

**PREPARATION AND CHARACTERIZATION OF BIODEGRADABLE POLY  
LACTIC ACID (PLA) COMPOSITES WITH OIL PALM EMPTY FRUIT  
BUNCH (EFB) FIBER**

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## ABSTRACT

Application of natural fibers as reinforcing material of polymer matrix is the prime attention in this research. Oil palm empty fruit bunch (EFB) fiber has been considered as reinforcing material of Poly lactic acid (PLA) for preparation of EFB/PLA biocomposites. The limitation in the broad use of EFB fiber in PLA matrix is poor compatibility between fibers and matrix due to presence of non cellulosic components and the hydroxyl groups of cellulose. Moreover, the hydroxyl groups form hydrogen bonds inside the macromolecule itself (intra-molecular) and also with hydroxyl groups from moist air that restrict the fiber matrix adhesion and also bring about dimensional changes in the fiber. These limitations has been successfully overcome by removing the non cellulosic components, altering the fiber surface, through conventional alkali (ALK) and non conventional ultrasound (ULS) pre-treatment methods. The Pre-treatment were conducted with variation of sodium hydroxide (NaOH) concentration, soaking or exposing time and treatment temperature. Fiber characterization was done by the single fiber strength, FTIR spectrum, SEM and TGA-DTG thermal analysis. The ULS EFB fiber was given best properties compare to ALK EFB fiber at mild treatment conditions. The treatment parameters were optimized on the basis of that treated EFB/PLA composites mechanical properties and by using Design Expert Software. Optimization of fiber loading was carried out by 10 wt%, 20wt%, 30 wt% and 40wt% raw EFB fiber, composite was prepared by extrusion with PLA followed by injection molding. The composites properties were examined by mechanical tests such as tensile strength (TS), tensile modulus (TM), elongation at break (EB) and impact strength (IS). It was found that 30wt% EFB fiber incorporated composite represented good TS, TM, EB and IS. By considering these mechanical properties, 30wt% EFB was considered as optimum loading in EFB/ PLA composite. Beside this comparative analysis was done for 30wt% EFB fiber incorporated raw EFB/PLA, ALKEFB/PLA and ULSEFB/PLA composites. This comparison was carried out by the analysis of melt flow index (MFI), mechanical properties (TS, TM, EB, IS), kinetic property (activation energy,  $E_a$ ) by TGA-DTG data and crystallinity index ( $I_{DSC}$ ) by DSC thermograms. The ULSEFB/PLA composite was shown better properties, such as higher MFI (3.55 g/10min), mechanical strength (TS= 63MPa, TM=2468 MPa, IS=18.67 J/m<sup>2</sup>), crystallinity index ( $I_{DSC}$ =43.12) and lower activation energy ( $E_a$ =69.73 kJ/mol), compare to ALKEFB/PLA composite. Moreover, these properties were obtained when the ULSEFB fiber was treated at lower NaOH concentration (3 wt%) and treatment temperature (80<sup>0</sup>C) at 90 minutes exposing time. The ULSEFB/PLA composite properties were increased by treating that ULSEFB fiber with HBPE as coupling agent in ULSEFB/HBPE/PLA composite. It shows highest MFI (4.15 g/10min) and mechanical properties (TS=66.78 MPa, TM=2629MPa, IS=19.33), greater thermal stability, highest crystallinity index ( $I_{DSC}$ =45.13) and lowest activation energy ( $E_a$ =67.89 kJ/mol) among all composites.

## ABSTRAK

Aplikasi fiber semulajadi sebagai bahan penguat matrik plastik menjadi perhatian utama dalam kajian ini. Serat tandan kelapa sawit kosong (EFB) merupakan bahan penguat kepada asid polilaktik (PLA) bagi penyediaan biokomposit EFB/PLA. Dalam penggunaan serat EFB di dalam matrik PLA, kesesuaian antara serat dan matrik plastik adalah terhad disebabkan kehadiran komponen yang bersifat bukan selulosik dan terdiri daripada kumpulan hidroksil pada struktur selulosa. Tambahan lagi, kumpulan hidroksil membentuk ikatan hidrogen di dalam makromolekul itu dan kehadiran kumpulan hidroksil kesan dari kelembapan udara menghadkan lekatan antara serat-matrik yang akhirnya menyebabkan perubahan dimensi pada serat tersebut. Faktor-faktor yang menghadkan lekatan ini dapat diatasi melalui penyingkiran bahan yang tidak bersifat selulosa, pengubahsuaian permukaan serat melalui kaedah pra-rawatan alkali konvensional dan ultra-bunyi bukan konvensional. Pra-rawatan telah dijalankan dengan kepelbagaian tahap kepekatan natrium hidroksida (NaOH), tempoh rendaman atau masa pendedahan dan suhu rawatan. Pencirian serat telah dijalankan melalui kaedah analisis kekuatan gentian tunggal, spektrum FTIR, imbasan SEM dan terma TGA-DTG. Serat ULS EFB menunjukkan sifat yang terbaik berbanding dengan ALK EFB dengan keadaan rawatan yang sederhana. Parameter rawatan telah dioptimumkan berdasarkan sifat mekanikal komposit EFB/PLA dan menggunakan perisian *Design Expert*. Pengoptimuman muatan serat dijalankan dengan peratusan berat kandungan gentian EFB yang berbeza iaitu 10wt%, 20wt%, 30wt% dan 40wt%, komposit telah disediakan oleh kisaran campuran dengan PLA diikuti oleh pembentukan acuan. Sifat-sifat komposit telah dianalisa melalui ujian mekanikal seperti kekuatan tegangan (TS), modulus tensil (TM), pemanjangan pada takat putus (BP) dan kekuatan kesan (IS). Didapati bahawa gentian EFB 30wt% gabungan komposit menunjukkan sifat yang baik bagi sifat-sifat TS, TM, EB dan IS. Dengan mengambil kira sifat-sifat mekanik ini, EFB 30wt% dianggap sebagai muatan yang optimum dalam komposit EFB / PLA. Selain analisis ini, perbandingan telah dilakukan terhadap gentian EFB yang mengandungi 30wt% serat dan PLA, ALK EFB / PLA dan ULS EFB / PLA komposit. Perbandingan komposit dilakukan melalui analisis indeks pengaliran leburan (MFI), sifat mekanik (TS, TM, EB, IS), sifat kinetik (tenaga pengaktifan,  $E_a$ ) menggunakan TGA-DTG dan indeks penghabluran ( $I_{DSC}$ ) oleh DSC termogram. Komposit ULSEFB / PLA telah menunjukkan sifat yang lebih baik, iaitu nilai yang tinggi bagi MFI (3.55 g/10min), kekuatan mekanikal (TS = 63MPa, TM = 2468 MPa, IS = 18.67 J/m<sup>2</sup>), penghabluran indeks ( $I_{DSC}$  = 43.12%),. Manakala, tenaga pengaktifan lebih rendah ( $E_a$  = 69.73 kJ / mol), berbanding dengan komposit ALKEFB / PLA. Selain itu, sifat-sifat ini telah diperolehi apabila ULSEFB serat dirawat pada kepekatan NaOH yang lebih rendah (3%) dan suhu rawatan (80°C) selama 90 minit bagi masa pendedahan. Sifat-sifat komposit ULSEFB / PLA meningkat dengan perawatan ULSEFB serat dengan HBPE sebagai agen gandingan pada komposit ULSEFB / HBPE / PLA. Ia menunjukkan MFI tertinggi (4.15 g/10min) dan sifat mekanik (TS = 66.78 MPa, TM = 2629MPa, IS = 19.33 J/m<sup>2</sup>), kestabilan terma yang lebih baik, indeks penghabluran tertinggi ( $I_{DSC}$  = 45.13%) dan tenaga pengaktifan terendah ( $E_a$  = 67.89 kJ / mol) di antara kesemua komposit.

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**LIST OF SYMBOLS**

$E_a$	Activation Energy (kJ/mol)
$I_{DSC}$	% Crystallinity determined by DSC
$T_c$	Crystallization Temperature (°C)
$y$	Fraction of materials not been decomposed
$Z$	Frequency factor
$R$	Gas constant (J/mol K)
$T_g$	Glass Transition Temperature (°C)
$\Delta H$	Heat of fusion (J/g)
$\beta$	Heating Rate (°C/min)
$T_m$	Melting Temperature (°C)
$\mu\text{m}$	Micrometer
$T_{\text{max}}$	Temperature at maximum reaction rate (°C)

**LIST OF ABBREVIATIONS**

ALK	Alkali
ASTM	American Standard Testing Method
DSC	Differential scanning calorimetry
DTG	Differential thermo gravimetry
EB	Elongation at break
EFB	Empty fruit bunch
EDX	Energy dispersive X-ray
ENR	Epoxidized Natural Rubber
ETP	Engineering thermoplastics
GPa	Giga Pascals
HBP	Hyper branched polyester
HBPEA	Hyper branched polyester amide
HMDI	Hexamethylene diisocyanate
IS	Impact strength
MPa	Mega Pascals
MA	Methyl acrylate
MCC	Microcrystalline cellulose
MFI	Melt flow index
NFRPC	Natural fiber reinforced polymer composites
OPF	Oil palm fiber

PF	Phenol formaldehyde
PLA	Poly(lactic acid)
PP	Poly(propylene)
SEM	Scanning electron microscopic
TDI	Toluene diisocynate
TGA	Thermo gravimetric analysis
THF	Tetra hydrofuran
TM	Tensile moldulus
TPM	3-(trimethoxysilyl)-propylmethacrylate
TS	Tensile strength
ULS	Ultrasound
UTS	Ultimate tensile strength
UV	Ultra-violet

# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 INTRODUCTION**

In recent years there has been an expanding search for new materials with high performance at affordable costs. Due to environmental awareness, this search particularly emphasis on environment friendly materials, in terms of renewable, recyclable, sustainable and triggered biodegradable. In this perception composite materials make from renewable resources are very prospective in the field of composite science. Several lignocellulosic fibers such as jute, sisal, pineapple, coconut etc. are source of raw materials in plastic industries. These fibers have established their potentiality as reinforcing fillers in many polymers to develop new composite materials. In recent years it has found that the demand of these materials increasing on a commercial scale. (Satyanarayana et al.,2008; Singh, et al.,2008; Zheng et al., 2008) . These examples give emphasis to the development of new materials based on renewable materials.

Similarly, use of natural polymers is not new, since bamboo, straw, paper, silk, etc., have been used from historical times. The use of natural polymers was superseded in the 20<sup>th</sup> century as a wide-range of synthetic polymers was developed based on raw materials from low cost petroleum. However, since the 1990s, increased attention has been paid to the use of natural polymers and lignocellulosic fibers. The reasons for this

include: (a) growing interest in reducing the environmental impact of polymers or composites (b) finite petroleum resources, decreasing pressures for the dependence on petroleum products with increasing interest in maximizing the use of renewable materials and (c) the availability of improved data on the properties and morphologies of natural materials such as lignocellulosic fibers, through modern instruments at different levels, and hence better understanding of their structure–property correlations. These factors have greatly increased the understanding and development of new materials such as biocomposites (Kestur et al., 2009).

Synthetic polymer-based composite materials are now well established all over the world for a wide variety of applications because of their high specific strength and modulus compared to conventional materials such as metals and alloys, along with their long durability (Bledzki and Gassan 1999; Marikarian 2008). However, the use of large volumes of polymer-based synthetic fiber composites in different sectors in spite of their high cost has led to disposal problems. In fact, several countries have already approved laws for the reduction of such environmentally abusive materials, triggering greater efforts to find materials based on natural resources in view of the latter’s eco-friendly attributes.

Natural fibers are sourcing of organic materials also a source for carbon and a host of other useful materials and chemicals, particularly for the production of “green” materials. Several countries such as India, Malaysia, Indonesia, Philippines, Brazil and some of the African countries have national projects for the utilization of their agro wastes such as coconut based materials, wastes from rubber and palm oil industries, rice husk, etc., These materials thus form inexpensive “new or secondary resources”, which could make them more valuable for extensive utilization (Rijswijk and Brouwer, 2002).

Lignocellulosic fibers have some unique attributes, such as being less abrasive to tooling and not causing as many respiratory problems for workers (Kandachar, 2002 and Sanadi, 2004). Furthermore, because they are inexpensive and have load bearing capacity, the use of natural fiber based composites has spread to various sectors, including aircraft, construction, grain and fruit storage and footwear. Natural fiber reinforced polymer composites are used in cars behind the vinyl carpeting on the doors, consoles and seat backs. Residential construction applications include windows, sidings, and roof tiles. Many window and door manufacturers are considering natural fiber