UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLYHYDROXYBUTYRATE/POLYCAPROLACTONE/STEARATE MAGNESIUM-ALUMINIUM LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

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FS 2013 60

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By

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

November 2013

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

PREPARATION AND CHARACTERIZATION OF POLYHYDROXYBUTYRATE/POLYCAPROLACTONE/STEARATE MAGNESIUM-ALUMINIUM LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

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Disposal of non-biodegradable polymer waste leads to environmental problems which produce highly toxic to living organisms. Therefore, production of biodegradable polymer is necessary to resolve environmental problems and to obtain materials with excellent properties for other uses. The anionic clay Mg-Al layered double hydroxide (Mg-Al LDH) nanofiller with Mg^{2+}:Al^{3+} (3:1) ratio was synthesized by co-precipitation method from nitrate salt solution at pH 9. Stearate Mg-Al LDH nanofiller was prepared by anion exchange method where the nitrate anions replace by stearate anions between the LDH interlayer. This chemical modification leads to expand the interlayer d-spacing of LDH and easier for the polymer chain intercalated into the LDH interlayer.

Polyhydroxybutyrate (PHB)/polycaprolactone (PCL) polymer blends and PHB/PCL/stearate Mg-Al layered double hydroxide (stearate Mg-Al LDH) polymer nanocomposites with distinct contents were prepared via a solution casting intercalation method to avoid thermal instability of pure PHB. Blend of both biodegradable polymer to achieve unique properties and the additional of stearate Mg-Al LDH nanofiller is to improve the compatibility between the filler and polymer matrix. The characteristics of prepared samples were investigated in term of spectroscopic, thermal, mechanical and morphology.

Fourier Transform Infrared Analysis (FTIR) spectra shows stearate anions are successfully replaced the nitrate anion due to the presence of carboxylic acid (COOH) functional group. Moreover, the formation of polymer nanocomposites only involves physical interaction as there are no new functional groups or new bonding present. In addition, XRD results shows increasing interlayer d-spacing from 8.66 Å to 32.97 Å in stearate Mg-Al LDH nanofiller due to the intercalation of long chain hydrophobic tail

stearate anions into the LDH interlayer. TEM results revealed that additional of 1.0 wt % stearate Mg-Al LDH nanofiller shows a homogeneous dispersion in the 80PHB/20PCL polymer blend matrix. Thus, higher miscibility and strong interaction between filler and polymer matrix lead to the higher thermal stability in TGA characterization.

The presence of 1.0 wt % of the stearate Mg-Al LDH nanofiller improved drastically in elongation at break (around 300 %) and tensile strength (around 66 %) when compare with PHB/PCL polymer blends. Besides, investigation of scanning electron microscopy (SEM) shows fracture surface of polymer nanocomposites are less porosity, homogeneous dispersed and well stretched before it breaks. This suggests that filler act as compatibilizer to improve the mixing between filler and polymer matrix. As a conclusion, 80PHB/20PCL/1stearate Mg-Al LDH polymer nanocomposite as an optimum ratio between filler and polymer matrix due to the enhancement drastically in properties when compare with those pure PHB, pure PCL and PHB/PCL polymer blends.

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

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT POLIHIDROKSIBUTIRAT/POLIKAPROLAKTON/STEARAT MAGNESIUM-ALUMINIUM HIDROKSIDA LAPISAN GANDA DUA

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Pelupusan sisa polimer yang bukan terbiodegradasikan akan menyebabkan masalah alam sekitar yang menghasilkan toksik kepada organisma hidup. Oleh itu, menghasilkan polimer terbiodegradasi adalah diperlukan untuk menyelesaikan masalah alam sekitar dan mendapat bahan dengan sifat cemerlang untuk kegunaan lain. Sintesis anionik tanah liat hidroksida lapisan ganda dua (Mg-Al LDH) nanopengisi pada nisbah molar Mg^{2+}:Al^{3+} bersamaan dengan 3:1 telah dilakukan dengan menggunakan kaedah ke-pemendakan daripada larutan garam nitrat pada pH 9. Stearat Mg-Al LDH nanopengisi telah disediakan oleh kaedah pertukaran anion di mana anion nitrat digantikan oleh anion stearat di ruangan antara lapisan LDH. Pengubahsuaian kimia ini membawa kepada mengembangkan ruangan antara lapisan LDH dan lebih mudah untuk rantaian polimer diinterkalasi ke dalam ruangan antara lapisan LDH.

Polimer adunan polihidroksida (PHB) /polikaprolakton (PCL) dan nanokomposit polimer PHB/PCL/stearat Mg-Al hidroksida lapisan ganda dua (stearat Mg-Al LDH) dengan pelbagai kandungan telah disediakan melalui kaedah interkalasi penuangan larutan untuk mengelakkan ketidakstabilan terma PHB tulen. Campuran kedua-dua polimer terbiodegradasi untuk mencapai ciri-ciri unik dan tambahan stearat Mg-Al LDH nanopengisi adalah untuk meningkatkan keserasian antara pengisi dan matriks polimer. Ciri-ciri sampel yang disediakan telah disiasat dari segi spektroskopi , terma, mekanikal dan morfologi.

Analisis spectra Inframerah transformasi fourier (FTIR) membuktikan bahawa anion stearat berjaya menggantikan anion nitrat kerana kehadiran kumpulan berfungsi iaitu asid karboksilik (COOH). Selain itu, pembentukan nanokomposit polimer hanya

melibatkan interaksi fizikal kerana tidak ada pembentukan kumpulan-kumpulan berfungsi baharu atau kehadiran ikatan baharu. Di samping itu, keputusan pembelauan sinar-X (XRD) menunjukkan bahawa ruangan antara lapisan meningkat daripada 8.66 Å ke 32.97 Å di dalam nanopengisi stearat Mg-Al LDH kerana interkalasi rantai panjang ekor hidrofobik anion stearat ke dalam ruangan antara lapisan LDH. Keputusan mikroskop electron penghantaran (TEM) mendedahkan bahawa tambahan sebanyak 1.0 % berat nanopengisi stearat Mg-Al LDH menunjukkan pengisi tersebar secara homogen dalam 80PHB/20PCL polimer adunan. Oleh itu, pencampuran yang lebih baik dan interaksi kuat antara pengisi dan matriks polimer membawa kepada kestabilan terma yang lebih tinggi pada pencirian analisis termogravimetri (TGA).

Kehadiran 1.0 % berat nanopengisi stearat Mg-Al LDH bertambah secara drastik dalam pemanjangan pada takat putus (kira-kira 300 %) dan kekuatan tegangan (kira-kira 66 %) bila dibandingkan dengan polimer adunan PHB/PCL. Selain itu, kajian mikroskop imbasan elektron (SEM) menunjukkan bahawa permukaan pecah nanokomposit polimer adalah kurang keliangan, tersebar secara homogen dan juga keregangan yang baik sebelum ia pecah. Ini menunjukkan bahawa pengisi sebagai ‘compatibilizer’ meningkatkan pencampuran keserasian antara pengisi dan matrik polimer. Sebagai kesimpulan, nanokomposit polimer 80PHB/20PCL/1stearate Mg-Al LDH sebagai nisbah optima antara pengisi dan matriks polimer kerana peningkatkan sifat-sifat berbanding dengan PHB tulen, PCL tulen dan polimer adunan PHB/PCL.

ACKNOWLEDGEMENTS

I sincerely emphatic my foremost thank to God because of His blessing and guidance. Besides, I sincerely extend my warming gratefulness and appreciation to my honourable project supervisor Prof. Dr Mansor B Hj Ahmad, co-supervisors Professor Dato' Dr. Wan Md Zin Wan Yunus, Dr. Nor Azowa Ibrahim and Dr. Norhazlin Zainuddin for their supervision, brilliant ideas, invaluable advice, constructive criticisms, inspiring guidance, unfailing help and superb tolerance throughout the course of this work. Their supports encouraged and motivated me to strive harder for success.

Also, I dedicated my appreciation to all laboratory assistants in Chemistry Department and Institute Biological Science UPM for their willingness to help, encouragement and sincere contribution that has made this research work possible. In addition, special thanks to Mr. Then Yoon Yee and Mr. Chieng Buong Woei for their consolation and support. I have learned a lot from them while I conducted this project.

Not forgettable are my beloved family members who have always believe in me, and endured with me during difficult times. A word of appreciation and deepest affection is inadequate to them. Their love and understanding ways inspire me and give me hopes whenever I am disappointed. Lastly, my gratefulness will dedicate to all my friends in polymer group for their direct or indirect help, suggestions, encouragement and companion are of great help in sustaining the morale and enthusiasm. Without their unconditional and endless love, it would not have been possible for me to complete this Master of Science thesis.

Financial support from Universiti Putra Malaysia for the Graduated Research Fellowship and MyBRAIN MyMaster National Science Fellowship Award is gratefully acknowledged.

I certify that a Thesis Examination Committee has met on 19th November 2013 to conduct the final examination of Liau Cha Ping on her thesis entitled "**Preparation and Characterization of Polyhydroxybutyrate/Polycaprolactone/Stearate Magnesium-Aluminium Layered Double Hydroxide Nanocomposites**" in accordance with the Universities and University Colleges Act 1971 and the Constitution 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 OF ABBREVIATIONS

PHB	Polyhydroxybutyrate
PCL	Polycaprolactone
Mg-Al LDH	Magnesium-Aluminium Layered Double Hydroxides
Stearate Mg-Al LDH	Stearate Magnesium-Aluminium Layered Double Hydroxides
FTIR	Fourier Transform Infrared
XRD	X-ray Diffraction
Ǻ	Angstrong
TGA	Thermogravimetric Analysis
DTG	Differential Thermogravimetric
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy

CHAPTER 1
INTRODUCTION

1.1 Background

The production of packaging and plastic materials including composites has increased from year to year. Polymers play an important role in human beings with great contribution into market. But very few pure polymers are used commercially without any additives. In order to improve and modify polymers' properties, several types of material which is non-biodegradable are added to it. Non-biodegradable polymers use in synthetic packaging films will cause environmental deterioration and ecological problems due to slow degradation rate and predicted exhaustion.

Consequently, many wastes that produced from fossil fuels are non-biodegradable, widely used of these polymers created a long-term disposal problem and have significant adverse effects on the environmental pollution. Many solutions have been proposed for soil waste management of plastics, like recycling, incineration, landfill disposal and degradable plastics. Polymer recycling is an environmentally attractive solution, but the results on a worldwide scale have not been successful because recycling will not yield quality products due to the heterogeneous nature of plastics. Incineration of plastics will release toxic gasses and vapors, which results in a serious health hazard. The use of plastic in landfill operations is least preferred because of space constraint.

On the other hand, much attention had been focused on biodegradable polymers to instead the role of non-biodegradable polymers due to its short-lived degradation when exposed to a biologically active environment and solve the environment problems. High cost, poor mechanical properties and poor processing ability restricted the application of biodegradable polyesters even it's considering as high performance environmental friendly biodegradable plastics. Abdel-Rehim *et al*. (2004) reported that synthesis and manufacture of new environmental friendly and sustainable polymeric materials have been focused by researchers. The purpose to extend the shelf life and enhance food quality while reducing packaging waste has encouraged the exploration of new bio-based packaging materials, such as edible and biodegradable films from renewable resources (Sorrentino *et al*., 2007).

Consequently, biodegradable polymers polyhydroxybutyrate (PHB) and polycaprolactone (PCL) are chosen for much of the researchers in order to solve the environmental problems. However, some of the drawbacks of pure PHB and pure PCL lead to restrict their application. For pure PHB, it is brittleness, thermal instability at above its melting temperature and very high cost production. Besides, pure PCL is low melting point (60 °C), poor availability, poor process ability, low durability and high cost production (Chen *et al*., 2005 (a); Wang *et al*., 1998). Sorrentino *et al*. (2007) reported that polymer nanocomposites using inorganic or natural fillers were explored as an alternative way of acquiring green materials with desired properties. Furthermore, numerous researchers had studied blends of the polymer as potential applications in packaging to medical sutures.

However, the main problem exists in the biodegradable polymer blends are incompatibility between both polymers which lead to a poor mechanical properties. Therefore, reinforcing nanofillers such as layered double hydroxide (LDH) are often introduced into the polymer blends in order to enrich their properties, solve disposability problems and reduce cost production. For example, Pandey *et al*. (2005) reported that insertion of equitably low concentration filler can enhance materials properties in term of mechanical and thermal properties. Besides, Kumar *et al*. (2009) studied the aim of nano-additives incorporated into polymer is to improve physical, mechanical, thermal properties, degradability and stabilization of polymers.

Meanwhile, nanofillers have much smaller size with larger surface areas than bulk materials and exhibit excellent mechanical properties. Furthermore, Zhao *et al*. (2011) reported that polymer-based nanocomposites have good mechanical properties and compatibility caused by the high interfacial reactivity of the nanofiller incorporate with the polymer matrix. Issue in using LDH nanofiller is the hydrophilic nature which may lead to poor interfacial adhesion with the hydrophobic polymer matrix and hence decreased toughness, mechanical and thermal properties of polymer nanocomposites. Thus, chemical modification of LDH nanofiller is necessary to reduce the hydrophilicity of LDH nanofiller and lead to much easier incorporation between filler and polymer matrix.

1.2 Statement of Problems

Disposal of non-biodegradable wastes is one of the most serious environmental problems facing by modern society. This has given a great impact on the environment such as emissions of the greenhouse and toxic gases from incineration, damage to wildlife and marine species, and landfill accumulation. Increased environmental awareness and consciousness throughout the world has lead to an increasing the need to investigate more environmental friendly and/or sustainable materials to replace it.

During the past decade, numbers of significant industries such as the automotive, construction or packaging industries have shown massive interest in the progress of new biocomposite materials. The development of biodegradable polymers has attracted a great deal of interest recently. Most of the biodegradable polymers are mainly polyester which is promising materials for the production of high performance and environmental friendly biodegradable plastics. The biodegradable polyesters including poly(butylene adipate-coterephthalate) (PBAT), polyhydroxybutyrate (PHB), polycaprolactone (PCL), poly(lactic acid) (PLA) and poly(butylenes succinate) (PBS). Although biodegradable polyesters have started making inroads into the commercial application, they are far from becoming substitutes for traditional non-degradable polymers.

The major reason is the disadvantages properties of the biodegradable polyesters, such as poor mechanical properties and poor process ability which limit their application. Taking this situation into consideration, researchers have been focused on the necessity and urgency of modification to these biodegradable polymers. The most important question is does the use of polymer nanocomposites safes to the environment? Is it really practical and cost effective in large scale production? Properties and cost of biodegradable polymers can be also modified and improved through the use of nanofillers that reduce the cost of the material without modifying their biodegradability (Iannace *et al*., 1999).

Lack of the researchers reported that the polymer nanocomposites with the use of synthetic fillers. Jonas and Kuykendall (1966) reported that the drawback of natural filler montmorillonite (MMT) is the tendency of MMT crystallites to aggregate and the permanent negative charge of MMT filler is completely neutralized with sodium cation, Na^+ with very high stability lead to ion exchange reaction become more difficult. Thus, in this study has been focused on the introducing of synthetic nanofiller into biodegradable polymer matrices to produce polymer nanocomposites in order to enhance the properties of pure polymers. In spite of the above findings, an idea of present study will investigate the properties of polymer nanocomposites which prepared from the incorporation of biodegradable polyesters PHB/PCL polymer blends with stearate Mg-Al LDH nanofiller.

Recently, many studies are focused on the preparation of polymer/filler nanocomposites via melt intercalation mixing technique. This is because high temperature and large shear forces in melt intercalation mixing often cause strong chemical and/or physical interactions between inorganic fillers and polymer matrices. However, solution intercalation mixing technique has taken place in this study because of the thermal instability and/or thermal decomposition of PHB at above its melting temperature. Meanwhile, PHB will undergo thermal decomposition with rapid decrease in molecular weight during melt processing.
On the other hand, the purpose of blending both biodegradable polyester polymer, pure PHB and pure PCL is to reduce the brittleness and cost production of PHB and improved the flexibility of the PHB/PCL polymer blends. Besides, the challenge is thus, how to improve the interfacial adhesion between both polymers? Therefore, incorporation of stearate Mg-Al LDH nanofiller is necessary to act as a reinforcing nanofiller and/or compatibilizer in order to increase the miscibility and compatibility between filler and polymer matrices.

The advantages of synthetic stearate Mg-Al LDH nanofiller are light weight, reasonable flexible, renewable, low cost production, environmental friendly and biodegradable. Besides, co-precipitation method is defined that incorporation of trace elements into mineral structure during solid solution formation. This synthesis method will lead to produce the nanofiller with the character such as smaller size particles, high surface areas, average pore diameters, homogeneous reaction and accurate control charge density (Mg^{2+}:Al^{3+} ratio) etc. Therefore, the polymer nanocomposites provide economical and ecological properties.

Moreover, strong bonding between filler and polymer matrix is essential for imparting polymer nanocomposites with the desired properties for many specific applications. The bonding between hydrophilic filler and the hydrophobic polymer matrix is weak and poor interfacial adhesion. Thus, this problem can be improved by addition of a coupling agent and/or surface modifications of filler. In this study, a surface chemical modification method was carried out by exchange nitrate anions with stearate anions in the interlayer LDH. For example, the long hydrophobic tail of stearate anions will radiates away from the surface and anion head group resides on the surface of LDH layer. This leads to expand interlayer d-spacing and change hydrophilic surface to hydrophobic surface which make more compatible with hydrophobic PHB/PCL polymer matrix.

1.3 Objectives of This Study

The objectives of this study are listed as below:

1 To modify the Mg-Al LDH nanofiller by anion exchange method using sodium stearate as Mg-Al LDH modifier.
2 To prepare PHB/PCL polymer blends and PHB/PCL/stearate Mg-Al LDH polymer nanocomposites of various compositions using solution casting technique.
3 To characterize the spectroscopic, thermal, mechanical and morphology properties of prepared PHB/PCL polymer blends and PHB/PCL/stearate Mg-Al LDH polymer nanocomposites.

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