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Chemically Modified Sago Starch Reinforced Poly(lactic) acid Biocomposite

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CHEMICALLY MODIFIED SAGO STARCH REINFORCED POLY(LACTIC)ACID BIOCOMPOSITE

AMIRUL HAZIZIE BIN HAMDAN

A dissertation submitted in partial fulfilment
of the requirement for the degree of
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Dedicated to my beloved parents and my family who always bestow me sustainable motivations and encouragements

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ABSTRACT

The research aims to investigate the outcome of interaction of poly (lactic acid) with chemically treated sago starch at different weight percentages. Biodegradable polymer is one of the most promising alternatives to replace conventional petroleum-based polymers. Poly (lactic acid) is derived from renewable resources and many researchers had conduct studies to improve the mechanical properties of PLA biocomposite. PLA-based biocomposites are applied in industrial applications such as food packaging and biomedical. The limitation of PLA matrix such as poor mechanical properties and low thermal resistance can be improved by using chemically treated sago starch as biodegradable fillers. Sago starch are hydrophilic and polymer matric are hydrophobic. These two distinct nature forms weak covalent bond. To improve the properties, three different chemicals suggested for this research project. Three different types of chemical treatment which are grafting with acrylonitrile, grafting with benzenediazonium salt and with tetrahydrofuran. PLA matrix and chemically treated sago starch are mixed at different weight percentage by solvent casting method. The addition of biodegradable filler improve the mechanical properties of PLA based biocomposites. Morphological study, mechanical study, FTIR and thermal behavior characterization were carried out to analyze the specimen.

ABSTRAK

Kajian ini menumoukan untuk menyiasat hasil interaksi di antara poli(laktik asid)(PLA) dengan kanji sagu yang dicampur dengan bahan kimia pada komposisi yang berbeza.Polimer biodegradable adalah di antara alternative yang mempunyai potensi untuk menggantikan polimer berasaskan petroleum. poli(laktik asid) diterbitkan daripada sumber yang boleh diperbaharui dan ramai pengkaji telah menjalankan kajian untuk meningkatkan kekuatan mekanikal bio-komposit untuk poly(laktik) acid.Bio-komposit berasaskan poli(laktik) asid telah digunakan dalam industry seperti biomedical dan pembungkusan makanan. Kekurangan polilaktik asid adalah lemah kekuatan mekanikal dan ketahanan haba. Kanji sagu adalah bersifat menyerap air manakala PLA bersifat kalis air. Ini akan membentuk jaringan kovalen yag lemah. Dengan memperbaiki sifat kanji sagu melalui campuran kimia dapat menguatkan interaksi di antara PLA dengan kanji sagu. Untuk mencapai matlamat ini, tiga jenis bahan kimia digunakan sepanjang kajian ini. PLA dan kanji sagu yang telah dicampurka bahan kimia akan dicampurkan mengikut komposisi yang berbeza. Analisis morphologi, mekanikal, FTIR dan ketahanan haba akan dilakukan.

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ABBREVIATIONS

PLA	Poly (lactic acid)
FTIR	Fourier Transform Infrared Spectroscopy
PVA	Poly (vinyl) alcohol
PVC	Poly (vinyl) chloride
PS	Polystyrene
PP	Polypropylene
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
DSC	Differential Scanning Calorimetry
-OH	Hydroxide group
$-CH_3$	Methyl group

NOMENCLATURE

˚C	Degree celcius
g	Gram
g/10 min	Gram per 10 minute
g/cm^3	Gram per cubic centimetre
g/L	Gram per litre
kPa	KiloPascal
J/g	Joules per gram
K	Kelvin
kN	Kilo Newton
kg/m^3	Kilogram per cubic metre
Kg/mol	Kilogram per mole
J/L	Joule per liter
kg	Kilogram
MPa	Mega Pascal
%	Percentage
mol^{-1}	Per mole
wt%	Weight Percentagge

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Sago (Metroxylon sago) is a palm species which is commercialized in Southeast Asia region especially in Malaysia, Indonesia, Papua New Guinea and Philippines. Sago palm is able to grow in wet growing condition and also can adapt to harsh environment(Mohamad Naim, Yaakub, & Awang Hamdan, 2016). Sago can resist to extreme weather and require less observation. Sago need to be replanted for every 25 years (Abdul Aziz, 2002).Malaysia is currently the third largest sago producer in the world behind Indonesia and Papua New Guinea (Liestianty, Rodianawati, Patimah, & Muliadi, 2016). Four district in Sarawak which are Mukah, Dalat, Matu, and Daro have estimated plantation are of 11,112 hectares, 28,169 hectares, 4,306 hectares and 3,149 hectares respectively (Mohamad Naim et al., 2016). Malaysia is currently the largest world exporter with 96 % of the supply is from Sarawak (Uthumporn, Wahidah, & Karim, 2014).

Starch from different source differ in physicochemical, rheological, thermal, gelatinization and retrogradation properties. There are two types of applications for sago starch which are food applications and non-food applications. For food applications, one of the main application of sago starch is as gelling agent in jelly gum and hard gum candies (Liestianty et al., 2016). Meanwhile for non-food application, starch based hydrogels are usually applied in biomedical and pharmaceutical applications. This is due to the properties of the sago starch itself which includes hydrophilicity, biocompatibility and biodegradability (Kumar, Pandey, Raj, & Kumar, 2017). Other than that, sago starch also non-toxic and renewable raw materials. But there is some drawback of sago starch. It has short shelf life and prone to bacterial attack. Native sago starch also shows high sensitivity toward water and lack of mechanical strength. This is caused by the hydrophilic character which cause poor bonding with hydrophobic polymers in starch-polymers blends (Wu, 2005). The nature of starch which is highly hydrophilic caused agglomeration of starch paste when direct addition is added into latex material (Misman, Azura, & Hamid, 2016) In order to improve the mechanical properties, sago starch should be introduced with reactive functional group to blend with synthetic polymer. One of the material is poly(lactic acid) (PLA).

PLA is biodegradable thermoplastic polyester that manufactured by biotechnological processes from renewable resources. PLA have several good properties which are good strength, film transparency, biodegradability, biocompatibility and availability. PLA and copolymer able to degrade to non-toxic breakdown products under certain minimum conditions of temperature and moisture content and degradation happened with non-enzymatic hydrolytic process (Talbamrung, Kasemsook, Sangtean, Wachirahuttapong, & Thongpin, 2016). There are several additives added such as plasticisers, lubricants and impact modifier during the processing of PLA (Pivsa-Art et al., 2016). The applications of PLA in industries are biomedical and food packaging. PLA also show weakness with low deformation at break and quite high price (Setiawan, 2015). In this report, sago starch is modified as filler to improve the mechanical properties of PLA. These efforts include modifying sago starch with three different chemical which are acrylonitrile, benzediazonium chloride and tetrahydrofuran. Graft copolymerization is most common technique for modifying polysaccharides (Ekebafe, Ogbeifun, & Okieimen, 2016). Other than that, graft copolymerization only cause minimum loss of native properties of starch.(Celli, Sabaa, & Jyothi, 2016).

The main aim of this research is to investigate the outcome of interaction of poly(lactic acid) with chemically treated sago starch at different weight percentage. In order to achieve the main aim, three objectives are developed to be investigated throughout this research project. The first objective is to prepare three different chemical modification of starch. Second objective is to prepare PLA bio-composite with three different chemical modification. Third objective is to characterize and propose for interior and exterior application.

1.2 Problem Statement

There is some drawback for using starch as biodegradable filler with poly (lactic acid). The hydrophilic character of sago starch cause poor adhesion with hydrophobic polymer in starch-polymer blends. The properties of sago starch make the covalent bonding with hydrophobic polymer less strong until chemical modification is carried out. Lack of these properties prevent biomaterial from performing its function and cause undesirable side effects. Native starch shows high water sensitivity and lack of mechanical strength which induce brittleness and limits the application in industries. Waste disposal issue has urged the contributions of research in effort to develop new advanced material. Biodegradable polymer have potential in solving environmental issue. The properties of the biodegradable polymer need to be improved.

1.3 Research Objectives

This research project was conducted and carried out based on objectives as following:

a. To prepare PLA based bio-composite with three different chemical modification of sago starch
b. To characterize in term of morphology, mechanical strength and structural properties and propose for interior and exterior application
c. To study the effect of different weight percentages of treated sago starch and PLA matrix

1.4 Scope of Study

Not many studies have been done to investigate the chemical treatment of sago starch to improve the properties of PLA- based biocomposites. PLA-based biocomposite has been applied in medicinal, food packaging, interior finishing products, and aerospace industries. The potential of biodegradable polymer to produce biocomposite including advantages and disadvantages will be discussed. The enhancement of properties of PLA-based biocomposites are analysed with appropriate techniques. This includes morphology, mechanical strength and structural properties will be analysed.

1.5 Expected Outcomes of Research

The chemical treatment on sago starch as biodegradable filler in preparing biocomposites will change the mechanical properties, chemical structure and morphology. Different weight percentage of treated sago starch as fillers shows different characteristics in PLA biocomposites.

1.6 Summary

In this chapter, the background of study is discussed. The properties of sago starch should be improved after undergo chemical treatment. The reinforced biocomposite can be applied to industrial applications. With the addition of biodegradable filler of treated sago starch, the properties of biocomposite can be reinforced. The effect of chemically treated sago starch on the interaction with PLA matrix will be determined and analysed. Problem statement and objectives of this research project are discussed in this chapter.

CHAPTER 2

RESEARCH LITERATURE REVIEW

2.1 Overview

This chapter comprised the literature review of the research project. Biocomposite, starch grafting and chemical treatment were discussed. The potential of biocomposite used in the research, poly (lactic acid) was discussed as well. The type of techniques for preparing biocomposite were explained. Besides, the important and advantages of biocomposite by using poly (lactic acid) were also involved in discussion. The type of application for bio-composite also explained and discussed.

2.2 Biocomposite

A composite material is made up of at least two distinct intended material to improve product performance and lower manufacturing cost (Panchagnula & Palaniyandi, 2017). Biocomposite had attracted the attentions of researchers due to the issues of depletion of conventional fossil fuels and environmental problems. Most of the polymers available are produced from conventional fossil fuels and contributed as largest source of monomers. By considering the advantage of environmentally friendly materials, the application of natural/biofibre reinforced composites had expanded significantly due to the availability of renewable resources with other synthetic and biocomposite (Rahman et al., 2014).

There are many ways to solve disposal problems. The way for solving disposal problems is by biodegradation especially for agriculture waste. Poly (lactic acid), poly-3-hydroxybutyrate (PHB) and thermoplastic starch are the examples of biodegradable polymers. Most of the applications are food packaging, engineered fabrics, biomedical applications, automotive, aerospace and interior construction. Bicomposite showed great enhancements in terms of physical, material and other properties. The progress shown in researches could become alternative choice for global environmental problem on plastic waste. In achieving the solution, some of the properties need to be improved.

The main constraint in producing biocomposite is to find the appropriate procedure to combine the matrix and reinforcement materials. Appropriate method produces better properties of matrix and reinforcement. There are several drawbacks for biocomposite. The poor performance in the properties can be improved by adding multiphase materials and other type of composite.

2.2.1 Advantages of reinforced composites

The advantages of composite materials are light and strong. Composite materials also have good acoustic insulation properties and source of the fibers are renewable (Talbamrung et al., 2016). A good mixture of matrix and reinforcement material lead to fulfil the requirement of particular applications. Other than that, composites also able to be used design as composites are able to perform complex shapes. Existing reinforced composites enable industry to explore and do more research on improving the properties. Any increase in the properties added the value of biocomposite as alternative to replace carbon fiber and glass fiber reinforced materials (Mohammed, Ansari, Pua, Jawaid, & Islam, 2015).

2.2.2 Shape-forming and curing of composite-material parts

The type of reinforcing filler, the nature of the polymer binder and the design of the part determine the particular features of the technological process of reprocessing a composite into an item by which the required orientation of reinforcing filler and its combination with the binder, shape forming and monolithic form of the item are to be provided. According to Bratukin and Bogolyubov (1995) stated that the combination of a reinforcing filler with a binder is done as follows (p. 126):

1. Application of a binder solution or melt on surface of the reinforcing fibers as they pass through the liquid binder or with aid of a rotating roller plunged into the binder
2. Deposition of a liquid binder by a sprayer