EFFECT OF RICE STRAW FIBER AND POLYETHYLENE GLYCOL ON POLYLACTIC ACID/POLYHYDROXYBUTYRATE-VALERATE BLENDS

by

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LIST OF ABBREVIATIONS

ASTM	American standard testing method
DSC	Differential scanning calorimeter
FTIR	Fourier transform infrared
HDPE	High density polyethylene
PBAT	Poly(butylenes adipate-co-terephthalate)
PCL	Poly-Ɛ-caprolactone
PE	Polyethylene
PEG	Polyethylene glycol
PE-g-MA	Polyethylene-grafted maleic anhydride
PHA	Polyhydroxy alkanoate
PHBV	Poly(hydroxybutyrate valerate)
PLA	Polylactic acid
PP	Polypropylene
RS	Rice straw
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UTM	Universal testing machine

LIST OF SYMBOLS

%	Percentage
kg/capita	kilogram per capita
^oC	degree celcius
g/cm^3	gram per cubic centimetre
g	Gram
µm	Micrometer
wt%	weight percentage
mm/min	millimetre per minute
kV	Kilovolt
mg	Milligram
$^oC/min$	degree celcius per minute
ΔH^*_f	heat fusion for 100% crystalline polylactic acid
ΔH^o_f	heat fusion for semicrystalline polylactic acid
L	Litre
ml	Millilitre
cm^3	cubic centimetre
Mm^3	cubic millilitre
cm^{-1}	reciprocal wavelength
MPa	mega pascal

Kesan Serat Jerami Padi dan Polietilena Glikol Terhadap Campuran Polilaktik Asid / Polihidroksibutirat Valerat

ABSTRAK

Polimer terbiodegradasi adalah salah satu alternatif yang mempunyai potensi untuk mengatasi masalah pencemaran alam sekitar dan pengurangan minyak mentah. Antara bahan yang digunakan dalam kajian ini adalah polilaktik asid (PLA), polihidroksibutirat-valerat (PHBV), serat jerami padi dan polietilene glikol (PEG). PLA and PHBV adalah salah satu polimer terbiodegradasi yang dapat memenuhi sifat antara satu sama lain. Komposit ini telah diproses menggunakan pemanasan pengisar dua gelek (DW5110). Campuran antara PLA dan PHBV telah mengurangkan sedikit kekuatan regangan tetapi telah meningkatkan pemanjangan pada takat putus (E_b). Selain itu, modulus Young turut meningkat. Kadar optimum campuran adalah 50% PLA dengan 50% PHBV. Kajian turut memfokuskan terhadap kesan serat jerami padi dan PEG sebagai bahan peliat terhadap campuran PLA/ PHBV. Kandungan serat jerami padi telah divariasikan daripada 5 sehingga 25 peratus kandungan. Kandungan PEG dalam PHBV telah ditambah sebanyak 5 peratus daripada kandungan serat jerami. Kehadiran serat jerami padi telah mengurangkan sedikit sifat mekanikal dan kestabilan terma. Walaubagainapun kadar penyerapan air telah meningkat. Tujuan menambahkan bahan peliat ke dalam campuran PLA/ PHBV dengan serat jerami padi adalah untuk meningkatkan E_b dan mengurangkan kerapuhan disamping mengekalkan kekuatan polimer pada tahap yang optimum. Kehadiran PEG turut mengurangkan ketegangan regangan tetapi telah meningkatkan E_b dan modulus Young. Sifat amfifilik yang ada pada PEG mengurangkan sedikit kadar serapan air. Berdasarkan spectra tranformasi inframerah Fourier (FTIR), intensiti kumpulan –OH adalah lebih rendah berbanding dengan intensiti serat jerami padi diisi dengan komposit PLA/ PHBV. Ujian biodegradasi dibuat dengan mendedahkan polimer pada persekitaran semulajadi dan ujian tanaman ke dalam tanah selama 6 bulan. Ujian tersebut telah disahkan dengan menilai sifat mekanikal, morfologi permukaan, indeks karbonil dan penghabluran. Penambahan serat jerami padi telah mengurangkan sifat mekanikal tetapi mengurangkan indeks karbonil dan penghablura. Imej imbasan mikroskopi electron (SEM) menunjukkan bahawa terdapat keretakan, lubang dan kolonisasi kulat pasa bahan yang mengandungi serat jerami padi. Penambahan PEG kedalam komposit telah membantu meningkatkan degradasi dengan meningkatkan pendedahan permukaan untuk kolonisasi kulat. Kesimpulannya, penambahan serat jerami padi telah meningkatkan degradasi dan kehadiran PEG kedalam komposit tersebut telah meningkatkan E_b antara campuran tersebut.

Effect of Rice Straw (RS) Fiber and Polyethylene Glycol (PEG) on Polylactic Acid/ Polyhydroxybutyrate Valerate (PLA/PHBV) Blends

ABSTRACT

Biodegradable polymer is one of the alternatives that have potential to overcome serious environmental problem and depletion of crude oil. The materials that have been used in this study are polylactid acid (PLA), polyhydroxybutyrate-valerate (PHBV), rice straw (RS) fiber and polyethylene glycol (PEG). PLA and PHBV are one of biopolymer that can complement each other properties. The mixing process of these composites was carried out using heated two-roll mill (DW5110). The blends between PLA and PHBV slightly reduced tensile strength but increased E_b. Besides, it also increased the Young's modulus. The optimum ratio of the blends is 50% PLA with 50% PHBV. This study also focused on the effect of RS fiber and PEG as plasticizer on PLA/PHBV blends. The RS fiber content was varied from 5 to 25 wt%. 5 wt% PEG based on RS fiber content was added. The addition of RS fiber into the blends reduced the mechanical properties and thermal stability however the water absorption increased. The incompatibility of RS fiber with PLA/ PHBV blends was proven by SEM micrographs. PLA/PHBV blends show high modulus and high tensile strength but it is quite brittle. . The goal of adding plasticizer to PLA/ PHBV blend with RS fiber is to enhance the polymer elongation and to reduce the brittleness while maintaining optimum polymer strength and stiffness. After the addition of PEG, the tensile strength reduced, while the E_b and Young modulus increased. The amphiphilic properties of PEG slightly reduced the water absorption. From FTIR spectra, it can be seen that the presence of PEG into PLA/PBV blends filled with RS fiber reduced the –OH group intensity. Natural weathering and soil burial test until 6 months were performed to determine the biodegradability of the polymer and were confirmed by evaluating the mechanical, morphological, carbonyl index and crystallinity. The addition of RS fiber had reduced the mechanical strength but carbonyl index and crystallinity increased. The crack, pores and fungus colonization was shown in SEM micrograph, indicated that the biodegradation was more pronounced with the addition of RS fiber. The addition of PEG also helps to increase the degradability by increasing the surface area for microbial attack. In conclusion, the addition of RS fiber increased the degradability and the presence of PEG as plasticizer improved the E_b between the blends.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Any synthetic or semi-synthetic organic polymer is called plastic. Plastic is made from crude oil, which is very limited amount as it is from a non-renewable resource. Packaging materials largely contribute to the high demand for plastics. Although the plastic can be recycled, it still generate amount of solid waste that cannot be decomposed. Plastics bags are the true threat to our ecosystems and our waste diversion goals (Lee et al., 2013). Environment and Plastics Industry Council indicates about two hundred billion tones of plastic are produced worldwide every year. Some types of non-biodegradable polymers are polypropylene (PP), polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC) (Sam et al., 2011)[a]

As environmental concerns of waste disposal and pollution become issues, new biodegradable polymers offer a good substitute for non-biodegradable petroleum-based plastics which can create an age of green plastics. An approach is made to produce plastics from agricultural products which are produced by nature. This includes starch, sugar molasses, protein and cellulose (Swain et al., 2004). Besides, by blending two or more biodegradable polymer would one of the options to reduce the waste disposal and pollution issues. Some examples of the biodegradable polymers are polylactic acid (PLA), polyhydroxybutyrate-valerate (PHBV) and polybutylenes succinates (PBS).

Polymer blends are physically blended of different kind of polymers to obtain a material with desirable properties. The important characteristic of polymer blends from two or more polymers is the phase behaviour either it miscible or immiscibility as it can affect the mechanical properties of the polymer. The advantage of polymer blends is their potential to solve application requirements without alternating to develop new monomer and a new polymer. The specific interactions that promote miscibility are the hydrogen bonding, ionic interactions and electron donor-acceptor complexes (Corre et al., 2011). The physical properties and degradation characteristics of polylactic acid/polyhydroxybutyrate-valerate (PLA/PHBV) blends can be modified by compounding different ratio of PLA and PHBV. Zhang and Thomas (2011) found the PHBV can enhance the recrystallization of PLA and consequently increased heat temperature.

Natural fiber reinforced materials offer environmental advantages as it reduced the dependence on non-renewable sources (Grazdanov et al., 2006). Besides their renewability and abundantly available, the utilization of agricultural residues provides many advantages to economy and environment. Bamboo, jute, and rice straw (RS) are the most commonly reinforcement natural fiber that are incorporated in polymers (Qin et al., 2011). The abundant of RS fiber can be converted to a useful material as it can be degraded naturally, consequently fasten the degradation process of the polymer (Chen et al., 2011). Like other agricultural wastes, RS is an abundant biomass consists of hemicellulose, cellulose, lignin and others such as ash and wax. They contribute to mechanical strength of the straw cell walls.

As plasticizers for the polymers, various types of compounds such as citrate ester, polyethylene glycols (PEG), glucose monoesters, partial fatty esters, oligomeric lactic acid and glycerol have been used to improve the flexibility of the composites.

PEG with the general formula $H(OCH_2CH_2)n$ OH are liquid or solid polymers. Low molecular weight of PEG is in the liquid form, while the higher molecular weight of PEGs is in the solid form at room temperature. PEGs are appropriate plasticizer for PLA due to their miscibility, biodegradability and food contactable application (Chieng et al., 2013).

In this study, the performance of RS particulate filled PLA/PHBV composites were studied using tensile test, thermogravimetry analysis (TGA), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), fourier transform infrared (FTIR) and water absorption. The PEG was used as the plasticizer in the composites. The natural weathering and soil burial test were carried out to test its degradability test.

1.2 Problems Statement

Biopolymer are a growing research issue since they appear as a solution to emerging environment concerns. The design of biodegradable plastics is an appropriately eco-efficient approach to enhance the environmental quality for many products as well as to minimize the waste disposed in landfills. Unfortunately, the utilization of biodegradable polymer as bulk commodity materials is still restricted to a few applications because of the strong cost-competition with cheaper petroleum-based polymer and their limited thermo mechanical properties (Gamez et al., 2011). Biodegradable polymer likes PLA and PHBV are produced from renewable resources which make them most potential for production of plastics which are more environmental-friendly. However, there are very high in cost and have several drawback. Commercially available PLA cannot fully satisfy the industrial requirements due to its brittleness and lack of ductability. On the other hand, the applications of

PHBV based materials are limited due to the poor stability and low rate of crystallization resulting in aging after processing. Therefore, this study aims to produce a promising PLA/PHBV blends. Blending is a cost-effective, strategy which combines the advantages of different polymers to obtain a material with the desirable properties. Therefore, by blending PLA and PHBV can overcome and complete each other limitation (Modi et al., 2013). On the other hand, the cost can be reduced by incorporation the natural filler such as RS fiber, jute and ramie. Nevertheless, most of the filler are covered with non-cellulosic and hydrophobic compounds which obstruct adhesion between fibers and polymer matrix. Therefore, plasticizers are normally added to overcome the brittleness of the blends and increase the adhesion of the polymer composites.

1.3 Objectives

This study aims to evaluate the properties of PLA/PHBV blends with different loading of RS fiber. The objectives of the research are listed as following:

i. To investigate the properties of PLA/PHBV blends with different blends ratio.
ii. To explore the effect of RS fiber content on the properties of PLA/PHBV blends.
iii. To evaluate the performance of PEG as a plasticizer in RS fiber filled PLA/PHBV composites.

1.4 Scope of Study

In this study, biopolymers that have been considered are PLA and PHBV. In the first series, the study focused on the blends of PLA with PHBV while the second series focused on the addition of natural filler into the blends by varying the RS powder content between 5% and 25%. The third series represented the effect of PEG on 50% PLA 50% PHBV with 5% to 25% of RS fiber content. The mixing process was carried out using heated two-roll mill (DW5110). The blends were then subjected to mechanical, morphological, thermal and physical test. For biodegradation test, the blends were investigated through natural weathering and soil burial test.

1.5 Thesis Organization

This thesis contains five chapters where chapter 1 consists of research background, problem statements, objectives and scope of research. Chapter 2 explains and summaries the previous research about biodegradable polymers. Chapter 3 outlines the methodology the preparation and production of the blends and the test that performed. Chapter 4 covered the discussion of the result and chapter 5 covered conclusion and recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradable Polymers

The biodegradable plastics were introduced during the oil crisis in 1970's. The plant based material become increasingly popular as the renewable resource is more economic. Recently, biodegradable polymers such as polycaprolactone (PCL), polyhydroxyalkanoates (PHA) and polylactic acid (PLA) have been produced. These materials properties have similar properties to petrochemical-based polymers (Sam et al., 2010). Biodegradable polymers present a large range of properties which now can compete with non-biodegradable thermoplastics in different fields such as packaging, textile and biomedical (Berkesch, 2005).

Different materials can be sources to make biodegradable plastics. The previous research shows that the biodegradable plastics can be made from starch based plastics which mainly harvested from potatoes, rice, corn and wheat (Berkesch, 2005). The most commonly used is corn because it is cheaper than others. The starch based plastics have limitation in use because it is soluble in water and cause them to swell and deform when exposed to moisture (Berkesch, 2005). Another alternative to produce biodegradable plastic is by using bacteria. These bacteria based plastic use the polymer chain polyhydroxyalkanoate (PHA) that produce inside the bacteria cells (Berkesch, 2005).

There are several families that related to the biodegradable plastics. According to Macy et al. (2007), the degradable plastics is a plastic that designed to undergo