

MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF  
MONTMORILLONITE FILLED LINEAR LOW DENSITY  
POLYETHYLENE-TOUGHENED POLYLACTIC ACID NANOCOMPOSITES

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*'To mankind, may knowledge and wisdom endeavor us with capabilities for our  
challenging future ahead'*

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## ABSTRACT

Linear low density polyethylene (LLDPE) toughened polylactic acid (PLA) nanocomposites containing organophilic modified montmorillonite (MMT) were prepared by melt extrusion using a counter-rotating twin-screw extruder followed by injection molding in order to examine the mechanical, morphological and thermal properties of the nanocomposites. The mechanical properties of PLA/LLDPE nanocomposites were studied through tensile, flexural and impact tests. Scanning electron microscopy (SEM) was used to investigate the phase morphology and LLDPE particle's size in PLA/LLDPE blends and nanocomposites. X-ray diffraction (XRD) was employed to characterize the formation of nanocomposites while the thermal properties were determined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The dynamic mechanical properties were examined via dynamic mechanical analysis (DMA) while moisture permeability properties of the PLA/LLDPE nanocomposites were assessed through water absorption and hygrothermal aging. Subsequently, for PLA/LLDPE blends, the loadings of LLDPE were varied from 5-15 wt% and PLA/LLDPE nanocomposites with 2 phr and 4 phr loadings of MMT were prepared only for the optimum formulation (10 wt% of LLDPE). The results showed that the blending of LLDPE significantly increased the toughness but at the expense of stiffness and strength. Conversely, the incorporation of the MMT increased the stiffness, while the toughness and strength decreased. The PLA/LLDPE nanocomposites containing 2 phr of MMT and 10 wt% of LLDPE had the best balance of stiffness, strength and toughness. The impact strength results also proved that PLA nanocomposites were successfully toughened with LLDPE. XRD established that MMT were well dispersed and preferentially embedded in the PLA phase. SEM revealed that blend ratio and the presence of MMT were found to influence the morphology (e.g. LLDPE particle size and distribution) of the system. Finer particles' size and better distribution of LLDPE has been observed in higher MMT loadings in the system. The SEM micrographs also revealed that increasing content of LLDPE has increased the particle size of LLDPE in PLA. DMA analysis discovered that the storage modulus at 30°C increased with the presence of MMT for PLA nanocomposites. The DSC results showed that the crystallization temperature ( $T_c$ ) dropped gradually with increasing content of MMT for both PLA and PLA/LLDPE nanocomposites while the glass transition ( $T_g$ ) and melting temperature ( $T_m$ ) remained unchanged. TGA also exhibited an increase in  $T_{10\%}$  decomposition temperature for PLA and PLA/LLDPE nanocomposites. Water absorption curves obeyed the Fick's law with rapid moisture absorption to maximum saturation level ( $M_m$ ) and the value of  $M_m$  of PLA increased with addition of LLDPE and 2 phr of MMT. Hygrothermal aging revealed that the  $M_m$  increased significantly at elevated temperatures (60°C and 90°C) and addition of LLDPE and MMT improved the hygrothermal stability of PLA.

## ABSTRAK

Nanokomposit asid polilaktik (PLA) yang mengandungi montmorillonite (MMT) yang diubahsuai secara organofilik, diliat dengan polietilena berantai lurus berketumpatan rendah (LLDPE), telah disediakan melalui penyemperitan leburan menggunakan penyemperit skru berkembar berlawanan arah diikuti proses acuan suntikan untuk mengkaji sifat mekanikal, morfologi dan terma nanokomposit tersebut. Sifat mekanikal nanokomposit PLA/LLDPE dikaji berdasarkan ujian tegangan, lenturan dan hentaman. Mikroskop Imbasan Elektron (SEM) digunakan untuk mengkaji morfologi dan saiz partikel LLDPE dalam adunan PLA/LLDPE dan nanokompositnya. Pembelauan sinar-X (XRD) digunakan untuk pencirian pembentukan nanokomposit sementara sifat termal ditentukan dengan menggunakan analisis termogravimetrik (TGA) dan kalorimeter pembezaan imbasan (DSC). Sifat dinamik diperiksa dengan menggunakan penganalisis terma dinamik (DMA) sementara sifat kebolehtelapan lembapan nanokomposit PLA/LLDPE dikaji melalui penyerapan air dan penuaan higroterma. Seterusnya, untuk adunan PLA/LLDPE, kandungan LLDPE diubah dari 5 hingga 15 wt% dan nanokomposit PLA/LLDPE dengan kandungan MMT 2 phr dan 4 phr disediakan hanya untuk formulasi yang optimum (10 wt% LLDPE). Keputusan menunjukkan adunan LLDPE jelas meningkatkan keliatan tetapi menyebabkan penurunan kekakuan dan kekuatan bahan. Sebaliknya campuran dengan MMT meningkatkan kekakuan namun keliatan dan kekuatan menurun. Nanokomposit PLA/LLDPE yang mengandungi 2 phr MMT dan 10 wt% LLDPE adalah formulasi yang terbaik dengan keseimbangan kekakuan, kekuatan dan keliatan. Keputusan kekuatan hentaman membuktikan bahawa nanokomposit PLA berjaya diliatkan dengan LLDPE. XRD menunjukkan MMT diselerakkan dengan baik dan berada di dalam matrik PLA. SEM mendedahkan nisbah adunan dan kehadiran MMT didapati mempengaruhi morfologi sistem (saiz partikel dan keserakan LLDPE). Partikel saiz LLDPE yang kecil dan keserakan yang baik dapat dilihat dengan kandungan MMT yang banyak. Mikrograf SEM juga mendedahkan peningkatan kandungan LLDPE telah meningkatkan saiz partikel LLDPE dalam PLA. Analisis DMA mendapati bahawa modulus simpanan pada 30 °C meningkat dengan kehadiran MMT dalam nanokomposit PLA. Keputusan DSC menunjukkan suhu penghabluran ( $T_c$ ) turun beransur-ansur dengan peningkatan kandungan MMT dalam kedua-dua PLA dan nanokomposit PLA/LLDPE, sementara suhu peralihan kaca ( $T_g$ ) dan takat lebur ( $T_m$ ) kekal tidak berubah. TGA juga menunjukkan suhu penguraian  $T_{10\%}$  meningkat untuk PLA dan nanokomposit PLA/LLDPE. Lengkungan penyerapan air mematuhi hukum Fick dengan penyerapan lembapan pantas ke tahap ketepuan maksimum ( $M_m$ ) dan nilai  $M_m$  untuk PLA meningkat dengan penambahan LLDPE dan MMT. Penuaan higroterma menunjukkan bahawa  $M_m$  meningkat pada suhu (60°C dan 90°C) dan penambahan LLDPE dan MMT meningkatkan kestabilan higroterma PLA.

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**LIST OF ABBREVIATIONS AND SYMBOLS**

ASTM	American Society for Testing and Materials
CEC	Cation Exchange Capacity
<i>D</i>	Diffusivity
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimeter
<i>d</i>	Spacing between diffractive lattice plane (interspacing)
<i>E'</i>	Storage Modulus
<i>E''</i>	Loss Modulus
ENR	Epoxidized Natural Rubber
HDPE	High Density Polyethylene
<i>Hz</i>	Hertz
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MFR	Melt flow rate
MMT	Montmorillonite
$M_m$	Moisture absorption at maximum
$M_t$	Percentage weight at time, <i>t</i>
NBR	Acrylonitrile butadiene rubber
NR	Natural rubber
PA	Polyamide
PA6	Polyamide 6
PE	Polyethylene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PLA	Polylactic acid
PS	Polystyrene

PVC	Polyvinyl chloride
SBR	Styrene butadiene rubber
SEM	Scanning electron microscopy
$\tan \delta$	Tangent delta
TEM	Transmission electron microscopy
$T_g$	Glass transition temperature
$T_m$	Melting temperature
$T_c$	Crystallization temperature
TGA	Thermogravimetric analysis
$W_d$	Weight of dry sample
$W_w$	Weight of samples after exposure to distilled water
XRD	X-ray diffraction
$X_c$	Degree of crystallinity
$\theta$	Diffraction angle
$\lambda$	Wave length
$\Delta H_m$	Heat of fusion for sample
$\Delta H_{mideal}$	Heat of fusion for 100% crystalline

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

Biopolymers have been studied extensively due to environmentally aware consumers, increased price of crude oil and global warming. These polymers are derived from naturally occurring polymers that are found in all living organisms. Biopolymers which sourced from renewable resources will reduce our dependence on petroleum (Peterson and Oksman, 2006). Today, biopolymers are used in a variety of applications such as therapeutic aids, medicines, coatings, food product and packaging materials.

Polylactic acid (PLA) has caught 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 on PLA had concluded 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 (Ray *et al.*, 2003). However, PLA, similar to polystyrene, is a

comparatively brittle and stiff polymer with low deformation at break and low impact strength (Jacobsen and Fritz, 1999).

One main task will be to modify these properties in such a way that PLA is able to compete with other more flexible commodity polymers such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) or polyvinyl chloride (PVC). Previous researchers (Jacobsen and Fritz, 1999; Baiardo *et al.*, 2003; Kulinski and Piorkowska, 2005) had used plasticizers to enhance PLA's elongation at break and reduce its brittleness. Jacobsen *et al.* (1999) had studied the introduction of plasticizers such as polyethylene glycol (PEG), glucosemonoesters and partial fatty acid esters into PLA. They showed that the impact strength of PLA had increased significantly from 31 to 80 J/m with the addition of 10% PEG, leading to a toughened PLA.

The recent achievements in nanocomposite technology has fueled the need for new knowledge and findings resulting development of respective polymer nanocomposites; polyamide (Kelnar *et al.*, 2005), polypropylene (Lim *et al.*, 2006), polycaprolactone (Lepoittevin *et al.*, 2002), polystyrene (Fu and Qutubuddin, 2000) and others. In recent years, the field of PLA nanocomposites (Ray *et al.*, 2003; Lee *et al.*, 2003; Petersson and Oksman, 2006) based on layered silicates, such as MMT, has steadily increasing interest from scientist and industrialist. The nanoscale distribution of such high aspect ratio fillers brings up some large improvements to the polymer matrix in terms of mechanical, fire retardant, rheological, gas barrier and optical properties, especially at low clay content (as small as 1wt%) in comparison with conventional microcomposites (>30 wt% of microfiller). In order to reach this nanoscale distribution, the naturally hydrophilic clay filler has to be organically modified to be compatible with the organic polymer matrix.

Interestingly, the distribution of nanoclay is proven to be well dispersed in PLA without introduction of compatibilizing agents due to the interaction of hydrogen bonding between ammonium group in the organic "surfactant" of the MMT with the

carbonyl group of PLA chain segments contributes to this process (Pluta, 2006). There are also strong interactions between the PLA hydroxyl end groups and the MMT platelet surfaces or the ammonium group of the ammonium surfactant in the organically modified MMT reported in previous studies (Jiang *et al.*, 2007). Regardless of the improvements achieved in the development of PLA nanocomposites, the polymer's brittleness had become more inherent. This had limited its applications.

Similar brittleness problems had been solved before by researches with the approach of introduction of tough materials into a brittle nanocomposite system. Ahn *et al.* (2006) had examined the rubber toughening of nylon 6 nanocomposites in terms of impact strength, ductile–brittle transition temperature, and tensile properties. Lim *et al.* (2006) had successfully developed the poly(ethylene-co-octene) toughened polypropylene nanocomposites and studied its morphology, thermal and mechanical behaviour. Only several studies had been conducted recently in the development of plasticized PLA nanocomposites (Pluta, 2004; Paul *et al.*, 2003; Thellen *et al.*, 2005) but the mechanical properties of these nanocomposites were not studied in detail. Thellen *et al.* (2005) had investigated the influence of MMT layered silicate on plasticized PLA blown films and concluded that the plasticized PLA/MMT nanocomposites did not see highly significant enhancements with addition of MMT but the toughness is at least maintained in the nanocomposites unlike other filled polymeric systems. They found that the plasticization effect reduced the brittleness of the nanocomposites and the breakthrough will widen PLA's applications.

Although the addition of plasticizers such as PEG will overcome the brittleness, it comes with a sacrifice of stiffness of the material which is also important for structural applications (Baiardo *et al.*, 2003). Jacobsen *et al.* (1999) had proved that the addition of a plasticizer (PEG) leads to a decrease of the elasticity modulus and the addition of 2.5 wt% already lowers the modulus by 10% to 15% and this result was nearly independently of the type of plasticizer used. Thus, a new toughener was needed to overcome the brittleness nevertheless significantly reducing the stiffness. The introduction of LLDPE as a toughener for PLA indeed showed a remarkable

enhancement in terms of toughness of the material. The results showed a significant improvement in impact strength with considerable reduction in tensile and flexural strength and modulus. It was also concluded that the partial miscibility of LLDPE in PLA enabled it to perform as an impact modifier for PLA (Anderson *et al.*, 2003). Although it seems that the use of LLDPE as an impact modifier for PLA may defeat the purpose of developing a ‘green’ polymer, it shall be noted that the main aim of this research is for utilization of PLA in structural applications such as furniture and automobile parts.

## 1.2 Objectives of the study

One of the most important aspects of materials development in thermoplastics engineering is to achieve a good combination of mechanical properties and processability at a moderate cost. As far as mechanical properties are concerned, the main target is to strike a balance of stiffness, strength and toughness. To the best of our knowledge, no study on LLDPE toughened PLA nanocomposites have been reported yet. Thus, the aim of the research is to develop an environmentally friendly polymer nanocomposite with enhanced toughness namely LLDPE-toughened PLA/MMT nanocomposite.

The main objective can further be divided into:

- To explore the effect of LLDPE contents on the mechanical, thermal and morphological properties of PLA/LLDPE blends.
- To investigate the effect of MMT concentration on the mechanical, thermal and morphological properties of PLA/MMT and PLA/LLDPE/MMT nanocomposites.

- To evaluate the water absorption behavior and hygrothermal aging of PLA/MMT and PLA/LLDPE/MMT nanocomposites.

### **1.3 Scope of Research**

In order to achieve the objectives of the research the following activities were carried out:

#### **1. Sample preparation**

In this research project, sample preparation and blending was performed via melt intercalation method. This involves:

- i) Blending of LLDPE with PLA to produce PLA/LLDPE blends with twin screw extruder.
- ii) Blending of MMT with PLA to produce PLA/MMT nanocomposites with twin screw extruder.
- iii) Blending of LLDPE and MMT with PLA to produce PLA/LLDPE/MMT nanocomposites with twin screw extruder.
- iv) The blends and nanocomposites fabricated into test specimens via injection molding for analysis.

#### **2. Physical and mechanical analysis**

- (i) Water absorption
- (ii) Hygrothermal aging
- (iii) Tensile test
- (iv) Flexural test
- (v) Izod impact test

### 3. Characterization and morphological study

- (i) X-ray Diffraction (XRD)
- (ii) Scanning electron microscopy (SEM)
- (iii) Transmission electron microscopy (TEM)

### 4. Thermal properties analysis

- (i) Differential scanning calorimeter (DSC)
- (ii) Thermogravimetric analysis (TGA)
- (iii) Dynamic mechanical analysis (DMA)

## **1.4 Importance of Research**

The research expects to develop a toughened nanocomposite from a renewable resource with balanced mechanical properties. The success of this project will widen the applications of PLA such as furniture, automobile parts and enables it to be considered as a possible substitute for conventional petroleum based plastics.