BIODEGRADABLE POLY (LACTIC ACID)/ CLAY NANOCOMPOSITE BY MELT INTERCALATION: A STUDY OF MECHANICAL PROPERTIES

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ABSTRACT

Polymer nanocomposites have highly improvement in mechanical properties compared to conventional polymer. In this project, polylactic acid was reinforced with the organoclay (Cloisite 20A) as nanofiller by using twin screw extruder at 210°C and 100 rpm. Fourier Transform Infrared Spectroscopy (FT-IR) was used to identify the attendance of nanoparticle in polymer matrix. The mechanical properties were evaluated by measuring their tensile stress, Modulus Young's and hardness. In FT-IR results, PLA/ C20A nanocomposite shows the peak between 1580 cm^{-1} and 1610 cm^{-1} which is representing amine group of Cloisite 20A. However, in pure polylactic acid matrix the peak is absent. Mechanical studies indicate that a significant increasing by 70.5% in tensile stress and 394.3% in Modulus Young's shows in PLA/1 wt. % C20A. It is expected because this behaviour is mainly due to high stiffness and modulus of nanoclay that reinforce the blend matrix. Further, PLA/ 1 wt. % C20A also give the high increasing by 3.23% in hardness testing because the strong interfacial interaction between nanofiller and polymer matrix. As a conclusion, an addition of Cloisite 20A significantly improves mechanical properties of polylactic acid matrix and PLA/ 1 wt. % C20A had the higher increasing in tensile strength, Modulus Young's and hardness.

ABSTRAK

Polimer nanokomposit mempunyai peningkatan yang sangat tinggi dalam sifat mekaniknya berbanding dengan polimer biasa. Dalam kajian ini, asid polilaktat telah diperkuatkan dengan tanah liat organik (Cloisite 20A) yang digunakan sebagai nano penguat dengan menggunakan pengisar skru berkembar pada suhu 210ºC dan 100 rpm. Spektrometri infra merah (FT-IR) telah digunakan untuk mengenalpasti kehadiran nanopartikel dalam polimer matrik. Sifat mekanikal dinilai dengan mengukur tegangan tarik, Modulus Young's dan kekerasan. Daripada keputusan FT-IR, PLA/ nanokomposit C20A menunjukkan puncak di antara 1580 cm^{-1} and 1610 cm^{-1} yang merupakan kumpulan amina Cloisite 20A. Namun, puncak ini tidak hadir dalam asid polilaktat tulen. Kajian mekanik menunjukkan bahawa peningkatan sebanyak 70.5% pada tegangan tarik dan 394.3% pada Modulus Young dalam PLA/ 1 wt. % C20A kerana kekerasan tinggi dan modulus nano tanah liat organik yang memperkuatkan campuran matrik. Selanjutnya, PLA/ 1 wt. % C20A juga memberikan peningkatan yang tinggi sebanyak 3.23% dalam ujian kekerasan kerana interaksi yang kuat antara nano penguat dan matrik polimer. Sebagai kesimpulan, penambahan Cloisite 20A meningkatkan sifat mekanik asid polilaktat matrik dan PLA / 1 wt. % C20A memiliki peningkatan yang paling tinggi dalam tegangan tarik, Modulus Young, dan kekerasan.

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SYMBOL	DEFINITION
PLA	Poly (Lactic Acid)
PBAT	Polybutylene adipate co-terephthalate
C20A	Cloisite 20A
^oC	Degree celcius
Wt%	Percentage Weight
FTIR	Fourier Transform Infrared Spectroscopy
GMA	Glycidyl methacrylate
Na^+	Natrium
PNCs	Polymer nanocomposites
µm	Micrometer
nm	Nanometer
σ	Stress
ϵ	Strain
O-H	Hydroxy group
C=O	Carbonyl group
CH	Alkyne group
C-O	Epoxy and Oxirane rings
-COO	Peroxides group

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CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 History of Polymer Nanocomposite

In the last 20 years, there has been a strong emphasis on the development of polymeric nanocomposites, where at least one of the dimensions of the filler material is of the order of a nanometer. The final product does not have to be in nanoscale, but can be micro- or macroscopic in size. This surge in the field of nanotechnology has been greatly facilitated by the advent of scanning tunneling microscopy and scanning probe microscopy in the early 1980s. With these powerful tools, scientists are able to see the nature of the surface structure with atomic resolution. Simultaneously, the rapid growth of computer technology has made it easier to characterize and predict the properties at the nanoscale via modeling and simulation. In general, the unique combination of the nanomaterial's characteristics, such as size, mechanical properties, and low concentrations necessary to effect change in a polymer matrix, coupled with the advanced characterization and simulation techniques now available, have generated much interest in the field of nanocomposites. In addition, many polymer nanocomposites can be fabricated and processed in ways similar to that of conventional polymer composites, making them particularly attractive from a manufacturing point of view (Hojjati *et al.*, 2006).

The history and growth in synthesis, characterization, and understanding of microscopic structures has given rise to a new chapter, the nanoscience and nanotechnology. There is a continuing effort to take advantage of recent advances in nanotechnology, in the polymer and fibre industry. In its most basic form, nanotechnology refers to the manipulation of materials at the atomic or molecular level. The name derives from the nanometer, a scientific measurement unit representing one billionth of a meter. With various manufacturing techniques such as vapor deposition, sputtering, scanning tunneling microscopy, and supersonic molecular beams, it is now possible to produce materials of nanometer size (Bhat *et al*., 2008).

In the last two decades there has been a continuous increase of research for the improvement of material properties employing nanometric engineered structures taking advantage of the inherent high surface area volume ratio of nanomaterials. Nanocomposite materials often show an excellent balance between strength and toughness and usually improved characteristics compared to their individual components. As a matter of fact, natural bone matrix is an organic/inorganic composite material of collagen and apatite. From this point of view, composite materials are excellent choices as bone tissue engineering scaffolds. Indeed, current opportunities for polymer nanocomposites in the biomedical field arise from the multitude of applications and the vastly different functional requirements (Armento *et al*., 2010).

1.1.2 Polymer Nanocomposite

Polymer nanocomposites are polymers that have been reinforced with small quantities of nano-sized particles. These systems consist of a polymer matrix with nanoparticle filler. Polymer nanocomposite is one of radical alternative to conventional polymers because the interaction between nanostructures and polymer matrix is the basis for enhanced mechanical and functional properties of the nanocomposites as compared to conventional polymer. The examples of application polymer nanocomposites are automotive and cover for portable electronic equipment. The nanoparticles are nano-sized that have at least one dimension in the range 1 to 100nm. Because of their smaller size, nanoparticles have a high surface to volume ratio and provide high energy surfaces. The nanoparticles are used to increase the surface area available for interaction with the matrix. Polymer composite theory predicts that improved bonding between polymer and matrix leads to improved mechanical properties.

1.1.3 Polylactic acid-Organoclay Nanocomposite

In this research, polylactic acid is use as a matrix material and organoclay (Cloisite 20A) is use as new filler. Polylactic acid (PLA) is biodegradable aliphatic polyester derived from lactic acid which can be obtained from the fermentation of renewable resources. Most processes to produce lactic acid rely on bacterial fermentation of dextrose in aqueous slurry with a continual addition of a base, such as calcium hydroxide, to maintain a neutral pH. It is friendly for the environment and has many good properties, such as biodegradability, mechanical strength, transparency, and processibility. It has high potential applications as commodity plastics, packaging, agricultural products, disposable materials, medicine, surgery and pharmaceuticals. The polymer is relatively hard, with the glass transition temperature in the range 60–70 ^{o}C and melting at 170–180 ^{o}C.

Starch-polyester blends are being produced with the objective of maintaining the excellent physical properties of the polyesters while reducing cost. A process was developed at the University of Nebraska-Lincoln to produce starch-based plastic foam with 70% starch combined with a variety of ingredients and plastics found that addition of PLA to regular and waxy corn starches improved the physical and mechanical properties of the foams (Lee *et al.,* 2008).

Cloisite 20A is a natural montmorillonite modified with dimethyl dihydrogenated tallow quaternary ammonium (MMT-20A). It was purchased from Southern Clay (Gonzales, TX, USA). These modified clays are called organoclays, and are more compatible with polymers because they increase the spacing between the layers and reduce the surface energy of the filler. Specific gravity of Cloisite 20A is 1.77. Particle size distribution is such that 90 % are less than 13 micron and 50 % are less than 6 micron and 10% less than 2 micron.

PLA has attracted the attention of polymer scientist recently as a potential biopolymer to substitute the conventional petroleum based plastics. Apart from being in the category of biodegradable polymer, PLA has wide applications in biomedical field due to its biocompatibility characteristics. Recent studies and findings on PLA had proven that the biopolymer has good mechanical properties, thermal plasticity and biocompatibility, and is readily fabricated, thus being a promising polymer for various end-use applications (Balakrishnan *et al*., 2010).

1.2 Problem Statement

Polymer systems are widely used because of their light weight, design flexibility, and process ability. These systems, however, generally exhibit less attractive mechanical properties such as low strength and low elastic modulus as compared to metals and ceramics. To improve the mechanical properties of these systems is by adding nanoparticle filler. Because of their small size, nanoparticles have a high surface to volume ratio and providing more surface area for bonding with the matrix.

1.3 Research Objective

The objective of this research is to study the mechanical properties of poly (lactic acid)-organoclay (Cloisite 20A) nanocomposite by mean of the tensile strength and the hardness.

1.4 Research Scopes

1. Prepare polylactic acid-organoclay nanocomposite by twin screw extruder.
2. Characterize of polylactic acid-organoclay nanocomposite using Fourier Transform Infrared Spectroscopy (FT-IR).
3. Study the tensile strength of polylactic acid-organoclay nanocomposite using Universal Testing Machine.
4. Study the hardness of polylactic acid-organoclay nanocomposite using Rockwell Brinell Hardness machine.

1.5 Rationale and significance

The rationale of this research is to improve the tensile strength and hardness of polymers. The significance is by adding nanoparticle filler it will increase the tensile strength and hardness of polymers.

CHAPTER 2

CHEMISTRY AND PHYSICAL PROPERTIES OF POLY (LACTIC ACID) AND POLY (LACTIC ACID) NANOCOMPOSITES

2.1 Introduction of Polymer Nanocomposite

Polymer nanocomposites (PNCs) have drawn a great deal of interest in recent years because these materials possess high potential to achieve great property improvement by adding a small amount of nanoparticles in the polymer matrices. Nanocomposites are a new class of materials providing superior properties when compared to their microcomposite counterparts. An addition of a small amount of nanoparticles can significantly improve a variety of properties without sacrificing the lightweight of polymer matrices (Lee *et al*., 2005).

2.2 Comparison of a macro-composites and nano-composites

There are three main material constituents in any composite: the matrix, the reinforcement (fiber), and the so-called interfacial region. The interfacial region is responsible for communication between the matrix and filler and is conventionally ascribed properties different from the bulk matrix because of its proximity to the surface of the filler. To convey the origin and interrelation of these distinguishing characteristics, Figure 2.1 compares the dominant morphological scale of a classic filled polymer containing 1 μm x 25 μm fibers in an amorphous matrix to that of a nano-filled system at the same volume fraction of filler, but containing 1 nm x 25 nm fibers (Gacitua E. *et al*., 2005).

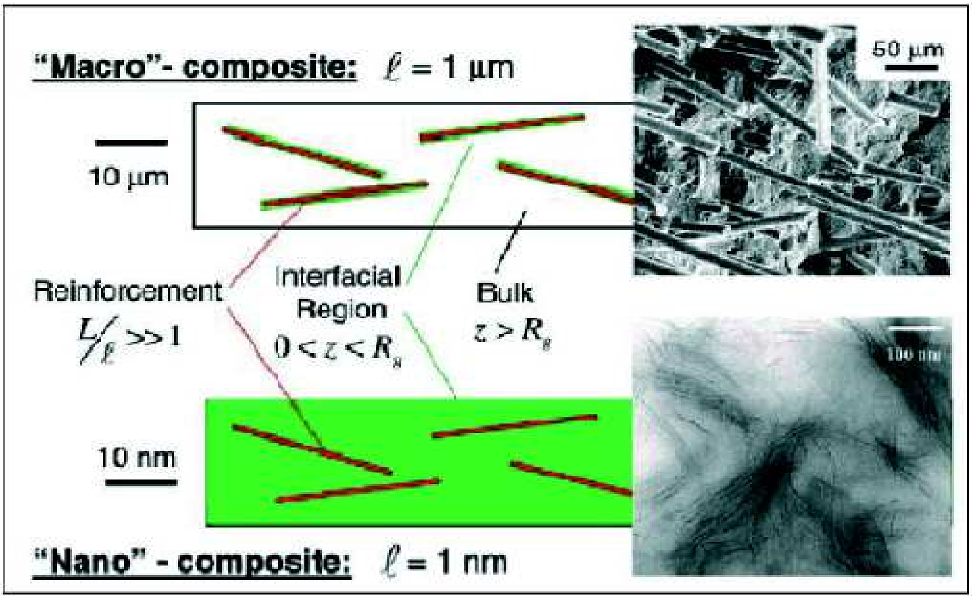

Figure 2.1: Schematic comparison of a macro-composite containing 1 μm x 25 μm fibers in an amorphous matrix to that of a nano-composite at the same volume fraction of filler, but containing 1 nm x 25 nm fibers. Constituents in any composite: the matrix (white), the reinforcement (fiber, red), and the so-called interfacial region (green) (Gacitua E. *et al*., 2005).

2.3 Poly (Lactic Acid)

Poly (lactic acid) is one of the promising biodegradable polymers, which has been produced in a rather complicated two-step process by first producing lactic acid by fermentation followed by ring opening polymerization of lactide, a cyclic dimer of lactic acid (Kyung and Lee, 2010). Polylactic acid is a versatile polymer derived from lactic acid and is made from completely renewable resources like sugar beets and sugarcanes or even corn, wheat, and other starch-rich products (Nakagaito *et al*., 2009).

2.3.1 Synthesis of Poly (Lactic Acid)

The properties of lactic acid based polymers vary to a large extent depending on the ratio between and the distribution of the two stereoisomers. The polymers can be manufactured by different polymerization routes, which are schematically described in Figure 2.2 (Anders Sodergard and Mikael Stolt, 2002). The polymers derived from lactic acid by polycondensation are referred to poly (lactic acid) and the polymers prepared from lactide by ring-opening polymerization referred to poly (lactide). Both types are generally referred to PLA.

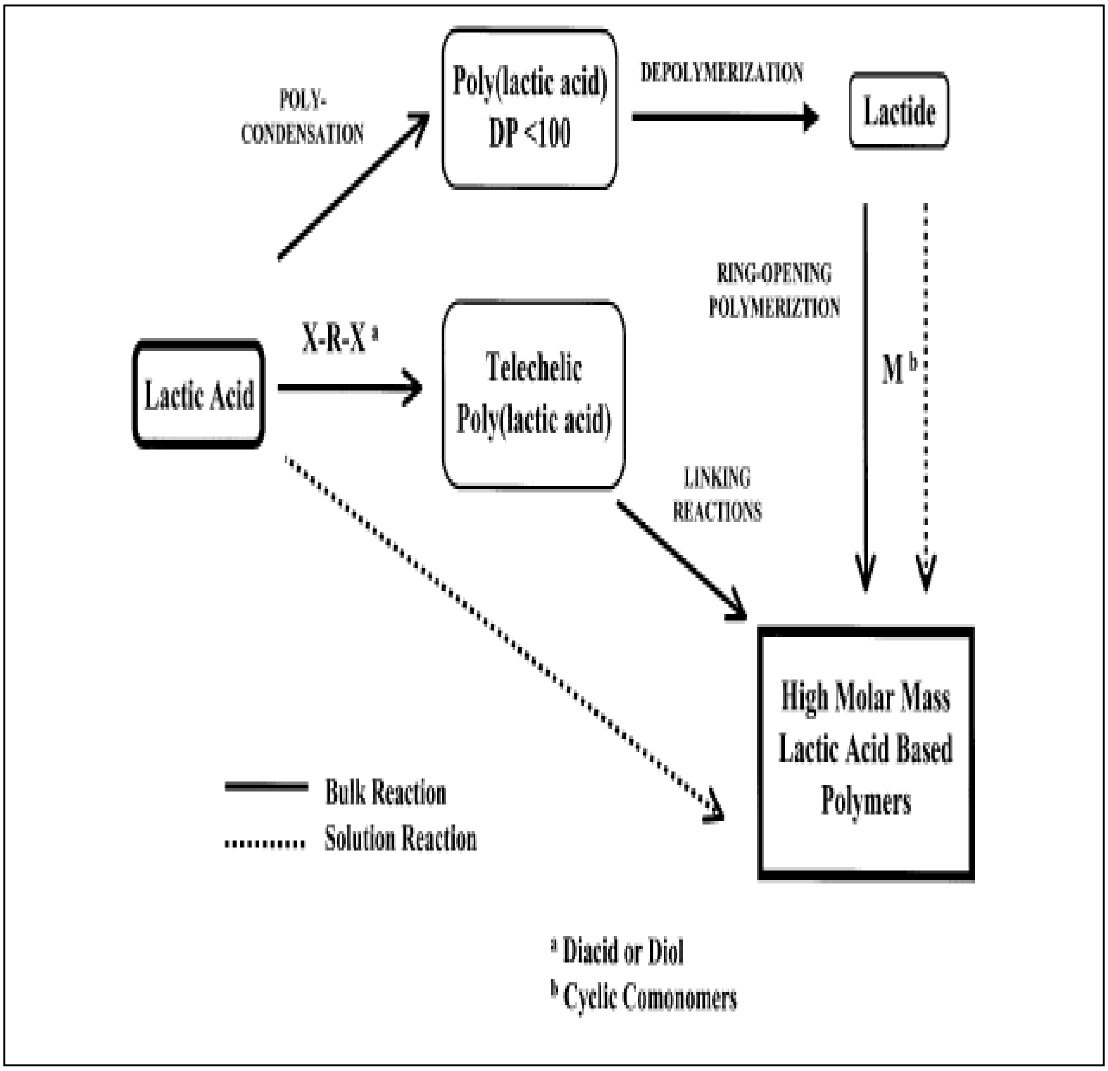

Figure 2.2: Different routes for the preparation of lactic acid based polymers (Sodergard and Stolt, 2002)

2.3.2 Physical properties of Poly (Lactic Acid)

The most important ability of PLA is that one can tailor its physical properties by material modifications. The polymer is relatively hard, with the glass transition temperature in the range 60–70 °C and melting at 170–180 °C. Some of physical characteristic of PLA are listed in Table 2.1.

Table 2.1: Physical characteristic of PLA (Gupta *et al.*, 2007)

Property	Units	Condition	Value
Degree of crystallinity, Xc	%	L-PLA	0–37
Density, ρ	g/cm^3	Amorphous Single crystal	1.248 1.290
Heat of fusion, ΔHf	KJ/mol	L-PLA complete crystalline L-PLA fiber As-extruded After hot drawing	146 2.5 6.4
Heat capacity, Cp	J/K/g	L-PLA with Mv = 5300 $Mv = (0.2–6.91) x10^5$	 0.60 0.54
Glass transition temperature	K		326–337
Melting point	K		418–459
Decomposition temperature	K		500–528
Swelling in water, %		pH 7 buffer	2
Intrinsic viscosity (η) in chloroform at 25 °C	dl/g		3.8–8.2
Radiation resistance	G value	Under nitrogen	
Co60 in benzene solution, 30 °C		Chain scission Cross linking	26.5 4.5

In water		Chain scission Cross linking	23.0 6.5
IR peaks	cm^{-1}		
OH (alcohol/carboxylic)			3700–3450
–C = O			1750–1735
–COO			1600–1580
C-O			1200–1000
CH			950–700

2.3.3 Application of poly (lactic acid)

As one of the most prominent biodegradable polymers, poly (D, L-lactic acid) (PLA) is widely used in the fields of tissue engineering and drug delivery due to its nontoxic, biocompatible and bioabsorbable characteristics (Dedai Lu et al., 2008). Polylactic acids are of considerable interest as biodegradable polymers in medical applications and also potentially for use as environmentally friendly packaging materials (Amass *et al*., 1999).

Recently, the demand for plastics made from biomass (bioplastics) has increased because they can reduce environmental carbon dioxide emissions, which induces global warming, and their production does not require fossil fuel resources, thus reducing the environmental load required to produce these plastics. If bioplastics are going to be able to address the issues of global warming or fossil fuel use, they will need to be used in large quantities (Achmad *et al*., 2009).

Biopolymers are expected to be an alternative for conventional plastics due to the limited resources and soaring petroleum price which will restrict the use of petroleum based plastics in the near future. PLA has attracted the attention of polymer scientist recently as a potential biopolymer to substitute the conventional petroleum based plastics. Apart from being in the category of biodegradable polymer, PLA has wide applications in biomedical field due to its biocompatibility characteristics. Recent studies and findings on PLA had proven that the biopolymer has good mechanical properties, thermal plasticity and biocompatibility, and is readily fabricated, thus being a promising polymer for various end-use applications (Balakrishnan *et al*., 2010).

2.3.4 Polylactic acid-nanocomposites

The incorporation of nanoparticles in certain biodegradable matrices could significantly affect the crystallization behavior, morphology, mechanical properties as well as biodegradation. Also, water barrier and antimicrobial properties are very important characteristics when using biodegradable polymers for special purposes like packaging. For example, PLA nanocomposites based on different types of nanoclays such as Cloisite® Na+, Cloisite® 30B and Cloisite® 20A are effective in improving the water vapor barrier properties and bacteriostatic function against certain microbes (Avella *et al*., 2009).

Polymer–clay nanocomposites are a new class of composites, based on intercalation of polymer chains into organically modified clay. It is believed that the formation of nanocomposites offers improving flame retardancy, increasing heat distortion temperature, improving flexural modulus, decreasing in permeability and ionic conductivity at lower filler concentration, relative to the neat polymers and conventional composite (Paiva *et al*., 2007).

2.4 Layered silicate organoclay

The crystal lattice of 2:1 layered silicates (or 2:1 phyllosilicates), consists of two-dimensional layers where a central octahedral sheet of alumina is fused to two external silica tetrahedra by the tip, so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheets, as shown in Fig. 2.3. The layer thickness is around 1 nm and the lateral dimensions may vary from 300A to several microns, and even larger, depending on the particulate silicate, the source of the clay and the method of preparation (e.g. clays prepared by milling typically have lateral platelet dimensions of approximately 0.1–1.0_m). Therefore, the aspect ratio of these layers (ratio length/thickness) is particularly high, with values greater than 1000 (Pavlidou and Papaspyrides, 2008).

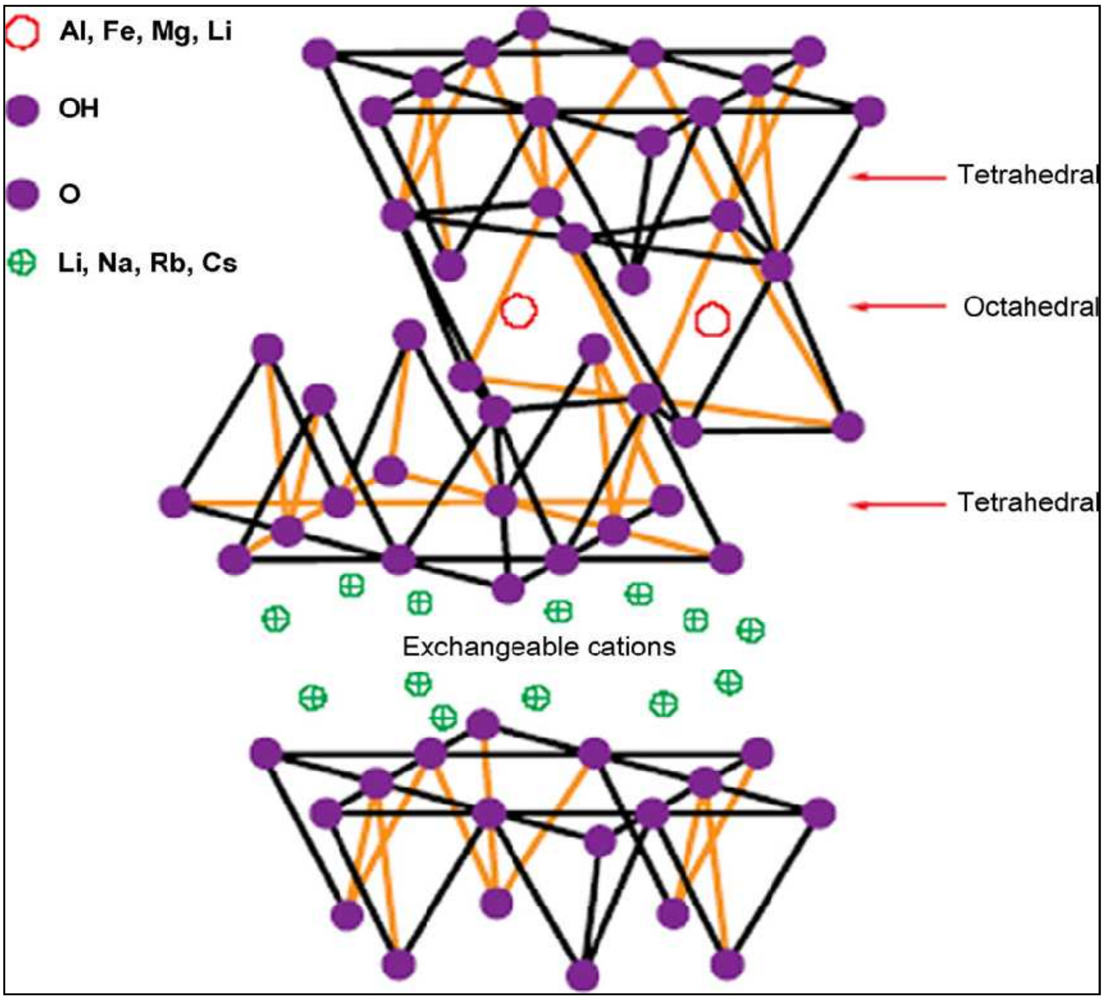

Figure 2.3: The structure of a 2:1 layered silicate (Pavlidou and Papaspyrides, 2008)

2.4.1 Organoclay modified layer silicate

Cloisite 20A treated with a surfactant (2M2HT) having the chemical structure dimethyl dihydrogenated tallow alkyl quaternary ammonium chloride. The chemical structures of the surfactants, 2M2HT is given in Figure 2.4 below:

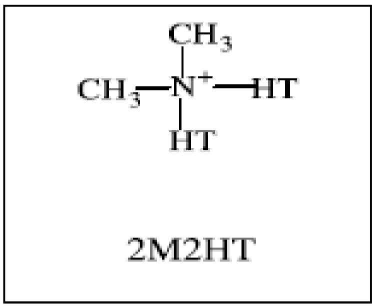

Figure 2.4: Chemical structure of surfactant (2M2HT) (Huang and Han, 2006)

Recently, nanocomposites prepared by melt mixing such ionomers with organically modified montmorillonite clays (organoclays) have attracted a great deal of technological and scientific interest because of their potential for significant improvements in physical and barrier properties at low filler levels. The key to achieving these benefits is exfoliating the organoclay into the polymer matrix to generate high aspect ratio particles (Shah and Paul, 2006).

Polymer nanocomposites are a class of reinforced polymers containing small quantities (1–5 wt%) of nanometric- sized clay particles. Smectite-type clays, such as hectorite, synthetic mica, and montmorillonite were employed as fillers to enhance the properties of the composites. The functional properties of the nanocomposites were improved markedly compared to those of the unfilled polymer or conventional composites. These improvements included high moduli increased tensile strength (and thermal stability; decreased gas permeability, flammability and water absorbance; and increased biodegradability of biodegradable polymers (Lee *et al.*, 2008).

2.5 Structure of Polymer Nanocomposite

Polymer/layered nanocomposites in general, can be classified into three different types, namely (i) intercalated nanocomposites, (ii) flocculated nanocomposites, and (iii) exfoliated nanocomposites (see Figure 2.5) (Gacitua E. *et al.*, 2005).