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Synthesis, Characterization and Optimization of Carbon Micro-Nano Filler and its Bio-composites

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

Synthesized carbon (biochar) from microwave assisted pyrolysis *Jatropha* seeds demonstrate great potential as bio-filler for bio-composite development. However, no research has been done so far on the pyrolysed *Jatropha* seed using ball milling approach for the biochar fabrication and develop bio-composite for engineering applications including biomedical. Therefore, the main aim of this research is to synthesis and characterize microwave-pyrolysis biochar using ball milling approach to develop micro-nano bio-filler reinforced poly lactic acid (PLA) bio-composites. After 30 hours of ball milling, the biochar manages to reduce into micro-nano size range. The Scanning Electron Microscopy (SEM) show *Jatroph*a seed biochar reduced from macro-size to micro-nano range 10 µm - 600 nm. Energy Dispersive X-ray Spectroscopy (EDS) results indicated an increase in carbon mass percentage from 72.6% to 81.2%, while the Brunauer-Emmett-Teller (BET) analysis showed an increased in surface area from 0.10 m^2/g to 3.67 m^2/g after 30 hours of ball milling. Fourier Transform Infrared Spectroscopy (FTIR) showed an increase in the percentage of transmittance after ball milling the biochar for 30 hours, with a reduction of moisture (alcohol, phenol, and water). The developed bio-composites are PLA/BC, which is PLA and bio-filler only, and PLA/PEMA/BC which is with the added compatibilizer Poly (Ethylene-Alt-Maleic Anhydride) (PEMA). Percentage of weightage for all materials for bio-composite fabrication are based on the D-optimal model design via StatEase Design Expert software. D-optimal mixture design models help to predict the mechanical properties of the bio-composites, as according to the response input (Mechanical Tensile and Microhardness Test Result). Noise level of the model dictates the accuracy and reliability to obtain the predicted values. Predicted optimum mixture content is found to be around PLA/BC 2wt% and PLA/PEMA/BC 1.25wt%. The developed bio-composites showed that higher bio-filler content increases the microhardness. However, the tensile strength and modulus of elasticity did not improve with higher bio-filler content, due to the brittle nature of the bio-composite structure, which could be observed in the SEM results. FTIR results for PLA/BC bio-composites were similar to PLA/PEMA/BC. Bio-composites with lower bio-filler content showed peak intensities which were more pronounced than higher bio-filler content. This correlated to the performance of the tensile strength and optimum bio-filler content. The additional PEMA in PLA/PEMA/BC showed peaks that were more pronounced, which showed the interaction between bio-filler and matrix to be better, hence affecting the mechanical performance. Overall, the introduction of bio-filler did not have much alteration in functional groups. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis demonstrated that the developed bio-composites had slightly better thermal stability compared their neat control samples. The improve thermal stability of PLA/PEMA/BC was attributed to the additional hydroxyl group by the introduction of PEMA, which improved interaction between bio-filler and polymer matrix.

Keywords: Jatropha, biochar, composite, micro, nano, carbon

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Sintesis, Pencirian dan Pengoptimuman Karbon Mikro-Nano pengisi dan Bio-kompositnya

ABSTRAK

Karbon disintesis (biochar) daripada pirolisis bantuan gelombang mikro biji benih Jatropha menunjukkan potensi besar sebagai pengisi bio untuk kemajuan biokomposit. Walau bagaimanapun, tiada kajian dilakukan setakat ini untuk pirolisis biji benih Jatropha menggunakan pengilangan bebola untuk fabrikasi biochar dan kemajuan biokomposit untuk aplikasi kejuruteraan termasuk bioperubatan. Oleh itu, matlamat utama penyelidikan ini adalah untuk mensintesis dan mencirikan biochar pirolisis bantuan gelombang mikro menggunakan pengilangan bebola untuk kemajuan biokomposit asid poli laktik (PLA) bertetulang bio-pengisi mikro-nano. Selepas 30 jam pengilangan bebola, biochar berjaya dikurangkan kepada julat saiz mikro-nano. Imbasan Elektron Mikroskopi (SEM) menunjukkan biochar dari benih Jatropha dikurangkan dari saiz makro menjadi dalam lingkungan mikro-nano10 µm - 600 nm. Hasil Spektroskopi sinar-X Tenaga Menyebar (EDS) menunjukkan peningkatan peratusan jisim karbon dari 72.6% hingga 81.2%, sementara analisis Brunauer-Emmett-Teller (BET) menunjukkan peningkatan luas permukaan dari 0.10 m^2/g hingga 3.67 m^2/g selepas 30 jam pengilangan bola. Spektroskopi Transformasi Fourier Inframerah (FTIR) menunjukkan peningkatan peratusan transmisi setelah penggilingan bola biochar selama 30 jam, dengan pengurangan kelembapan (alkohol, fenol, dan air). Bio-komposit yang dikembangkan adalah PLA/BC, yang hanya PLA dan bio-filler, dan PLA/PEMA/BC yang disertakan dengan penambah Poli (Etilena-Alt-Maleik Anhidrida) (PEMA). Peratusan wajaran untuk semua bahan-bahan untuk pembuatan bio-komposit adalah seperti mengikut reka bentuk model D-optimum dengan menggunakan perisian "StatEase Design Expert". Model reka bentuk campuran D-optimum *membantu meramalkan sifat mekanik bio-komposit, seperti yang sesuai dengan input tindak balas (Hasil Ujian Ketegangan Mekanikal dan Kekerasan Mikro). Tahap kebisingan model menentukan ketepatan dan kebolehpercayaan untuk mendapatkan nilai yang diramalkan. Kandungan campuran optimum yang dijangkakan didapati sekitar PLA/BC 2wt% dan PLA/PEMA/BC 1.25wt%. Bio-komposit yang dikembangkan menunjukkan bahawa kandungan pengisi bio yang lebih tinggi meningkatkan kekerasan mikro. Walau bagaimanapun, kekuatan tegangan dan modulus keanjalan tidak bertambah baik dengan kandungan pengisi bio yang lebih tinggi, kerana sifat rapuh struktur biokomposit, yang dapat diperhatikan dalam hasil SEM. Hasil FTIR untuk bio-komposit PLA/BC adalah serupa dengan PLA/PEMA/BC. Bio-komposit dengan kandungan pengisi bio yang lebih rendah menunjukkan intensiti puncak yang lebih ketara daripada kandungan pengisi bio yang lebih tinggi. Ini berkaitan dengan prestasi kekuatan tegangan dan kandungan pengisi bio yang optimum. PEMA tambahan dalam PLA/PEMA/BC menunjukkan puncak yang lebih ketara, yang menunjukkan interaksi antara pengisi bio dan matriks menjadi lebih baik, sehingga mempengaruhi prestasi mekanikal. Secara keseluruhan, penambahan pengisi bio tidak mempunyai banyak perubahan dalam kumpulan berfungsi. Analisis Termogravimetrik (TGA) dan Analisis Kalorimetri Pembezaan Berbeza (DSC) menunjukkan bahawa biokomposit yang dikembangkan mempunyai kestabilan haba yang sedikit lebih baik berbanding dengan sampel kawalan yang rapi. Peningkatan kestabilan terma PLA/PEMA/BC disebabkan oleh kumpulan hidroksil tambahan oleh penambahan PEMA, yang meningkatkan interaksi antara pengisi bio dan matriks polimer.*

Kata kunci: *Jatropha, biochar, komposit, mikro, nano, karbon*

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
BET	Brunauer-Emmett-Teller
BBM	Biochar before ball milling
ABM4hours	After ball milling for 4 hours
ABM8hours	After ball milling for 8 hours
ABM12hours	After ball milling for 12 hours
ABM16hours	After ball milling for 16 hours
ABM25hours	After ball milling for 25 hours
ABM30hours	After ball milling for 30 hours
DSC	Differential Scanning Calorimetry
DOE	Design of Experiment
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
MOE	Modulus of Elasticity
PLA	Polylactic Acid
PLA/PEMA	Polylactic Acid + Poly (ethylene-alt-maleic anhydride)
PLA/BC	Polylactic acid + Bio-filler
PLA/PEMA/BC	Polylactic acid + Poly (ethylene-alt-maleic anhydride) + Bio-filler
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TS	Mechanical Tensile Strength

CHAPTER 1

INTRODUCTION

1.1 Research Background

The importance of this research is to showcase the potential of microwave pyrolysis *jatropha* seed biochar and its bio-composites through characterization tests and determining the optimum mechanical properties. Comparing to other oil extraction processes, microwave pyrolysis of *jatropha* seeds has the advantage of the yielding not only bio-oil, but also biochar (Kanaujia et al., 2016; Odetoye et al., 2019). This research uses ball milling processes on the microwave pyrolysis *jatropha* seed biochar to develop a micro-nano size bio-filler mainly use to modify the polymer matrix's properties. The development of bio-composites shows the bio-filler application, which may be used to develop products in the biomedical industry. Biodegradable and biocompatible composites with overall good mechanical properties are sought after in the biomedical industry (Indira Devi et al., 2019; Umerah et al., 2020) .

The drawback of current published research regarding microwave pyrolysis of *jatropha* seeds is the lack of characterization and further development involving the resulting end product which is the biochar. There is a lack of data and information regarding specifically characterization of *jatropha* seed biochar via microwave pyrolysis (Figueiredo, 2011; Kadry, 2015; Kanaujia et al., 2016; Sugumaran et al., 2017; Odetoye et al., 2019). research showed biochar and/or activated carbon derived from a variety of biomass are used as adsorption material for heavy metals, toxins and chemicals (Ho et al., 2011; Belhamdi et al., 2016; Wu et al., 2019). Moreover, current published research is also scarce involving *jatropha* seed biochar via microwave pyrolysis being used as fillers for developing bio-composites with biodegradable polymer matrix. The drawback of using biochar as fillers may be due to the poor adherence to the polymer matrix and dispersion influenced by the physical, mechanical and chemical properties (Nan et al., 2015; Das et al., 2016; Aup-Ngoen & Noipitak, 2020). In addition, most bio-composite fabrication weightage percentage ratio are mostly random by selection through trial and error (Nan et al., 2015; Indira Devi et al., 2019; Umerah et al., 2020) .

This research is important to showcase the properties and characteristics of both microwaved pyrolysis *jatropha* seeds biochar as filler and the development of bio-composites. To overcome the inadequacies of current published research, characterization tests are required to determine the properties of the biochar and bio-composites and showcasing the materials characteristics. Examples of characterization tests includes Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), Mechanical Tensile Strength Test, Vickers Microhardness Test, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). These characterization tests showcase the physical, mechanical, chemical and thermal properties which defines the biochar and bio-composites. The ball milling process might have the capability to yield a product within micro-nano size range. Hence the microwave *jatropha* seed biochar, would undergo the ball milling process, which may assist dispersion within the matrix and adhesion (El-Eskandarany, 2020).

This research could be split into two sections which involves the development and characterization of the bio-filler and its bio-composites. The first section involves synthesizing microwaved pyrolysis *jatropha* seeds biochar, followed by a ball milling process to reduce the overall size of the biochar converting into bio-filler. The second section involves the combining a biodegradable polymer matrix with the micro-nano size bio-filler, developing a bio-composite. Analysis of characterization tests such as Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), Mechanical Tensile Strength Test, Vickers Microhardness Test, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are used to relate the developed micro-nano microwave pyrolysis *jatropha* seed biochar as bio-filler and its bio-composite towards biomedical applications. Design of experiment (DOE) *via* D-optimal mixture design is used to determine the weightage percentage or ratio for developing the bio-composites. D-optimal mixture design is statistical approach to optimise responses based on the effect of variables by mathematical modelling *via* software (Homkhiew et al., 2014). It is a useful tool to improve the design process, by managing materials usage and determining material ratios (Radfar et al., 2020).

1.2 Problem Statement

Jatropha seed biochar has potential as a reinforcement material in polymer bio-composites. However, a number of technical issues need to be addressed. It is recognized that the mechanical performances of bio-composites strongly depend on the characteristics and properties of the reinforcement, the type of polymer matrix, and the quality of adhesion between the two components. The poor compatibility between biochar and matrix, make it less desirable as biochar exhibits hydrophobic behaviours with well-organized C layers characterized by lower percentage of H and O containing functional groups due to the pyrolysis process of the medium (Agnieszka et al., 2020). Therefore, to improve the interfacial adhesion with polymer, modification *via* ball milling is used to physically reduce the size of the biochar and increase surface area, aiding the dispersion and adhesion of the reinforcement in the matrix._Some studies fabricate bio-composites using non-degradable and non-environmentally friendly polymers, such as polypropylene (PP), polyethylene (PE), and etc. but very few studies conducted using degradable and environmentally friendly polymer, such as poly lactic acid (PLA) for fabricating *jatropha* seed biochar reinforced polymer bio-composites. There are many studies conducting fabrication of bio-composites material is mostly conducted with ratio selection *via* trial and error. This method may result is material wastage, increased fabrication time, and increased difficulty in determining the optimum range for mechanical performance. Design of Experiment (DOE) can determine material usage or ratios for fabrication and for analysing experimental data and information. Furthermore, DOE has an option for the optimization of material usage or ratio in response to the bio-composites mechanical properties performance.

1.3 Research Gap

Bio oil and biochar yield are some parameters which could be seen in some research which investigate microwave pyrolysis of *jatropha* seed. Pyrolysis conditions such as gas flowrate, processing temperature, microwave power and chamber pressure are parameters that some researchers have considered for the study. However, there is research gap for the characterization and development of carbon micro-nano size bio-filler *via* microwave pyrolysis of *jatropha* seed and its bio-composites. Reinforcements used for the bio-composites is the carbon micro-nano size bio-fillers, synthesized from the biochar of microwave pyrolysis *jatropha* seeds. Other research shows bio-composites material ratios are mostly selection through trial and error, hence presents a disadvantage of the inability to include parameters affecting the performance of the bio-composites (Nan et al., 2015; Indira Devi et al., 2019; Umerah et al., 2020). Utilizing design of experiment (D-optimal mixture design) approach to determine material ratios for fabrication and optimizing the bio-composites properties may serves as a better mode of study for analysing experimental data and information.

1.4 Hypothesis

The mechanical, morphological, infrared spectral, and thermal characterisation on biochar (carbon) micro-nano bio-filler and its bio-composites were established and optimized. Ball milling process proves to be capable to convert microwave pyrolysis *jatropha* seed biochar and into micro-nano size bio-filler. Hence, an improvement in dispersion and increased surface area enables better adhesion between polymer matrix and bio-filler. The established material ratios and optimization via design of experiments (D-optimal mixture design), prove to be reliable to achieve high desirability for good mechanical properties in respect to the material ratios. The developed bio-composites using the carbon micro-nano size bio-filler improves properties such as material hardness and stiffness by filling gaps and pores within the matrix, thus enhancing the integrity of the matrix.

1.5 Objectives

i. To develop micro-nano bio-filler with microwave pyrolysis *jatropha* seed biochar
ii. To characterize the micro-nano bio-filler and its bio-composites.
iii. To determine bio-composites optimal material ratio and mechanical properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Important highlights have been made in this literature review in order to understand published research, material findings and factors influencing the properties of bio-composites. *Jatropha* seeds, biochar, polymer types, and characterization techniques have also been documented. Methods, observations and contributions made by others in this area are reviewed in this chapter.

2.2 Jatropha Seeds (Jatropha Curcas L.)

Jatropha seeds have gained interest with researchers due to their potential as a source of bio-oil. *Jatropha curcas* L. belongs to the family Euphorbiaceae and is a deciduous shrub that can grow to a height of 3 m to 5 m, with a productive lifespan of 50 years (Ugbogu et al., 2014). Srivastava et al. (2013) reported numerous case studies showing that *jatropha* seeds have high oil content, with potential application as an alternative to diesel (Srivastava et al., 2013). Depending on the variety, the seeds may contain 40% to 60% of oil. In recent years, several studies have been conducted to examine *jatropha* seeds for production of bio-oil, measuring their properties and characteristics (Ugbogu et al., 2014; Kadry, 2015; Audu, Irtwange & Satimehin, 2018). After extraction of the bio-oil, an alternative method of disposal alongside other organic waste utilizes microwave-assisted pyrolysis to yield biochar, which may be beneficial for numerous applications. There are several studies supporting pyrolysis of *jatropha* seeds and seed cakes obtaining biochar and syngas (Figueiredo, 2011; Kanaujia et al., 2016; Odetoye, Abu Bakar & Titiloye, 2019).