UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLY-3-HYDROXYBUTYRATE/POLY(BUTYLENE-ADIPATE-TEREPHTHALATE) STEARATE-MODIFIED Zn3Al- LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

PAK YEN LENG

FS 2014 30

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By

PAK YEN LENG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of University of Putra Malaysia in fulfillment of the requirement for the degree of Master Science

PREPARATION AND CHARACTERIZATION OF POLY-3-HYDROXYBUTYRATE/POLY(BUTYLENE-ADIPATE-TEREPHTHALATE) STEARATE-MODIFIED Zn_3Al- LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

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January 2014

Chairman **: Prof. Mansor b Hj Ahmad, PhD**

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The present research aims at studying the influence of layered double hydroxide (LDH) on the properties of Poly(3-hydroxybutyrate)/Poly(butylene adipate-co-terephthalate), (PHB/PBAT). LDH is a synthetic clay which can be easily prepared through co-precipitation method. However, it is incompatible with organic material due to its hydrophilic nature. The LDH was modified via ion exchange method using organic surfactant, sodium stearate to increase its hydrophobicity and compatibility with organic materials. The characterization of modified sterarate LDH was carried out by X-ray Diffraction (XRD), Fourier Transfrom Infrared Spectroscopy (FTIR) and Thermogravimetric analysis (TGA). XRD and FTIR results indicated LDH was successfully modified through the ion exchange method. XRD showed that the basal spacing of pristine LDH increased with the formation of modified LDH.

The PHB/PBAT blend was successfully prepared by solvent casting method. FTIR spectra revealed that the blends involved only physical interaction as there were no new functional groups or new bonding present. Tensile strength and modulus decreased as the PBAT contents increased due to elastic characteristic of PBAT. SEM micrograph of the PHB/PBAT clearly demonstrated a two phase morphology, which indicated the immiscibility of the component. For the result of PHB/PBAT blend, the onset temperature, the temperature at the T_{max} of PHB and the T_{max} of PBAT are found to decrease as compared to the pristine polymer. This indicated that the PHB/PBAT blend have an effect on the acceleration of thermal decomposition. Thus, the addition of PBAT to PHB in the weight ratio of 10% has decreased the thermal stability of virgin PHB.

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The PHB/PBAT nanocomposites were prepared by solvent casting technique. The expansion of the basal spacing of the modified LDH indicated the formation of intercalated types of nanocomposites which supported by the presence of diffraction peak in XRD diffractograms and TEM images. TEM images results revealed that the modified LDH layers are homogeneously distributed in the PHB/PBAT polymer blends matrix. Mechanical property of the nanocomposites with 2 wt% modified LDH content show 56% improvement in elongation at break compared to those of the blend. The significant enhancement in the elongation at break of the nanocomposites is due to the presence of modified LDH that act as a plasticizer.

Furthermore, the thermogravimetric analysis showed the presence of modified stearate LDH resulting in significant improvement in thermal stability of nanocomposites, especially 2 wt% nanocomposite as compared to pristine polymer blend.

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Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT POLI-3-HIDROBUTIRAT/ POLI(BUTILENA-ADIPAT-TEREFTALATE) STEARATE Zn_3Al- LAPISAN BERGANDA HIDROKSIDA TERMODIFIKASI

Oleh

PAK YEN LENG

Januari 2014

Pengerusi : Prof. Mansor b Hj Ahmad, PhD

Fakulti : Sains

Matlamat kajian ini adalah untuk mengetahui kesan penggunan lapisan berganda hidrosida ke atas sifat poli(3-hidrobutirat)/poli(butilena adipat-ko-tereftalat), (PHB/PBAT). Lapisan berganda hidrosida adalah sintetik tanah liat yang boleh disediakan melalui kaedah pemendakan serentak. Walau bagaimanapun, ia adalah tidak serasi dengan bahan organik kerana ia bersifat hidrofilik. Leapisan berganda hidrosida telah diubahsuai melalui kaedah pertukaran ion menggunakan surfaktan organik, natrium stearate untuk meningkatkan hidrofobik dan keserasian dengan bahan organik. Pencirian lapisan berganda hidrosida termodifikasi telah dijalankan melalui pembelauan sinar-X (XRD), spektroskopi Infrared transformasi Fourier (FTIR) dan analaisis termogravimetri (TGA). Keputusan XRD dan FTIR menunjukkan bahawa lapisan berganda hidrosida telah berjaya diubahsuai melalui kaedah pertukaran ion. XRD menunjukkan bahawa jarak basal lapisan berganda hidrosida meningkat dengan pembentukan lapisan berganda hidrosida termodifikasi.

Adunan PHB/PBAT telah berjaya disediakan dengan kaedah tuangan pelarut. Spektrum FTIR menunjukkan bahawa campuran hanya melibatkan saling tindakan fizikal kerana tidak ada kumpulan baru dan ikatan baru. Kekuatan tegangan dan modulus menurun dengan penambahan kandungan PBAT kerana PBAT besifat elastik. SEM mikrograf daripada PHB/PBAT mempamerkan morfologi dua fasa dan menunjukkan adunan tersebut tidak bercampur. Suhu awal, suhu di T_{max} PHB dan T_{max} PBAT didapati berturun berbanding dengan polimer asli dalam adunan PHB/PBAT. Ini menunjukan bahawa adunan PHB/PBAT mempunyai kesan untuk meningkatkan terma penguraian Oleh itu, penambahan PBAT untuk PHB dalam nisbah sebanyak 10% telah menurunkan kestabilan haba PHB.

Nanokomposit PHB/PBAT telah disediakan melalui teknik tuangan pelarut. Pertambahan jarak basal daripada lapisan berganda hidrosida termodifikasi menunjukkan pembentukan nanokomposit berjenis interkalasi yang disokong oleh

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kehadiran puncak belauan dalam XRD dan imej TEM. Keputusan imej TEM nenunjukkan lapisan berganda hidrosida termodifikasi diedarkan secara homogen dalam aduanan PHB/PBAT. Sifat mekanik nanokomposit dengan 2 wt% lapisan berganda hidrosida termodifikasi menunjukkan peningkatan 56% dalam pemanjangan pada takat putus berbanding dengan adunan PHB/PBAT. Peningkatan ketara dalam pemajangan nanokomposit menunjukkan kehadiran lapisan berganda hidrosida termodifikasi bertindak sebagai pemplastik. Tambahan pula, analisis termogravimetri menunjukkan kehadiran lapisan berganda hidrosida termodifikasi telah meningkatkan kestabilan haba dalam nanokomposit terutamanya 2 wt% nanokomposit berbanding dengan adunan PHB/PBAT.

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APPROVAL

I certify that a Thesis Examination Committee has met on 2nd of January 2014 to conduct the final examination of Pak Yen Leng on her master thesis entitled "Preparation and characterization of Poly-3-hydroxybutyrate acid/Poly (butylene adipate-co-terephthalate)/stearate modified Zn_3Al layered double hydroxide nanocomposites" in accordance with Universities and University Colleges Act 1971 and the Consitutution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the degree of Master of Science.

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LIST ABBREVIATIONS

B109	Bentonite
C30B	Cloisite 30B
CP	Cellulose propionate
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimeter
FTIR	Fourier Transform Infrared Spectroscopy
GMA	Glycidyl methacrylate
LDH	Layered double hydroxide
PBA	Poly(butylene Adipate)
PBAT	Poly(butylene adipate-co-terephthalate)
PBS	Poly(butylene succinate)
PCL	Poly(caprolactone)
PEOPAs	Poly(ethylene glycol) phosphonates
PHA	Polyhydroxyalkanoate
PHB	Poly(3-hydroxybutyrate)
PHBV	Poly(hydroxybutyrate-co-hydroxyvalerate)
PIP	Poly(cis-1,4-isoprene)
PLA	Polylatic acid
PMLDH	phosphonates (PEOPAs)-modified Layered Double Hydroxide
PPC	Poly(propylene carbonate)
PVA	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
SEM	Scanning Electron Microscopy
SLDH	Stearate- Zn_3Al LDH
TEM	Transmission Electron Microscopy
T_g	Glass transition temperature

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TGA	Thermogravimetric Analysis
wt%	Weight percentage
XRD	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background

Great contributions have been made by introducing polymers into the market to enhance the grade of living and lifestyle. Polymers are composed of many repeating units and known as macromolecules. Monomer is the basic molecular unit that builds up polymer. Monomers are linked to each other by covalent bond
.

Natural polymers and synthetic polymers are the classes of polymer. Polymers that exist naturally are known as natural polymer. It can be classified into biological and plant origins. Enzymes and nucleic acid are the examples of biological origin polymers. It can be very complex. Meanwhile, the plant origin polymers may have relatively simple structures likes starch and rubbers. Man-made polymers are known as synthetic polymers. Fibers, plastics and adhesives are examples of synthetic polymers.

Polymer can be divided into three groups that consist of thermoplastic, thermosets and elastomers. Under the glass transition temperature (T_g), thermoplastics become brittle and become rubbery beyond T_g. Poly(ethylene) (PE), Poly(propylene) (PP), and Polystyrene (PS) are examples of thermoplastics. Thermosets are polymer that cannot be softened by heating. Due to formation of cross linking among polymer chains by intermolecular bonding, it is hardened upon heating. To achieve cross linking, chemicals, heat or radiation is used during fabrication. This process is known as vulcanization. Phenolic resins and silicones are examples of thermoset. Elastomers are amorphous polymers with elastic property. Segmental motions occur above the T_g. Thus, elastomers are soft and convert to its original shape after deformation. Polybutadiene, polyisoprene, and polychloroprene are examples of elastomer (Shanks and Kong, 2013).

1.1.1 Biodegradable Polymer

Plastics are being used throughout the world. Plastics are extremely important to the job market, especially in packaging field. Production of eco-friendly plastics that compatible with the environment is needed since plastics created ecological concern due to the lack of deprivation. Therefore, biodegradable plastics began being sparking interest. Creating of biodegradable materials draws high attention as oil prices increased and they are considered to assist to reduce the waste issue (Gatenholm *et al*., 1992).

There has been much attention in research dedicated to create biodegradable matter because of the abundant waste amount in the world. Biodegradable polymer can be obtained from renewable sources and derived from petrochemicals resources. Some of the commonly obtainable biodegradable polymers are polylactic acid (PLA), poly(caprolactone) (PCL), polyhydroxyalkanoate (PHA), poly(butylenes succinate) (PBS), poly(butylene adipate-co-terephthalate) (PBAT), cellulose, thermoplastic starch, and etc (Tokiwa and Calabia, 2007).

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1.1.2 Polymer Nanocomposites

Combination of very discrete elements (particles/fibres) within a polymer matrix deliberated to hold the reinforcements together is defined by the term ‘‘advanced composite’’. Strength and stiffness of the particles are combined in this type of composite. ‘‘Nanocomposite’’ is referred to a material when the microstructural scale is between the range of a few nanometers.

Polymer nanocomposites consist of two parts which are polymeric material and reinforcing nanoscale material (nanoparticle). The nanoparticle aforementioned must have at least one dimension in one billionth of a meter (10^{-9} m). Many researches have been proven that major enhancement in tensile properties, thermal stability and other areas of polymer nanocomposites. To improve or modify the mechanical and physical properties of elastomeric materials, organoclay is used in the polymer field (Malas and Kumar Das, 2013). Significant improvements which have been confirmed in materials properties of polymer-clay nanocomposites at very low clay content as compared to its pure polymer or conventional composites have generated excitement from both the industry and academia (Sinha Ray and Okamoto, 2003b). Remarkable improvements in thermal properties, mechanical properties, barrier properties, and biodegradability of the pristine polymer have been revealed by polymer-clay nanocomposites (Sinha Ray and Okamoto, 2003b).

In recent years, attention was drawn on polymer/layered crystal nanocomposites due to their wonderful and distinct characteristics which may provide a wide range in application (Zhao *et al*., 2002). In addition, there is a great attention of layered materials as guests and hosting polymers in the preparation of nanocomposites. For examples, manganese oxides (Liu *et al*., 2002), layered silicates (Alexandre and Dubois, 2000), titanates (Sukpirom and Lerner, 2001) and layered phosphates (Nakato *et al*., 2000) are most generally used layered material (Ding *et al*., 2007). Nevertheless, most of the earlier conducted studies have concentrated on layered silicate, also named as clay and majority are natural clay minerals. The cations are interlayer ions, as well as K^+, $Na^+$and Ca^{2+} (Sinha Ray and Okamoto, 2003b). For the making of clay organophilic, alkylammonium cations could be used to replace these alkaline cations. Since the researchers done the first work on exfoliated nylon/clay nanocomposites at Toyota Research Center, different kind of polymers used for the research of nanocomposites (Usuki *et al*., 1993).

1.1.3 Layered Double Hydroxide

Layered double hydroxide (LDH) is synthetic clay. By co-precipitation reaction, it can be easily synthesized under the laboratory conditions. LDH is also known as hydrotalcite- like compounds because of similarity in their structural with hydrotalcite (Bravo-Suảrez *et al*., 2004). LDH is a thin crystalline inorganic layer in two dimensional type layered structure consisting of thickness of a few nanometers. Both organic and inorganic anions are allowed to host in the structure of LDH with different sizes in interlayer spaces. In polymer, appropriately modified clays, natural or synthetic can be dispersed (Manzi-Nshuti *et al*., 2009)

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1.1.4 Poly(butylene adipate-co-terephthalate)

Poly(butylene adipate-co-terephthalate) (PBAT) is an eco-friendly polymers which totally biodegraded with the assist of naturally occurring enzymes in a few weeks (Witt *et al*., 2001) It has the properties same as low density polyethylene (LDPE), but with superior mechanical properties and it can be manufactured using most common polymer processing systems. PBAT is flexible and tough (strain at break ~710%). PBAT is belonging to aliphatic/aromatic copolyester family that produced from terephthalate acid, 1,4 butanediol, and adipic acid. Its density is 1.26g/cm^3. Polydispersity of PBAT is 2.4 with a glass transition temperature of -29°C and melting point of 115°C (Jiang *et al*., 2006). Figure 1.1 is the structure of PBAT (Chivrac *et al*., 2007).

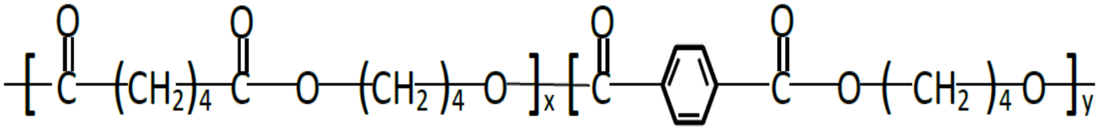

Figure 1.1: Structure of poly(butylene adipate-co-terephthalate) (PBAT).

1.1.5 Poly(3-hydroxybutyrate)

For replacement of petroleum-derived thermoplastics, Poly(hydroxyalkanoate) (PHA) is considered as potentially valuable polyester because it is a biodegradable, biocompatible and microbial thermoplastic. PHA also known as Poly(hydroxyalkanoic acid) (Herrema and Kemmel, 2009). Poly(3-hydroxybutyrate), (PHB) is accumulated by many species of bacteria as a carbon or energy storage material and it is the well known member of the PHA series. PHB is composed of 3-hydroxybutyric acid monomer (Ojumu *et al*., 2004) which also known as 3-hydroxybutyrate or hydroxybutyrate monomer. Therefore, PHB can be named as Poly(3-hydroxybutyric acid) or Poly(hydroxybutyrate). Figure 1.2 is the structure of 3-hydroxybutyric acid and PHB. It is a high melting temperature and a high degree of crystallinity of semicrystalline polymer. It is not soluble in water and 100% biodegraded. PHB has a few of weakness that limited its applications such as inefficient and high cost of the fermentation and extraction process, poor mechanical properties, poor formability and very low melt viscosity (Avella *et al*., 2000). Cracking and brittleness properties of PHB are because of the large spherulites in its structure. However, PHB nanocomposites still attracted a lot of attention due to its uses in few areas such as biomedical, agricultural and packaging (Scott, 2002). Figure 1.2 is the structure of 3-hydroxybutyric acid and PHB (Bucci *et al*., 2005).

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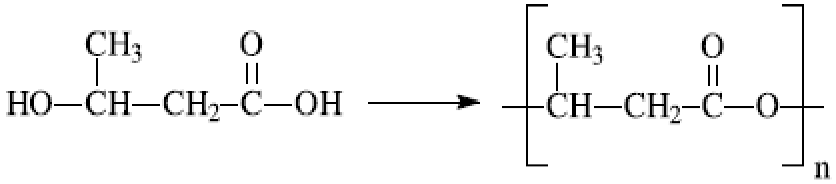

Figure 1.2: Structucre of 3-hydroxybutyric acid and PHB.

1.2 Problem Statements

The use of plastics for packaging is one of the fast growing areas. The factors such as convenience, safety, cheap and fine aesthetic behavior determine the rapid growth for manufacturing of packing using plastics. In general, they are formed from polyolefins that produced from fossil fuels. They ended up as spontaneously non degradable wastes after used and discarded to the surroundings or incinerated. So, the issue of plastics refuse becomes a worldwide ecological crisis (Kirwan and Srawbridge, 2003).

An enormous research challenge is to modify the biodegradable materials with controlled properties throughout the world today. PHB is biodegradable polyester. However, applications of PHB are limited due to its high cost and poor mechanical property. Therefore, PBAT is a natural pick to blend with PHB since it is a flexible polyester. Conventional composites or blend preparation with inorganic or natural fillers, respectively are alternative methods to enhance few of the properties of eco-friendly polymers. Therefore, in this research, layered double hydroxide will be studied as compatibilizer in biodegradable PHB/PBAT blend to form nanocomposites.

1.3 Objectives of the Study

The objectives of this study are:

1. To prepare Zn_3Al layered double hydroxide.
2. To modify Zn_3Al LDH with sodium stearate via ion exchange method.
3. To prepare PHB/PBAT stearate-Zn_3Al LDH nanocomposites by solution casting method.
4. To study the effect of layered double hydroxide on mechanical, thermal properties and morphology of the PHB/PBAT/stearate-Zn_3Al LDH nanocomposites.

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