OIL PALM EMPTY FRUIT BUNCH (EFB) FIBER REINFORCED POLY(LACTIC) ACID COMPOSITES: EFFECTS OF FIBER TREATMENT AND IMPACT MODIFIER

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ABSTRACT

The use of natural fibers as reinforcement in polymer composites has become necessary based on the several advantages of lignocellulosic fibers over their inorganic counterparts. However, limitations to the use of natural fiber in composites are the inherent reduced adhesion between the fiber and matrix, high moisture absorption and UV degradation owing to non-cellulosic components of natural fibers. In this research, composites were fabricated from oil palm empty fruit bunch fiber (EFB) and poly lactic acid (PLA) with different loading percent of 10-40 wt%. Mechanical testing revealed that 30 wt% of fiber content produced the highest mechanical properties and this was selected as the optimum fiber content based on treated EFB fiber that were fabricated. To enhance the compatibility of EFB with PLA, the fiber surface was treated by ultrasound in both water and alkali medium and optimization was done by response surface methodology (RSM), which selected 100 mins exposure time at 90^{o}C in 2 wt% NaOH as the optimum treatment condition. Fibers were further treated with poly(dimethysiloxane) coupling agent to increase bonding of EFB with PLA. Effects of fiber treatment were investigated through mechanical, structural, morphological and thermal analysis. Characteristic strength analysis of fibers was also done by Weibull characteristic model. Fabrication of composites was done by extrusion followed by pelletizing after which test samples were prepared using injection moulding machine, and composite characterization was carried out. Furthermore, biostrong impact modifier was incorporated into the composites up to 2 wt% to improve the impact properties and it was found to increase the IS of PLA by 38%, but also led to reduction in other mechanical properties of EFB/PLA composites. Morphological analysis of composites fractured surface by scanning electron microscopy (SEM) and functional groups analysis by Fourier transforms infrared spectroscopy (FTIR) revealed improved adhesion of treated fibers with PLA. Structural analysis by X-ray diffraction (XRD), supported results from differential scanning calorimetric (DSC) analysis which showed that composites prepared with the combination of ultrasound alkali and silane treated fibers has the highest crystallinity index (CrI% = 75.44%). Thermogrvimetric analysis (TGA) also showed that silane ultrasound and alkali treatment of EFB fibers increased the thermal stability of the composites by raising the peak decomposition temperature, with an increase of 43% in activation energy (E_a = 56.52 kJ/mol). Natural degradation analysis also confirmed the reduced effect of environmental factors on silane and ultrasound treated fiber based composites compared to untreated fiber based composites. Besides that, water uptake analysis and contact angle measurements revealed the increased hydrophobicity of composites after silane treatment of EFB fibers, with about 106^{o} contact angle value and less than 5% water uptake after 150 days soaking period. The highest mechanical properties were obtained from composites based on combined ultrasound, alkali and silane treated fibers.

ABSTRAK

Penggunaan gentian semula jadi sebagai komponen penguat dalam komposit polimer amat penting berasaskan kepada beberapa kelebihan gentian lignoselulosa berbanding bahagian bukan organik. Walau bagaimanapun, terdapat kekangan kepada penggunaan serat semula jadi dalam komposit seperti kelemahan lekatan di antara gentian dan matriks, penyerapan kelembapan yang tinggi dan degradasi UV oleh komponen bukan selulos gentian semula jadi. Dalam kajian ini, komposit diperbuat dari gentian tandan kosong kelapa sawit (EFB) dan poli asid laktik (PLA) dengan berat di antara 10-40 %. Ujian mekanikal menunjukkan bahawa 30 % berat kandungan gentiant menghasilkan sifat mekanikal tertinggi dan dipilih sebagai kandungan gentian optimum berdasarkan komposit EFB terawat yang dihasilkan. Untuk meningkatkan keserasian di antara EFB dengan PLA, permukaan gentian telah dirawat dengan kaedah ultrasound dalam medium air dan sederhana alkali dengan pengoptimuman dilakukan melalui kaedah gerak balas permukaan (RSM), dengan 100 minit masa pendedahan pada 90^0C di dalam 2% berat NaOH sebagai kaedah rawatan yang optimum. Gentian juga dirawat dengan ejen gandingan *poly(dimethysiloxane)* untuk meningkatkan ikatan di antara EFB dengan PLA. Kesan rawatan gentian diuji melalui analisis mekanikal, struktur, morfologi dan terma. Analisis kekuatan ciri gentian juga telah dilakukan dengan menggunakan Weibull model. Penghasilan komposit dengan gentian dilakukan melalui kaedah penyemperitan diikuti dengan *pelletizing* selepas sampel ujian dihasilkan dengan menggunakan mesin pengacuan suntikan, dan seterusnya pencirian komposit dilakukan. Seterusnya, 2% berat pengubahsuai impak (*biostrong*) dicampurkan ke dalam formulasi komposit dan didapati meningkatkan IS PLA IS PLA sebanyak 38%, namun juga mengurangkan sifat mekanikal yang lain dalam komposit EFB/PLA. Analisis kegagalan permukaan komposit dilakukan dengan menggunakan *scanning electron microscopy* (SEM) dan analisis kumpulan fungsi menggunakan Fourier transforms infrared spectroscopy (FTIR) menunjukkan pelekatan yang lebih baik di antara gentian EFB terawat dengan PLA. Analisis struktur menggunakan *X-ray diffraction* (XRD), yang disokong dengan *differential scanning calorimetric* (DSC) analisis menunjukkan bahawa komposit yang dihasilkan dengan gabungan *ultrasound* gentian alkali dan dirawat *silane* mempunyai indeks penghabluran tertinggi (CRI% = 75.44%) Analisis thermogravimetrik (TGA) juga menunjukkan bahawa ultrasound *silane* dan rawatan alkali gentian EFB meningkat kestabilan terma komposit dengan menaikkan suhu penguraian puncak, dengan peningkatan sebanyak 43% dalam tenaga pengaktifan (Ea = 56.52 kJ / mol). Analisis degradasi alam juga mengesahkan pengurangan kesan alam sekitar terhadap komposit gentian terawat *silane* dan ultrasound berbanding dengan yang lain. Di samping itu, analisis pengambilan air dan pengukuran sudut menunjukkan *hydrophobicity* komposit meningkat selepas rawatan *silane* gentian EFB, dengan nilai sudut 106^0 dan kurang dari 5% penyerapan air selepas 150 hari tempoh rendaman. Sifat-sifat mekanikal yang paling tinggi diberikan oleh komposit dengan gabungan ultrasound alkali dan silane yang digunakan untuk merawat gentian.

TABLE OF CONTENTS

CHAPTER 2 LITERATURE REVIEW

CHAPTER 4 RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

β	Heating Rate (^{o}C/min)
T_g	Glass Transition Temperature (^{o}C)
T_m	Melting Temperature (^{o}C)
T_c	Crystallization Temperature (^{o}C)
F_{max}	Maximum peak load (N)
σ_t	Tensile Strength (MPa)
$P_f(\boldsymbol{\sigma})_L$	Probability of failure at particular length
$\boldsymbol{\sigma}_o$	Characteristic strength (MPa)
$\boldsymbol{\sigma}_u$	Lowest strength value (MPa)
τ	Interfacial shear strength (MPa)
μl	Micro liter
y	Fraction of non-volatilized material yet undecomposed
T_{max}	Temperature of maximum reaction rate (^{o}C)
Z	Frequency factor
E_a	Activation energy (J mol^{-1})
R	Gas constant
I_{DSC}	Degree of crystallinity (%)
ΔH	Heat of fusion of sample
ΔH_m	Heat of fusion of 100% crystalline reference material
W	Mass fraction of matrix in composite
L_o	Initial measured length (m)
L	Length at breaking point (m)
E_f	Flexural modulus (MPa)
d	Interplaner spacing

θ	Bragg angle
λ	X-ray wavelength.
β	Full width at half maximum (FWHM).
K	Scherrer's constant

LIST OF ABREVIATIONS

AIR	Acid-insoluble residue
ANOVA	Analysis of variance
ASTM	American Standard Testing Method
EB	Elongation at break
EFB	Empty fruit bunch
DSC	Differential scanning calorimetry
DTG	Differential thermo gravimetry
ENR	Epoxidixed natural rubber
FM	Flexural modulus
FS	Flexural strength
FTIR	Fourier transforms infrared spectroscopy
FWHM	Full width at half maximum
GPa	Giga pascals
HDPE	High density polyethylene
HMDI	Hexamethylene diisocyanate
IFSS	Interfacial shear strength
IMFPC	Impact modified fiber reinforced PLA composite
IS	Impact strength
ISO	International Organization for Standardization
MAPP	Maleic anhydride grafted polypropylene
MPa	Mega pascals
NDE	Non-destructive evaluation
NDT	Non-destructive testing
NR	Natural rubber

ORFPC	Optimum raw fiber reinforced PLA composite
OUFPC	Optimized ultrasound treated fiber reinforced PLA composite
OUSFPC	Optimized ultrasound treatment silane treated fiber reinforced PLA composite
PBS	Poly butylene succinate
PDMS	Poly (dimethylsiloxane), chlorine terminated
PE	Polyethylene
PEKK	Polyetherketoneketone
PF	Phenol formaldehyde
PLA	Poly lactic acid
PMPPIC	Polymethylene (polyphenyl isocyanate)
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinyl chloride
RSM	Response surface methodology
SEM	Scanning electron microscopy
SIMFPC	Silane treated impact modified fiber reinforced PLA composite
TAPPI	Technical Association of the Pulp and Paper Industry
TDI	Toluene diisocynate
TGA	Thermo gravimetric analysis
THF	Tetrahydrofuran
TM	Tensile modulus
TPM	(Trimethoxysilyl)-propylmethacrylate
TS	Tensile strength

ULSALK	Ultrasound alkali treated
ULSALKSIL	Ultrasound alkali silane treated
UTS	Universal tensile strength
UV	Ultra-violet
WUFPC	Water medium ultrasound treated fiber reinforced PLA composite
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

The use of natural fibers in more diversified fields came alongside the emergence of polymers in the 19th century. This followed the success of the German Chemist Hermann Staudinger's ability to prove his earlier proposed hypothesis about polymers to be true. At the same time, researchers also developed interest in synthetic fibers due to their superior dimensional properties, making it to slowly replace the natural fibers in several applications. However, fabrications of synthetic fiber reinforced polymer composites required a lot of energy, as well as pollute the environment especially during production and recycling (Mohanty et al., 2005).

This again brought attention back to the natural fibers based on their distinct advantages (Mohanty et al., 2005; Wambua et al., 2003). The renewed interest therefore opened grounds for a large number of modifications to bring the natural fibers at par, and where possible superior to the synthetic fibers. These modifications therefore made natural fibers suitable for such applications as packaging, medicine, furniture and automatic parts (Rijswijk & Brouwer, 2002, Nickel et al., 2003; Netravali et al., 2003; Marsh, 2003; Wambua et al., 2003; Suddell and Evans, 2003; Schloesser, 2004; Mathur, 2006). Hydrophilic character of natural fibers however led to composites with weak interface but pre-treatments were sought, which aims at improving the adhesion between fibers and polymer matrices.

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In pre-treatments, either the cellulose hydroxyl groups of the fiber get activated or new moieties are added that can effectively interlock with the matrix (Khalid et al., 2008; Cabedo et al., 2006). Despite this necessity for surface treatment in order to obtain desirable results from natural fiber reinforced polymer composites, the unique attribute of natural fibers, such as being less abrasive to processing equipment as well as reduced respiratory tract related problem for worker, makes them highly esteemed (Bledzki et al., 1999; Mohanty et al., 2000; Kandachar, 2002; Mohanty et al., 2002; Evans et al., 2002; Sanadi, 2004, Maya and Thomas, 2008). Moreover, they are less expensive and also possesses good load bearing potential which contributes to its wide spread application in several sectors such as aircraft, construction, storage facilities and even in foot wears. In countries where improved sustainability is legislation due to environmental consciousness, there is high priority to the incorporation of lignocellulosic fibers in polymer composites especially in automotive applications (Bledzki et al., 2002; Evans et al., 2002). Among the various natural fibers; flax, bamboo, sisal, hemp, ramie, jute, oil palm and wood fibers are of particular interest.

Oil palm (*Elaeis guineensis Jacq.*) is one of the oil crops in the world that produces the largest quantity of edible oil. Cultivation of oil palm has an extension of over 42 countries with an estimated value of about 11 million hectare on a worldwide basis (Khalil et al., 2008). Some countries which possess the largest areas for oil palm cultivation includes West African countries like Nigeria, South East Asian countries like Indonesia and Malaysia, Latin America countries and India (Joseph et al., 2006). The estimated amount of dry matter produced from an annual oil palm plantation is about 55 ton per hectare, in form of fibrous biomass alongside an equivalent 5.5 ton of oil (Hasamudin and Soom, 2002).

Apart from palm oil which is the main product from palm oil industries, vast quantities of biomass from which fibers can be obtained are also produced. The fibers can be gotten either from the palm frond, palm trunk, fruit mesocarp and especially oil palm empty fruit bunch (EFB). Oil palm empty fruit bunch is the fibrous mass which remains after palm fruits had been separated from the fruit bunches. Oil palm empty fruit bunch had been said to possess a yielding capacity of up to 73% fibers; higher than other sources in the oil palm industry (Wirjosentono et al., 2004). This led to the preference of EFB both in terms of availability as well as cost (Rozman et al., 2000). Oil palm empty fruit bunch is a hard and tough fiber which is in many ways similar to coir fibers (Ibrahim et al., 2005). Surface of EFB fibers has many pores which offer it good interlocking properties with polymer matrix during composite fabrication. However the presence of porous surface morphology could lead to high water absorption by the action of capillary whenever it is exposed to water (Hill and Khalil 2000). Analysis of EFB would reveal some granules of starch on the interior of the vascular bundle (Law et al., 2007).

Report from several authors had shown that oil palm empty fruit bunch fiber, among several other natural fibers had been used to reinforce polymers in different applications and at varying degrees. A notable example is the incorporation of natural fibers into thermoplastics like PLA, wherein the issue of fiber matrix interaction is always contentious from one researcher to another (Bax & Müssig, 2008; Bledzki, et al., 2009; Huda et al., 2006; Huda et al., 2008; Huda et al., 2005; Mathew et al., 2003; Petersson et al., 2007; Petinakis et al., 2009; Plackett et al., 2003; Suryanegara et al., 2009; Sykacek et al., 2009; Van de Velde & Kiekens, 2002). However, most of these researches show that there is apparently poor adhesion between the fiber and the PLA matrix interface, hence the need for further modifications to improve the surface interaction of EFB fibers and PLA matrix. The essence of surface modification is to make the hydrophilic fiber become more susceptible to the hydrophobic polymer matrix through surface treatment of the fiber. This is to enhance fiber matrix interaction which is a major perquisite for composites in which mechanical, tensile, abrasive and other desirable properties are priorities. There is this possibility through surface treatment, in which case the hydroxyl groups get activated or through the addition of new moieties that can interlock effectively with the polymer matrix.

Several modifications have been made on fiber surface in times past, and their effect noted. These studies have been undertaken to modify the performance of natural fibers in varying degrees. Different surface treatment methods such as alkali treatment (Chang et al., 2009), isocyanate treatment (Maiti et al., 2004,) acrylation (Huda et al., 2008), benzoylation (Mohanty et al., 2001), latex coating (Sreekala, 2000), permanganate treatment (Joseph, 2000), acetylation (Larsson-Brelid et al., 2008), silane

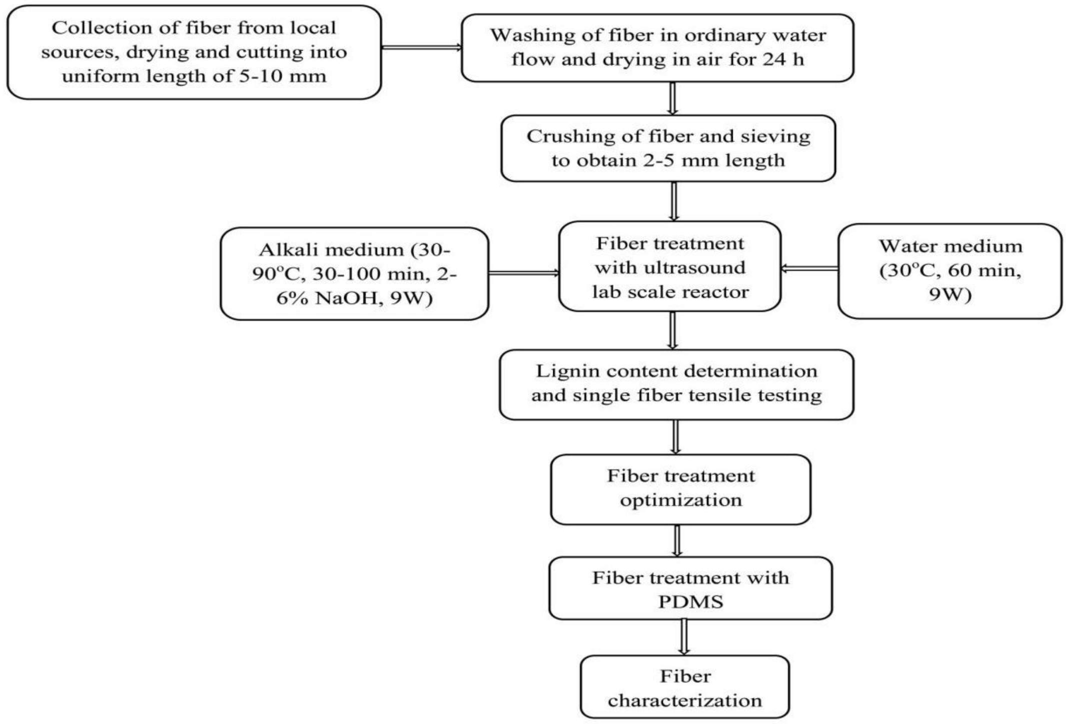
CHAPTER 3

MATERIALS AND METHODOLOGY

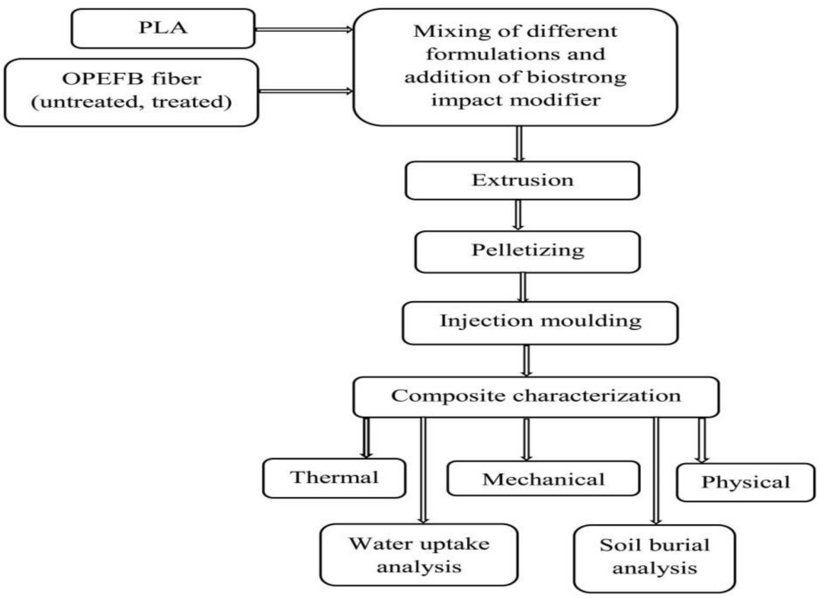
3.1 INTRODUCTION

In this research, composites were from oil palm empty fruit bunch fiber (EFB) and poly (lactic) acid (PLA) matrix. The selection of materials and experimental procedures were selected based on literature review as discussed in Chapter 2. Modifications were made to the surface of oil palm empty fruit bunch (EFB) through ultrasound treatment in both water and alkali medium. Composites were prepared from EFB fiber and PLA matrix. To further enhance the adhesion of fiber to the matrix, silane coupling agent; poly (dimethylsiloxane), chlorine terminated (PDMS) was used incorporated onto the fiber surface. Improvements were offered to make up for the brittleness of the poly (lactic) acid (PLA) matrix through the incorporation of impact modifier. Different characterization procedures were carried out in order to study the effect of surface treatment on performance of EFB fiber reinforced poly (lactic) acid composites, as well as the influence of impact modifier on the composite.

This chapter describes the various materials used for the research as well as the experimental procedures, the different treatment methods applied to the fiber surface, the composite fabrication steps, the characterization and standard testing methods such as ASTM, ISO, etc. as well as little details on the equipment and machines implored for the various testing. The flow process of the experimental design is as represented in Figure 3.1.



(i)



(ii)

Figure 3.1: Experimental flow of research methodology showing (i) fiber treatment and characterization and (ii) composite fabrication and characterization

3.2 MATERIALS

3.2.1 Polymer Matrix

The polymer matrix used for this research is thermoplastic poly (lactic) acid resin. It is a Poly lactic acid of Natureworks Ingeo™ Biopolymer 3051D grades supplied by Unic Technology Ltd, China. It has a density of 1.24 g/cm^3, melt flow index of 30-40g / 10 min. (190^{o}C/2.16kg) and a melting temperature of 160-170^{o}C.

3.2.2 Reinforcing Fiber

The fiber used is oil palm empty fruit bunch (EFB) fibers which were collected as waste materials from LKPP Corporation Sdn. Bhd., Kuantan, Malaysia.

3.2.3 Chemicals

The chemicals used for this research and the suppliers are listed in Table 3.1.

Table 3.1: List of chemicals

Chemical	Supplier
Acetone	Merck
Acetic acid	Sigma
Sodium hydroxide (NaOH)	Merck
Potassium Bromide (KBr)	Merck
Tetraoxosulphate (VI) acid (H_2SO_4)	Sigma

3.2.4 Impact Modifier

The impact modifier used (Biomax® Strong 120) was collected for experimental purposes from Dupont, Switzerland. Dupont™ Biomax® strong (biostrong) is an ethylene-epoxy based copolymer specially designed to be grafted on to modify PLA.