MECHANICAL, THERMAL AND FLAMMABILITY PROPERTIES OF POLY (LACTIC ACID)/BANANA FIBRE/GRAPHENE NANOCOMPOSITES TOUGHENED BY CORE SHELL RUBBER

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

School of Chemical and Energy Engineering
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FEBRUARY 2021

DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time.

ACKNOWLEDGEMENT

In the process of preparing this thesis I have come across many people who are willing to contribute either directly or indirectly. First and foremost, I would to express my gratefulness to god for getting me through all the resistance upon finishing this thesis. For my main supervisor, Associate Prof. Dr. Zurina binti Mohammad, I would like to express my gratitude for all the guidance, helps and encouragement given. Secondly, to my co-supervisor, Prof Azman bin Hassan who has provided guideline, ideas and knowledge.

I also appreciate the help from all the technicians especially Mr. Suhee Tan, Mr. Fairuz and a long list of others who have given me all the technical supports while carrying out the experiments in various laboratories in UTM. My deep appreciation also to my family, friends and other lecturers who provide me with moral supports and experience sharing which have all contributed to help me finish this thesis.

ABSTRACT

A biocomposite consists of Poly (lactic acid) (PLA) and Banana Fiber (BF) was prepared responding to high demand of biodegradable product. The mechanical as well as the morphological studies were done to find the optimum BF loading for the biocomposite system. Nevertheless, the optimum BF loading could not determine since most of the mechanical properties exhibit a decremental trends and the scanning electron microscope (SEM) analyses revealed that there was an interfacial gap presence between the PLA/BF due to poor compatibility between those two. An epoxy-based compatibilizer (brand name Joncryl) was then incorporated into the biocomposite system to improve the overall mechanical properties of PLA/BF biocomposite. However, addition of Joncryl only gave a slight improvement on impact strength but adversely affected the tensile and flexural strength. Hence, graphene (Gr) was added to improve the properties of the nanocomposite. Sample of PLA/10% BF with 0.5 phr Gr loading recorded the highest tensile and flexural strength compared to other formulations thus was selected as the optimum loading for the PLA/BF/Gr nanocomposite. Thermal gravimetry analysis (TGA) and differential scanning calorimetry tests (DSC) revealed that increased amount of Gr had enhance the thermal stability of the biocomposite. On the contrary, the increase contents of Gr had decreased the nanocomposite toughness, which was shown by the impact test results. In order to overcome the drawback, a core shell rubber (CSR) was introduced to the system as a toughening agent. Based on the overall mechanical properties, 15 phr CSR content showed the highest impact strength and elongation at break while having an acceptable thermal stability. The limiting oxygen index (LOI) for 15 phr CSR content was at 21 volume%, which exceeded the threshold mark of 20.8 volume%. This indicate that the nanocomposite produced at this formulation can be classified as a safe material.

ABSTRAK

Biokomposit yang terdiri daripada campuran poli (asid laktik) (PLA) dan serat pisang (BF) telah disediakan bagi memenuhi permintaan tinggi produk biodegrasi pada masa kini. Kajian mekanikal serta kajian morfologi telah dijalankan bagi menentukan kadar pemuatan optimum BF didalam sistem komposit. Walau bagaimanapun, pemuatan optimum BF tidak dapat ditentukan kerana kebanyakkan sifat mekanikal menunjukkan nilai penurunan manakala imbasan miskroskop electron (SEM) pula mendedahkan bahawa terdapat ruang antara muka PLA dan BF disebabkan oleh keserasian yang kurang baik antara keduanya. Joncryl kemudiannya dimasukkan ke dalam komposit untk memperbaiki sifat mekanikal PLA/BF komposit. Penambahan Joncryl bagaimanapun, hanya memberi sedikit peningkatan kekuatan hentaman tetapi melemahkan sifat mekanikal lain seperti kekuatan tegangan dan lenturan. Grafene (Gr) kemudiaanya ditambah untuk meningkatkan sifat nanokomposit. Formulasi PLA/10% BF beserta 0.5 phr mencatatkan kekuatan tegangan dan lenturan tertinggi berbanding formulasi lain. Analysis terma gravimeti (TGA) dan pengimbas kalori berbeza (DSC) telah menunjukkan bahawa peningkatan kandungan Gr dapat meningkatkan kestabilan terma nanokomposit. Namun demikian, peningkatan kandungan Gr turut mnyebabkan penurunan daya tahan hentaman, seperti yang ditunjukkan oleh keputusan ujian hentaman. Bagi mengatasi masalah ini, getah teras bercengkerang (CSR) telah ditambah kedalam sistem nanokomposit. Berdasarkan sifat mekanikal secara keseluruhan, kandungan 15 phr CSR telah menunjukkan kekuatan hentaman tertinggi dan mempunyai keseimbangan terma yang baik. Indeks penghad oksigen (LOI) juga mencatakan 21/vol%, yakni melebihi paras 20.8/vol%. Ini menunjukkan bahawa nanokomposit yang dihasilkan pada formulasi ini dapat diklasifikasikan sebagai bahan selamat.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

PLA	-	Poly (lactic acid)
BF	-	Banana Fiber
Gr	-	Graphene
CSR	-	Core Shell Rubber
SEM	-	Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared Spectroscopy
DSC	-	Differential Scanning Calorimetry
LOI	-	Limiting Oxygen Index
APS	-	Bis-3-triethoxy silylpropyl
CNT	-	Carbon Nanotubes
PVC	-	Poly (Vinyl) Chloride

CHAPTER 1

INTRODUCTION

1.1 Background of Research

These few decade, various synthetic material has been explored as an alternative to iron and steel in various area such as automotive, packing and even housing application. Among those, thermoplastic has simulated immense interest and became the perfect replacement for metal. Nowadays, plastics are used for almost everything from the articles of daily use to complicated structures, machine components etc. (Raj et al. 1986). Plastics find an extensive application due to their properties such as less weight, low water absorption, high stiffness and strength. The same chemical building blocks that make plastics so versatile are the same components that harm people and the environment. Until now, there is no safe and convenient way to disposed plastics and it end up become an iconic of symbol of waste, 'the white pollution' that is harmful to environment. Another detriment of using plastic material was due to the fact that plastics were made from crude oil, a valuable natural resource that cannot be replenished once diminished. Most plastics are derived from petrochemicals process produced from fossil oil and gas. As the manufacture of plastics also requires energy, its production is responsible for the consumption of a similar additional quantity of fossil fuels.

Biodegradable polymer, a polymer that breaks down after its intended purpose to result in natural byproducts such as gases, water, biomass, and inorganic salt may serve as a promising replacement for thermoplastic. This type of polymer can be classified into two main groups based on the structure and occurrence, agro polymer and bio polyester. Agro polymer consist polysaccharides and protein while bio polyester usually obtained from microorganism or synthetic monomer. Among these biodegradable polymer, poly (lactic acid) (PLA) can be considered as the most famous and suitable alternative material for synthetic plastic due to it distinct features.

PLA is biodegradable thermoplastic aliphatic polyester that derived from renewable resources, such as corn starch, tapioca roots, or sugarcane. PLA has many desirable properties such as environmentally friendly, ease of processability and non-toxicity applications (Kumar et al., 2010). Even though PLA have those desirable properties as mention earlier, PLA also have several impediments that restricted it usage for several applications. In term of mechanical properties, PLA inherent brittleness, low elongation at break and low toughness. Apart from having moderate mechanical properties, the biggest concern regarding PLA was its high raw material cost. Due to this, scientists have come up with a new way, adding a natural fiber into PLA matrix and turn it into biodegradable composite or biocomposite. Various natural fibers such as flax, ramie, jute, bambo, pineapple, kenaf, hemp and banana have been investigated as reinforcements in biopolymers by various researchers (Shalwan and Yousif, 2013; Oksman et al., 2003)

Almost all biocomposite consist of biodegradable polymer as matrix and a natural fiber as the reinforcing filler. Since both components are biodegradable, the biocomposite will also become biodegradable as well. Natural fiber such as banana fiber (BF) surely can become a promising biocomposite filler because it is abundantly available and considered as one the most planted tree on whole world. Although BF does provide the biodegradability needed, but on its own, BF does not possess the necessary thermal and mechanical properties desirable for engineering application. In order to compensate these limitations, BF was combined with PLA to obtained the desirable property without obstructing green polymer images. The main problem with PLA/untreated banana fiber (UBF) is it tend to undergo various damage phenomenon's such as matrix cracking, interfacial debonding, fiber pull outs, and fracture due to incompatibility between hydrophobic PLA and hydrophilic UBF. The poor interfacial interaction between the hydrophobic matrix and hydrophilic natural fiber is a pondering subject for material scientists in this area. Several attempts have been tried by numerous researchers to solve these incompatibility problems.

Various modification techniques such as physical treatments using solvent extraction and the others use different type of coupling agent to improve the compatibility between PLA and BF (Dupraz et al.,1996; Luo and Netravali, 1999; Okubo and Fujii, 2002; Plackett et al., 2003). All of these researchers reported that most of the treatment used does improved the compatibility and thus, enhance both mechanical and thermal properties of the biocomposite.

The addition of compatibilizer certainly can improve the compatibility between matrix and natural fiber, thus, enhancing the mechanical properties of the PLA/BF composite. In a similar fashion, this research hope to utilize the usage of new additive named Joncryl, that will act as a compatibilizer, in order to improve the interfacial bonding between the hydrophilic fibers with hydrophobic PLA. This novel approach was expected to increase the mechanical properties of PLA/BF biocomposite. Despite several improvement in term of mechanical properties, the PLA/BF biocomposite might still possessed the poor thermal properties and high flammability.

According to Feng et al., (2014), high performance nanofillers like nanotube, nanoclay, and graphene can improve the thermal properties and flame retardancy of natural fiber reinforced PLA composites. However, the drawback of nanofiller is their high production cost while nanoclay only provided slight enhancing effect toward electrical and thermal conductivity properties. As Nicholas (2012) wrote in his review for Springer Nature, “When carbon fibers just won’t do, but nanotubes are too expensive, where can a cost-conscious materials scientist go to find a practical conductive composite? The answer could lie with graphene sheets”.

Graphene (Gr) is two-dimensional carbon nanofiller, with one-atom-thick planar sheet of bonded carbon atoms, that are densely packed in a honeycomb crystal lattice. It is regarded as the “thinnest material in the universe” with tremendous application potential (Geim and MacDonald., (2007); Si and Samulsky., (2008). Cao et al., (2010)) reported that the incorporation of 0.2 mass % of Gr into PLA induces a significant enhancement in mechanical and thermal stability of polymer.

More recent study conducted by Pinto et al. (2013) has discussed the effect of small amounts (0.2 to 1 mass %) of graphene oxide (GO) and graphene nanoplatelets (GNP) on functional properties of PLA film. The results obtained show that the yield strength as well as Young's modulus certainly improved with the addition of GO and GNP compared to pristine PLA. Mat Desa et al., (2019), on the other hand, study the effect of GNP toward the thermal stability and LOI value of PLA composite. It was found out that GNP certainly enhanced both of the thermal stability and LOI value of PLA composite. Even though all of these studies highlight the enhancing effect of Gr, some of them also highlight the low impact strength yield PLA/Gr blend.

Low impact strength yield by PLA/Gr blend can be remedied by adding an elastomer or rubber component that can act as impact modifier. Elastomer or rubber is very important class of polymeric materials with major application in various areas of polymer industry. Among earlier work on PLA/Gr toughening was reported by Wu et al., (2009) and Ko et al., (2009) that used (PCL) and poly (butyleneadipate-co-butyleneterephthalate) (PBAT) as impact modifier. The toughening of PLA/Gr nanocomposites was later examined by Shi et al. (2011) using ethylene-co-vinyl acetate (EVA) as impact modifier. All of them had showed that addition of elastomeric material does give a slight toughening effect toward PLA/Gr nanocomposites. However, the materials stiffness becomes too low and this affected the tensile and flexural strength. Apart from the previously mention works, there was a very few attempts made thus far to enhance the toughness of PLA/Gr nanocomposites. Therefore, it is interesting to see the effect of new generation impact modifier called Core Shell Rubber (CSR) toward PLA/Gr nanocomposites system. CSR can be defined as a material that contain of a rubber core (inner material), encapsulated by a glassy shell (outer layer material). The advantage of CSR was its compatibility with non-polar polymer such as PLA since the outer shell were also made up from non-polar polymer as well. This will prevent the core rubber from sticking with each other thus, lead to a better toughening effect.

1.2 Problem Statement.

Recent consciousness in reducing the environmental impact materials lead to the development of newer materials. In light of potential future petroleum shortages and pressures for decreasing the dependence on petroleum products, there is an increasing interest in maximizing the use of renewable material. Polylactic acid (PLA), linear aliphatic thermoplastic polyester, offers a fine solution toward those problems due to its biodegradability and agricultural origin. It is an auspicious polymer with inherent biodegradability character, offers good aesthetics, relatively good mechanical strength, and non-toxicity. Even though PLA has many desirable properties, it does have several impediments that restricted its use in several applications. High brittleness, low heat deflection temperature and high cost in particular have limited the wide application of PLA in various aspect (Kumar et al., 2010)

Mention before on the introductory part that the stumbling block of using PLA was its high cost. Many research studies have been conducted on modification of PLA by blending with other biodegradable polymers or incorporated PLA with natural fiber in order to reduce the cost (Dupraz et al., 1993, Jandas et al., 2011 and Plackett et al., 2013). Unfortunately, the fabrication method of blending with others biodegradable polymer will also result in high cost. The more approvable method is producing a biocomposites by impregnating natural fibers into biodegradable polymer to reduce the cost as well as to improve the mechanical properties without compromising green composite image. That being said, the hydrophobic nature of PLA is not very compatible with hydrophilic natural fiber such as banana fiber (BF). PLA is an aliphatic polyhydroxyacid which mean chemically, there is no site for effective interaction with hydroxide (-OH) of natural fiber but many sites for hydrophobic reaction. This low compatibility of BF with PLA will result on ineffective stress transfer between them, that leads to poor mechanical properties in the composites. The poor mechanical properties may result from various type of failure such as matrix cracking, interfacial debonding, fiber pull outs, and fracture due to incompatibility between hydrophobic PLA and hydrophilic BF. It is believed that the addition of compatibilizer will improve the interfacial bonding between fiber and matrix, thus, further enhancing the compatibility between the matrix and fibers.

Since several researchers have proved that the addition of compatibilizer will enhance the compatibility of PLA and BF, this research hope to pounce of the same idea, utilizing the usage of new additive named Joncryl, that will act as a compatibilizer, in order to improve the interfacial bonding between the hydrophilic fibers with hydrophobic PLA This novel approach expected to increase the mechanical properties of PLA/BF biocomposite. That being said, since Joncryl is a new type of additives, there is no paper published regarding the effectiveness of this additives as a compatibilizer. The only guideline was the technical data provided by the supplier (D-BASF), which contain the information stating that Joncryl can react with various reactive group such as epoxide, anhydride, -COOH and –OH. This opens the possibility for Joncryl to react with both PLA and BF. That being said, the reaction between PLA with Joncryl and Joncryl with BF might varies compared with silane or other type of coupling agent.

The addition of Joncryl might remedied the compatibilities issues between PLA and BF, thus slightly enhance the mechanical properties of biocomposite. However, PLA/BF biocomposite still inherent the poor thermal properties and high flammability, which limit it usage in various applications of polymer fields. According to Jandas et al. (2013), irrespective of the BF treatment and surface modifications, the thermal stability of PLA/BF remain unchanged. He also claimed that for the Limiting Oxygen Index (LOI), the value also constant at 20 volume% with or without BF treatment. This showed that the addition of compatibilizer or BF surface treatment will not improve the thermal properties as well as the flame-retardant properties of biocomposite.

In order to improve the thermal and flame retardancy properties of PLA/BF biocomposite, nano fillers such as nanoclay (Nc), carbon nanotubes (CNT) and graphene (Gr) (Feng et al., 2014; Geim and MacDonald, 2007; Si and Samulsky, 2008) were incorporated into PLA/BF biocomposite. Nc was reported to give just a slight improvement to PLA/BF biocomposite while CNT are very pricy, Gr was proved to be the most suitable candidate to be used as reinforcing filler for this project. Mention in introduction that there was plenty of studies in recent year that proved the addition of graphene already improved the mechanical, thermal and more importantly, compensate poor fire resistant inherent by PLA/BF biocomposite (Cao et al., 2010; Pinto et al., 2013). Although various research proved the effectiveness of Gr as reinforcing filler, incorporation of a rigid Gr into an already brittle PLA will create a very stiff and brittle material, that have low toughness and impact strength.

Adding an impact modifier can proved to be an effective way to tackle the brittleness issues experience by PLA/Gr blend. However, most traditional impact modifiers were made from elastomer/rubber that doesn't synergy well with PLA matrix. There's always the chance of agglomeration among rubber particle that could lead to even poorer mechanical properties. The emerging of new generation impact modifier called Core Shell Rubber (CSR) could prove to be the answer due to its compatibility with PLA. It is interesting to see whether the presence of CSR can improve toughness and at the same time, retained good mechanical, thermal and flame retardancy properties obtained by PLA/BF/Gr compatibilized with Joncryl nanocomposite.

1.3 Objectives of Research

The aims of this research were to develop a new smart material based on PLA and BF composite toughened by core shell rubber (CSR) as an impact modifier, with the addition of graphene (Gr) as nanofillers. The aims were further divided into:

(1) To determine the best BF loading for PLA matrix based on the mechanical properties and morphological study.

(2) To study the effectiveness of Joncryl as a compatibilizer for PLA/BF biocomposite.

(3) To examine the reinforcing effect of Gr toward the mechanical, thermal and flammability properties of PLA/BF/Gr composite

(4) To investigate the toughening effect of CSR toward the mechanical, thermal and flammability properties of PLA/BF/Gr nanocomposite

1.4 Scope of Research

In order to achieve the research aims, several requirements were carried out such as:

(1) Preparation of PLA/BF composite by using melt blending method, with BF loading varies between 0 to 20 wt%. Analysis on PLA/BF composite are:

   (a) Evaluation of optimum BF load of PLA composites was determine based on tensile, flexural, and impact properties.
   (b) Morphological observation using Scanning Electron Microscopy (SEM)
   (c) Finding possible interaction between PLA, and BF by using Fourier Transform Infrared Spectroscopy (FTIR).

(2) Preparation of PLA/BF composite compatibilized with Joncryl by using melt blending method, with BF loading varies between 0 to 20 wt%. Analysis on PLA/BF compatibilized with Joncryl composite are:

   (a) Evaluation of optimum BF load of PLA composites compatibilized with Joncryl was determine based on tensile, flexural, and impact properties.
   (b) Morphological observation using SEM.
   (c) Finding possible interaction between PLA, BF and Joncryl by using FTIR

(3) Preparation of PLA/BF/Gr compatibilized with Joncryl biocomposite using melt blending method, with Gr loading varies between 0,0.5,1,1.5 and 2 phr. Analysis on PLA/BF/Gr compatibilized with Joncryl nanocomposite are:

   (a) Evaluation of optimum Gr loading was determine based on tensile, flexural, and impact properties.
   (b) Morphological observation using FESEM.
   (c) Finding possible interaction between PLA, BF, Joncryl and Gr by using FTIR

(d) Thermal properties characterization using Thermal Gravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC).

(e) Investigate the flame retardancy property using Limiting Oxygen Index (LOI).

(4) Preparation of PLA/BF/Gr/CSR compatibilized with Joncryl nanocomposite using melt blending method, with CSR content varies between 0,5,10,15 and 20 phr. Analysis on PLA/BF/Gr/CSR compatibilized with Joncryl nanocomposite are:

(a) Evaluation of optimum CSR loading was determine based on tensile, flexural, and impact properties.

(b) Morphological observation using FESEM.

(c) Finding possible interaction between PLA, BF, Joncryl, Gr and CSR by using FTIR

(d) Thermal properties characterization using TGA and DSC.

(e) Investigate the flame retardancy property using LOI.

1.5 Significance of Study

This study was originated from the desire to utilize biopolymer from renewable resources. Utilization of PLA and BF will enrich values to our local commodity and help to reduce dependency on non-renewable petroleum-based polymers. The addition of core shell rubber was essential to remedied the brittleness issues caused by PLA and BF composite. The addition of graphene (Gr) meanwhile, act as the reinforcement filler so that the composite can improved its mechanical, thermal, and flammability properties which consequently drive PLA based composite towards greater application. This research was expected to yield new findings and providing new knowledge regarding biopolymeric nanocomposites material with enhanced mechanical, thermal stability and flame-retardant characteristics. This PLA nanocomposites is expected to find ways into wider applications such as in automotive parts, medical devices, and coating application that required certain level of mechanical, thermal and flame retardancy property.

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