PREPARATION AND CHARACTERIZATION OF POLYLACTIC ACID/ MODIFIED ROCK STONE/STARCH BIOCOMPOSITES

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To my beloved mother and father

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ABSTRACT

The main purpose of this study was to investigate the effects of starch and a new phthalate-free plasticizer, which was modified rock stone (MR) on the mechanical, physical, thermal and biodegrability properties of polylactic acid (PLA). The biocomposites of PLA, MR and starch were prepared by extrusion method and injection molded into standard tensile and flexural shape. The properties of the biocomposites were tested and characterized by using tensile and flexural tests, melt flow index, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and water absorption test. The investigation of biodegradation of the biocomposites was done by soil burial test. Test results showed that MR improved the mechanical properties up to 30 w/w% and the optimum MR content was 16.6 w/w% (PM0). The test results also showed that MR acted as reinforcement filler but not as plasticizer because there was a decrease in flow rate and no change in glass transition temperature. When starch was added to the PLA/MR biocomposites, the mechanical properties of the biocomposites were reduced probably due to the agglomeration of starch particles. Optimum starch content was 15 w/w% (PMS15). After the blending of PLA with MR and starch, the pure PLA, PM0 and PMS15 samples were compared. FTIR and SEM results showed that MR was compatible with PLA and that starch interfered with the compatibility of PLA and MR. DSC results also showed that the addition of MR and starch to PLA did not affect the crystallinity of the biocomposite. Addition of starch improved the amount of water uptake and the percentage weight loss during soil burial test because starch is hydrophilic and can be hydrolyzed by microorganisms.

ABSTRAK

Tujuan utama kajian ini adalah untuk mengkaji kesan bahan pemplastik baru yang tidak mengandungi ftalat iaitu batu-batuan terubahsuai (MR) dan kanji terhadap sifat-sifat mekanikal, fizikal, termal dan kebolehuraian polilaktik asid (PLA). Biokomposit-biokomposit bagi PLA, MR dan kanji telah disediakan dengan menggunakan kaedah penyemperitan dan diacu suntikan ke dalam bentuk-bentuk piawai untuk ujian regangan dan kelenturan. Sifat-sifat biokomposit tersebut telah diuji dengan ujian regangan dan kelenturan, ujian indeks kelikatan, spektroskopi inframerah transformasi Fourier (FTIR), mikroskopi elektron pengimbas (SEM), kalorimetri pengimbasan pembezaan (DSC) dan ujian keserapan air. Kajian terhadap kebolehuraian biokomposit dengan penanaman di dalam tanah. Hasil ujian telah menunjukkan MR telah meningkatkan sifat-sifat mekanikal sehingga ke tahap 30 w/w% dan kandungan optimum MR adalah 16.6 w/w% (PM0). Hasil ujian juga menunjukkan MR telah bertindak sebagai bahan pengisi pengukuhan dan bukan sebagai bahan pemplastik kerana terdapat pengurangan kadar pengaliran dan tiada perubahan pada suhu peralihan kaca. Apabila kanji ditambah kepada biokomposit PLA/MR, sifat-sifat mekanikalnya telah jatuh berkemungkinan disebabkan oleh penggumpalan partikel-partikel kanji. Kandungan optimum kanji adalah 15 w/w% (PMS15). Setelah pengadunan PLA dengan MR dan kanji, sampel PLA asli, PM0 dan PMS15 telah dibandingkan. Keputusan FTIR dan SEM menunjukkan MR adalah serasi dengan PLA dan kanji pula mengganggu keserasian antara PLA dan MR. Keputusan DSC juga menunjukkan penambahan MR dan kanji ke dalam PLA tidak mengakibatkan perubahan kepada penghabluran biokomposit tersebut. Penambahan kanji telah meningkatkan kebolehanserapan air dan kebolehuraian di dalam tanah kerana kanji cenderung untuk menyerap air dan mengalami hidrolisis oleh mikroorganisma.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS/ABBREVIATIONS

Al_2O_3	-	Alumina
ASTM	-	American Standard Testing Method
ATR-FTIR	-	Attenuate total reflectance Fourier transform infrared spectroscopy
CO_2	-	Carbon dioxide
CO_2^{-3}	-	Carbonate ion
DSC	-	Differential scanning calorimetry
MFI	-	Melt flow index
MR	-	Modified rock stone
OH	-	Hydroxyl group
PLA	-	Polylactic acid
PM	-	Polylactic acid/modified rock stone biocomposite
PMS	-	Polylactic acid/modified rock stone/starch biocomposite
TPS	-	Thermoplastic starch
PCL	-	Polycaprolactone
PHA	-	Poly(hydroxy alkanoates)
PEG	-	Poly(ethylene glycol)
PET	-	Poly(ethylene terephthalate)
PS	-	Polystyrene
SEM	-	Scanning electron microscopy
UV	-	Ultraviolet
%	-	Percent or percentage
w/w	-	Weight over weight
T_g	-	Glass transition temperature
T_c	-	Crystallization temperature

T_m	-	Melting temperature
χ_c	-	Degree of crystallinity
ΔH_m	-	Enthalpy of fusion melting
ΔH_c	-	Enthalpy of crystallization
ΔH_f	-	Enthalpy of fusion of purely crystalline

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polylactic acid (PLA) is the current momentum in the biopolymer technology, which defies other synthetic polymers and caught the eyes of scientists and industrialists, in term of biodegradability. This is PLA, the next generation saviour and the weapon to fight for the greener earth.

PLA belongs to the family of aliphatic polyesters commonly made from α-hydroxy acids which are considered biodegradable and compostable (Garlotta, 2001). Compared to other polymers, its stereochemical structure can be easily modified by polymerizing a controlled racemic mixture of L- and D- isomers to yield high molecular weight amorphous or crystalline polymers which are food grade material and is considered as safe (Conn, *et al*., 1995).

PLA is a thermoplastic, high-strength, high-modulus polymer that can be made from renewable materials for either industrial field or medical device market (Garlotta, 2001). It is also widely used as a biodegradable and renewable plastic as in service ware, grocery, waste-composting bags, mulch films, controlled-released matrices for fertilizers, pesticides and herbicides (Fang and Hanna, 1999). While its biodegradability ranges from several months up to two years compared to synthetic polymers which take 500-1000 years to biodegrade (Wang, *et al*., 2001).

However, despite these advantages, PLA also has its limitations that restrict its use in certain applications. The most important limitation is the brittleness due to its glass transition temperature (T_g) is higher than room temperature and with less than 10% elongation at break (Rasal and Hirt, 2008). Given that, its mechanical properties and elastic modulus are comparable to synthetic polymers such as polystyrene (PS) and poly(ethylene terephthalate) (PET) (Auras, *et al*., 2003, 2004 and Lim, *et al*., 2008).

Several modifications had been done to improve the processability, flexibility and ductility of PLA. Some incorporated other polymers into PLA to improve these properties. Another method is by blending PLA with plasticizer. A lot of studies had been done on the incorporation of plasticizer into PLA (Martin and Averous, 2001 and Labrecque, *et al*., 1997).

Ljungberg and Wesslen (2003) had studied the effect of tributyl citrate (TbC) and synthesized TbC oligomers which were long (heptamer, TbC-7) and short (trimer, TbC-3). Both oligomers and TbC were blended with PLA at 15 % (w/w). They found that the plasticers were able to reduce the T_g of PLA where TbC had the lowest T_g (25 ^oC).

Lemmouchi *et al*. (2009) studied the plasticization of PLA by using plasticizer, tributyl citrate (TBC) and synthesized copolymers poly($_{D,L}$-lactide)-b-poly(ethylene glycol) copolymers (PLA-b-PEG) designated as COPO1-5. Various formulations were used and all of the formulations were able to plasticize PLA. The lowest T_g was 15 ^oC owned by PLA:(COPO1/TBC) (75:25 w/w). The T_g was lowered when the amount of the plasticizers were increased.

While, the mechanical properties of PLA such as tensile strength and modulus can be improve by incorporation of additives for example inorganic materials. Gregorova, *et al.* (2011) studied the addition of mica and wood flour (WF) to the properties of PLA. The PLA was plasticized with 10 v/v% polyethylene glycol (PEG) before being blended with mica and WF 30 v/v% and mica/WF at 15/15 v/v%. They found that the tensile strength of the PLA composites were decreased when WF and mica/WF were added but increased when mica was added. While, the modulus of the PLA composites of three fillers were increased drastically. However, the tensile strain were decreased with the addition of the fillers.

Ayana, *et al.* (2014) studied the effect of nanoclay to the blend of PLA and thermoplastic starch (TPS). They used 40/60 w/w% PLA/TPS matrix and the percentage of nanoclay added was 0.5 and 1.0 phr clay with respect of dry starch. They found that the tensile strength, modulus and elongation at break of the nanocomposites were increased significantly up to 1.0 phr of nanoclay compared to the PLA/TPS composite.

On the other hand, PLA alone is expensive, and its biodegradability is from several months up to two years, which is still considered too long (Wang, *et al*., 2001 and Lee, *et al*., 2008a). The assimilation of starch into PLA as filler can improve the properties of PLA in a cheaper way. The introduction of starch to polyester-starch blends can maintain the great physical properties of the polyester, at the same time, reducing cost (Lee, *et al*., 2008a and Ayana, *et al.*, 2014). This is due to starch is cheap and fast biodegradability rate due to its water solubility (Simmons and Thomas, 1995).

Avella *et al*. (2000) had studied the properties of, polycaprolactone (PCL)/starch blends. They found out that the addition of starch maintains the tensile strength of the blends up to 30 w/w% starch with significant decrease of the values, 20-30 % lower. Further increase of the starch composition had drastically reduce the tensile strength due to poor adhesion between PCL and starch.

Yew *et al*. (2005) studied the effect of rice starch with PLA and found out that the maximum starch composition in the blend was 20 w/w%. Further addition of the starch had led to agglomeration and thus greatly reduce the tensile strength. They also reported that the addition of starch to PLA had increase the water absorption of PLA/starch biocomposites. This is due to the hygroscopic nature of starch. Moreover, the addition of starch also accelerated the enzymatic degradation of the biocomposite based on drastic decrease in tensile strength and surface erosion showed by SEM micrographs.

Shogren *et al.* (2003) also reported similar results where starch helped the degradation of PLA/starch biocomposites. They studied the biodegradation of PLA and poly(hydroxyester-ethers) (PHEE) with starch. Significant weight loss was observed up to 60 w/w% of starch content. Drastic decline in tensile strength was also observed in the PLA/starch biocomposites.

In order to improve the properties of PLA, a new inorganic phthalate-free plasticizer was used in this study. The new material is considered biodegradable and harmless to the environment since the major component of the material is rock stone powder. The addition of starch was also studied in order to reduce the amount of PLA and improve the biodegradability of the blends.

1.2 Problem Statements

Non-biodegradable plastic bags are posing threat to the environment because they are non-totally recyclable and/or biodegradable, thus causing municipal waste disposal problem to increase every year (Kirwan and Strawbridge, 2003 and Sorrentino, *et al.*, 2007). Hence, PLA offers to solve the problem due to its biodegradability.

Compostability of the biopolymer is important since recycling is cost expensive while composting allows the disposal of the wastes by soil burial (Siracusa, *et al*., 2008). However, based on previous studies (Hughes, *et al*., 2012, Jacobsen and Fritz, 1999, and Lim, *et al*., 2008), PLA is significantly brittle which bottleneck the application of the polymer. Therefore there is a need to improve the properties of the polymer.

The brittleness of PLA is due to the high glass transition temperature (T_g) above room temperature (around 50 - 60 ^oC) which limits its application in certain field (Garlotta, 2001). Therefore, to overcome this problem, various low molecular weight plasticizers are used for example glycerol, sorbitol and triethyl citrate (Shah, *et al*., 2008) in order to lower the T_g.

Since the study is aimed to produce a packaging product, soft and ductile characteristics are required. However, transparency is not necessary. Hence, miscibility of the plasticizer is not crucial. On the other hand, low mobility of the plasticizer is a must.

Modified rock stone (MR), a new phthalate-free plasticizer, patented and provided by Blapol Plastic Sdn. Bhd. looks promising. This is due to its composition which consists of 90% natural stone powder and the rest 10% are the additives, consist of alkane, stearic acid, ethylene propylene diene monomer (EPDM), silane (SiH_4), and amides. Since MR is a new material, it is of interest to study the effects of MR to PLA. Besides that, there were very few studies done on the blending of PLA with inorganic materials.

Apart from that, PLA is also quite expensive compared to the petroleum-based polymers due to its complicated processes. One way to reduce this is by adding a filler by reducing the amount of PLA in the composite. Starch is a cheap and biodegradable material due to its water solubility (Simmons and Thomas, 1995). Starch can also maintain the physical properties of PLA, at the same time, reducing cost (Lee, *et al*., 2008a). Thus, it is relevant to study the effects of starch as a filler and to improve biodegradability of the PLA/MR blends.

1.3 Research Objectives

Biodegradable biocomposites of PLA, MR and starch were manufactured by using an injection moulding. The objectives of this research were:

1. To study the effects of MR concentrationon on the tensile and flexural properties of PLA and PLA/MR biocomposites (PM).

2. To study the effects of starch concentration on the tensile and flexural properties of PLA/MR/starch biocomposites (PMS) at an optimum MR concentration as determined from objective 1.

3. To compare between optimal PM and PMS biocomposites in term of mechanical properties, melt flow index, thermal, infrared spectroscopic, morphological characterization, water absorption, and biodegradability.

1.4 Scopes of the Research

Preparation of PM biocomposites were carried out by varying the amount of PLA/MR (90/10, 80/20, 70/30 and 60/40 w/w%.). The blending was done by using a twin-screw extruder and then injection moulding to mould into standard tensile and flexural shapes. Tensile and flexural tests were conducted to find the optimum amount of MR in PM biocomposites.

Next, was the preparation of PMS biocomposites. The biocomposites were prepared by varying the amount of starch (10, 15 and 20 w/w%) with constant amount of PLA and MR (obtained from PM biocomposites optimization). The blending was also done by using twin-screw extruder and injection moulding. Tensile and flexural tests were conducted to find the optimum amount of starch of PMS biocomposites

Then, the optimum PM and PMS biocomposites were compared by using these testing and characterizations listed below.

a) Mechanical properties by using tensile and flexural tests.
b) Thermal behaviour by using differential scanning calorimetry (DSC).
c) The viscosity by using melt flow index (MFI).
d) The structural characterization by using Fourier transform infrared spectroscopy (FTIR).
e) Morphological characterization by using scanning electron microscopy (SEM).
f) Water absorption test.
g) Biodegradability test by using soil burial method.

1.5 Significance of Study

This study was focused on polylactic acid (PLA) as an effective alternative material for synthetic polymer products. This is because it can be recycled and is synthesized from renewable sources compared to other products which are derived from the non-renewable source; petroleum. PLA is also biodegradable plus harmless, which makes it a powerful tool for green technology without harming the environment.

Besides that, the properties of PLA is comparable or much better than that synthetic polymers. In the meantime, the brittleness of the PLA can be overcome by using plasticizer. Plasticizer used to plasticize PLA usually using glycerol, sorbitol and triethyl citrate but rarely plasticized by using other plasticizer. However, in this study, a new, non-toxic plasticizer was used which is modified rock stone (MR). MR not only can improve the properties of the PLA, but also environmental friendly.

Thus this study can help reduce the humongous amount of solid waste which mainly composed of non-degradable plastic materials. This means the tremendous cost used to manage those wastes can be reduced. Besides environmental friendly, this study can be applied in food and beverages field as packaging product since the materials that were used in this study are non-toxic.

On the other hand, the method used to process PLA is not complicated which is by using injection moulding. Processing PLA composites using injection moulding can produce maximum results, plus homogeneous blends. The new knowledge from this study is hoped can be applied to greater measures either in industrial, medical or environmental field.

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