

**MECHANICAL PROPERTIES OF POLY (LACTIC ACID) (PLA)/CLAY  
NANOCOMPOSITE**

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## ABSTRACT

Polymer nanocomposite (PNC) is a polymer or copolymer having dispersed in its nanoparticles. These may be of different shape (platelets, fibers, spheroids), then dimension must be in the range of 1 to 50 nm. PNC represent a new class of material alternative to the conventional filled polymers. Nanosized inorganic filler (at least one dimension) are dispersed in polymer matrix offering tremendous improvement in performance properties of the polymer. Poly (lactic acid) or polylactide (PLA) is biodegradable, thermoplastic, aliphatic polyester derived from renewable resources which is environmentally friendly, low density and cost and commercially available. In this project, the pure PLA will reinforce by adding the nanoclay type Cloisite® 30B in percentage of 1, 3 and 5 wt% inside the PLA matrix by melting processing using co-rotating twin-screw extruder at 210°C and 100rpm. The material was dried in the dryer at 80°C for 2 hours before through the melting process. The influence of nano particles in the PLA matrix was investigated on the morphology and mechanical properties. The Fourier transform infrared (FTIR) spectroscopy spectrum shows the attendance of Cloisite® 30B clay in the PLA matrix. Brinell hardness test and tensile and tensile modulus properties result prove mechanical properties of PLA were improve after by dispersion of nanoclays.

## ABSTRAK

Polimer nanokomposit adalah polimer atau asas polimer yang mengalami penyebaran zarah yang bersaiz nano. Zarah-zarah itu mempunyai bentuk yang berbeza (platlet, gentian, sferoid) dan dimensinya mesti diantara 1 hingga 50nm. Polimer nanokomposit mewakili klas bahan alternatif yang baru untuk kebiasaan gembung polimer. Nano saiz pengisi yang tidak organik (sekadar mempunyai satu dimensi) yang disebarkan dalam matrik polimer menawarkan peningkatan yang besar dalam prestasi sesuatu polimer itu sendiri. Poly lactic acid atau poly lactide (PLA) adalah polimer yang biodegradasi, termoplastik, alifatik polyester yang diterbitkan melalui pembaharuan sumber iaitu mesra alam, rendah ketumpatan dan kos, dan boleh di kormesialkan. Dalam projek ini, PLA asli akan diperkuatkan dengan penambahan nanoklay jenis Cloisite® 30B dalam 1, 3, dan 5 peratusan berat ke dalam matik PLA melalui proses pencairan menggunakan putaran-bersama skru-berkembar pada suhu 210°C dan 100rpm. Bahan-bahan dikeringkan terlebih dahulu di dalam alat pengering pada suhu 80°C dalam masa 2 jam sebelum melalui proses pencairan. Kesan-kesan zarah-zarah nano penguat di dalam matrik PLA disiasat berasakan morfologi dan sifat mekanikalnya. Spektrum yang terhasil dari ujian menggunakan alat Fourier penukar infrared (FTIR) spektroskopi membuktikan kehadiran klay jenis Cloisite® 30B dalam matrik PLA. Ujian kekerasan Brinell, kekuatan dan ketegangan membuktikan sifat mekanikal PLA telah meningkat selepas berlakunya penyebaran penguat nanoklay.

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**LIST OF ABBREVIATION**

PNC	-	Polymer nanocomposite
PLA	-	Poly lactic acid
APES	-	Aliphatic polyester
TPS	-	Thermoplastic starch
PCL	-	Polycaprolactone
PEG	-	Poly (ethylene glycol)
URP	-	Unsaturated polyester
MBDAC	-	methacryloxyethyl benzyl dimethyl ammonium chloride
CTAB	-	n-Hexadecyl trimethylammonium bromide
wt. %	-	Weight percent
TEM	-	Transmission electron microscopic
FTIR	-	Fourier transform infrared spectrometry
XRD	-	X-ray Diffraction
WAXS	-	Wide angle x-ray scattering
T	-	Tetrahedral
O	-	Octahedral
C	-	Intercalated cations
OMLS	-	Organomodified layered silicates
ODA-MMT	-	Octadecylamine-montmorillonite
MMT	-	Montmorillonite
OMMT	-	Organomodified montmorillonite
2 $\theta$	-	Range of angles
BHr	-	Brinell hardness number

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**LIST OF NOMENCLATURE**

F	-	Applied force (N)
D	-	Indenter diameter (mm)
$D_i$	-	Indentation diameter (mm)
BHr	-	Brinell hardness ( $\text{N}/\text{mm}^2$ )
m	-	Meter
Nm	-	Nanometer
g	-	Gram
N	-	Newton
mm	-	Milimeter
d	-	Interlayer distance (nm)
E	-	Modulus Young (GPa)
BHr	-	$\text{N}/\text{mm}^2$

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. The true start of polymer nanocomposites history is in 1990 when Toyota first used clay/nylon-6 nanocomposites for Toyota car in order to produce timing belt covers. This obviously includes polymer science and technology and even in this field the investigations cover a broad range of topics. This would include microelectronics (which could now be referred to as nanoelectronics) as the critical dimension scale for modern devices is now below 100 nm (D.R Paul et al., 2008). The concept of combining nanocomposites as matrix material with fiber reinforcement in a new three-phase composite reinforcement has been shown to be very successful. Lighter, thinner, stronger, and cheaper structures are the goals of materials science and engineering applications nowadays (J. Njuguna et al., 2007). Such properties can indeed be tailored by changing the volume fraction, shape, and size of the filler particles (S.C Tjong 2006) and engineering materials at the atomic and molecular levels are creating a revolution in the field of materials and processing. The discovery of new nanoscaled materials such as nanoclays, carbon nanotubes, and others offer the promise of a variety of new composites, adhesives, coatings, and sealant materials with specific properties (J. Njuguna et al., 2007).

Nanoparticles are presently considered to be high-potential filler materials for the improvement of mechanical and physical polymer properties. The nanometric size, leading to huge specific surface areas of up to more than 1000m<sup>2</sup>/g, and their unique properties (of at least some of these nanoparticles) have caused intensive research activities in the fields of natural and engineering sciences (J. Njuguna et al., 2007). The improved properties of the nanocomposite matrix material may upgrade the properties of relatively low-cost composites up to the level of high performance composites and further increase the temperature resistance of existing high-performance composites. The added cost of the nano-filled matrix can be small due to the low amounts of filler necessary for a significant improvement (J. Njuguna et al., 2007). The dispersion of nanofillers in the polymers is rather poor due to their incompatibility with polymers and large surface-to-volume ratio. Therefore, organic surfactant and compatibilizer additions are needed in order to improve the dispersion of these nanofillers in polymeric matrices (S.C Tjong 2006).

Advantage of the use of polymer nanocomposites compared to the use of different polymers to improve the high-temperature behavior of fiber composites is that the properties can be improved without any change in the melting temperature and processing conditions (J. Njuguna et al., 2007). Polymers can be used as matrix material at temperatures up to 50 C higher at the same composite strength without changes in the impregnation and forming temperature. However, a common drawback is the fact that the flow properties of the nanocomposites often hinder fiber bundle impregnation, result in void formation and reduce adhesion (J. Njuguna et al., 2007). All these factors often lead to a reduction of the strength instead of the expected increase, and therefore the nanocomposites used in these fiber composites have to be carefully selected.

The objective of this study were to prepare the Poly lactic acid (PLA)/clay nanocomposite using for different percentage of clay Cloisite® 30B, 1,3 and 5 wt % by melt processing, extruded in co-rotating twin-screw extruder. The experiment is to investigate the characterization, physical morphological and mechanical properties.



## **1.2 Problem Statements**

PLA is biodegradable and biocompatible polymer widely use in textile industry, clinical usage and automotive. Have great potential with respect to application in agriculture. There are many limitation because poor thermal and mechanical resistance (Wisam et al., 2010). To enhance the application and improve the mechanical properties, the addition of nanoclay in pure PLA is able to increase the mechanical properties even at low fillers content 1-5 wt %.

## **1.3 Research Objective**

Based on the aforementioned research background and problem statement, the objectives of this study are:

- i. To study the mechanical properties of PLA/clay nanocomposite.

## **1.4 Research Scope**

In order to achieve the objectives stated above, the following scopes of study have been drawn.

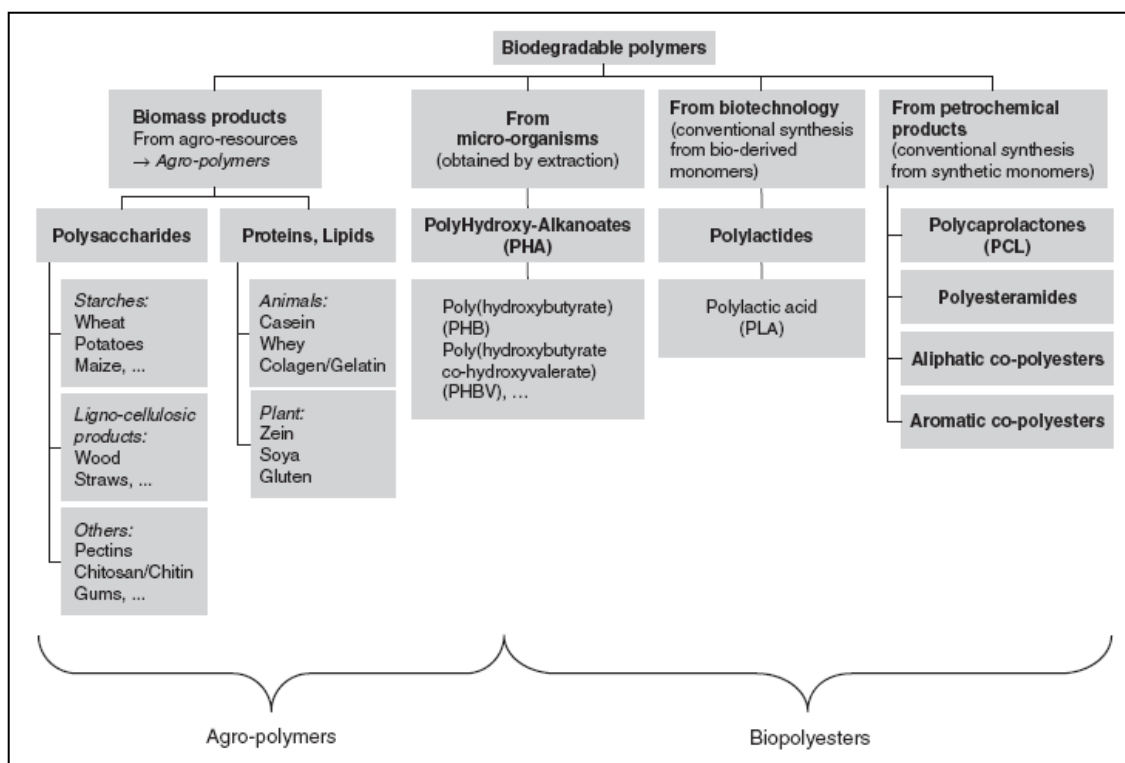
- i. Produce the PLA/clay nanocomposite through the melt processing.
- ii. Increase the mechanical properties of the PLA in addition of nanoclay as filler.
- iii. Characterize the PLA/clay nanocomposite structure using Fourier transform infrared (FTIR) spectroscopy.
- iv. Compare the mechanical properties result between pure PLA and PLA/clay nanocomposite

## CHAPTER 2

### CHEMISTRY AND PHYSICAL PROPERTIES OF POLY (LACTIC ACID) (PLA) AND PLA/CLAY NANOCOMPOSITE

#### 2.1 Introduction

In recent year's biopolymers, i.e., biodegradable polymers have attracted more and more interest due to increasing environmental concern and decreasing fossil resources. This evolution motivates academic and industrial research to develop novel materials labeled as “environmentally-friendly”, i.e., materials produced from alternative resources, with lower energy consumption, biodegradable and non-toxic to the environment. Since biopolymers are biodegradable and the main productions are obtained from renewable resources such as agro-resources, they represent an interesting alternative route to common non-degradable polymers for short-life range applications (packaging, agriculture, etc.) (P. Bordes et al., 2008). Nevertheless, until now, most biopolymers are costly compared to conventional thermoplastic and they are sometimes too weak for practical use. Therefore, it appears necessary to improve these biopolymers to make them fully competitive with common thermoplastics. Figure 2.1 shows an attempt to classify the biodegradable polymers into two groups and four different families. The main groups are (i) the agro-polymers (polysaccharides, proteins, etc.) and (ii) the biopolyesters (biodegradable polyesters) such as polylactic acid (PLA), polyhydroxyalkanoate (PHA), aromatic and aliphatic copolyesters (L. Averous, 2008; P. Bordes et al., 2008).



**Figure 2.1:** Classification of the biodegradable polymers (L. Averous, 2008).

Biodegradable polymers show a large range of properties and can now compete with non-biodegradable thermoplastics in different fields (packaging, textile, biomedical, etc.). Among these biopolyesters, PLA is at present one of the most promising biopolymer (L. Averous, 2008; P. Bordes et al., 2008; S. Y. Lee et al., 2008).

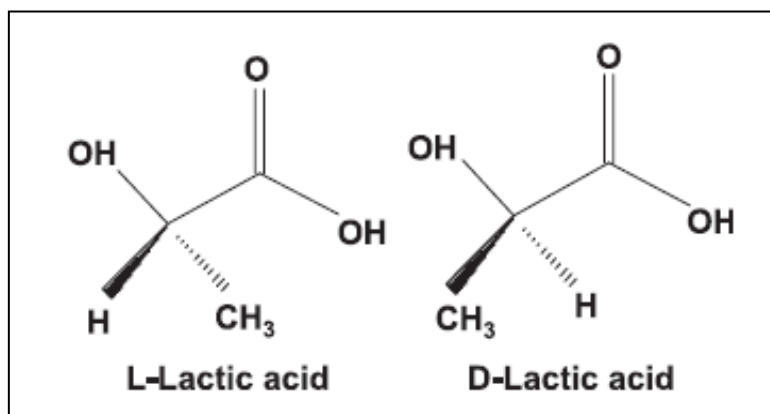
### 2.1.1 Poly (lactic acid) (PLA)

Interest in the manufacture of aliphatic polyester from lactic acid was pioneered by Carothers in 1932. This product was of a low molecular weight, and possessed poor mechanical properties. Further work by DuPont resulted in a higher-molecular weight product that was patented in 1954. However, as with all the completely aliphatic

polyesters investigated at this time, the susceptibility to hydrolytic degradation led to discontinuation of work in this area. In 1972, Ethicon introduced high-strength, biocompatible fibers for medical restorable sutures. These products, which are copolymers of lactic and glycolic acids, slowly hydrolyze within the body to the constituent acids. Further applications, also in the medical field, include implants and controlled drug release (James, 1997). Cargill Inc. has been the company most active in the development of poly (lactic acid) (polylactide, PLA). After nine years of lactic acid and poly (lactic acid) development, a Cargill Dow polymer LLC was created in 1997 as a joint venture of Cargill and the Dow Chemical company. Commercial production of PLA by the new company started in 2002. The polymer products are finding an enormous number of applications in technologically important fields (B. Gupta et al., 2007).

### **2.1.2 Synthesis of PLA**

There is growing interest in developing biodegradable polymers to replace synthetic nondegradable materials. Poly (lactic acid) (polylactate or polylactide) (PLA) is a biodegradable polyester that can be used to alleviate the waste disposal problem. It is synthesized from L- and D-lactic acid. For L-lactic acid, the plane is rotated in a clockwise (dextro) direction, whereas the D form rotates the plane in an anticlockwise (laevo) direction (James, 1997). The chemistry of PLA involves the processing and polymerization of lactic acid monomer. Lactic acid  $\text{HOCH}_2\text{CHCOOH}$  is a simple chiral molecule which exists as two enantiomers,  $L$ - and  $D$ -lactic acid (B. Gupta et al., 2007). It illustrates in Figure 2.2.

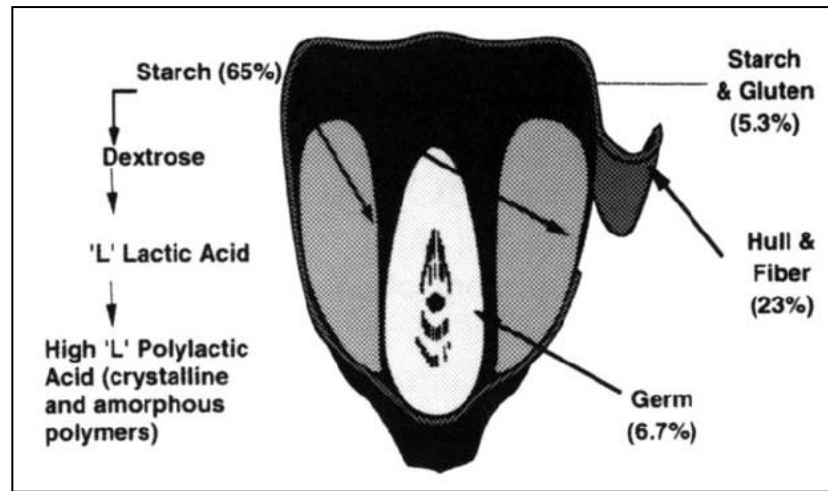


**Figure 2.2:** Lactic Acid stereoisomers form (James, 1997; B. Gupta et al., 2007).

Today the most popular route is fermentation, in which corn starch is converted into lactic acid by bacterial fermentation using an optimized strain of *Lactobacillus* (B. Gupta et al., 2007). PLA were produces from fermentation of sugar and (poly)saccharides such as sugar feedstock's and corn, wheat and other starch sources, either by ring-opening polymerization or by condensation polymerization (Steven, 2002; James, 1997) (Figure 2.3), and petrochemical route (James, 1997; B. Gupta et al., 2007) (Figure 2.4). Polymerization of lactic acid to high molecular weight PLA can be achieved in two ways (Figure 2.5):

- i. Direct condensation—which involves solvents under high vacuum.
- ii. Formation of the cyclic dimer intermediate (lactide)—which is solvent free.

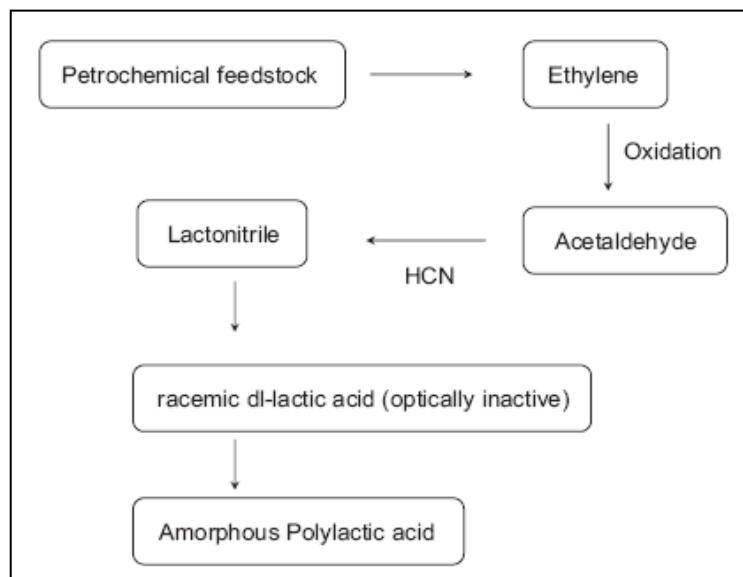
In direct condensation, solvent is used under high vacuum and temperatures for the removal of water produced in the condensation. This approach was used by Carothers and still used by Mitsui Chemicals. The resultant polymer is a low to intermediate molecular weight material, which can be used as is, or coupled with isocyanates, epoxides or peroxide to produce a range of molecular weights.



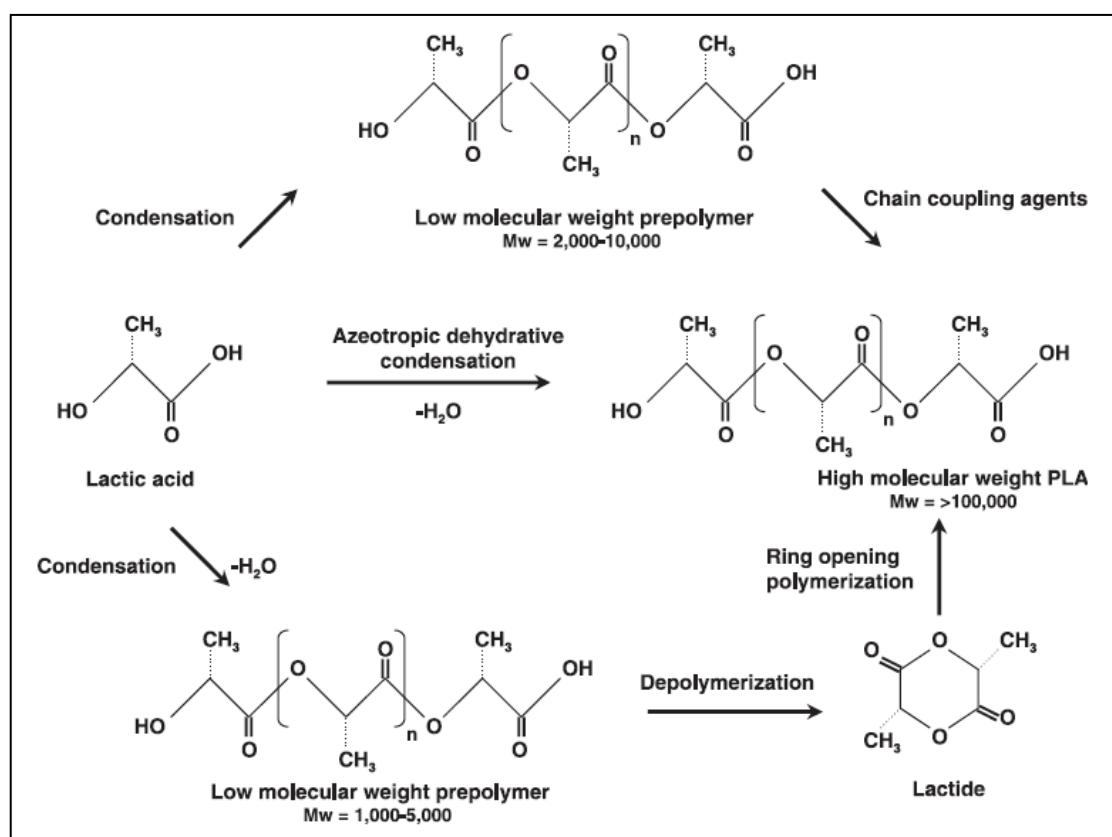
**Figure 2.3:** Fermentation route to lactic acid (using corn as a feedstock) (James, 1997).

In the solvent-free process, a cyclic intermediate dimer, commonly referred to as lactide (Figure 2.5) is produced and purified by distillation. Catalytic ring-opening polymerization of the lactide intermediate results in PLA with controlled molecular weight. By controlling residence time and temperatures in combination with catalyst type and concentration, it is possible to control the ratio and sequence of D- and L-lactic acid units in the final polymer.





**Figure 2.4:** Petrochemical route to lactic acid (James, 1997; B. Gupta et al., 2007).



**Figure 2.5:** Synthesis of poly (lactic acid) (PLA) (James, 1997; B. Gupta et al., 2007).



Advance in the bacterial fermentation of  $D$ -glucose obtained from corn introduced the potential to obtain lactic acid considerably cheaper than previously achievable from the petrochemical derived product. Within six years, the technology to produce poly lactic acids economically on a commercial scale was developed.

PLA is insoluble in water and has good moisture and grease resistance. Its mechanical properties can be modified by varying its molecular weight and its crystallinity. PLA is used widely as a biodegradable and renewable plastic for uses in service ware, grocery, waste-composting bags, mulch film, and controlled release matrices for fertilizers, pesticides and herbicides (Fang and Hanna, 1999). However PLA is expensive due to the complicated synthesis.

## **2.2 Nanofillers**

Fillers play important roles in modifying the desirable properties of polymers and reducing the cost of their composites (W. H. Hoidy et al., 2010; J.-H. Chang et al., 2003; S. Y. Lee et al., 2007; B. Guo et al., 2004; S. Tanoue et al., 2006; M.-A. Paul et al., 2004; P. K. Maji et al., 2009; E. A. J. Al-Mulla et al., 2010; T.-M. Wu and C.-Y. Wu, 2005; P. S. G. Krishnan, 2005; J. Njuguna et al., 2007; P. Bordes et al., 2008). In conventional polymer composites, many inorganic fillers with dimensions in the micrometer range, e.g. calcium carbonate, glass beads and talc have been used extensively to enhance the mechanical properties of polymers (S.C. Tjong, 2006). Smectite-type clays such as hectorite, synthetic mica, and montmorillonite (S.Y. Lee et al., 2008) were nanofiller that commonly use nowadays in the material engineering to increasing the properties of the polymer matrix itself.

