized soybean oil plasticized pol (lactic acid) /fatty nitrogen compounds modified clay preparation and characterization . Industrial Crops and Products,0926-6690,v33(1):PP, 23- 29,(2011).

8- Al-Mulla, E.A.J.Polyactic acid / expoxidized palm oil / fatty. Nitrogen compounds modified clay nanocomposites , preparation and characterization . Korean Journal of Chemical Engineering ,0256-1115,v 28(2):PP, 620-626, (2011).

9- Dick . Rubber Technology Compounding&Testing for Performance . Hanser publishers :PP, 523 ,(2001) .

10 - Franta .Elastomers and Rubber Compounding Materials . Elsever, NeW York : PP, 588 , (1989) .

11–Burnside , S. D. and Gianelis . Synthesis and properties of New Poly(dimethylsiloxane) nano composities . chem. Mater: PP ,1597-1600, (1995) .

12- Arroyo, M., Lopez-Manchado, M., and Herrero, B., Organo - montmorillonite as substitute of carbon black in natural rubber compounds. Polymer 44 :PP, 2447- 2453, (2003).

13- Al-Mulla, E. A. J., Preparation of new polymer nanocomposites based on poly(lactic acid) fatty nitrogen comounds modified clay by a solution casting process . Fibers and Polymers, 1229-9197,v12(4):PP, 444 -450,(2011).

14-Yunus,W.M.Z., Al-Mulla,E.A.J., Ibrahim,N.A.,&Rahman,M.Z.A. Polym. Polym. Compos.: PP ,18, 451,(2010) .

15- W.M. Yunus et al. Polymer Testing UPM 24,211-21, (2005) .

16- Xi,Y., Martens ,W., He ,H., Frost ,R., J. Therm. Anal. Cal. PP, 81, 91,(2005)

17- Eid Moneer Alosime . Preparation and Characterization of Natural Rubber / Polyproplene / Fatty Hydrazide – Octadecel Ammonium Modified Nanocomposites . University Putra Malaysia ,: PP 5-15 .(2008) .

18- Hoidy,W.H., Al-Mulla,E.A.J., and Al-Janabi, K.W., Mechanical and thermal properties of PLLA/PCL modified clay nancomposities. Journal of Polymers and the Environment, 1566-2543,v18(4): PP, 608-616,(2010).

19- Hoidy,W.H., Ahmad, M.B., Al-Mulla, E.A.J.,and Ibrahim,N.A.B. Preparation and characterization of polylactic acid/polycaprolactone clay nanocomposite . Journal of Applied Sciences, ,v10 (2) :PP,97 106,(2010) .

20-Al-Mulla,E.A.J., Ibrahim, N.A.B., Shameli, K., Ahmad,M.B., and Yunus,W. M.Z.W. Fatty amides synthesized from vegetable oil as extactant of molybdenum (VI) .Research on Chemical Intermediates

,0922-6168,doi: 10.1007/s11164-012-0687-6,(2012).

21-Al-Mulla,E.A.J., Yunus,W. M.Z.W., Ibrahim, N.A.B., &Rahman, M.Z .A.Enzymatic synthesis of fatty amides from palm olin . Journal of Oleo Science, 1345-8957, 59(2):PP ,59-64,(2010).

22- Vu, Y.T.,Mark,J.E.,&Pham, L.H., et al. Clay nanolayer einforcement of cis- 1,4- polyisoprene and epoxidized natural rubber. Appl. Polm. Sci. 82:PP,1391-1403, (2001) .

23 -Robert, A. D., Editor . Natural Rubber Science and Technology . Oxford Science Publications, :PP ,1078,(1988).

24- Rattana Tanterdtam . Reinforcement of Natural Rubber Latex by Nanosize MMT Clay . the Pennsylvania state University, :PP ,4-56 .(2003) .

25- Coran ,A. Y. & PateL ,R. P. Rubber Chem.Technol : PP, 53, 141, (1980) .

26-Morton , M . Editor Rubber Technology , 3 ed . Van Notstrand Co. New York ,:PP 631 ,(1987) .

27-Bateman , L . Chemistry and physics of Rubber –like ey and Sons , : PP 777, (1963) .

28- S. Kaufhold and R . Dohrmann . Effect of extensive drying on the cation exchange capacity of bentonites, Clay Minerals*, 45, :*PP 441-448,(2010) .

29- Giannelis , E . P. polymer – layered silicate nanocomposites : Synthesis , properties and applications . Applied Organometallic Chemistry 12 :PP, 675, (1998).

30- Z . Gökalp , M ., Başaran , and Uzun , O . Compaction swelling characteristics of sand-bentonite and pumice-bentonite mix. Clay Minerals*,* v. 46,: PP,449-459, (2011).

31-Blow , C . M . Editor Rubber Technology and Manufacture , The Chemical Rubber Co. Ohio :PP, 509, (1971).

32-Wang, M. J. Effect of Polymer-Filler and Filler-Filler neractions on Dynamic Properties of Filled Vulcanizates . Rubber Chemical Technolgy, (1998).

33-Eirich, F. R., Editor Science and Technology of Rubber Academic press . New York :PP 633, (1978).

34-Walf , S ., Chemical aspects of Rubber Reinforcement by Fillers. Rubber Chemical Technology . :PP 69, 346, (1996).

35-Arroyo, O. H., Huneault, M. A., Favis, B. D., and Bureau, M. N. Processing and properties of PLA / thermoplastic starch / montmorillonite nanocomposite. Poylmer Composites. : PP31, 114-127, (2010) .

36-Thength , B . K. G. Formation and Properties of Clay - polymer Complexes , Elsevier Scientific Publishing Company, NewYork :PP 353, (1979) .

37-Blackley, D .C .High Polymer Lattices ; Their Science and Technology Volume 1 Fundamental Principles, Palmerton Publishing Co , New York : PP 351, (1966) .

38-Brindley, G. W., & Brown, G. Crystal Structure of Clay Minerals and their X-ray Identification , mineralogical Society: PP485,(1980).

39-Moore , D. M. and Renolds , R. C. Jr. X-ray Diffraction and the Identification and Analysis of Clay Minerals . New York :PP ,378, (1997) .

40- Newman ,A. C. D. Chemistry of Clays and Clay Mineral York : PP, 480,(1987) .

41- Nanocomposites : Model Systems for Confined polymers and polymer Brushes . Advance in polymer Science : PP , 107 -143 , (1999).

42- Biswas , M ., and Sinha Ray , S. Recent progress insynthesis and evaluation of polymer–montmorillonite nanocomposites. Advance Polymer Science 155:PP ,167–221 , (2001) .

43- Aranda , P., and Ruiz- Hitzky , E. Poly (ethylene oxide) - silicate Intercalation materials . Chemistry of Material 4: PP1395–1400 , (1992) .

44- Krishnamoorti, R., Viva, R.A. 7and Giannelis, E.P. Structure and Dynamics of Polymer-Layered Silicate Nanocomposite. Chemistry of Materials 8:PP 1728-1734, (1996).

45- Lagaly , G. Interaction of alkyl amines with different type of layered compound , (1986) .

46- LeBaron , P. C. et al . Polymer-Layered Silicate Nanocomposites : An Overview, Applied Clay Science,15: PP 11-19 , (1999).

47- Messersmith , P. B., and Giannelis . E. P. Synthesis and Barrier Properties of Poly (ε - Caprolactone) – Layered Silicate nano - composites , J. of poly Sci-Part A: Polymer Chemistry,33 :PP , 1047-1057, (1995).

48- Yano, K. et al. Synthesis and Properties of Polyimide-Clay Hybrid, J. of poly Sci-Part A: Polmer Chemistry :31PP,2493- 2498,(1993)

49- Qutubuddin , S., and Fu, X. Polymer - Clay Nano – composites : Synthesis and Properties. in Nano-Surface Chemistry M. Rosoff.ed. (2001).

50- Al-Mulla, E.A.J., Ahmad ,M.B., Hoidy ,W.H., and Ibrhim , N.A.B. Modification of montmorillonite by new surfactants.Journal of Eng. And Applied Sciences,1816-949x, v4(3) :PP184-188, (2009).

51- Medalia ,A . I., Effective Degree of Immobilization of Rubber occluded within Carbon Black Aggregat Rubber Chem.Technology, 45 pp *Marcel Dekker* :PP 653-673,(1972).

52- ASTM D638-03, Standard Test Method for Tensile Properties of Plastics, vol. 08.01, (2004) .

53- Al-Mulla,E.A.J., Preparation of polytactic acid/epoxidized palm oil/ fatty nitrogen compounds modified clay nanocomposites by melt blending . Polymer Science – Series A,0965-545X,v53(2): PP 149-157,(2011).

54- Mark , L . and Rex , P. X-Rays and X-Ray Diffraction . Structure Determination by X-ray Crystallography : Analysis by X-rays and Neutrons Boston, MA: Springer US. PP.111-159 (2013).

55- He, B.B. X-ray technology and its brief history. Two-Dimensional X-ray Diffraction. John Wiley & Sons (2009).

56- Yoshio, W., Eiichiro , M. and Kozo, S. Diffraction from Polycrystalline Samples and Determination of Crystal Structure. X-Ray diffraction crystallography: introduction, examples and solved problems (pp107 -167). Berlin ; Heidelberg ; New York: Springer (2011) .

57 - Chih Te Huang . Physicochemical Characterization of Portuguese Clay and Nanocomposite Preparation with Polyactide , University Of Ottawa. Canda: PP 19-26 .(2014) .

58- Nielsen , L . E . and Landel , R . F . Mechanical Properties of Polymers and Composites , 2 nd ed , Marcel Dekker , Inc ., 545 pp . (1994) .

59- Plante, A. F., Fernandez, J. M., & Leifeld, J. Application of thermal analysis techniques in soil science . Geoderma *, 153* (1-2) , 1-10 . (2009) .

60- Prime, R. B., Bair, H. E., Vyazovkin, S., Gallagher, P. K. &Riga, A. Thermogravimetric analysis (TGA). In Menczel, J. D., Prime, R. B., Bair (Eds.) Thermal analysis of polymers : fundamentals and applications. Hoboken, NJ : John Wiley. (2009).

61- Brown, M. E. Introduction to thermal analysis: techniques and Applications . Dordrecht ; Norwell , Mass : Kluwer Academic Publishers. (2001) .

62 - Sandler, S. R., Karo, W., Bonesteel, J. A.and Pearce, E. M. Polymer synthesis and characterization: a laboratory manual (PP.108-119). San Diego : Academic Press. (1998).

63 - Mittal, V. Thermal Characterization of Fillers and Polymer nano-composites . Characterization techniques for polymer nano – composites Weinheim : Wiley-VCH. PP.13-32 (2012).

64- Guggenheim, S. and van Groos Koster , A. F. Baseline studies of the clay minerals society source clays : Thermal analysis . Clays and Clay Minerals, 49(5), 433-443. (2001).

65- Gunning, W.T. and Calomeni, E.P. A brief review of transmission electron microscopy and applications in pathology . Journal of Histotechnology 23(3)PP. 237-246. (2000).

66- Elsass, F. Transmission electron microscopy. In F. Bergaya, B. K. G. Theng & G. Lagaly (Eds.), Handbook of Clay Science (pp 939-963). Amsterdam: Elsevier Science. (2006).

67- Williams, D. B. & Carter, C. B. Transmission electron microscopy: a textbook for materials science . New York ; London : Springer (2009).

68- Reimer, L. & Kohl, H. Transmission electron microscopy: physics of image formation. New York, NY : Springer (2008) .

69- Vu,Y.T, Mark, J,E,& Pham ,L.H et al.,Clay nanolayer reinforcement of cis-1,4-polyisoprene and epoxidized natural rubber. J Appl. Polm . Polm. Sci. 82:PP1391–1403, (2001).

70- Al-Mulla, E.A.J., Preparation of Polylactic Acid/Epoxidized Palm Oil/Fatty Nitrogen Compounds Modified Clay Nanocomposites by Melt Blending. Polym Sci Series A 53:PP149– 157, (2011).

71- Nielsen, L . E. Mechanical Properties of Polymers and Composites , 2nd edn . Marcel Dekker, New York , (1974).

72- Agag ,T., Koga, T., Takeichi ,T. Studies on thermal an mechanical properties of polyimide - clay nano - composites. Polymer 42 : PP 3399–3408, (2001) 73- Hoidy, W. H., Ahmad ,M. B., Ibrahi, N.A .et al . Synthesis and characterization of organoclay from sodium montmorillonite and fatty hydroxamic acids. Amer J Appli Sci 6:PP1567–1572, (2010).

74- Yunus ,W.M.Z., Ibrahim ,N.A., Mohm, Z.A. et al. Epoxidized palm oil plasticized polylactic acid / fatty nitrogen compound modified clay nanocomposites: preparation and characterization. Polymer Comp. 18(8): PP 451-460, (2010).

75-Yunus ,W.M.Z., Ibrahim, N.A., Zaki, A.et al . Difatty acyl urea from corn oil: synthesis and characterization. Journal Oleo Science, 59:PP 157-160, (2010).

APPENDICES

APPENDIX (A1)

FIGURES

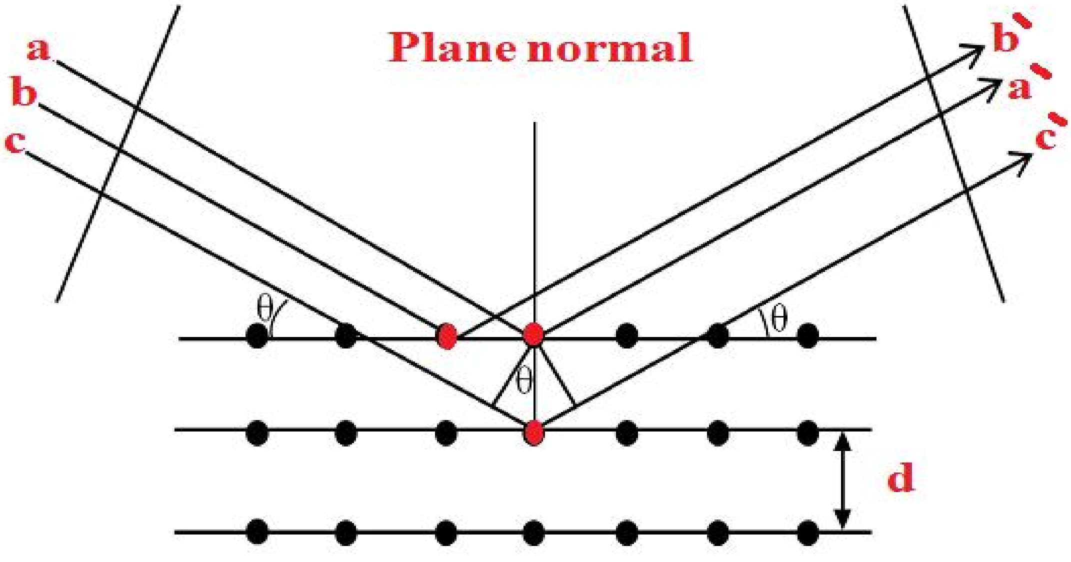


Figure A1-1: Clearly measured incident angle by X-ray diffraction from a layered structure

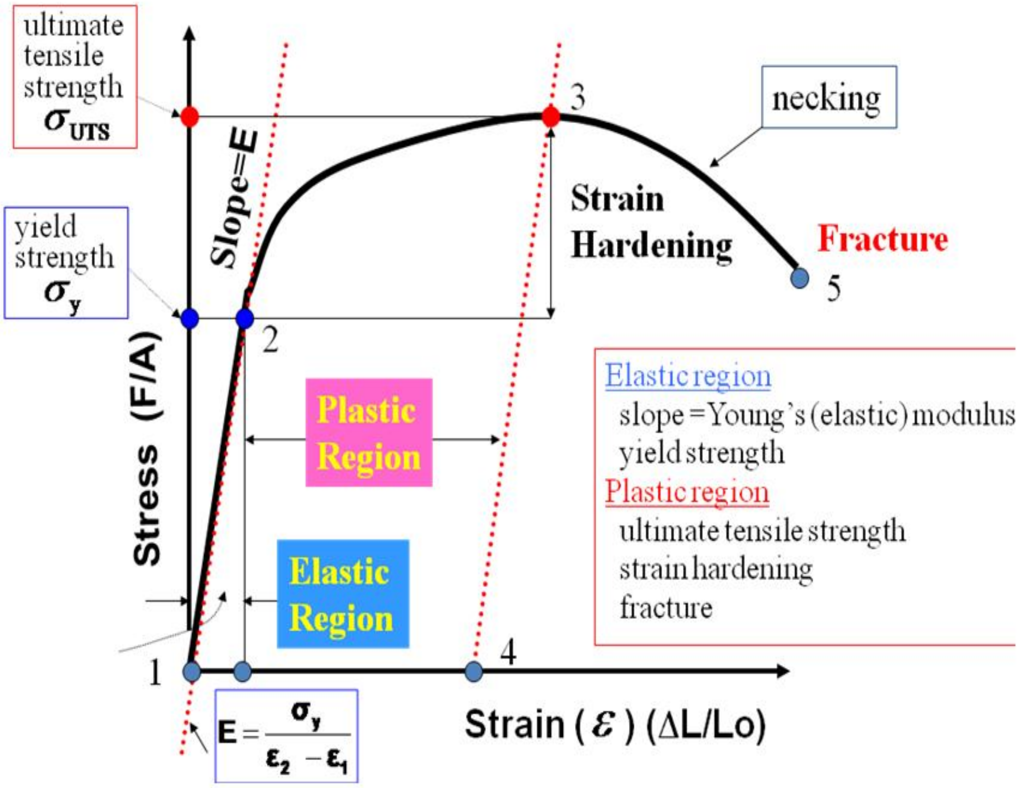


Figure A1-2 : Stress-strain diagram of **tensile** sample, natural rubber/ organoclay nanocomposite (nano-NR)

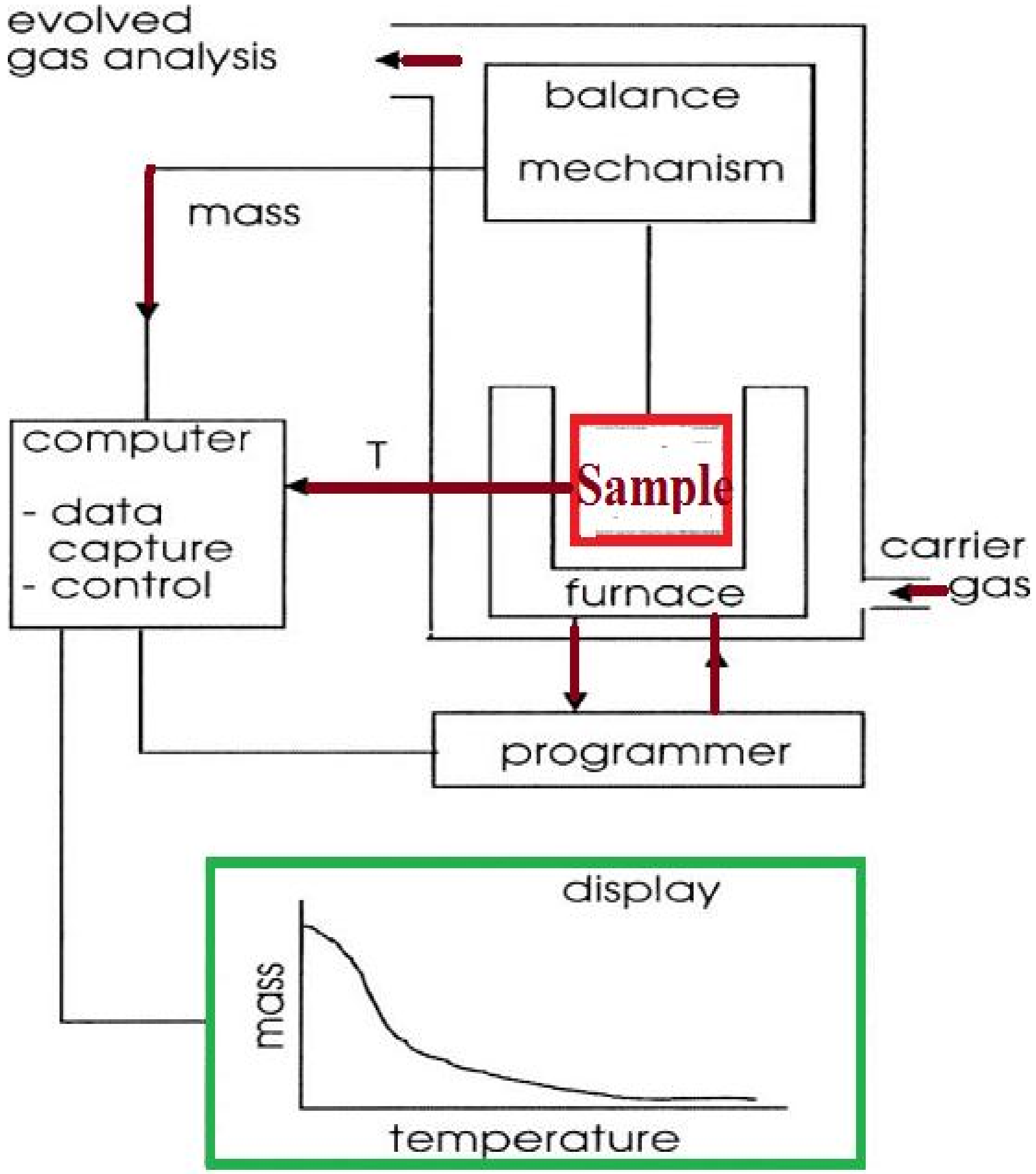


Figure A1-3: The scheme of **TGA** instrument

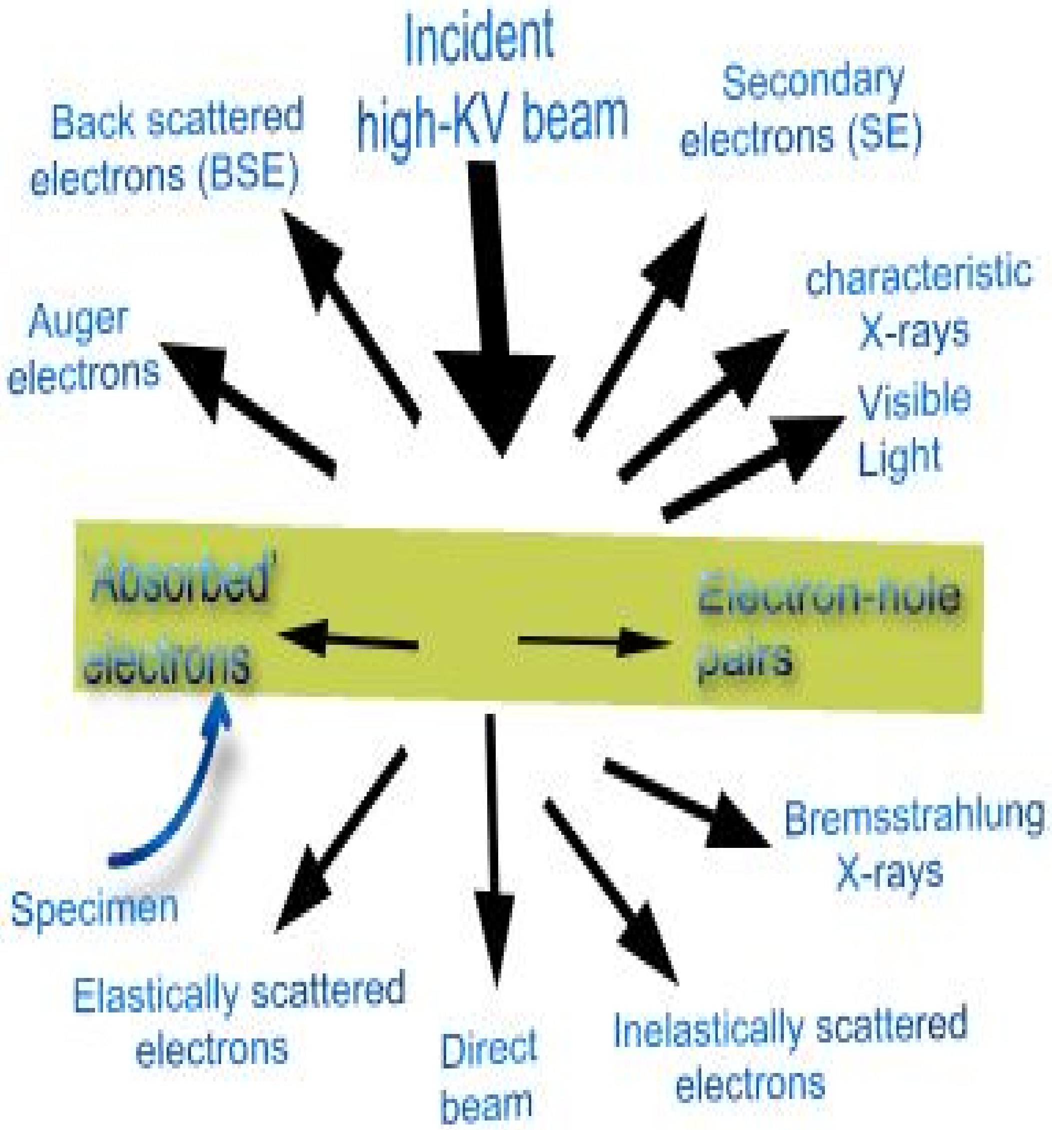
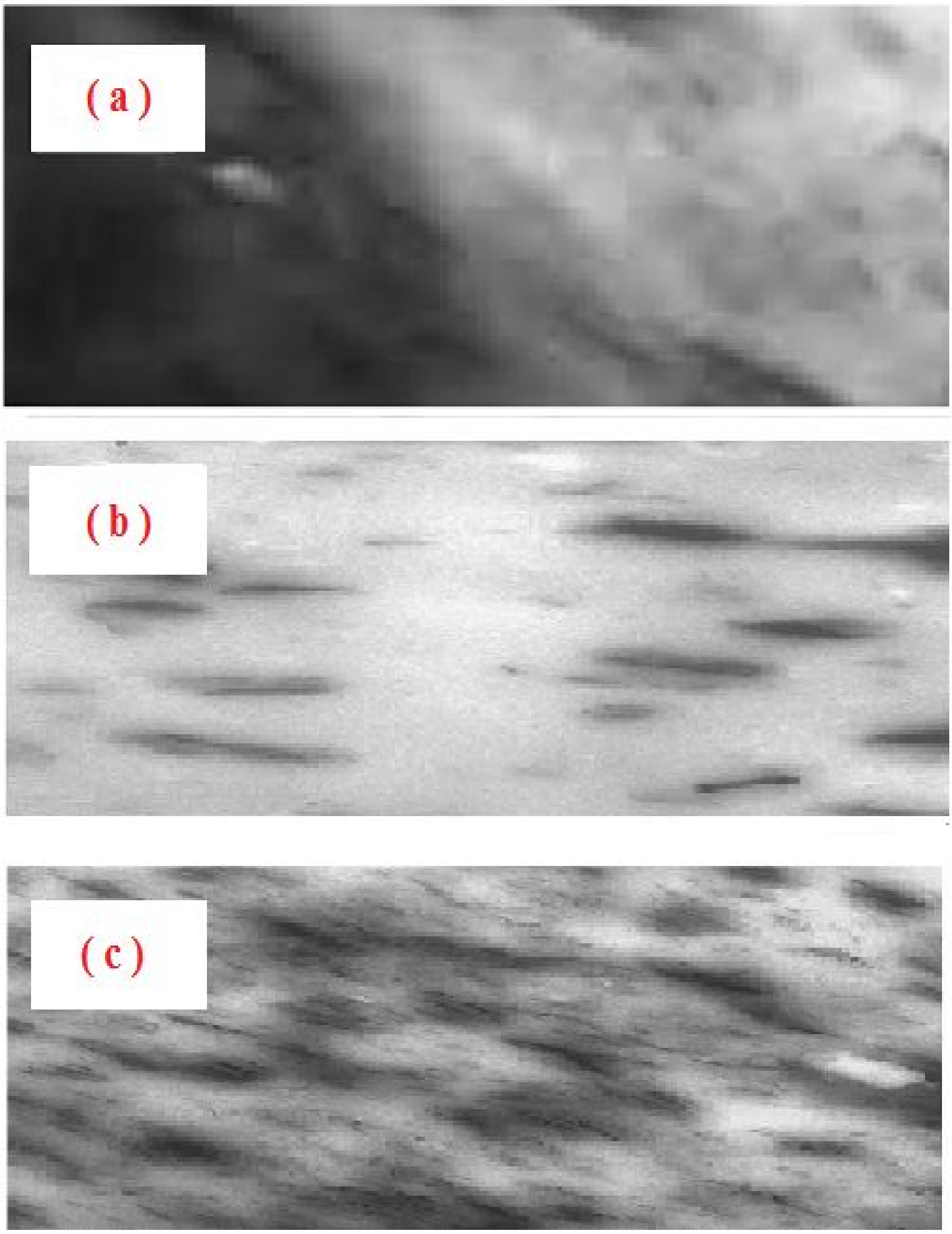


Figure A1-4: The signals generated by electron-specimen interction of **TEM** instrument



FigureA1-5:_TEM image at of a-NR/2 Phr Na-MMT microcomposite & b- NR/2phr DDA-MM , c- NR/3 Phr FAs-MMT nanocomposites

APPENDIX (A2)

TABLES

Table A2-1 The amounts of NR and modified clay in the nano-composite

Sample identity	Weight of NR,g	Weight of orgclay, g
NR mod0	20.00	0.00
NR mod2	19.60	0.40
NRmod3	19.40	0.60
NRmod4	19.20	0.80
NRmod5	19.00	1.00

mod0, mod1, mod2, mod3, mod4, mod5 = 0, 1, 2, 3, 4 and 5 phr weight of organoclay, respectively

Table A2-2 Optimum conditions for microcomposite& nanocomposites

				Ultimate tensile properties		
NR/ clay	Clay,phr	d,nm	Dec.,°C	TS, MPa	E, MPa	Elong.%
NR/Na-MMT	2	1.38	285±15	8.4±0.4	1.1± 0.2	780±10
NR/DDA-MMT	2	2.85	320 ±7	10.3±0.2	2.1± 0.1	830±5
NR/FAs-MMT	3	3.14	365 ±7	11.7±0.2	3.2± 0.1	880±5

APPENDIX (A3)

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Preparation and characterization of natural rubber latex/modified montmorillonite clay nano-composite

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Abstract In this study, new biopolymer nano-composites have been prepared. Fatty amides (FAs) which were synthesized from palm olein, have been used as an organic compound to modify natural clay, sodium montmorillonite. The clay modification was carried out by stirring the clay particles in an aqueous solution of FAs by which the clay layer distance increases from 1.24 to 2.65 nm. The modified clay was then used in the preparation of the natural rubber (NR) nano-composite. The interaction of the modifier in the clay layer was characterized by ray diffraction (XRD), and Fourier transform infrared. The nano-composite was synthesized by melt blending of the modified clay and NR. The nano-composite was then char- acterized using XRD, transmission electron microscopy, thermogravimetric analysis (TGA), and tensile properties measurements. The XRD and transmission electron microscopy results confirmed the production of nano-composites. NR-modified clay nanocomposites show higher thermal stability and significant improvement of mechanical properties in comparison with those of the pure NR.

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Introduction

Montmorillonite clay (MMT) has attracted a lot of attention due to its features such as high cation exchange capacity, swelling ability, and the high platelet aspect ratio. Therefore, it represents the most commonly used non-black filler in polymers and rubber [1–3]. MMT is considered an economical filler to modify processing and performance of natural and synthetic rubbers. However, its reinforcing ability is poor because it has a large particle size and low fatty amides (FAs) surface activity [4, 5].

MMT is hydrophilic in nature because it contains inorganic cations on the basal planar. So, the clay particles can only be dispersed on the microscale in the polymer matrix even though the clay is comprised of silicate layers. Modification of MMT is required to improve its reinforcing ability [6]. A recent way of enhancing this ability is by changing MMT from hydrophilic to organophilic material via ion exchange of the clay interlayer cations with organic cations, such as alkyl ammonium or alkylammonium, to produce organoclay. This process leads to an expansion in the basal spacing of the clay layers [7–9].

The incorporation of organoclay in the polymers and rubber can offer an attractive method to create nano-composites.The improvements in thermal stability and physical and mechanical properties can be achieved by the addition of 2–5 % weight of organoclays in comparison to the neat rubber [10, 11].

In this study, mixed of fatty amides (FAs) synthesized from vegetable oil were used for modification of the MMT. The presence of long-chain Fatty acids (mainly 16 and 18 carbon atoms) in FAs containing O and N donor sets suggests they should be very useful as surfactants for clay modification [12, 13]. The use of FAs will reduce the dependence on petroleum-based surfactants. Modified MMT was used to prepare new rubber/clay nano-composite.

Experimental

Materials

Montmorillonite clay (Kunipia F) with a cation exchange capacity of 119meq 100 g^{-1} was obtained from Kunimine , Japan. Palm olein was obtained from Ngo Chew Hong Oils and Fats (M) Sdn. Bhd., Malaysia. The immobilized lipase used was the product from Novo Nordisk, Denmark. Urea, sodium hydroxide, and hexane were purchased through local suppliers from Merck, Germany. Natural rubber (NR) of SMR (CV60) grade was kindly provided by the Malaysian Rubber Board (MRB), Malaysia.

Preparation of organoclay

Organoclay was prepared with a cationic exchange process, where Na$^+$ in the MMTwas exchanged with the alkylammonium ion from FAs synthesized from triacylglycerides, which was prepared applying the procedure reported by Al-Mulla and coworkers [13], in an aqueous solution. Sodium montmorillonite (Na-MMT) (4.00 g) was stirred vigorously in 600 mL of hot distilled water for 1 h to form a clay suspension. Subsequently, FAs (4.50 g), which had been dissolved in 400 mL of hot water and concentrated hydrochloric acid (16.00 mL) was added into the clay suspension of FAs [14]. After being stirred vigorously for 1 h at 80°C, the organoclay suspension was filtered and washed with distilled water until no chloride was detected with a 1.0 M silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay was ground until the particle size was less than 100 µm before the preparation of the nano-composite.

Preparation of rubber–clay nano-composites

The designed amount of NR was prepared by an internal mixer (Haake Polydrive). The NR was first softened for 1 min and mixed with a required amount of the modified clay in the second and third minutes. The compounds were then moulded in an electrically heated hydraulic press at 130 °C for 10 min and a pressure of 150 kg cm^{-2}. At the end of the molding time, the compounds were immediately cooled for 5 min. The amount of NR and the modified clay used in this study are listed in Table 1.

Characterization

Tensile properties measurements

The tensile strength, tensile modulus, and elongation at the break were measured by using an Instron Universal Testing Machine 4301 at 5 mm min^{-1} of crosshead speed in accordance with ASTMD638 [15]. Seven samples were used for the tensile test and an average of five results was taken as the resultant value.

X-Ray diffraction (XRD) analysis

X-Ray diffraction study was carried out using Shimadzu XRD 6000 diffractometer with CuK radiation ($\lambda = 0.15406$ nm). The diffractogram was scanned in the ranges from 2° to 10° at a scan rate of 1° min^{-1}.

Table 1 The amounts of NR and modified clay in the nano-composite

Sample identity	Weight of NR,g	Weight of organoclay, g
NR mod0	20.00	0.00
NR mod1	19.80	0.20
NR mod2	19.60	0.40
NRmod3	19.40	0.60
NRmod4	19.20	0.80
NRmod5	19.00	1.00

mod0, mod1, mod2, mod3, mod4, mod5 = 0, 1, 2, 3, 4 and 5 % weight of organoclay, respectively

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the samples were recorded by the FTIR spectrophotometer (Perkin Elmer FT-IR-Spectrum BX, USA) using the KBr disc technique.

Thermogravimetric analysis (TGA)

The thermal stability of the samples was studied by using a Perkin Elmer model TGA 7 Thermo gravimetry analyzer. The samples were heated from 35 to 800 °C with a heating rate of 10°C min^{-1} under nitrogen atmosphere with a nitrogen flow rate of 20 mL min^{-1}.

Transmission electron microscopy (TEM)

The dispersion of clay was studied by using energy filtering transmission electron microscopy (EFTEM). TEM pictures were taken in a LEO 912 AB EFTEM with an acceleration voltage of 120 keV. The specimens were prepared using a Ultracut E (Reichert and Jung) cryomicrotome. Thin sections of about 100 nm were cut with a diamond knife at −120 °C .

Figure 1 shows the effect of clay content on the tensile strength properties of NR/ Na-MMT microcomposite and NR/FAs-MMT nanocomposites. The reinforcing effect of unmodified MMT in the NR matrix was increased with a low rate of increment. The maximum tensile strength was obtained when the clay content was 2 % of the weight. Further increasing the clay content decreases the tensile strength. Na - MMT acts as conventional particulate filler in the NR matrix.

Low tensile strength is obtained for NR/Na-MMT because the clay–clay interactions are stronger than those NR–clay interactions [16]. A poor compatibility between the clay and the MR matrix is expected as the mixing is at micro-level [5]. A similar behavior of the clay content affects the modulus and elongation at the break of NR/ Na-MMT is observed (Figs. 2, 3).

The increment of tensile strength, modulus, and elongation at the break for the nano-composite with FAs-MMT loadings are similar to that of microcomposite. However, the rate of the increment of tensile properties for the nano-composite increases. The highest tensile strength, modulus, and elongation at the break of the FAs-MMT nano-composite is obtained when 3 % of FAs-MMT loadings are used (Figs. 1, 2, 3). The enhancing effect of the FAs-MMT on the mechanical properties is probably due to the increase of the amount of the incorporated NR chains in the clay layers. The rubber–clay interactions include the interactions of the intercalated NR chains with surface layers of the silicates. However, the tensile strength modulus and elongation at the break decrease when the FAs-MMT loadings are increased to more than 3 %. The decrease of tensile strength, modulus, and elongation at the break is due to the decrease of the NR chains interaction with the clay as the clay coagglomerates.

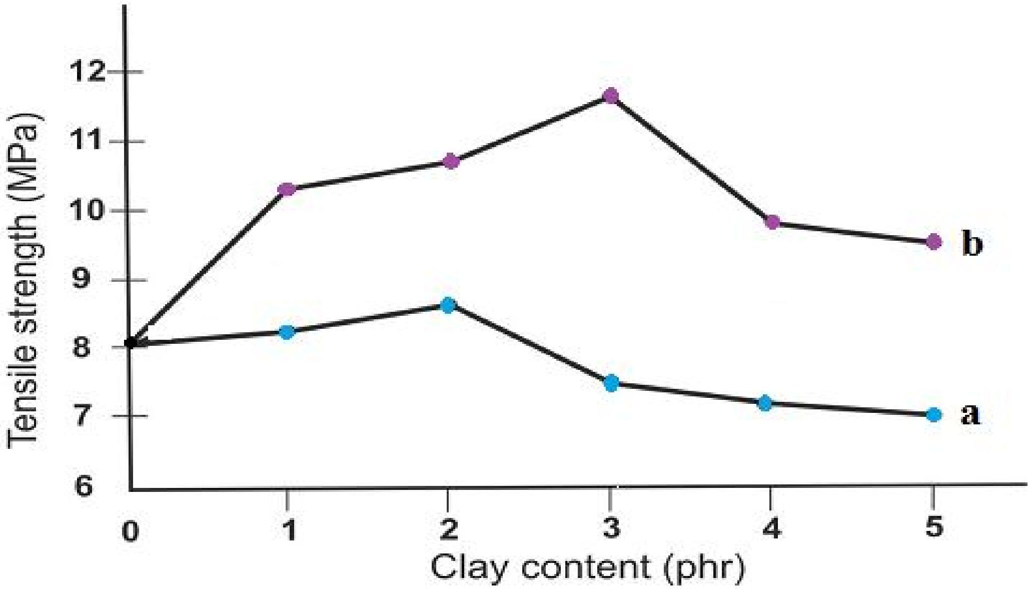

Fig. 1 Tensile strength of a NR/Na-MMT and b NR/FAs-MMT

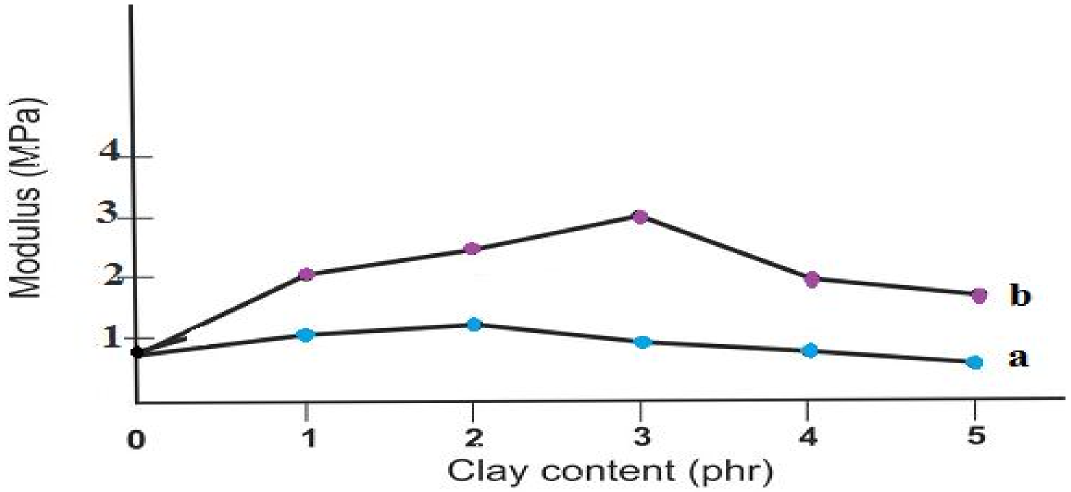

Fig. 2 Modulus of a NR/Na-MMT and b NR/FAs-MMT

The clay galleries were changed from the originally hydrophilic to organophilic silicate resulting in increases in the layer-to-layer spacing of Na-MMT due to the presence of FAs chain in the clay galleries [14]. Based on Bragg's law (n $\lambda = 2d \sin \theta$), the d refers to the distance of two consecutive clay layers, and k is the wavelength of the intercept X-rays at the incident angle h. By using the XRD test, Na-MMT assigns to d the diffraction peak at $2\theta = 7.21$. This value indicates an interlayer distance of the Na-MMT with a basal spacing of 1.24 nm. The Na-MMT surface was treated by FAs as an intercalation agent through a cation exchange process. The cationic head groups of the intercalation agent molecule would preferentially reside at the layer surface and the aliphatic tail will radiate away from the surface (Fig. 4).

The maximum basal spacing of FAs-MMT increases from 1.24 to 2.65 nm (Table 2), indicating that these FAs were successfully intercalated into the Na-MMT galleries.

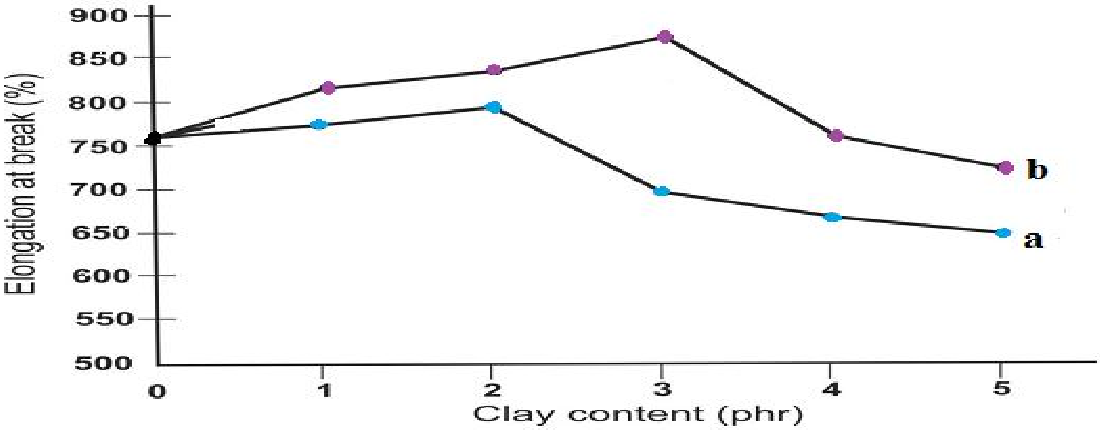

Fig. 3 Elongation at break of a NR/Na-MMT and b NR/FAs-MMT

Figure 5 shows the XRD patterns of the composites prepared using unmodified and modified MMT by FAs. The basal spacing of the clay increased to 3.08 nm in the nano-composite but with no significant improvement of basal spacing in the microcomposite (Table 3). The XRD pattern suggests that the nano-composite produced is an intercalated type.

The presence of ion FAs in the MMT was determined by FTIR spectroscopy. FTIR spectra of Na-MMT, FAS-MMT, and FAS are shown in Fig. 5. The spectra show the presence of two peaks corresponding to the Si–O stretching and interlayer water deformation vibration from the infrared spectrum of the Na-MMT, which were found at the wavelengths of 1,043 and 1,631 cm^{-1}, respectively. The FAs- MMT spectrum shows the presence of C–H asymmetric at 2,927 cm^{-1}, while the C–H symmetric stretching is shown by 2,850 cm^{-1}. The band at 1,471 cm^{-1} is assigned to an amide salt [7].

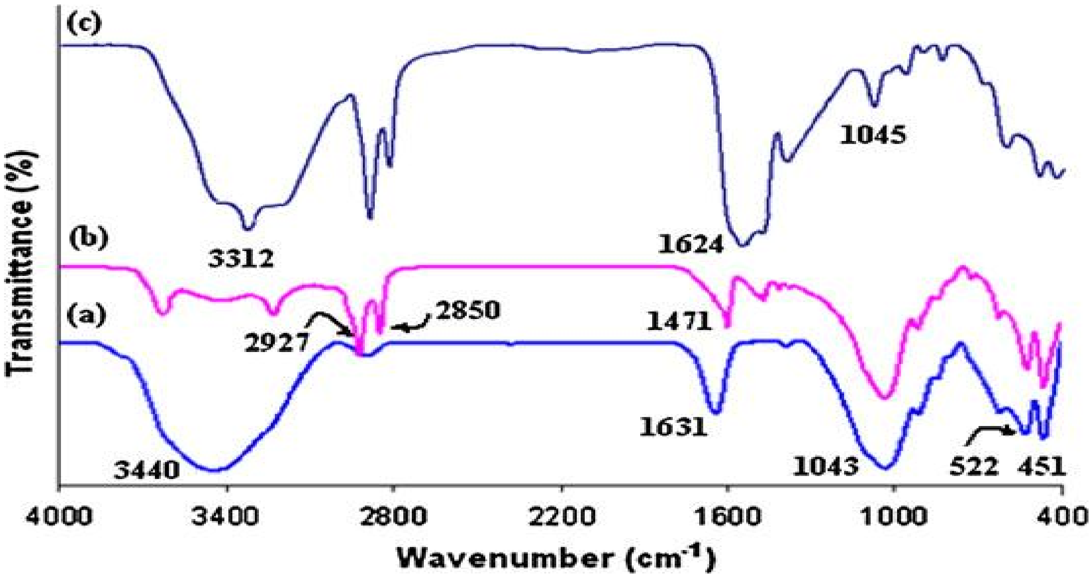

Fig. 4 FTIR spectra of a Na-MMT, FAs-MMT and c FAs

Table 2 Diffraction angle and basal spacing of natural clay (Na-MMT) and modified clays with the FAs-MMT

Sample	Exchanged cation	2θ,degree	d- spacing, nm
Na-MMT	Na+	7.19	1.24
FAs-MMT	$RCO\text{-}NH_3^+$	3.47	2.65

The band at 3,440 cm^{-1} is due to the O–H stretching vibration of the Na-MMT. The other strong absorption bands at 522 and 451 cm^{-1} indicate the presence of Al–O stretching and Si–O bending, respectively, in the clay. The absorption bands at 3,312, 1,624, and 1,045 cm^{-1} are attributed to –NH$_2$ group stretching, C=O stretching, and C–N stretching of amide, respectively.

Figure 5 shows the weight loss curves of Na-MMT, FAs, NR, NR / Na-MMT microcomposite, and NR/FAs-MMT nano-composite. Na-MMT contains water due to hydrated sodium (Na^{+}) cations intercalated inside the clay layers. The presence of alkylammonium groups within the MMT interlayer spacing lowers the surface energy of the inorganic structure and will transform organophobic to organophilic materials. The major difference between the thermogram of the unmodified clay and that of the organoclay is that the organic the organic constituent in the organoclay decomposes in this range (Fig. 5a).

The FAs decomposed as the temperature is increased from 155 to 600 °C. The decomposition process ends at around 310 °C (Fig. 5b). It can be observed that the decomposition temperatures of the FAs-MMT (Fig. 5c) are higher than those of the pure FAs and Na-MMT. The increase in the decomposition temperatures of the FAS in the organoclays implies that there is a strong intermolecular interaction between the alkylammonium cations and the clay. In other words, after the ion of the FAs is intercalated and attached to the silicate layers of the clay, their decomposition temperature increases.

Thermogravimetric analyses were also done on the NR/Na-MMT microcomposite and the NR/FAs-MMT nano-composite in order to determine the effect of unmodified and modified clay content in the rubber matrix on thermal properties. The results of the TGA are shown in (Fig. 5e, f). The onset of the degradation of the nano-composite is higher, at 365 °C, for NR containing FAs-MMT, compared to that of the pure NR (Fig. 5d) and NR/Na-MMT microcomposite, which are 264 and 285 °C, respectively. The results show that the thermal stability increases with the addition of the FAs. The presence of silicate layers dispersed homogeneously in the polymer sheet hinders the permeability of volatile degradation products out from the material and helps delay the degradation of the nano-composite

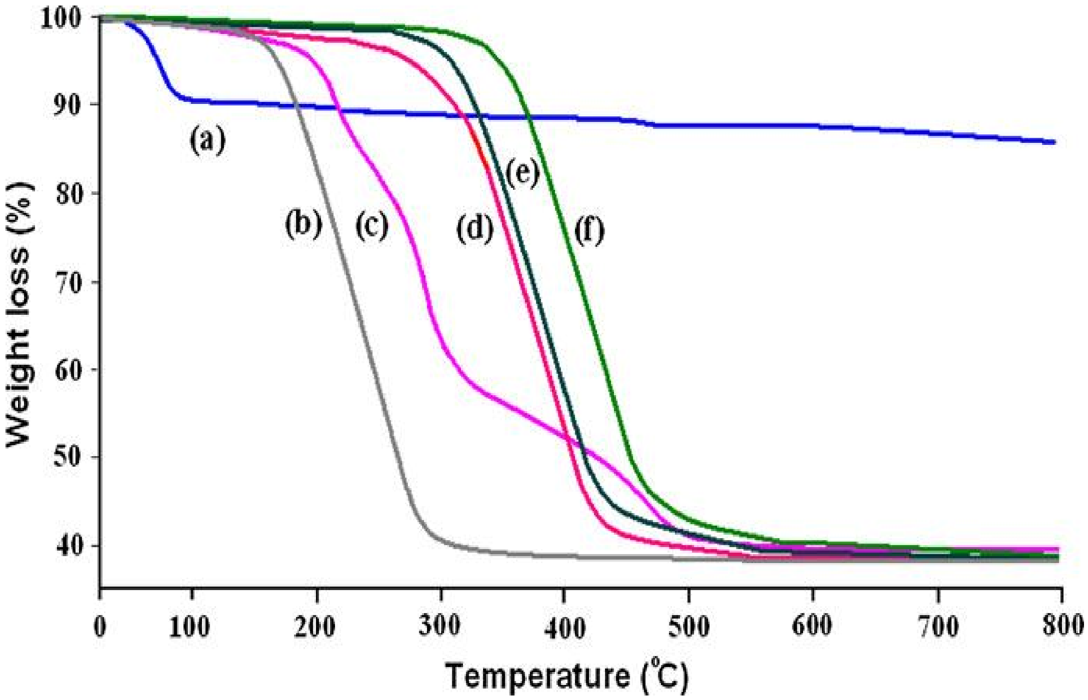

Fig. 5 TGA thermograms of a Na-MMT, b Fas, c FAs-MMT, d NR, e NR/Na-MMT microcomposite and f NR/FAs-MMT nano-composite

Table 3 Diffraction angle and basal spacing of NR/FAs unmodified and modified clay composites

Sample	2θ,degree	d-spacing, nm
NR	0.00	0.00
NR/Na-MMT	6.91	1.29
NR/FAs-MMT	2.75	3.14

Transmission electron microscopy micrographs of the NR composites reinforced with Na-MMT and FAs-MMT are illustrated in Fig. 6. The NR/Na-MMT micrograph shows that the original Na-MMT stack morphology is fully preserved in the NR matrix due to the incompatible nature of both constituents (Fig. 6a). Dark bundles represent the thickness of the individual clay layers or agglomerates. Figure 6b exhibits the TEM images of NR/3 % FAs-MMT nano-composites, which shows good properties and composite effects. The dark bundles of the modified clay are dispersed in the NR matrix with an intercalated state, which can be observed clearly in the images.

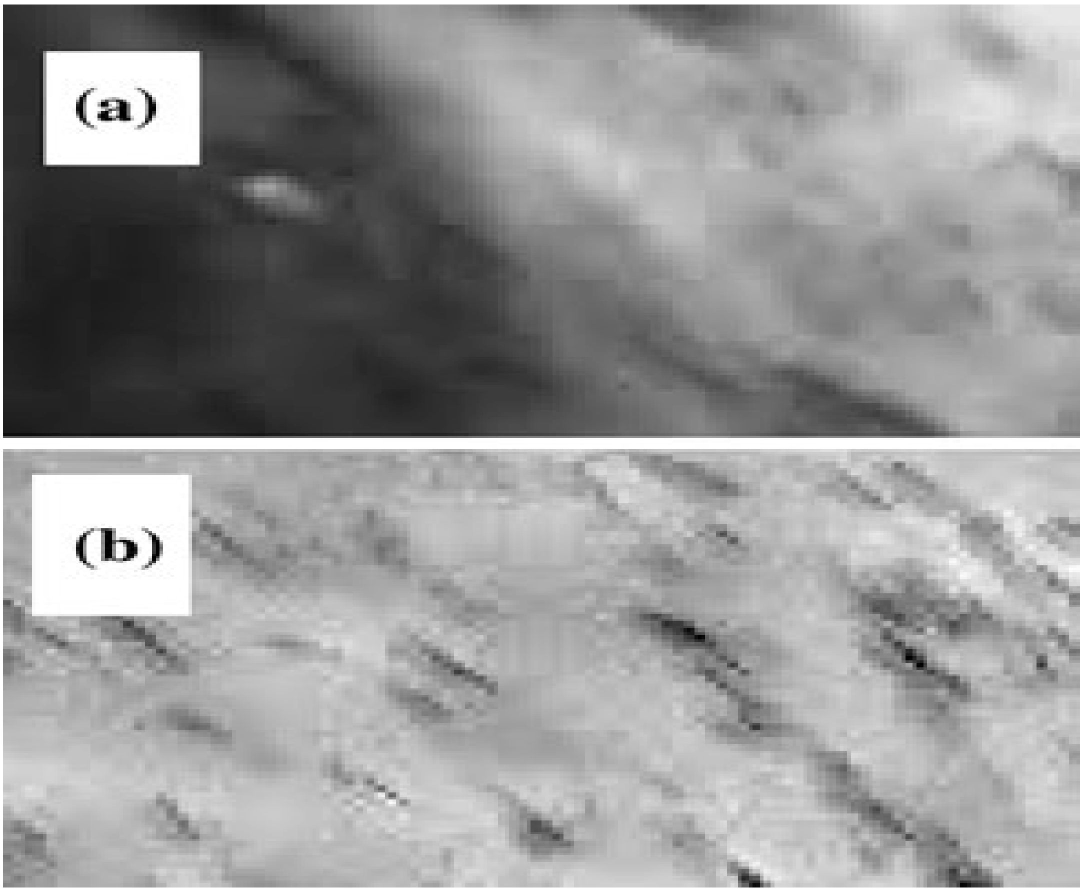

Fig. 6 TEM micrographs of a NR/2 % Na-MMT microcomposite and b NR/3 % FAs-MMT nano-composite

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References

1. S. Varghese, J. Karger-Kocsis, J. Appl. Polym. Sci. 91, 813 (2004)
2. A.H. Suhail, E.A.J. Al-Mulla, S.A. Aowda, Ind. Crop. Prod. 33, 23 (2011)
3. E.A.J. Al-Mulla, Korean J. Chem. Eng. 28, 620 (2011)
4. Y. Li, H. Shimizu, Macromol. Biosci. 7, 921 (2007)
5. M. Arroyo, M. Lopez-Manchado, B. Herrero, Polymer 44, 2447 (2003)
6. Y. Xi, W. Martens, H. He, R. Frost, J. Therm. Anal. Cal. 81, 91 (2005)
7. E.A.J. Al-Mulla, Fiber. Polym. 12, 444 (2011)
8. W.M.Z. Yunus, E.A.J. Al-Mulla, N.A. Ibrahim, M.Z.A. Rahman, Polym
. Polym. Compos. 18, 451 (2010)

9. A.Y. Coran, R.P. Patel, Rubber Chem. Technol. 53, 141 (1980)
10. W.H. Hoidy, E.A.J. Al-Mulla, K.W. Al-Janabi, Polym. Environ. 18, 606 (2010)
11. W.H. Hoidy, M.B. Ahmad, E.A.J. Al-Mulla, N.A. Ibrahim, J. Appl. Sci. 10, 97 (2010)
12. E.A.J. Al-Mulla, N.A.B. Ibrahim, K. Shameli, M.B. Ahmad, W.M.Z.W. Yunus, Res. Chem. Inter- med. (2012). doi:10.1007/s11164-012-0687-6
13. W.M.Z. Yunus, E.A.J. Al-Mulla, N.A. Ibrahim, M.Z.A. Rahman, J. Oleo Sci. 59, 59 (2010)
14. E.A.J. Al-Mulla, Polym. Sci. Ser. A 53, 149 (2011)
15. ASTM D638-03, Standard Test Method for Tensile Properties of Plastics, vol 08.01 (2004)
16. Y. Vu, J. Mark, L. Pham, M. Engelhardt, J. Appl. Polym. Sci. 82, 1391 (2001)

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DOI 10.1007/s12210-014-0307-z .

A comparative study of different surfactants for naturalrubber clay nanocomposite preparation

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Abstract Nanocomposites on the basis of natural rubber and highly anisotropic nanoclay have gained significant attention due to their excellent thermal, barrier, and mechanical (tensile) properties. A nanocomposite based- natural rubber (NR) with fatty amides (FAs) (which was synthesized from vegetable oil)-modified clay was pre- pared using montmorillonite (MMT) as a natural clay. The product was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results were compared with those nanocomposites produced based on dodecyl ammonium chloride (DDA) as surfactant. It was observed that the NR-modified clay nanocomposites based on FAs show higher thermal stability and significant improvement of tensile properties in comparison with those of the NR-modified clay nanocomposites based on DDA as surfactant. The use of FAs for clay modification will reduce the dependence on petroleum-based surfactants. In addition to renewable resources, these nanocomposites are considered as environmentally friendly.

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Keywords Nanocomposites Natural rubber DDA FAs

1 Introduction

Thermoplastic elastomers are a class of polymers that have rubber-like behavior, but can be melting processed like thermoplastic polymers (Bohmick 2001). The most spec- tacular results in the search for thermoplastic elastomers have been achieved by blending rubbers and plastics. Among the various rubber–plastic, thermoplastic natural rubber is the most useful for natural rubber-producing countries. Several studies have been made in this field regarding processability and rheological behavior (Tinker1987), mechanical properties, strength and other behaviors (Roy and Bhowmick 1990).

Clay (montmorillonite) is one of the most widely used nonblack fillers for rubber. It is an in expensive natural mineral which has been an important part of the rubber industry. In this type of industry, it is used as economical filler to modify processing and performance of natural and synthetic rubbers but the reinforcing ability of clay is poor due to its large particle size and low surface activity. The clay particles could only be dispersed on the microscale in the polymer matrix even though the clay comprised of silicate layers having a 1-nm-thick planar structure (Al- Mulla 2011a). The layers cannot be separated from each other through general polymer processing methods. The recent way of improving the reinforcing ability of clay is done by changing the hydrophilic nature of clay to orga- nophilic. This is done by ion exchange of the clay inter- layer cations with organic cations such as alkylammonium or alkylphosphonium. Using the modified clay, many researchers have succeeded in intercalating various polymers in the clay interlayer to prepare polymer/clay nanocomposites (Masoud et al. 2006; Al-Mulla 2011b).

Dodecyl ammonium chloride (DDA) was used as surfactant based on petroleum to produce organoclay using montmorillonite as a natural clay for polymer nanocomposite preparation (Vu et al. 2001), in our previous report (Al-Shemmari et al. 2012). Mixed fatty amides (FAs) synthesized from vegetable oil were used for modification of the MMT. Modified MMT was used to prepare new rubber/clay nanocomposites.

In this study, two types of rubber nanocomposite properties were discussed using the above surfactants. With FAs as a modifier for production of rubber nanocomposites, more thermal stability and improvement in tensile properties were observed compared to those used DDA in rubber nanocomposites.

2 Experimental

2.1 Materials

Dodecyl ammonium chloride was obtained from Fluka A. G. Chemische Fabrik (Switzerland). Palm olein was obtained from Ngo Chew Hong Oils and Fats (M) Sdn. Bhd., Malaysia. Montmorillonite clay (Kunipia F) with a cation exchange capacity of 119 meq 100 g^{-1} was obtained from Kunimine, Japan. The immobilized lipase used was the product from Novo Nordisk, Denmark. Urea, sodium hydroxide, and hexane were purchased through local suppliers from Merck, Germany. Natural rubber (NR) of SMR (CV60) grade was kindly provided by the Malaysian Rubber Board (MRB), Malaysia. All chemicals used are of the highest purity available.

2.2 Preparation of organoclay

Organoclay was prepared with a cationic exchange process, where N^+ in the MMT was exchanged with the alky- lammonium ion from DDA or FAs synthesized from tria- cylglycerides, which was prepared applying the procedure reported by Al-Mulla and coworkers (Al-Mulla et al.2010), in an aqueous solution. Sodium montmorillonite (Na-MMT) (4.00 g) was stirred vigorously in 600 mL of hot distilled water for 1 h to form a clay suspension. Subsequently, FAs (4.50 g), which had been dissolved in 400 mL of hot water and concentrated hydrochloric acid (16.00 mL) was added into the clay suspension of DDA or FAs. After being stirred vigorously for 1 h at 80 °C, the organoclay suspension was filtered and washed with dis- tilled water until no chloride was detected with a 1.0 M silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay was ground until the particle size was silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay was ground until the particle size was less than100 µm before the preparation of the nanocomposites (Yunus et al. 2010a, b).

2.3 Preparation of NR/clay nanocomposites

The designed amount of NR was prepared by an internal mixer (Haake Polydrive). The NR was first softened for 1 min and mixed with a required amount of the modified clay in the second and third minutes. The compounds were then molded in an electrically heated hydraulic press at 130 °C for 10 min and a pressure of 150 kg cm^{-2}. At the end of the molding time, the compounds were immediately cooled for 5 min. The amount of NR and the modified clay used in this study are listed in Table 1.

Table 1 The amount of NR and modified clay (DDA-MMT or FAs- MMT) in the nanocomposites

Sample identity	Weight of NR (g)	Weight of orangoclay (g)
NR mod0	20.00	0.00
NR mod1	19.80	0.20
NR mod2	19.60	0.40
NR mod3	19.40	0.60
NR mod4	19.20	0.80
NR mod5	19.00	1.00

mod0, mod1, mod2, mod3, mod4, mod5 = 0, 1, 2, 3, 4 and 5 phr weight of organoclay, respectively

2.4 Characterization

2.4.1 Tensile property measurements

The tensile strength, modulus, and elongation at the break were measured by using an Instron Universal Testing Machine 4301 at 5 mm min^{-1} of crosshead speed in accordance to ASTM D638-03, standard test method for tensile properties, Vol. 08.01, 2004. Seven samples were used for the tensile test and an average of five results was taken as the resultant value.

2.4.2 X-Ray diffraction (XRD) analysis

X-Ray diffraction study was carried out using Shimadzu XRD 6000 diffractometer with CuK radiation ($\lambda = 0.15406$ nm). The diffractogram was scanned in the ranges from 2° to 10° at a scan rate of 1° min^{-1}.

2.4.3 Thermogravimetric analysis (TGA)

The thermal stability of the samples was studied using a Perkin Elmer model TGA 7 Thermo gravimetry analyzer. The samples were heated from 35 to 800 °C with a heating rate of 10 °C min^{-1} under nitrogen atmosphere with a nitrogen flow rate of 20 mL min^{-1}.

2.4.4 Transmission electron microscopy (TEM)

The dispersion of clay was studied using energy filtering transmission electron microscopy (EFTEM). TEM pictures were taken in a LEO 912 AB EFTEM with an acceleration voltage of 120 keV. The specimens were prepared using an Ultracut E (Reichert and Jung) cryomicrotome. Thin sections of about 100 nm were cut with a diamond knife at −120 °C.

3 Results and discussion

3.1 X-ray diffraction measurements

X-ray diffraction technique was used to measure the interlayer distance of the silicate layers of the clay and modified clay with alkyl ammonium cations. It was also used to measure the silicate layers' distribution of modified clays in the NR matrix. Table 2 shows the interlayer distance of natural clay (Na-MMT) and modified clays with the alkyl ammoniums (DDA-MMT and FAs-MMT) (Thength 1979). The interlayer distance of Na-MMT was expanded from 1.21 nm to about 1.67 and 2.65 nm for DDA-MMT and FAs- MMT.

The summary of the intercalated silicate layer in NR/ unmodified MMT and NR/modified MMT nanocomposites obtained from the XRD analysis is given in Table 3.

Table 2 Diffraction angle and basal spacing of natural clay (Na-MMT) and modified clays with the FAs-MMT

Sample	Exchanged cation	2θ ,degree	d -spacing, nm
Na-MMT	Na+	7.19	1.24
DDA-MMT	$C_{12}H_{25}NH_3^+$	5.26	1.67
FAs-MMT	$RCO\text{-}NH_3^+$	3.47	2.65

Table 3 XRD analysis of NR/unmodified MMT and NR/modified MMT composites

NR/Type of clay	d-Spacing, nm				
	1 phr	2 phr	3 phr	4 phr	5 phr
NR/Na-MMT	1.37	1.38	1.33	1.31	1.30
NR/DDA-MMT	1.83	2.85	2.73	2.03	1.69
NR/FAs-MMT	2.05	2.78	3.14	2.15	1.90

3.2 Tensile property measurements

Figure 1 shows the tensile strength of NR/Na-MMT microcomposite and organoclays' (NR/FAs-MMT and NR/ DDA-MMT) nanocomposites. As expected, the silicate- reinforced system prepared by melt mixing NR with vari- ous amounts of organoclay has superior tensile strength relative to pristine NR. The maximum tensile strength was obtained when clay content (Na-MMT) was 2 phr of the weight. Further increasing the clay content decreases the tensile strength. A poor compatibility between the clay and the NR of the clay content affects the modulus and elongation at the beak of NR/Na-MMT is observed (Figs. 2 and 3 matrix is at micro-level (Arroyo et al. 2003). A similar behavior of the clay content affects the modulus and elongation at the break of NR/Na-MMT is observed (Figs 2 and 3).

The Figs. 1, 2 and 3 also show that organoclay of FAs-MMT and DDA-MMT renforced nanocomposites have higher tensile properties (tensile strength , modulus

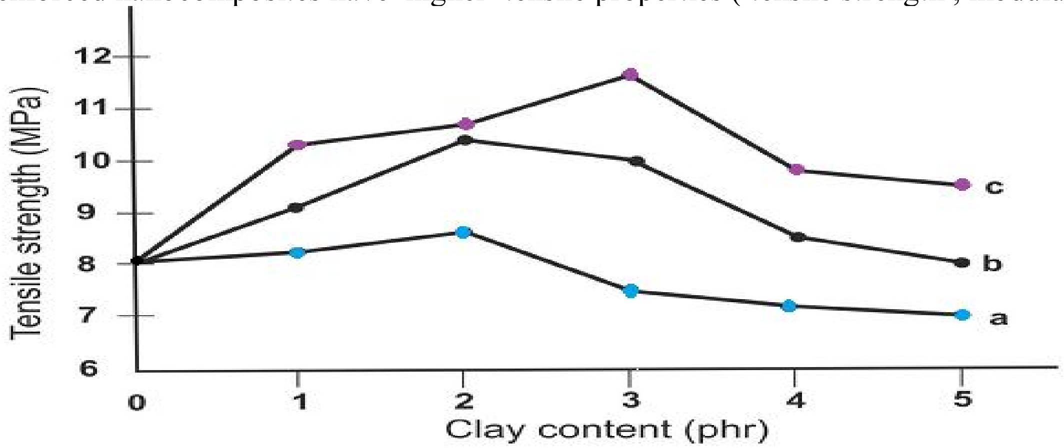

Fig. 1 Tensile strength of a NR/Na-MMT microcomposite and b NR/DDA-MMT, c NR/FAs-MMT nanocomposites

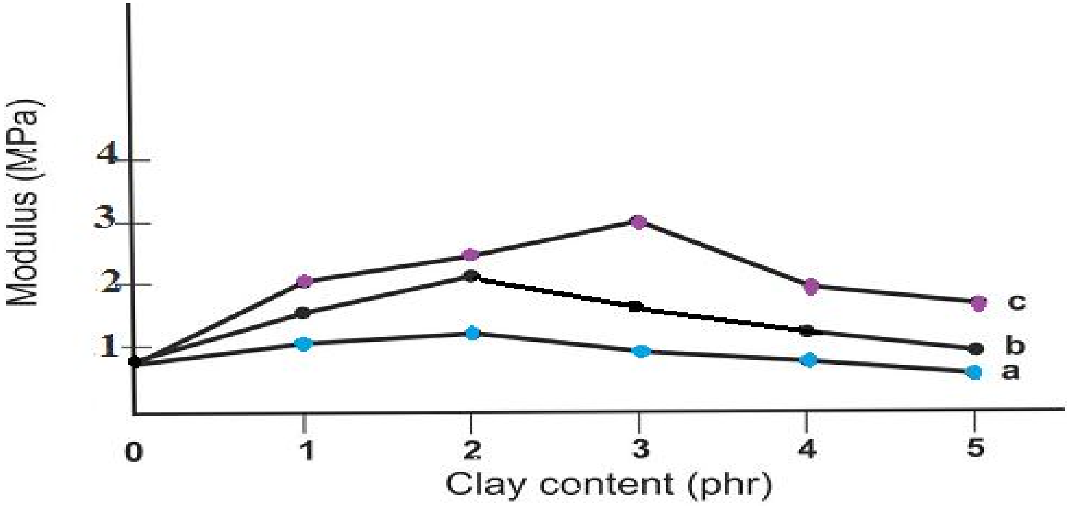

Fig. 2 Modulus of a NR/Na-MMT, b NR/DDA-MMT and c NR/ FAs-MMT nanocomposites

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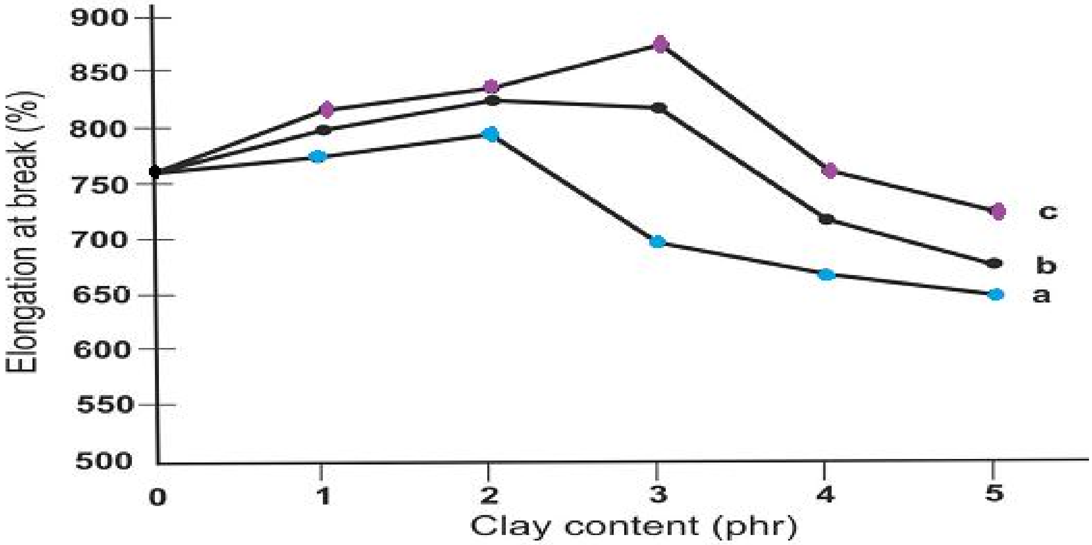

Fig. 3 Elongation at the break of a NR/Na-MMT, b NR/DDA-MMT and NR/ FAs-MMT nanocomposites

and elongation %) compared to unmodified montmorillonite because the clay galleries were changed from the originally hydrophilic to organophilic silicate resulting in increases in the layer to layer spacing of Na-MMT due to the presence of FAs or DDA chain in the clay galleries (Al-Mulla 2011c; Nielsen 1974; Agag et al. 2001).

The highest tensile properties of NR/DDA-MMT (2 phr) and NR/FAs-MMT (3 phr) nanocomposites obtained are shown in Figs. 1, 2 and 3.

However, at higher clay content i and e (2 phr and 3 phr) for DDA-MMT and FAs-MMT, respectively, tensile properties start to decrease and remain constant with increasing clay content up to 5 phr.From the above testing, it was shown that the mechan ical properties (tensile properties) of NR/FAs-MMT are superior to those of NR/DDA-MMT.

3.3 Thermogravimetric analysis (TGA)

Figure 4 shows the weight loss curves for increasing temperatures of NaMMT, DDA, FAs, DDA-MMT, FAs- MMT, NR and NR/2 phrNa-MMT and NR/2 phr DDA- MMT, NR/3 phr FAs-MMT nanocomposites.

Na-MMT contains water due to hydrated sodium (Na^+) cation intercalated inside the clay layers.The presence of alkylammonium groups from vegetable or petroleum-based surfactants within the MMT interlayer spacing lowers the surface energy of the inorganic structure and will transform organophobic to organophilic materials. The major differ- ence between the thermogram of the unmodified clay and that of the organoclay is that the organic constituents in the organoclay decompose in the range 200–500 °C.

The DDA and FAs decomposed as the temperature is increased from 120 to 580 °C and 155 to 600 °C, respectively. The decomposition process of DDA and FAs ends at around 295, 310 °C, respectively as shown in Fig. 4b, c. It can be observed that the decomposition temperature of the FAs-MMT Fig. 4e is higher than those of DDA-MMT and pure FAs, DDA and Na-MMT. The increase in the decomposition temperatures of DDA or FAs in the organoclays implies that there is a strong intermolecular interaction between the alkyl ammonium cations and the clay. In other words, after the ion of the DDA or FAs is intercalated and attached to the silicate layers of the clay, their decomposition temperature increases.

Thermogravimetric analysis (TGA) was also done on the NR/Na-MMT microcomposites and two types of nanocomposites (NR/DDA-MMT and NR/FAs-MMT) in the order to determine the effect of unmodified and modified by vegetable oil or petroleum oil clay content in the rubber matrix on thermal properties. The results of the TGA are shown in Fig. 4g–i. The onset of the degradation of the nanocomposites (NR/2 phrDDA-MMT and NR/3 phr FAs-MMT) is higher at (320–365 °C), respectively, compared to that of pure NR, NR/2 phrNa-MMT microcomposites.

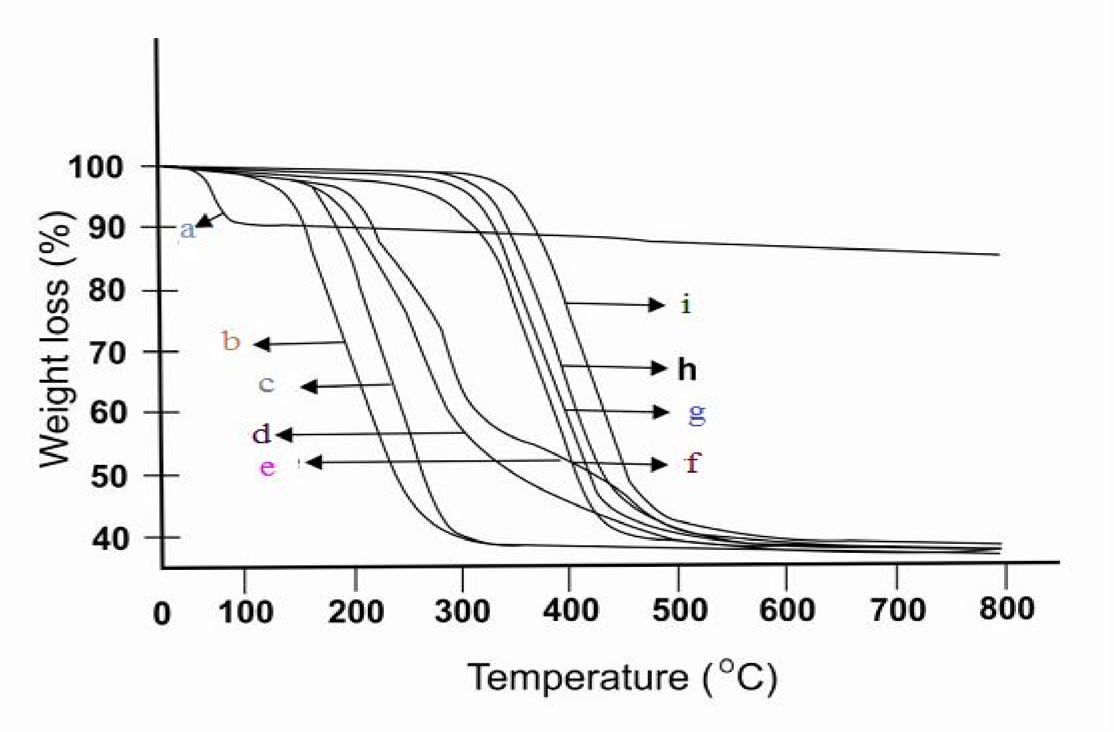

Fig. 4 TGA thermograms of a Na-MMT, b DDA, c FAs, d DDA- MMT, e FAs-MMT, f NR, g NR/2 phrNa-MMT, h NR/2 phrDDA- MMT, and i NR/3 phrFAs-MMT

The results from Fig. 4 showed that the NR with modified clay nanocomposites based on FAs shows higher thermal stability in comparison with those of the NR with modified clay nanocomposites based on DDA surfactant because NA/FAs-MMT has more homogeneous distribu- tion of silicate layer without clay aggregates and higher (d- spacing). The results also show that thermal stability increases with the increase of DDA-MMT and FAs-MMT loading up to 2–3 phr, respectively, and increase above this percentage does not improve the thermal stability.

On the other hand, NR/Na-MMT shows only slight improvement in the thermal stability compared to the nanocomposites because the hydrophilic clay sheets are not well dispersed (Hoidy et al. 2010; Yunus et al. 2010a, b), and the latest was greater than NR/Na-MMT.

3.4 Transmission electron microscopy (TEM)

Transmission electron microscopy micrograph observtions are shown in Fig.5a, b. NR/2 % DDA-MMT illustrates exfoliated lamellae and aggregates of tactoide.

However, the NR/%FAs-MMT shows more homogenous distribution of silicate layer without clay aggregates. Also the XRD pattern of both NR/DDA-MMT and NR/FAs-MMT clearly show that interlayer distance reduces with high increase of organoclay contents. The extent of intercalation depends on several factors such as the polymer transport process through the agglomerate micropores, agglomerate size, diffusion elastomer chain within the silicate layer and the nature of the elastomer itself (Vu et al. 2001). Table 3 shows the interlayer silicate distance of the clay layer obtained from the XRD analysis.

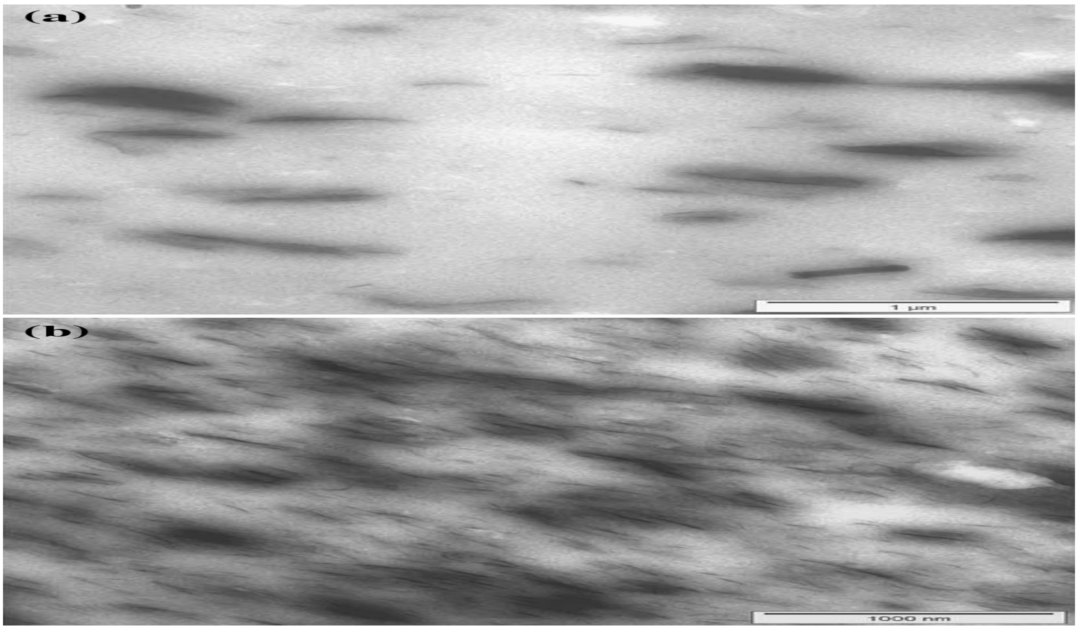

Fig. 5 TEM image at of a NR/2 phr DDA-MMT and b NR/3 phr FAs-MMT

References

Agag T, Koga T, Takeichi T (2001) Studies on thermal and mechanical properties of polyimide-clay nanocomposites. Pol- mer 42:3399–3408

Al-Mulla EAJ (2011a) Polylactic acid/epoxidized palm oil/fatty nitrogen compounds modified clay nanocomposites: preparation and characterization. Korean J Chem Eng 28:620–626

Al-Mulla EAJ (2011b) Preparation of new polymer nanocomposites based on poly (lactic acid)/fatty nitrogen compounds modified clay by a solution casting process. Fiber Polym 12:444–450

Al-Mulla EAJ, Yunus WMZ, Ibrahim NA et al (2010) Enzymatic synthesis of fatty amides from palm olein. J Oleo Sci 59:59–64

Al-Mulla EAJ (2011c) Preparation of Polylactic Acid/Epoxidized Palm oil/Fatty Nitrogen Compounds Modified Clay Nanocom- posites by Melt Blending. Polym Sci Series A 53:149–157

Al-Shemmari FHJ, Rabah AA, Al-Mulla EAJ et al (2012) Preparation and characterization of natural rubber latex/modified montmorillonite clay nanocomposite. Res Chem Intermed 39:4293–4301

Arroyo M, Lopez-Manchado M, Herrero B (2003) Organo-montmorillonite as substitute of carbon black in natural rubber compounds. Polymer 44:2447–2453
Bohmick AK, Stephens HL (2001)Handbook of Elastomers .Marcel Dekker, New York

Hoidy WH, Ahmad MB, Ibrahi NA et al (2010) Synthesis and characterization of organoclay from sodium montmorillonite and fatty hydroxamic acids. Amer J Appli Sci 6:1567–1572

Masoud F, Susan D, Zahra S (2006) Gas barrier properties of PP/EPDM blend nanocomposites. J Mem Sci 282:142–148

Nielsen LE (1974) Mechanical Properties of Polymers and Composites, 2nd edn. Marcel Dekker, New York

Roy NC, Bhowmick AK (1990) Strength of thermoplastic elastomers from rubber-polyolefin blends. J Mat Sci 25:161–167

Thength BKG (1979) Formation and properties of polymer clay complexes. Elsevier, Amsterdam 18:30

Vu YT, Mark JE, Pham LH et al (2001) Clay nanolayer reinforcement of cis-1,4-polyisoprene and epoxidized natural rubber. J Appl Polm Sci 82:1391–1403

Yunus WMZ, Ibrahim NA, Mohm ZA et al (2010a) Epoxidized palm oil plasticized polylactic acid/fatty nitrogen compound modified clay nanocomposites: preparation and characterization. Polym Polym Comp 18(8):451–460

Yunus WMZ, Ibrahim NA, Zaki A et al (2010b) Difatty acyl urea from corn oil: synthesis and characterization. J Oleo Sci 59:157–160

Appendix A3

ICAMN III 2013.

ICAMN III 2013

Next Generation of Sustainable Materials

09 Sept 2013

3rd International Conference on the
Advancement of Materials and Nanotechnology 2013
19-22 November 2013 . Panang, Malaysia

Dear Dr. Fayq Al-Shemmari,

The committee of ICAMN III 2013 has reviewed your abstract and we are delighted to inform you that your abstract entitled **“A COMPARATIVE STUDY OF DIFFERENT SURFACTANTS& CLAYS FOR NATURAL RUBBER CLAY NANOCOMPOSITE PREPARATION “** has been accepted.

You may check the reviewed abstract by login into the conference website (http://material.eng.usm.my/ICAMN2013/) using your username and password.
We hope to receive your full paper for the conference proceedings before 1st October 2013.
If your abstract has been accepted for presentation but you are unable to present it, please contact the committee as soon as possible to notify them that the abstract will be withdrawn.

The scheduled activities for **3rd International Conference on the Advancement of Materials and Nanotechnology 2013** would be made available soon. The conference will be held as follows

Venue : ParkRoyal Penang Resort, Penang, Malaysia.
Date : 19, 20, 21 & 22 November 2013.

The fee for this 4-day conference is :

i. Postgraduate (proof of I.D. is compulsory) : Local – MYR 850.00 International – USD280.00.
ii. Normal : Local – MYR 1,200.00 / International – USD 390.0

Thank you very much for your kind participation. Please do not hesitate to contact us if you need any assistance.

Best regards,

KHAIROL ANUAR MOHAMMED
ICAMN III 2013 Committee
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