UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PROCESSING AND CHARACTERIZATION OF POLYCAPROLACTONE (PCL) / SAGO STARCH BLENDS AS BIODEGRADABLE POLYMERS

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Engineering Technology (Automotive Technology) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Engineering Technology of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Mechanical Engineering Technology (Automotive Technology) with Honours. The member of the supervisory is as follow:

……………………………….

(Project Supervisor)

ABSTRACT

Biodegradable polymers undergo chain cleavage at the polymer chains as a result of the action of microorganisms and/or enzymes. The rate of the degradation may vary from hours to years depending on the molecular structures of the polymers. Polycaprolactone (PCL) is one of most-known biodegradable polymers. However, PCL is expensive and limited in resources. This study, therefore, attempted to blend PCL with naturally abundant sago starch at varied mass compositions to lower the cost and increase biodegradability. The blends were prepared by using solvent casting method which involved two main processes; dissolution of PCL and sago starch in chloroform and solvent evaporation of the blends obtained. The blends tend to shrink as sago starch increased suggesting that sago starch was an excellent filler that can be incorporated easily into the PCL polymer matrix phase. The thermal properties were measured by Differential Scanning Calorimeter (DSC). The melting temperatures and latent heats of fusion of the PCL/sago starch blends ranged between 64.92-67.07 °C and 27.97-51.21 kJ/kg, respectively. Based on DSC curve, it can be concluded that no significant change in the thermal properties indicates no chemical reaction occurred between sago starch molecules and PCL chains. The mechanical properties of the blends were measured by tensile machine of 50 kN load with constant crosshead speed of 50 mm/min. The strength and ductility of the blends were found to decrease with increasing starch content. For example, the ultimate tensile strength and elongation % at break for PCL 50 wt %/sago starch 50 wt % were 1.35 MPa and 156%, respectively, which were lower than that of pure PCL (ultimate tensile strength = 3.94 MPa, elongation % at break = 1528 %. The addition of starch to PCL, however, seems to increase the tensile Young's modulus of the blend suggesting that blends became stiffer with increasing starch contents. The biodegradability of PCL/sago starch blends was verified by soil burial biodegradation test which following ASTM 988-12 standard. The sample films were buried in a multilayer substrate consisting of mineral bed/soil mixture and left for 10 days. The mass loss of the sample films were ranged between 80-90 %. The sample with high starch contents found to degrade faster than that of pure PCL. The polyethylene film that was used as a control in this test did not degrade at all. Based on their biodegradability, mechanical and thermal properties, it can be concluded that these PCL/sago starch blends possess properties that make them technically and economically viable as biodegradable polymers that can be applied in various applications particularly in the field of packaging, biomedical and agricultural.

ABSTRAK

Polimer terbiodegradasi menjalani rantaian belahan pada rantai polimer akibat daripada tindakan mikroorganisma dan/atau enzim. Kadar degradasi mungkin berbeza dari jam ke tahun bergantung kepada struktur molekul polimer. Polycaprolactone (PCL) adalah salah satu polimer boleh biourai yang terkenal. Namun, PCL mahal harganya dan mempunyai sumber yang terhad. Oleh itu, dalam kajian ini PCL terlarut bercampur dengan kanji sagu pada komposisi jisim yang berbeza-beza untuk mengurangkan kos dan meningkatkan tahap biourai. Campuran telah disediakan dengan menggunakan kaedah pemutus pelarut yang merangkumi dua proses utama; percampuran PCL/kanji sagu dalam kloroform dan penyejatan pelarut campuran yang diperolehi. Campuran didapati mengecut apabila jumlah kanji sagu meningkat menunjukkan bahawa kanji sagu adalah pengisi yang bagus dan mudah dicampurkan ke dalam fasa polimer matriks PCL. Sifat haba diukur oleh kalorimeter pengimbas perbezaan (DSC). Suhu lebur dan haba pendam pelakuran campuran PCL / kanji sagu adalah antara 64.92-67.07 ° C dan 27.97-51.21 kJ / kg, masing-masing. Berdasarkan graf DSC, dapat disimpulkan bahawa tidak ada perubahan ketara dalam sifat haba yang menunjukkan tiada tindak balas kimia berlaku antara molekul kanji sagu dan rantai PCL. Sifat mekanik campuran diukur oleh mesin tensil dengan 50 kN beban dan kelajuan tetap kepala palang 50 mm / min. Kekuatan dan kemuluran campuran didapati berkurangan dengan meningkatkan kandungan kanji. Sebagai contoh, kekuatan tensil dan % pemanjangan apabila putus untuk PCL 50 wt% / kanji sagu 50 wt% masing-masing adalah 1.35 MPa dan 156%, lebih rendah daripada PCL tulen (kekuatan tensil = 3.94 MPa, % pemanjangan apabila putus = 1528%. Bagaimanapun, penambahan kanji kepada PCL, meningkatkan modulus Young ini menunjukkan bahawa campuran menjadi lebih keras dengan peningkatan kandungan kanji. Tahap biodegradasi PCL / campuran kanji sagu telah disahkan dengan ujian biourai tanah berdasarkan standard ASTM 988-12. Filem-filem sampel telah ditanamkan dalam substrat yang terdiri daripada pelbagai lapisan tanah dan dibiarkan selama 10 hari. Pengurangan jisim filem sampel adalah antara 80-90%. Kandungan kanji yang tinggi didapati mempecepatkan proses biodegradasi berbanding dengan PCL tulen. Filem polietilena yang digunakan sebagai kawalan tidak terurai sama sekali. Berdasarkan keputusan kajian biodegradasi, sifat-sifat mekanikal dan haba, bagi PCL /sagu kanji mempunyai ciri-ciri yang menjadikannya berpotensi dari segi teknikal dan ekonomi sebagai polimer boleh biourai yang boleh diaplikasikan dalam pelbagai kegunaan terutamanya dalam bidang pembungkusan, bioperubatan dan pertanian.

DEDICATION

This thesis is dedicated to my beloved parents, supervisor and friends for their endless help and great guidance to complete the final year project successfully.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

APES	-	Aliphatic Polyester
ASTM	-	American Society For Testing And Materials
ATR	-	Attenuated Total Reflectance
BPA	-	Bisphenol A
CH	-	Chitosan
cm	-	centimetre
CO_2	-	Carbon Dioxide
CS	-	Corn Starch
DEHP	-	di-(2-ethylhxyl) phthalate
DDS	-	Drug Delivery System
DNA	-	Deoxyribonucleic Acid
DSC	-	Differential Scanning Calorimeter
E	-	Young's Modulus
g	-	gram
ha	-	Hectare
kg	-	Kilogram
kJ/kg	-	Kilojoules per Kilogram
HDPE	-	High Density Polyethylene
H_2O	-	Water
LCDA	-	Land Custody and Development Authority
LCD	-	Liquid Crystal Display
LED	-	Light-emitting Diode
LDPE	-	Low Density Polyethylene
LLDPE	-	Linear Low Density Polyethylene
m	-	metre
mg	-	milligram
mL	-	millilitre
mm	-	millimetre

MPa	-	Megapascal
N_2	-	Nitrogen
PCL	-	Polycaprolactone
PET	-	Polyethylene Terephthalate
PE	-	Polyethylene
PP	-	Polypropylene
PS	-	Polystyrene
PUR	-	Polyurethane
PVA	-	Polyvinyl Acetate
PVC	-	Polyvinyl Chloride
RM	-	Ringgit Malaysia
SEM	-	Scanning Electron Microscopy
SiO_2	-	Silicon Dioxide
SS	-	Sago Starch
T_d	-	Decomposition Temperature
T_g	-	Glass Transition Temperature
Tm	-	Melting Temperature
TPS	-	Thermoplastic Starch
TS	-	Tensile Strength
WVPc	-	Water Vapour Permeability Coefficient
°C	-	Degree Celsius
wt%	-	Weight Percentage
%	-	Percentage
ΔHm	-	Heat of Fusion
σ	-	Yield Stress
ε	-	Epsilon

CHAPTER 1

INTRODUCTION

1.0 Introduction

This chapter discusses the background of this research in order to define its main focus. The problem statement is then defined in order to identify the real problems that are being focused in this study. General and specific objectives of the research are stated clearly as a guideline for the research. The specific focus and limitation of the research are also introduced in the scope of research.

1.1 Project Background

Awareness towards environmental threat had arisen from the uncontrollable usage of conventional non-biodegradable synthetic polymers which are made from petroleum by-products. These synthetic polymers have been discarded in vast amount through short period of time. The garbage disposal of domestic waste dumpsite, as shown in Figure 1.1, led to the generation of excessive amount of pollutant in the environment.

Figure 1.1 A garbage disposal dumpsite

There are two key solutions to overcome overloaded garbage disposal at the dumpsite. The solutions are; by recycling and by using biodegradable polymers to substitute the conventional polymers. Recycling involves reprocessing old materials into new products thus preventing the waste of potentially useful materials (M Spilka et al., 2008). Although recycling domestic waste can be helpful in reducing garbage disposal, it is not economically feasible because it consumes a huge amount of time and effort. Recycling tons of garbage will require separate factories that will result in more pollution and energy consumption for cleaning, sorting, storing and transporting waste materials.

The government also must set a firm and consistent recycling policy. The policy should be committed on reducing landfill waste to the maximum. Each residential area and state agency should facilitate practicable means to separate plastics, paper, metals and other recyclable items. The processes of separating waste into different types of bins, as shown in Figure 1.2, at every recycling centre needs high cost.

Figure 1.2 Locating recycling bins as part of recycling campaign

The awareness among the society also extremely important to ensure this recycling policy successfully implemented. The step of creating awareness through campaign will not only cost money but also take time for the society to practice recycling in a long run.

Another solution is by using biodegradable polymers. These polymers are now in high demand to overcome environmental problems of waste disposal. In some aspects, the initiative of using biodegradable polymers shows more promising results than recycling and it has been gradually implemented in line with the government attempt to reduce the amount of solid waste in dumpsite thus reduce the impacts of pollution towards environment.

Biodegradable polymers are polymers that can undergo a degradation process known as biodegradation. It is defined as polymers with similar properties of conventional polymer but can be decomposed after being disposed to the environment by the activity of microorganism (Tharanathan, 2003).

The “No Plastic Bag Day’ was launched by the Ministry of Domestic Trade Cooperative and Consumerism (MDTCC) in January 2011 (I. S. Zen et al., 2013). Recently, ban on plastic bags in Malaysia had been enforced more strictly by conducting periodical checks on all premises to ensure its effectiveness. Consumers need to bring along their own shopping bags after the declaration of total ban on plastic bags which are made from petroleum by-products at all supermarkets and shopping malls. Although, the total ban of using plastic bags from petroleum by-products had been implemented strictly, government still allow consumer to use plastic bags but only limited to the bags that are made from biodegradable polymers.

In this study, polycaprolactone (PCL) was used as a biodegradable polymer. Polycaprolactone (PCL) is an aliphatic polyester that is very well known for its biodegradability ; low melting point (60°C) and glass transition temperature (-60°C). Another unusual property of PCL is its high thermal stability with decomposition temperature, T_d of 350°C which is higher as compared to that of other aliphatic polyesters that in between 235 and 255°C (Pachence et al., 2007). Their hydrolysable ester linkages, of which the chemical structure is shown in Figure 1.3, make them biodegradable.

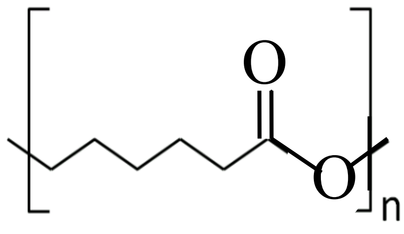

Figure 1.3 Chemical structure of PCL

PCL is hydrophobic and partially crystalline types of polyester with high biodegradability. PCL can completely degraded by the action of aerobic and anaerobic microorganisms in various environments. However, PCL is expensive and limited in resources as it is made from non-renewable sources. It needs to be blended with natural polymers such as starch to lower the cost and increase its biodegradability.

Starch is a natural polymer regenerated from carbon dioxide and water by photosynthesis in plants. It mainly composed of amylase and amylopectin. Figure 1.4 shows their chemical structures.

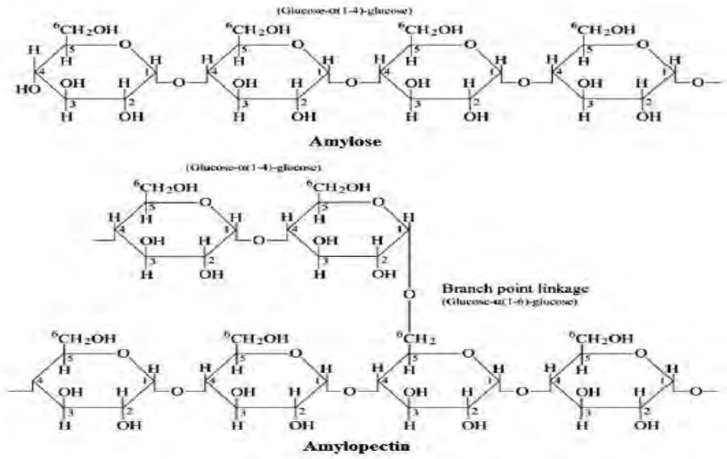

Figure 1.4 Chemical structure of starch

The use of starch in this study is especially important since Malaysia have abundant resources of sago starch majorly in Sarawak. For many centuries the people that inhabiting swamp forest of Oya, Mukah, Igan, Balingian and Dalat districts in Sarawak have live off the sago palm as their main resources (Morris, 1977).

Sago starch, as shown in Figure 1.5, is white and slightly pinkish in colour extracted from spongy centre of palm stems that have low solubility in water and alcohol. Sago starch is not only has unlimited renewable recourses but also exhibits complete biodegradability with inexpensive price.

Figure 1.5 Sago starch

Processing of PCL with starch blends in past research used various methods such as extrusion and melt blending method. In this study, PCL was blended with sago starch by using solvent casting method.

1.2 Problem Statement

Nowadays, environmental issues such as global warming and greenhouse effect have become greatest threat faced by the earth. The environment has taken its tolls because of irresponsible human activity. One of the major causes of the problems is poor waste management. The astounding amount of landfill waste produced each year is growing rapidly. Despite efforts by many of us to practice 4R (Refuse, Reduce, Reuse, Recycle), unfortunately we are still generating more garbage and it is unlikely to decrease.

Toxic gases that released from landfills undoubtly produce harmful greenhouse gases that will change the climate of its surroundings. Water pollution could also happens when toxic waste leaches from the landfills into soil and groundwater seeping through nearby river therefore, poisoning not only animal and plant but also human itself. Thus, the development of biodegradable polymers is extensively being studied as one alternative solution to overcome overloaded landfills waste problem. It is not only reduce the amount of waste but also promote cost saving.

Polycaprolactone (PCL) is well known biodegradable polymer. However, it is expensive and limited in resources. In order to reduce the cost of production, PCL usually blended with low cost natural polymer from renewable resources such as starch and cellulose. This study used sago starch to minimize the production cost of biodegradable polymers. Besides that, sago starch is easy to obtain locally due to it plenty resources.

In this study, PCL is blended with sago starch at varied mass composition. The effect of sago starch on the biodegradability, thermal properties and mechanical properties of the blends was investigated.

1.3 Objective of Research

The research objectives were divided into two; general and specific objectives. These objectives clearly articulate its purpose as a main guide in conducting this research and describe aim of it.

1.3.1 General Objective

To process and characterize the polycaprolactone (PCL)/sago starch blend as biodegradable polymers at varied mass compositions to lower its cost and increase the biodegradability.

1.3.2 Specific Objectives

i. To prepare PCL/sago starch blends as biodegradable polymers at varied mass compositions by using solvent casting method.

ii. To determine the thermal and mechanical properties of PCL/sago starch by using Differential Scanning Calorimeter (DSC) and tensile machine, respectively.

iii. To study the effect of sago starch to the biodegradability of the blends through soil burial biodegradation test.

1.4 Scope of Research

The main scope of this study was the processing the polycaprolactone (PCL)/sago starch blends as biodegradable polymers at varied mass compositions. The thermal and mechanical properties of the blends were characterized by using Differential Scanning Calorimeter (DSC) and tensile machine, respectively. Throughout this research, the biodegradability test for the blends was conducted in soil burial biodegradation test.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter first discusses the classification of biodegradable polymers. The properties and applications of biodegradable polymers are also highlighted. This review then introduces several researches findings on biodegradable polymers particular related to polycaprolactone (PCL) and sago starch. The mechanism of biodegradation has also been reviewed.

2.1 Polymer

The word 'polymer' was originated from Greek word: *poly* means many and *mer* means unit or parts. A polymer is a large molecule or macromolecule that composed of many repeated structural units joined by covalent bonds. Figure 2.1 illustrates that polymers, both natural and synthetic, which are created via polymerization of many small molecules, known as monomers.

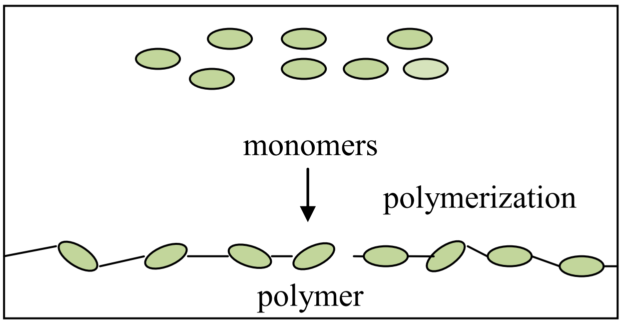

Figure 2.1 Conversion of monomers to polymer

R. Ebewele (2000) stated that polymers can be classified as addition or condensation polymers depending on the type of polymerization reaction involved in their synthesis. Other classifications are based on polymer structure, polymerization mechanism and thermal behaviour which serve as fundamental components to biological structures and functions.