修士論文

パームヤシ殻繊維/ポリ乳酸複合材料の 作製と力学特性

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Master Thesis

Preparation and Mechanical Properties of Palm Fiber/Polylactic Acid Composites

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Abstract

In recent years, the demand for environmental friendly materials based on biodegradable polymer and natural fiber has growth interest. In this work, a biodegradable composite from polylactic acid (PLA) and oil palm empty fruit bunch (palm fiber) were prepared by compression moulding. However there were several limitations especially related to the fiber matrix adhesion. So the palm fibers were treated by γ -aminopropyl trimethoxysilane (APS) and methyl trimethoxysilane (MS) and also coated by polylactic acid (PLA) in varied percentage (5%, 10% and 15%). The effect of APS and MS treatment and PLA coating on the mechanical and dynamic PLA/palm mechanical properties of fiber composites examined. was Thermogravimetric analysis showed the decomposition temperature of palm fiber was shifted to higher when treated by APS and MS. The density and flexural properties of composites were found to increase with increasing fiber coating and increased by introduction of APS and MS treatment. From dynamic mechanical analysis, it was also observed that the APS, MS treated fibers and PLA coating fibers have improved the dynamic mechanical properties of the composites respectively. The fiber-matrix morphology in the untreated and treated composites was confirmed by SEM analysis of fracture samples. The micrograph showed the improvement of fiber matrix adhesion by incorporation of APS and MS fiber treatment.

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Chapter 1 Introduction

1.1 Research background

In the past few decades, research and engineering interest has been shifting from monolithic materials to fiber reinforced polymeric composites materials. Fiber reinforced composites have received widespread attention because of unique combination of high performance and great versatility. These composite materials with high strength fibers like aramid, carbon and glass fibers now commonly used in aerospace, automotive, construction, leisure and sporting industries. However these fibers have several drawbacks such as no biodegradable, no renewability and reduce the wear of machinery¹⁻²⁾.

With the increasing global energy crisis and ecological risks, the interest in using natural fibers such as plant fibers and lignocellulosics fibers as reinforcement in plastics has increased dramatically. These fibers may not be strong as a carbon and glass fibers but they have several advantages which potential to serve as an alternative substitution for artificial fiber composites like renewable, environmental friendly, low cost, lightweight and relatively good stiffness and strength. The cellular structures of plant fibers also provide good insulation against heat and noise. It has been reported that composites based on natural fiber are used extensively in automotive applications, building materials and household products³⁻⁶⁾.

In Malaysia, palm oil industry is the one of the major plantation industry. A large quantity of biomass generated from this industries like empty fruit bunch

 $N_{o} = 2$

(EFB), oil palm frond (OPF) and oil palm trunks. EFB is the main fibrous left in the palm oil mill which obtained after the removal of oil seeds from fruit bunch for oil extraction. The production of EFB is estimated to be around 2.8-3.0 million tones per year and reported has increased by year. It also has been reported that the generated biomass from oil palm trunks is estimated to be around 0.5 to 1 million tones per year. These waste materials create tremendous environmental problems especially air pollution because they are disposed by burning. Therefore, economic utilization of these fibers will be beneficial⁷⁻⁹.

In recent years, the use of biodegradable polymers has created new interest as a similar purpose of natural fiber, to protect the natural environment. Polylactic acid is an example of biodegradable polymer. It is also known as a biopolyester polylactide or PLA which synthesis from lactic acid monomers. In details, the polylactic acid is produced by the ring-opening polymerization of the cyclic lactide dimmer. The lactic acid can be derived by bacterial fermentation from a number of different renewable resources. For examples are corn starch and sugarcanes. It has been reported that in North America, the production of PLA by Cargill Dow LLC mainly derived from a corn starch with an annual production capacity of 140,000 metric tons. PLA is a versatile material, exhibits many properties that are equal or better than many petroleum-based plastics which makes it suitable for a variety of application. PLA is currently used in medical, textile and packaging applications. Hence, the advantages of PLA are can be recycled or alternatively disposed of by incineration¹¹⁻¹⁶.

However in producing composite based on natural fiber, there are several limitations like high moisture absorption and poor wettability. The most important problem need to be concerned is the fiber-matrix adhesion because the properties of composites influenced by interfacial interaction between natural fiber and matrix. A good bond between polymeric matrix and fibers is required to transfer the load from matrix to stiff fibers through shear stresses at the interface²⁾. The compatibility and interfacial bond strength between natural fiber and polymer matrix are expected to be poor. This is due to the difference in nature between natural fiber and polymer matrix. Natural fibers are hydrophilic, contributed by hydroxyl groups in cellulose, lignin and hemicellulose, while thermoplastics are hydrophobic. The lack of good interfacial adhesion and poor resistance to moisture absorption made the use of natural fiber reinforced composites less attractive. This problem can be overcome by treating these fibers with suitable chemicals. Various chemical have been reported to enhance the compatibility between the constituent materials, these include 3-(trimethoxysilyl) propylmethacrylate and silane. These chemicals are incorporated hydroxyl groups on the fibers and increase the wetting effect of the PERPUSTAK resin on the fibers⁶⁻⁸⁾.

1.2 The purpose of research

In this research, composites were prepared from polylactic acid and palm fiber (natural fiber). In order to improve the adhesion between fiber and matrix, the palm fiber was treated by γ -aminopropyl trimethoxysilane (APS) and methyl trimethoxysilane (MS) and coated by PLA with varied percentage (5, 10 and 15wt%) in THF solution. The objectives of the research are

- To characterize the effects of fiber treatment by γ-aminopropyl trimethoxysilane (APS) and methyl trimethoxysilane (MS) on the mechanical and dynamic properties of Palm Fiber/Polylactic Acid Composites.
 - 2) To characterize the effects of fiber coating by polylactic acid (PLA) on the mechanical and dynamic properties of Palm Fiber/Polylactic Acid Composites.

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Chapter 2 Experimental

2.1 Raw material

2.1.1 Palm fiber

Palm fiber sheet used in this research was produced from the oil palm empty fruit bunch fiber in fibrous form by fiber sheet production. The pictures of oil palm empty fruit bunch fiber in fibrous form and palm fiber sheet are shown in Fig. 1.

2.1.2 Thermoplastic resin

Polylactic acid (PLA) in pellet form with density of 1.17g/cm³ was used as thermoplastic resin for fiber coating and sandwich composite. It was purchased from Mitsui Chemical Ltd. The synthesis and chemical structure of PLA is shown in Fig. 2.

2.1.3 Fiber surface treatment

Two types of silane coupling agent were used for the fiber surface treatment.

- γ-aminopropyl trimethoxysilane (APS) with molecular weight of 183.3 was supplied by Shin-etsu Chemical Ltd.
- (2) Methyl trimethoxysilane (MS) with molecular weight of 136 was supplied by Toray Dow Corning Silicon Ltd

The chemical structures of these two types of coupling agent are shown in Fig. 3.



Fig. 1 Palm fiber composition of untreated composites, APS treated composites and MS treated composites.





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2.2 Preparation of PLA sheet and palm fiber sheet

PLA sheet was prepared by using hot compress moulding. Firstly, the PLA pellets were dried in vacum oven at temperature of 60°C for 24 hours in order to remove the moisture. The dried PLA pellets were placed in stainless steel mould with thickness of 0.5 mm and pre heated for melting at temperature of 190° C for 10 minutes. Then it was pressed under pressure of 2.2 MPa for 1 minute and transferred to the water-cooling press machine. The melted PLA was cooled under pressure of 1.0 MPa for 10 minutes.

For the preparation of palm fiber sheet, the same method of preparing PLA sheet was used. However the palm fiber was prepared with thickness of 2 mm and the pre heated and press temperature was set to 200°C. The palm fiber sheet also cooled at the water-cooling press machine under pressure of 1.0 MPa for 10 Surface fiber treatment minutes.

2.3

Palm fiber mat was treated by γ -aminopropyl trimethoxysilane (APS) and methyl trimethoxysilane (MS). 800g of treatment solution was prepared by adding 1%wt (8g) of coupling agent (APS or MS) in 792g of distilled water and stirred for 3 minutes for mixing. For the treatment, the palm fiber mat was soaked in treatment solution and stirred for 3 minutes before dried in oven at temperature of 110°C for 20 minutes. The dried palm fiber mat then was cleaned by soaking and stirring in methanol for 10 minutes and dried at the room temperature for 24 hours before used. Diagram of the fiber treatment is shown in Fig. 4 and the chemical reaction of the fiber treatment by APS and MS are shown in Figs. 5 and 6.

2.4 PLA coating.

Palm fiber mat was coated by polylactic acid (PLA) with varied percentage of PLA (5, 10 and 15wt%) dissolved in tetrahydofouran (THF) solution. The palm fiber mat was soaked in solution and dried in vacuum oven at temperature of 60° C for 2 hours.

PERPUSTAKAAN TUNKU









2.5 Preparation of sandwich composite.

Composite with thickness of 3 mm was prepared by sandwiching one palm fiber mat between two layers of PLA sheets. Composite thickness was controlled using a 3 mm stainless metal mould plate. One layer of palm fiber mat was placed between two PLA sheets in parallel arrays and the whole assembly was carefully placed in a stainless stèel mould. The 3 mm stainless steel mould was placed on a carver hot press machine and pre heated at temperature of 190°C for 10 minutes before pressed under pressure of 2.2 MPa for 1 minute. Then the stainless steel mould was removed from the hot compress machine and quickly cooled down by water cooling press machine under pressure of 1.0 MPa for 10 minutes. Sandwich composite was removed from the stainless steel mould and then prepared for measurements and analysis. The flow chart of preparation of sandwich composite is shown in Fig. 7.



TUN AMINA

Chapter 3 Measurement

3.1 Thermogravimetric Analysis (TG/DTA)

The thermogravimetric analysis were carried out on untreated palm fiber, APS treated palm fiber, MS treated palm fiber and PLA by using a TG/DTA200 (SEIKO Electronic Ltd) in order to measure the weight loss in relation to change in temperature. The measurement condition is shown below.

Measurement condition

Sample weightabout 10mgMeasurement temperature 30° C~600°CHeating rate 10° C/minAtmosphereN₂, 200ml/min

3.2 Fourier Transform Infrared Spectrophotometer (FT-IR)

Untreated palm fiber, APS and MS treated palm fiber were analyzed by FTIR analysis. The equipment used was Fourier Transform Infrared Spectrophotometer Impact 400 (made by Nicolet Ltd). The purpose was to determine the hydroxyl group of palm fiber and the effect of APS and MS treatment on palm fiber. The analysis was carried out by using potassium bromide (KBr) and followed the following condition. Analysis condition

 $400 \text{ cm}^{-1} \sim 4000 \text{ cm}^{-1}$ Frequency area Number of scan 16Resolution 4cm^{-1}

3.3 Density

Samples with dimension (volume, V) of $10 \text{mm} \times 10 \text{mm} \times 3.5 \text{mm}$ were used for density measurement. The samples were dried in vacuum oven at temperature of 60°C for 12 hours before measure their weight (m). Density (ρ) of the samples UTUN AMINA were calculated from the weight and volume as a following equation.

 ρ [g/cm³] = $m \neq V$

Composition analysis 3.4

Composition were determined on samples with dimension of $70 \text{mm} \times 10 \text{mm} \times$ 3.5mm. The samples were dried in vacuum oven at temperature of 60°C for 12 hours in order to remove the moisture before measured their weight (m_l) . Then they were soaked and stirred in THF solution for 24 hours. The PLA was dissolved in THF and only palm fiber left. The weight of extracted palm fibers was measure and marked as m_2 . Composition of the samples were measured by weight ratio (W) as a below equation.

$$W = m_2 \swarrow m_1$$

Three point flexural testing 3.5

The flexural properties of PLA and composites were performed by using Universal Testing Machine, TENSILON/UTM-4 (made by Orientec Ltd). A constant bend was applied onto sample and a respond load was measured. The flexural modulus and flexural strength was calculated from the relation between obtained bend and load. The measurement condition and the calculation of flexural modulus and strength are shown below.

Testing condition

Temperature Sample size

Span length

STAKAAN TUNKU TUN AMIN $25^{\circ}C$

Crosshead speed

Flexural modulus

 $E_{f} = \frac{L^{3}}{4bh^{3}}.$ [MPa]

Flexural strength

$$\sigma_{f,max} = \frac{3LF_{max}}{2bh^2}$$
 [MPa]

L : Span length (mm)

b: Width of the sample (mm)

h : Thickness of the sample (mm)

F: Load at a chosen point on the initial linear portion of the load-deflection curve (N)

Y: Deflection corresponding to the load, F (mm)

Fmax : Maximum load (N)

3.6 Dynamic Mechanical Analysis (DMS)

Dynamic mechanical properties, the storage modulus (E') and loss factor $(\tan \delta)$ of the composites were measured as a function of temperature. The analysis was carried out by dynamic mechanical analysis DMS110 (SEIKO Electronic Ltd). The measurement condition is shown below.

Measurement Mode	Flexural mode
Sample size	55mm×10mm×2mm
Heating rate	2°C/min
Range of temperature	30°C∼160°C
Measuring frequency	1 Hz
Chuck distance	20mm
Atmosphere	Air 150ml/min

3.7 Scanning Electron Microscopy (SEM)

The morphology of fracture surface of composites were observed by scanning electron microscopy (SEM), using S-2150 type machine which made by Hitachi Ltd, Japan. The samples were prepared by immersing in liquid nitrogen for about 5 minutes before fracturing. The fracture surface all of the samples were sputter coated with gold about a few nanometers in thickness to provide enhanced conductivity. The samples were viewed perpendicular to the fracture surface.

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