



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS OF FATTY AND N,N'-CARBONYL DIFATTY AMIDES
FROM PALM OIL AND THEIR APPLICATION AS A CLAY MODIFIER
FOR POLYLACTIC ACID/EPOXIDIZED PALM OIL/CLAY
NANOCOMPOSITE PREPARATION**

EMAD A. JAFFAR AL-MULLA

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POLYLACTIC ACID/EPOXIDIZED PALM OIL/CLAY NANOCOMPOSITE
PREPARATION**

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 Doctor of Philosophy**

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Chairman: Professor Dato' Wan Md. Zin Wan Yunus, Ph.D

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N,N-carbonyl difatty amides (CDFAs) were synthesized from palm oil and urea using sodium ethoxide as a catalyst. Ethyl fatty esters (EFEs) and glycerol were produced as by-products. The synthesis was carried out by refluxing the reactants in ethanol. In this reaction, palm oil gave 79% CDFAs after 8 h and at molar ratio of urea to palm oil of 6.2: 1. Meanwhile, fatty amides (FAs) were synthesized from palm olein and urea by a one-step lipase catalyzed reaction. The use of immobilized lipase as the catalyst for the preparation reaction provides an easy isolation of the enzyme from the products and other components in the reaction mixture. The highest conversion percentage of 96% was obtained when the process was carried for 36 h using urea to palm olein ratio of 5.2: 1.0 at 40 °C. The method employed offers several advantages such as the use of renewable and abundant of the raw material, simple reaction procedure, environmentally friendly process and high yield of the product.



Both CDFAs and the FAs were characterized using Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (^1H NMR) technique and elemental analysis. The CDFAs, FAs and fatty hydroxamic acids (which were also synthesized from palm oil) were used as organic compounds to modify natural clay, Na-MMT, (sodium montmorillonite) by an ion exchange process. The clay modification was carried out by stirring the clay particles in an aqueous solution of FAs, CDFAs and fatty hydroxamic acids (FHAs). The interaction of the modifier in the clay layer was characterized by X-ray diffraction (XRD), and Fourier transform infrared (FTIR). Elemental analysis was used to estimate the presence of these fatty nitrogen compounds (FNCs) in the clay. The modified clay was then used in the preparation of the polylactic acid (PLA)/epoxidized palm oil (EPO) blend nanocomposites.

The EPO was used as a plasticizer for PLA using chloroform as a solvent for solution casting process of blending PLA/EPO. The FTIR spectra indicate that there are some molecular interactions by intermolecular hydrogen bond between PLA and EPO. All PLA/EPO blends show high thermal stability and significant improvement of mechanical properties compare to those of pure the PLA. The highest elongation at break (about 210%) was obtained when the ratio of PLA/EPO blend was 80/20. Morphological results of PLA/EPO blends show that EPO was miscible with PLA. Reduced viscosities of the blends decrease with increasing amount of EPO indicating that EPO was a good plasticizer for PLA.

The nanocomposites were synthesized by incorporating CDFA-MMT, FA-MMT or FHA-MMT into PLA/EPO blends. Preparation of nanocomposites were carried out

by solution casting of the modified clay and PLA/EPO blend of the weight ratio of 80/20 which has the highest elongation at break. The highest tensile strength, modulus, and elongation at break of the FA-MMT, FHAMMT, and CDFA-MMT nanocomposites were obtained when 2% of the CDFA-MMT and 3% of both FA-MMT and FHA-MMT loadings were used. These nanocomposites were characterized using XRD, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and tensile properties measurements. The XRD and TEM results confirm that the products are nanocomposites. PLA/EPO modified clay nanocomposites has higher thermal stability and significant improvement of mechanical properties in comparison with those of the PLA/EPO blend.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**SINTESIS AMIDA LEMAK DAN *N, N*-KARBONIL DWILEMAK DAN
PENGGUNAANNYA UNTUK UBAHSUAI TANAH LIAT DALAM
PENYEDIAAN NANOKOMPISOT POLI(ASID LAKTIK)/MINYAK KELAPA
SAWIT TEREPOKSI**

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N, N-Fenil difati karbonil (CDFAs) telah disintesis daripada minyak sawit dan urea menggunakan natrium etoksida sebagai pemangkin. Etil ester (Efes) dan gliserol dihasilkan sebagai produk simpanan. Sintesis dilakukan dengan merefluks minyak sawit dan urea dalam etanol. Dalam tindak balas ini, minyak sawit memberikan 79% CDFAs selepas 8 jam bertindak balas pada nisbah molar urea kelapa sawit adalah 6.2:1. Sementara itu fenil lemak (FAs) telah disintesis daripada minyak kelapa sawit dan urea dengan menggunakan lipase sebagai mangkin. Penggunaan lipase tersekat gerak membolehkan pengasingan enzim daripada produk dan bahan lain dalam campuran tindak balas dibuat dengan senang. Peratusan penukaran tertinggi (96%) diperolehi apabila proses dilakukan selama 36 jam dengan nisbah urea kelapa sawit sebanyak 5.2:1.0 pada 40⁰C. Kaedah yang dipergunakan menawarkan beberapa kelebihan termasuk bahan mentah yang banyak dan senang diperolehi, prosedur tindak balas mudah, proses yang mesra alam dan hasil yang tinggi.

CDFAs dan FAs dicirikan dengan menggunakan spektroskopi transformasi Fourier inframerah (FTIR), teknik proton resonansi nukleus (^1H NMR) dan analisis unsur. The CDFAs dan FAs dan asam lemak hidroksamik (yang juga disintesis dari minyak sawit) digunakan sebagai senyawa organik untuk menyesuaikan tanah liat semulajadi., Na-MMT (natrium montmorilonit) melalui proses pertukaran ion. Ubahsuai tanah liat dilakukan dengan mengacau zarah tanah liat dalam larutan mengandung air, FA, FHA, dan CDFAs. Saling tindak antara pengubah dengan tanah liat dikaji dengan belauan sinar-x (XRD), dan spektroskopi FTIR. Analisis unsur digunakan untuk menganggarkan kandungan nitrogen lemak (FNCs) dalam tanah liat. Tanah liat yang diubahsuai kemudian digunakan dalam penyediaan nanokomposit asid polilaktik (PLA)/minyak sawit terepoksi (EPO).

EPO digunakan sebagai pemplastik untuk PLA dengan kloroform sebagai pelarut bagi proses pengadunan larutan PLA dan EPO. Spektrum FTIR menunjukkan bahawa ada beberapa saling tindak intermolekul ikatan hidrogen antara PLA dan EPO. Semua adunan PLA/EPO menunjukkan kestabilan terma tinggi dan peningkatan sifat mekanik yang signifikan dibandingkan dengan PLA tulen. Pemanjangan takat putus tertinggi (sekitar 200%) diperolehi apabila nisbah PLA/EPO adunan adalah 80/20. Morfologi adunan PLA/EPO menunjukkan bahawa PLA/EPO adalah serasi dengan PLA. Pengurangan kelikatan adunan dengan peningkatan kandungan EPO menunjukkan bahawa EPO adalah pemplastik yang baik untuk PLA.

Nanokomposit telah disintesis dengan menggunakan 3% CDFAs-MMT atau 2% daripada kedua FA-MMT atau FHA-MMT dengan adunan PLA/EPO.

Nanokomposit yang disediakan daripada tanah liat yang diubahsuai dan adunan PLA/EPO pada nisbah 80/20 memiliki takat putus pemanjangan yang tertinggi. Nanokomposit ini dicirikan dengan menggunakan XRD, mikroskopi penghantaran elektron (TEM), analisis termogravimetri (TGA), dan pengukuran regangan. TEM mengesahkan penghasilan nanokomposit. PLA/EPO juga menunjukkan kestabilan terma yang lebih tinggi dan peningkatan sifat mekanik jika dibandingkan dengan adunan asal PLA/EPO.

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I certify that an Examination Committee met on 23 September 2010 to conduct the final examination of Emad A. Jaffar Al-Mulla on his Doctor of philosophy thesis entitled "Synthesis of Fatty and N,N'-carbonyl Difatty Amides from Palm Oil and Their Applications as a Clay Modifier for Polylactic acid/Epoxidized Palm Oil/Clay Nanocomposites Preparation" in accordance with 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 relevant degree.

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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.

EMAD A. JAFFAR AL-MULLA

Date: 23 September 2010



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