UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLYLACTIC ACID/ POLYCAPROLACTONE/ MODIFIED CLAY COMPOSITES

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By

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

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

PREPARATION AND CHARACTERIZATION OF POLYLACTIC ACID/ POLYCAPROLACTONE/ MODIFIED CLAY COMPOSITES

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March 2010

Chairman: Associate Professor Mansor B. Ahmad, PhD

Faculty: Science

In this study, synthesis and characterisation of fatty hydroxamic acid (FHA) from palm olein with hydroxylamine using reflux method. FTIR spectrum, ^{1}H NMR and elemental analysis tests conducted on FHA reveal that FHA was successfully produced from palm olein,. The conversion percentage of palm olein to FHA increases (81%) when the optimum reaction time to be 10 hours and a molar ratio of (hydroxylamine to palm olein) 7:1.

FHA was used as one of the organic compounds to modify natural clay (Na-MMT). The clay modification was carried out by stirring the clay particles in an aqueous solution of the FHA or octadecylammonium (ODA) by which the clay layer distance increases from 12.2 Å to 31.02 Å and 29.49 Å, respectively. The modified clays were then used in the preparation of polylactic acid/polycaprolactone (PLA/PCL) composites. The optimum clay contents that yielded maximum tensile strength were 2% and 3% for PLA/PCL-ODA-MMT and PLA/PCL-FHA-MMT, respectively. The

intercalation of the modifier in the clay layer was characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier Transform Infrared (FTIR). Elemental analysis (CHN) was used to estimate the amount of FHAs and ODA in the clay.

In the first part of the preparation, the composites were synthesized by melt blending of the modified clay and PLA/PCL by a two-roll-mill internal mixer blending at a temperature setting of 185°C, rotor speed of 50 rpm and the mixing time of 12 minutes. Mechanical properties of the produced composites were then characterized by an lnstron universal testing machine.

The composites were also synthesized by using solution casting in the second part of the study. In this process, Chloroform was chosen to dissolve PLA and PCL under magnetic stirrer for 1 h. The required amount of the modified clay was added to the mixture, the composites were poured into Petri dish and left to dry.

The results indicate that the presence of the modified clay has dramatically improved the properties. Both of PLA/PCL-ODA-MMT and PLA/PCL-FHA-MMT composites prepared by melt blending have high tensile strength 38.91 MPa and 39.31 MPa compared to those of solution casting 31.43 MPa and 32.84 MPa for PLA/PCL-ODA-MMT and PLA/PCL-FHA-MMT, respectively. These composites were further characterized by XRD, FTIR, TGA and scanning electron microscopy (SEM).

It was found that similar results of FTIR and TGA were obtained when solution casting and melt blending processes were used to produce PLA/PCL, PLA/PCL-ODA-MMT and PLA/PCL-FHA-MMT. Thermal stability of these composites was improved to 349.26 °C and 354.62 °C for PLA/PCL-ODA-MMT and PLA/PCL-FHA-MMT, respectively, compared with the blend of polymers 342.15 °C. While the values of basal spacing in melt blending were higher 34.61 Å and 36.15 Å compare with those of solution casting 31.15 Å and 33.18 Å for PLA/PCL-ODA-MMT and PLA/PCL-FHA-MMT, respectively.

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

PENYEDIAAN DAN PENCIRIAN KOMPOSIT TANAH LIAT ASID POLILAKTIK/POLIKAPROLAKTON

Oleh

WISAM H. HOIDY

March 2010

Pengerusi: Profesor Madya Mansor B. Ahmad, PhD

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Dalam kajian ini, sintesis dan pencirian lemak asid hidroksamik, FHA daripada olein sawit dan hidroksilamine dengan cara refluks. Spektrum FTIR, ^{1}H NMR dan ujian analisis unsur dijalankan keatas FHA menunjukkan FHA berjaya disintesis daripada olein sawit. Peratusan perubahan daripada olein sawit kepada FHA bertambah (81%) apabila masa tindak balas optimum sebanyak 10 jam dan molar berat (hidroksilamine kepada olein sawit) 7:1

FHA, digunakan sebagai salah satu sebatian organik untuk mengubahsuai tanah liat semulajadi (Na-MMT). Pengubahsuaian tanah liat dilakukan dengan mengacau partikel tanah liat dalam larutan akueus FHAs atau oktadesilammonium (ODA) yang mana jarak lapisan tanah liat masing-masing meningkat daripada 12.2 Å kepada 31.02 Å dan 29.47 Å. Tanah liat yang diubahsuai kemudiannya digunakan dalam penyediaan komposit asid polilaktik/polikaprolakton (PLA/PCL). Kandungan tanah liat optimum yang menghasilkan kekuatan tegangan yang maksimum ialah 2% dan

3% untuk masing-masing PLA/PCL-ODA-MMT dan PLA/PCL-FHA-MMT. Apitan untuk pengubahsuaian dalam lapisan tanah liat telah dicirikan menggunakan pembelauan X-ray (XRD), analisis termogravimetrik (TGA) dan Spektroskopi Inframerah (FTIR). Analisis unsure (CHN) digunakan untuk menganggarkan amaun FHA dan ODA dalam tanah liat.

Dalam bahagian pertama penyediaan, komposit disintesis melalui pengadunan lebur daripada tanah liat dan PLA/PCL dengan sebatian pencampur dalaman dua-giling-gulung pada suhu 185 °C, kelajuan rotor 50 rpm dan masa pencampuran 12 minit. Sifat mekanikal komposit yang dihasilkan kemudiannya dicirikan dengan mesin pengujian semesta lnstron.

Komposit juga disintesis dengan menggunakan penuangan larutan dalam bahagian kedua kajian ini. Dalam proses ini, kloroform telah dipilih untuk melarutkan PLA dan PCL menggunakan pengacau magnetik selama 1 jam. Tanah liat terubahsuai dengan amaun yang dikehendaki kemudiannya ditambahkan ke dalam campuran, Komposit tuang ke dalam piring Petri dan dibiarkan untuk kering.

Keputusan menunjukkan kewujudan tanah liat terubahsuai secara ketora telah memperbaiki sifat komposit. Kedua-dua komposit PLA/PCL-ODA-MMT dan PLA/PCL-FHA-MMT yang disediakan dengan pengadunan lebur mempunyai kekuatan tensil yang tinggi 38.91 MPa and 39.31 MPa berbanding yang dihasilkan melalui penuangan larutan 31.43 MPa and 32.84 MPa. Komposit ini telah dicirikan selanjutnya menggunakan XRD, FTIR, TGA. dan mikroskopi pengimbas an elektron (SEM).

Didapati bahawa keputusan FTIR dan TGA yang serupa diperolehi apabila proses adunan larutan dan pengadunan lebur digunakan untuk menghasilkan PLA/PCL, PLA/PCL-ODA-MMT dan PLA/PCL-FHA-MMT. Kestabilan TERMA komposit dipertingkatkan masing-masing kepada 349.26 °C and 354.62 °C untuk PLA/PCL-ODA-MMT, PLA/PCL-FHA-MMT berbanding odunan polimer 342.15 °C. Sementara itu, nilai jarak tapak dalam sebatian lebur adalah lebih tinggi 34.61 Å and 36.15 Å berbanding dengan adunan larutan 31.15 Å and 33.18 Å masing-masing untuk PLA/PCL-ODA-MMT dan PLA/PCL-FHA-MMT.

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I certify that an Examination Committee met on **18 march 2010** to conduct the final examination of **Wisam H. Hoidy** on his thesis entitled " **Fatty hydroxamic acid modified clay as an additive for polylactic acid/ polycaprolactone composite**" in accordance with Universities and the 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.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Purta Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Date: 10 June 2010

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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WISAM H. HOIDY

Date:

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile–butadiene-styrene
CBT	Cyclic butylene terephthalate
CEC	Cation exchange capacity
DTG	Derivative thermal gravimetry
ENR	Epoxidized natural rubber
EPDM	Ethylene-propylene-diene terpolymer
FHA	Fatty hydroxamic acids
FHA-MMT	Fatty hydroxamic acids modified montmorillonite
FTIR	Fourier transform infrared
HAF	Hydroxyapatite fibers
HRR	Heat release rate
MAgPP	Maleic anhydride grafted polypropylene
Na-MMT	Sodium montmorillonite
NR	Natural rubber
ODA	Octadecylamine
ODA-MMT	Octadecylamine modified montmorillonite
OMLS	Organically modified layered silicate
OMMT	Organophilic montmorillonite
PCL	Poly(ε-caprolactone)
PCN	Polymer-clay nanocomposites
PEO	Poly(ethylene oxide)
php	Part per hundared polymer
PLA	Polylactic acid

PLS	Polymer layered silicate
PLSN	Polymer layered silicate NANOCOMPOSITES
PMMA	Poly(methyl methacrylate)
PS	Poly styrene
PP	Polypropylene
SBR	Styrene butadiene rubber
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TPE	Thermoplastic elestomer
TPO	Thermoplastic polyolefin
TPV	Thermoplastic vulcanisation
WAXD	Wide angle X-ay diffraction
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of study

From the last decade of 20th century, petrochemical based polymers technology has achieved much benefit to mankind. One of these rapidly grown achievements is the use of plastics in packaging. The most important factor determining rapid growth in the use of plastic in packaging industries is convenient, safety, low price and good aesthetic qualities. The petrochemical-based polymers are produced from fossil fuel, consume and discarded into environment, ending up as spontaneously undegradable wastes. The increase of undegradable wastes are significantly disturbing and damaging the environment.

Till now, the environment specialists do not have the answer about how to deal with these undegradable wastes. Incineration of these wastes produces large amount of carbon dioxide that contribute to global warming. This can also direct us to global pollution if not controlled well.

Based on these backgrounds, there is a dire need for the development of green polymeric materials which would not involve the use of poisonous and toxic constituent in their manufacture. It means that it could be degradable in the nature environmental product. For these reasons, through the world today, the development of biodegradable materials with the controlled properties has been a subject of great research challenge to the community of material and engineers.

Biodegradable polymers are defined as those that undergo microbially induced chain scission leading to the mineralization (Ray and Bousmina, 2005). Biodegradable polymers may not been produced from bio source only, but it can be derived from the petroleum source. Polymers are also being produced from bio source such as polyhydroxybutyre (PHB) and polyhydroxyvalarate (PHV). On the other hand, biodegradable polymer which is produced from petroleum source is polylactic acid (Ray and Bousmina, 2005).

Polylactic acid (PLA) and polycaprolactone (PCL) are well known biodegradable polymers. Polylactic acid (PLA) has a good biocompatibility and physical properties, such as high strength, thermoplasticity and fabricibility. Polycaprolactone (PCL) however has high flexibility, good biodegradability (Wang *et al.*, 1997)

1.2 Problem statement

Most biodegradable polymers have good properties comparable to many petroleum-based plastics and readily biodegradable, and may soon be challenging with goods plastics. Biodegradable polymers have great commercial potential for bio-plastic. However, some of the properties such as brittleness, and low melt viscosity for further processing limit their use in wide-range of applications. Modification of the biodegradable polymers properties to reach end-users demands is required. Nanoreinforcement of pure polymers to prepare nanocomposite has already proven to be an effective way to improve these properties concurrently. Preparation to processing of biodegradable polymer-based nanocomposites, which is, green

nanocomposites are the wave of the future and considered as the next generation materials.

1.3 Scope of study

Thus, in this study, Fatty hydroxamic acid (FHA), synthesized from palm olein with hydroxylamine, and octadecylamine (ODA), were used to modify montmorillonite clay (MMT) for preparation polylactic acid (PLA)/polycaprolactone (PCL) nanocomposite.

This work is aimed at preparation and characterization PLA/PCL modified clay composites by both melt blending and solution casting. Properties of the prepared PLA/PCL modified clay nanocomposites by melt blending are compared with that of the prepared by solution casting method.

1.4 Objectives of the study

The aims of this study are to;

1. Synthesize and characterize the Fatty Hydroxamic Acid (FHA) from palm olein and hydroxamylamine;
2. Prepare of PLA/PCL/clay composites by melt blending;
3. Prepare PLA/PCL/clay composites by solution casting;
4. Study the effects of ODA and FHA/clay as organoclay on properties of composites; and

CHAPTER 2

LITERATURE REVIEW

2.1 Composites

Composites are combinations of two or more materials with the properties that are not shown by individual components. They are prepared to perform as a single material. Nature made the first composite in living things. Wood is a composite of cellulose fibers held together with a matrix of lignin. Most sedimentary rocks are composites of particles bonded together by many metallic alloys are composites of some quite different constituents. Steel reinforced concrete, medical pills are composite materials that are homogenous on a macro scale. The term composite was used in the reinforced plastic industry during the 1940s (Donald and Dominick, 1994).

Reinforced polymer is a combination of materials in composition or form on a macro scale. However, all of the constituents in the polymer composite have their identities and do not dissolve or otherwise completely combined into each other. This definition is not completely precise, and it includes some materials often not considered as composite. Some combinations may be thought of as composite structures rather than composite materials. The dividing line is not sharp, and differences of opinion do exist.