Preparation and Properties of Degradable Durian Seed Starch/Low Density Polyethylene and Durian Seed Starch/Poly(ε-caprolactone) Composites

by

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LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
DSS	Durian seed starch
DMA	Dynamic Mechanical Analysis
E_B	Elongation at break
FTIR	Fourier Transform Infra-Red
LDPE	Low-density polyethylene
MFI	Melt flow index
MSW	Municipal solid waste
PPC	Poly(propylene carbonate)
PCL	Poly(ε-caprolactone)
PLA	Polylactic acid
PVA	Polyvinyl alcohol
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TPS	Thermoplastic starch
TEM	Transmission Electron Microscopy
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

T_{deg}	Final degradation temperature
Tg	glass transition temperature
T_0	Initial degradation temperature
T_m	Melting temperature
μm	Micrometer
nano-SiO_2	Nano silicon dioxide
nm	Nanometer
wt.	Weight

Penyediaan dan Sifat-sifat Komposit Kanji Biji Durian/Polietilena Berketumpatan Rendah dan Kanji Biji Durian/Poli(ε-caprolactone) Terdegradasi

ABSTRAK

Komposit bagi kanji biji durian (DSS)/polietilena berketumpatan rendah (LDPE) dan kanji biji durian (DSS)/poly(ε-caprolactone) (PCL) telah dikaji. Kajian ini terbahagi kepada tiga bahagian. Bahagian pertama merangkumi penyediaan dan pencirian pengisi, bahagian kedua adalah untuk mengkaji kesan kandungan pengisi ke atas komposit DSS/LDPE dan DSS/PCL, manakala bahagian terakhir adalah untuk mengkaji kesan nisbah adunan ke atas komposit PCL/LDPE/DSS. Gliserol telah digunakan sebagai agen pemplastik untuk mengubahsuai DSS tersebut pada 20 % berat daripada DSS yang digunakan. Analisis saiz zarah menunjukkan bahawa saiz purata DSS yang digunakan dalam penyelidikan ini ialah 10 μm. Mikroskop pengimbas elektron (SEM) bagi kedua-dua DSS asli dan diubahsuai telah menunjukkan yang zarah-zarah adalah berbentuk tak sekata dan beragglomerak. Analisis Fourier Transform Infra Red (FTIR) bagi DSS asli dan yang diubahsuai menunjukkan pengubahsuaian tersebut adalah tidak mudah dikesan kerana kedudukan puncak-puncak penyerapan adalah sama. Suhu lebur (T_m) bagi DSS diubahsuai telah menunjukkan peningkatan kepada suhu lebih tinggi berbanding DSS asli seperti ditunjukkan oleh analisis permeteran kalori pengimbasan kebezaan (DSC). Tiga peringkat degradasi bagi DSS diubahsuai telah ditunjukkan oleh analisis permeteran graviti haba (TGA) melibatkan kemeruapan air, gliserol, dan penguraian kanji tersebut. Satu siri komposit DSS/LDPE, DSS/PCL, dan DSS/PCL/LDPE dengan 5, 10, dan 15 % kandungan berat pengisi telah disediakan dengan menggunakan pencampur dalaman Brabender Plastograph EC pada suhu 150 °C dan 30 pusingan per minit selama 6 minit. Nisbah adunan yang telah digunakan bagi komposit hibrid PCL/LDPE ialah 25/75. Kajian-kajian ke atas sifat-sifat komposit telah dijalankan oleh FTIR, ujian tegangan, indeks aliran leburan (MFI), TGA, DSC dan ujian terbiodegradasi mudah. Kekuatan tegangan dan pemanjangan dari ujian pemecahan (E_B) berkurangan setelah DSS ditambahkan ke dalam LDPE dan PCL disebabkan oleh pengaglomeratan DSS tersebut dan rekatan antara muka yang lemah di antara pengisi dan LDPE dan matriks PCL. Modulus anjal telah meningkat apabila DSS ditambah ke dalam LDPE dan PCL. Komposit DSS/PCL telah ditemui mempunyai sifat-sifat mekanikal yang lebih baik berbanding komposit DSS/LDPE. Analisis TGA menunjukkan bahawa penambahan DSS tersebut telah memperbaiki kestabilan haba bagi LDPE dan PCL. Tambahan pula, suhu degradasi (T_0) dan kehilangan berat menunjukkan DSS/LDPE mempunyai kestabilan haba yang lebih baik berbanding dengan komposit DSS/PCL. Suhu lebur (T_m) bagi komposit DSS/LDPE dan DSS/PCL menunjukkan penurunan apabila kenaikan kandungan pengisi telah ditambahkan seperti ditunjukkan oleh DSC. Pada kandungan pengisi yang sama, komposit LDPE/DSS tersebut memberikan suatu nilai T_m yang lebih tinggi berbanding dengan komposit PCL/DSS. Walaubagaimanapun, penggunaan DSS ke dalam komposit hibrid PCL/LDPE tersebut telah menurunkan sifat-sifat mekanikal serta sifat-sifat penurunan haba bagi komposit tersebut. Tiada perubahan ketara bagi nilai T_m pada komposit hibrid PCL/LDPE/DSS tersebut seperti ditunjukkan dalam analisis DSC yang menyatakan bahawa komposit hibrid LDPE/PCL adalah sukar larut campur atau tidak serasi pada skala molekul dengan DSS. SEM menunjukkan bahawa semakin tinggi kandungan pengisi akan menyebabkan luas antara muka di antara pengisi dan matriks polimer menjadi lemah dan menghasilkan ubah bentuk yang rapuh bagi komposit tersebut.

Walaubagaimanapun, SEM bagi komposit PCL/LDPE/DSS menunjukkan morfologi yang lebih lemah berbanding dengan komposit DSS/LDPE dan DSS/PCL yang mana lebih banyak pengisi yang terkeluar, ketidakbasahan bagi pengisi oleh matriks dan serakan pengisi yang lemah dalam matriks polimer telah diperhatikan. Ujian terbiodegradasi mudah telah dijalankan ke atas setiap siri komposit-komposit tersebut, di mana analisis FTIR telah dibuat untuk menentukan kebolehdegradasi komposit-komposit tersebut. Keputusan-keputusan menunjukkan bahawa semua komposit menunjukkan tanda-tanda kebolehdegradasi secara semulajadi.

Preparation and Properties of Degradable Durian Seed Starch/Low Density Polyethylene and Durian Seed Starch/Poly(ε-Caprolactone) Composites

ABSTRACT

Composites of Durian seed starch (DSS)/low-density polyethylene (LDPE) and durian seed starch (DSS)/poly(ε-caprolactone) (PCL) were investigated. The study is divided into three parts. The first part involves the preparation and characterization of the filler, second part is to study the effect of filler content on the DSS/LDPE and DSS/PCL composites, while the last part is to study the effect of blend ratio on the PCL/LDPE/DSS composites. Glycerol was used as the plasticizer agent to modify the DSS at 20 wt. % of the DSS. Particle size analysis revealed that average size of DSS used in this research is 10 μm. Scanning electron microscopy (SEM) of both native and modified DSS was found to be in irregular shape particles and shows agglomeration. The Fourier Transform Infra-Red (FTIR) analysis of native and modified DSS indicates that the modification is not easily detected because the positions of absorbance peaks are similar. The melting temperatures (T_m) of the modified DSS were observed to be shifted to higher temperature compared to the native DSS shown by the differential scanning calorimetry (DSC) analysis. Three-stage degradation of the modified DSS was observed by thermogravimetric analysis (TGA) attributed to the volatilization of water and glycerol, and the decomposition of the starch. A series of DSS/LDPE, DSS/PCL, and DSS/PCL/LDPE composites with 5, 10, and 15 wt. % of filler content were prepared using Brabender Plastograph EC internal mixer at temperature at 150 ºC for 6 minutes. The blend ratio used for PCL/LDPE hybrid composites was 25/75 ratio. Studies on their properties were carried out by FTIR, tensile test, melt flow index (MFI), TGA, DSC and simple biodegradability test. Tensile strength and elongation at break (E_B) decreased as DSS was added into LDPE and PCL due to the agglomeration of the DSS and poor interfacial adhesion between the filler and LDPE and PCL matrix. Elastic modulus was increased as DSS was added into LDPE and PCL. DSS/PCL composites were found to have better tensile properties than DSS/LDPE composites. TGA analysis shows that the addition of the DSS has improved the thermal stability of LDPE and PCL. Furthermore, DSS/LDPE composites show higher onset degradation temperature (T_0) and weight loss indicate that DSS/LDPE have better thermal stability compared to DSS/PCL composites. The T_m of the DSS/LDPE and DSS/PCL composites has reduced as filler content was increased as shown by the DSC results. In the same filler content, the LDPE/DSS composites give a higher T_m values than the PCL/DSS composites. The incorporation of DSS into the PCL/LDPE hybrid composites however has reduced its tensile properties as well as the thermal degradation properties of the composites. There is no significant change of the T_m values in the PCL/LDPE/DSS hybrid composites shown in DSC analysis indicate that LDPE/PCL hybrid composite is hardly miscible or incompatible at the molecular scale with the DSS. Scanning electron microscopy (SEM) shows that higher filler content caused poor bonding at the interfacial area between filler and matrix polymer which lead to the brittle deformation of the composite. However, SEM of PCL/LDPE/DSS composites show poorer morphology than DSS/LDPE and DSS/PCL composites which more filler pulled-out, de-wetting of the filler by matrix and poor filler dispersion in polymer matrix were observed. Simple biodegradability test was conducted on each series of the composites, where FTIR analysis was done to determine the degradability of the composites. Results showed that all composites are subjected to degradation.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Plastic wastes are becoming major environmental problem to the worldwide (Nawang et al., 2001). Many attempts have been created to solve this major problem. There are some methods have taken place to overcome the problem. These include recycling, pyrolysis and hydrolysis, chemical recovery, biodegradation, and incineration with energy recovery. With the excessive use of plastic material and at the same time increasing pressure because of this problem, the need of biodegradable plastics and plastic wastes biodegradation has gained high attention around the world (Shah et al., 2008). Recently, efforts have been focused more on the incorporation of the natural biopolymer into the synthetic polymers to produce biodegradable plastics due to the negative impacts of other methods such as pollution and consume high costs.

Polyethylene (PE) is one of the majorly used synthetic plastics as shown in Figure 1.1. This is due to its wide range of physical properties and suitability to most of the commercial thermoplastics fabrication process. One of the most important criteria in this resin is its cheaper price that can give a competitive edge compared to other materials; polymeric and non-polymeric materials (Peacock, 2000). Low-density polyethylene (LDPE) is used in the manufacture of blow-moulded bottles, film bags, food boxes, sacks and sheeting, flexible piping and hosepipes, household articles such as bowls and buckets, telephone cable sheaths, toys, etc. (UNEP, 2009). Their useful physical and chemical properties such as durable, easy to process, and characteristically inert have been the main cause of its broad applications in many industrial uses (Mark, 1999). LDPE is known to be hardly degraded after disposal and this can cause pollution to the environment and affects the ecological system (Bastioli, 2005). The hydrophobicity of LDPE is one of the reasons to its high resistance to the microorganism attack. Once it is discarded, large quantities of this material will result in undesired litter which will harm the sewage and further disturb the aquatic ecosystem. This situation will become worst when our environment become hazardous because of these problems.

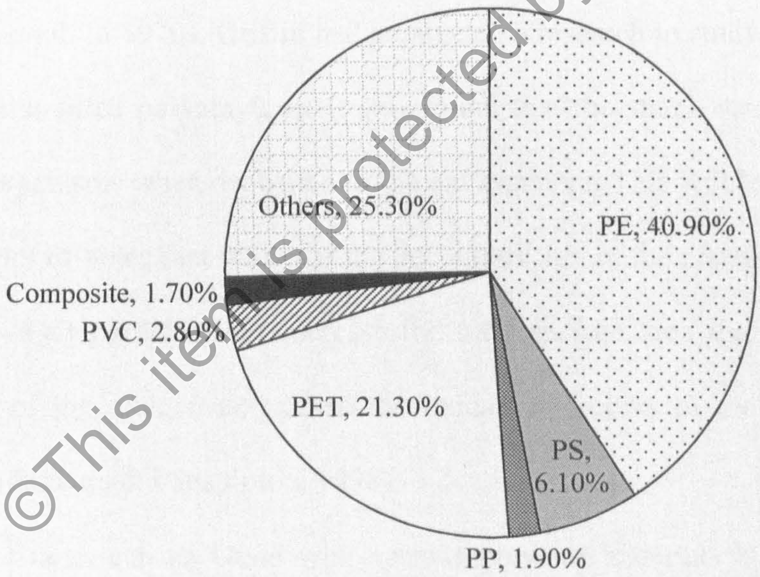

Figure 1.1: Waste plastics composition in the municipal solid waste (MSW) (UNEP, 2009).

Biodegradation is a natural process where the organic chemicals in the environment are being converted to simpler compounds, mineralized and redistributed through elemental cycles such as carbon, nitrogen, and sulphur cycles (Chandra & Rustgi, 1997). In terms of biodegradable polymer, it can be divided into naturally occurring and synthetic biodegradable polymers. Starch-based polymer is one of the naturally occurring biodegradable polymers which is low cost, abundant availability, and can be added as filler in blends with other polymers. Starch contain hydroxyl groups and readily biodegradable. Many efforts have been made to develop biodegradable polymers based on starch in order to overcome the problems caused by the petroleum-based polymers (Koenig & Huang, 1995; Avella et al., 2000).

Starch had been widely studied as an important natural polymer for many applications such as packaging, agricultural, and biomedical applications due to its low cost, abundant availability, and biodegradability (Prachayawarakorn et al., 2010). It can be mixed into the thermoplastics to increase the biodegradability and reduce the cost of the material. In 1970s, Griffin had conducted a research to study the biodegradability of the starch filled polyethylene. It was found that the starch was consumed by various microorganisms when deposited in the environment. This will leave the polymer blends with a lot of holes that will ease the decomposition of the materials into small particles. These small particles will increase the total surface area that will further allow the access of the oxygen and cause the oxidation process of the polyethylene becomes easier (Bikiaris & Panayiotou, 1998).

Starch can be blend with various polymer materials by conventional process. However, due to its hydrophilic properties of the starch, it cannot form a film solely. To obtain a homogenous blend, the interfacial tension needs to be reduced to improve the characteristics of the blend components. The addition of a plasticizer to the starch will allow the starch molecules to behave in a similar behaviour to common thermoplastic synthetic polymers. It will improve the incorporation of starch in LDPE and enhancing the biodegradability of the blends. Starch prepared in this way is known as thermoplastic starch (TPS) (Rodriguez et al., 2004). Lawton and Fanta (1994) reported that compounding of the starch-LDPE-plasticizer mixtures into pellets before film formation could improve the blending and dispersion of the two immiscible polymers. Palm oil based glycerol can be function as compatibilizer in LDPE/starch blend besides reducing the production cost (Sastry et al., 1998). Furthermore, the usage of this oil can also increase the degradation level of the LDPE/starch since it can be attacked by microorganism after being disposed.

On the other hand, the examples of synthetic biodegradable polymers are poly(ε-caprolactone) (PCL), polyvinyl alcohol (PVA), and polylactic acid (PLA) to name a few. PCL is aliphatic polyester which is obtained through petrochemical processes. PCL is highly flexible and attractive because of its good mechanical properties. PCL is a well-known polymer because it is a synthetic polymer that able to biodegrade and characterized by a high elongation at break. It is degradable in several water bodies such as lakes, river, sewage, and paddy soil (Eldsater et al., 2000). PCL is therefore suitable for many uses and able to be blend with various polymers due to its compatibility with them (Rezgui et al., 2005). However, PCL is often perceived as an obstruction for use as common thermoplastic due to its low melting point of around 60°C (Pierre et al., 2008).

It is known that the price for PCL resins is much higher compared to the other resins. Many attempts have been made to blend PCL with various types of starches to reduce the cost (Matzinos et al., 2002). The use of these types of polymers may benefits the environment by substituting the large number of non-biodegradable synthetic polymers that exist on earth (Eldsater et al., 2000). Therefore, this study is conducted to produce a biodegradable blend that utilizes the starch and the synthetic polymers which are LDPE and PCL.

1.2 Problem Statements

The high consumption of plastics due to economic development has caused pollution from the large amount of plastic wastes. LDPE was found to be the highest contributor to the number of plastic wastes since it is one of the majorly used synthetic plastics. Furthermore, it is hardly degraded by the microorganisms after disposal. The increasing public concern about environmental pollution has promoted the development of biodegradable plastics.

Synthetic biodegradable polymer such as PCL is a promising option in order to produce the biodegradable plastics. PCL is a plastic material with a very high flexibility. The elongation at break and tensile strength of PCL films have been reported to be higher than 1100 % and 33 MPa, respectively (Fujimaki, 1998). However, the high price of the PCL has limited in producing the biodegradable plastics. Therefore, many research attempts have been focused on the use of natural biopolymers such as starch which is also fully biodegradable.

The use of durian seed starch (DSS) as natural filler has not yet been widely used nor commercialized. In 2012, a study has been done by Osman & Zakaria that incorporates the durian seed flour in the PP and HDPE composites (Osman & Zakaria, 2012). However, the use of DSS as natural filler in the LDPE has not yet been studied. Therefore, this research will further study the incorporation of the DSS as natural filler in the LDPE and PCL. In order to reach a balance between cost and material properties, it is reasonably viable to incorporate the DSS to the mix of both types of synthetic polymer, which are LDPE and PCL in order to obtain their desired properties. This may enhance the degradability of the LDPE and reduce the cost of producing the biodegradable plastics.

1.3 Objectives

The main objective of this study is to prepare a degradable composite containing DSS and LDPE or PCL blends. This objective is divided into;

i. To investigate the effect of DSS on the properties of the DSS/LDPE and DSS/PCL composites;
ii. To investigate the effect of DSS on the properties of DSS filled PCL/LDPE hybrid composites; and
iii. To investigate the biodegradability of the DSS/LDPE, DSS/PCL and PCL/LDPE/DSS composites.

1.4 Scopes of Study

In order to achieve the objectives of this study, the DSS/LDPE and DSS/PCL composites were compounded by using the internal mixer at temperature of 150 ºC with rotor speed of 30 min^{-1}. Prior to compounding, the DSS was going through modification by using 20 wt. % of glycerol as plasticizer. The filler loadings used in this study were 0, 5, 10, and 15 wt. %. For PCL/LDPE hybrid composites, the ratio of 25/75 was used. To further investigate the properties of the composites, characterization and testing were conducted on all composites series. Melt flow index (MFI) measurement of each blend was conducted to determine the ability of the materials' melt to flow under pressure. The morphological analysis was studied through the use of scanning electron microscope (SEM), while the thermal analysis on the composites was determined by means of differential scanning calorimetry (DSC) and thermogravimetric analysis

(TGA). Fourier transform infra-red (FTIR) analysis was conducted to identify and study the chemical groups of the composites while the mechanical properties such as tensile strength, elastic modulus, and elongation at break were determined using the tensile testing machine. Finally, the simple biodegradability test was conducted to investigate the biodegradability of all composites.

1.5 Outline of Thesis Structure

The thesis has been divided into five (5) chapters and each chapter deals with an aspect of the overall problem of understanding the properties behaviour of the DSS filled LDPE or PCL composites.

- Chapter 1 covers the introduction of the thesis. It provides an overall introduction for the study including a brief introduction about research background, problem statements, objectives and scopes of the study, and outline of the thesis;
- Chapter 2 provides a comprehensive review on natural filler namely starch in polymer matrices, along with some review of related works reported in the literature;
- Chapter 3 details the materials, process flow, instruments, and experimental procedures applied in this research;
- Chapter 4 focuses the preliminary studies on filler characterization; provides the characterization and properties on the effect of the filler content on properties of DSS/LDPE, DSS/PCL, and PCL/LDPE/DSS composites;

- Chapter 5 presents conclusions on the present work and suggestions for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Plastics and Environment

Plastics were first invented in 1860, but have only been widely used in the last 30 years. Global production and consumption of plastics have increased, from less than 5 million tons in the year 1950 to 260 million tons in the year 2007 (Moinuddin, 2011). One of the major usages of plastics is in packaging due to its cheaper price and lightweight. In addition, plastics have good mechanical properties and transparency. However, besides its good properties, these petroleum-based products can be hazardous to the environment. Most plastics are non-biodegradable and they take long time to break down in landfill, estimated to be more than a century. These types of disposal of the plastics wastes release toxic gas; which has negative impact on environment. The resistance to natural biodegradation has becoming more and more problematic especially when they are use only a short period of time (Vert, 2009).

Besides the disposal on landfills, plastics wastes especially plastics packaging that float in water bodies such as rivers, seas and lakes may also endangering the animals that live in those habitats. Along with this, hundreds of thousands of sea turtles, whales and other marine mammals die every year eating discarded waste plastic bags which was mistaken as their food (Tomas et al., 2002). The aquatic ecosystem such as phytoplankton and algae may also been affected because of unreachable sunlight and oxygen from the atmosphere (Redford et al., 1997).

Until now, plastics have created so much pollution and landfill crisis that various attempts have been made to solve these problems. One of these attempts is to create a biodegradable polymer by adding natural biodegradable materials such as starch and lignocellulose materials into the synthetic polymer to produce biodegradable plastics.

2.2 Biodegradable Polymers

Biodegradable polymer is a newly emerging field. A vast number of biodegradable polymers have been synthesized and some microorganisms and enzymes capable of degrading them have been identified. In developing countries, environmental pollution by synthetic polymers has assumed dangerous proportions. As a result, attempts have been made to solve these problems by including biodegradability into polymers in everyday use through slight modifications of their structures.

Biodegradation is a natural process by which organic chemicals in the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles (Chandra & Rustgi, 1997). Biodegradation can only occur within the biosphere as microorganisms play a central role in the biodegradation process. Biodegradable polymers can be divided into two main categories; naturally occurring biodegradable polymers and synthetic biodegradable polymers (Danjaji, 2001). Naturally occurring biodegradable polymers including polysaccharides such as starch, cellulose, and chitosan, while the synthetic biodegradable polymers are normally polymers with hydrolysable backbone or