CHARACTERISATIONS OF BIOPLASTIC MADE FROM STARCHES TREATED WITH POTASSIUM PERSULFATE

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ABSTRACT

Starch-based bioplastic have been known as an alternative material to substitute the usage of petroleum-based plastic. The usage of starch-based bioplastic nowadays keep on growing as it is nature friendly, biodegrade faster, and consume less pollution if compared to traditional petroleum-based plastic. However, an issues of its absorbency arise when it faces incompatibility in certain application. This study concentrates on water absorbency properties and characteristics of starch-based bioplastic by employing chemical modification onto potato, cassava and corn starch using graft copolymerization method with potassium persulfate to act as the initiator. It was found that 0.8% of grafted starch obtained is the highest graft percentage for all types of starch. Graft copolymerization of starch is not affected much despite its increasing amount of moisture absorption rate due to concentration of initiator, synthesis temperature and surrounding humidity. For the production of bioplastic, both the native and grafted starches are applied to compare the water absorbency properties with the ratio of native starch to grafted starch are S100:MS0, S70:MS30, S50:MS50, S30:MS70 and S0:MS100. It was demonstrated that absorbency rate of potato starch bioplastic and cassava starch bioplastic increased with the increase of grafted starch ratio, meanwhile corn starch bioplastic showed no improvement. It can be concluded that more amount of grafted starch added onto bioplastic has increase its hydrophilicity properties. Corn starch bioplastic on the other hand, is not affected by the increasing amount of absorbency rate because of its low density value and is very brittle. The tensile test proved that corn starch bioplastic got weaker tensile strength with the increasing amount of grafted starch used. Meanwhile, both potato starch bioplastic and cassava starch bioplastic have higher tensile strength value at 0.2% grafted starch used but declines with increasing amount of grafted starch which suggests that the hydrophilicity properties has weaken the mechanical strength of bioplastic.

ABSTRAK

CIRI-CIRI PLASTIK BIO DARIPADA KANJI YANG DIUBAHSUAI DENGAN KALIUM PERSULFAT

Plastik bio berasaskan kanji telah dikenali sebagai bahan alternatif untuk menggantikan penggunaan plastik berasaskan petroleum. Penggunaannya kini semakin meluas kerana sifatnya yang mesra alam, cepat terbiodegradasi, dan mengurangi pencemaran. Walaubagaimanapun, isu-isu mengenai kadar penyerapannya muncul apabila ianya berdepan dengan masalah ketidakserasian terhadap penggunaan yang tertentu. Kajian ini tertumpu kepada sifat dan ciri-ciri penyerapan air terhadap plastik bio ini dengan menggunakan pengubahsuaian kimia ke atas kanji ubi kentang, ubi kayu, dan jagung melalui kaedah kopolimerisasi graf dengan kalium persulfat yang bertindak sebagai perangsang. Kajian mendapati bahawa 0.8% kanji terubahsuai memperoleh peratusan pengubahsuaian yang tinggi untuk kesemua jenis kanji. Kopolimerisasi kanji tidak terjejas banyak dengan peningkatan kadar penyerapan kelembapan disebabkan oleh kepekatan perangsang, suhu sintesis dan kelembapan persekitaran. Untuk penghasilan plastik bio, kedua-dua kanji asli dan kanji terubahsuai telah digunakan untuk membandingkan sifat-sifat penyerapan air dengan nisbah kanji asli kepada kanji yang diubahsuai ialah S100: MS0, S70: MS30, S50: MS50, S30: MS70 dan S0: MS100. Ia menunjukkan bahawa kadar penyerapan bagi plastik bio kanji ubi kentang dan plastik bio kanji ubi kayu meningkat dengan peningkatan nisbah kanji terubahsuai, manakala plastik bio kanji jagung tidak menunjukkan peningkatan. Plastik bio kanji jagung tidak terjejas dengan peningkatan penyerapan kerana ia mempunyai nilai kepadatan yang rendah dan sangat rapuh. Ujian tegangan membuktikan bahawa plastik bio kanji jagung mendapat kekuatan tegangan yang lemah dengan peningkatan jumlah kanji terubahsuai. Sementara itu, plastik bio kanji ubi kentang dan plastik bio kanji ubi kayu mempunyai nilai kekuatan tegangan yang lebih tinggi pada kepekatan kanji terubahsuai 0.2% tetapi nilai tegangan semakin menurun dengan peningkatan kanji terubahsuai mencadangkan bahawa sifat hidrofilik telah melemahkan kekuatan mekanikal plastik bio.

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LIST OF ABBREVIATIONS

–C=C–	-	Alkene molecule bond (stretch)
–C≡C–	-	Alkyne molecule bond (stretch)
=C–H	-	Alkene molecule bond (bend)
(C6H10O5)n	-	Cellulose compound
ANOVA	-	Analysis of Variance
ASTM	-	American Society for Testing and Materials
ASTM D570	-	Standard Test Method for Water Absorption of Plastics
ASTM D618	-	Standard Practice for Conditioning Plastics for Testing
ASTM D882	-	Standard Test Method for Tensile Properties of Thin Plastic Sheeting
C-H	-	Alkane molecule bond (stretch)
C=O	-	Carbonyl molecule bond (stretch)
C1	-	Carbon chain number 1
C2	-	Carbon chain number 2
C3	-	Carbon chain number 3
C6	-	Carbon chain number 6
CH_2	-	Methylene compound
CH_3	-	Methyl group
Fe^{2+}	-	Ferrous ion
FTIR	-	Fourier transform infrared spectroscopy
H_2O_2	-	Hydrogen peroxide
HCa	-	Hydrolised cassava
HCo	-	Hydrolised corn
HP	-	Hydrolised potato
HS	-	Hydrolised starch
IR	-	Infra-red
ISO	-	International Organization for Standardization
ISO 1183-1	-	Plastics – Methods for determining the density of non-cellular plastic. Part 1: Immersion method, liquid

pyknometer method and titration method

$K_2S_2O_8$	-	Potassium persulfate
$KMnO_4$	-	Potassium permanganate
min	-	Minute
MS	-	Modified starch
NCa	-	Native cassava
NCo	-	Native corn
Ni	-	Nickel
NP	-	Native potato
O–H	-	Alcohol molecule bond (stretch)
OH	-	Hydroxyl group
S	-	Native starch
S0:MS100	-	Ratio of starch is 0% to ratio of modified starch is 100%
S30:MS70	-	Ratio of starch is 30% to ratio of modified starch is 70%
S50:MS50	-	Ratio of starch is 50% to ratio of modified starch is 50%
S70:MS30	-	Ratio of starch is 70% to ratio of modified starch is 30%
S100:MS0	-	Ratio of starch is 100% to ratio of modified starch is 0%
SEM	-	Scanning electron microscope
SPSS	-	Statistical package for the Social Sciences
TGA	-	Thermogravimetric analysis
XRD	-	X-ray diffraction

LIST OF SYMBOLS

°C	-	Degree Celsius
%	-	Percentage
cm^{-1}	-	Reciprocal centimeters (wavenumber unit)
α	-	Alpha
M	-	Mole
V	-	Volt
±	-	Plus-minus sign
mm	-	Millimetre
g	-	Gram
ml	-	Millilitre
mg	-	Milligram
s	-	Second
°	-	Degree
kV	-	Kilovolt
mA	-	Milliampere
Cu K_{α}	-	Copper K-alpha
cps	-	Centipoise
µm	-	Micrometer
ρ	-	Rho
Kg	-	Kilogram
m^3	-	Cubic metre
ml/min	-	Millilitre per minute
°C/min	-	Degree Celsius per minute
°2θ	-	Degree 2-Theta

CHAPTER 1

INTRODUCTION

1.1 Research Background

As wood products nowadays face high demand from various industries and consumers, the high-value wood timber will be forced to extinction if there is no preservation or conservation action taken. To overcome this issue, there are several inventions that use plastic as the raw material to replace the usage of wood timber. Household materials such as furniture, kitchenware and decorations, as well as materials used in industries, mostly has been replaced by plastics to reduce the production of wood-based items. Plastics became widely accepted by consumers as it was cheaper and convenient. Recently, oil price has increased gradually and we should take this opportunity to create something that is cheaper and readily available to reduce plastics usage (Hopewell *et al.*, 2009).

The typical plastic commonly produced is using petroleum-based that can be recovered from underground oil deposit by drilling it out. The raw material then undergo the refineries process to obtain a Naphta, which is become a main material for most of the plastic products that were commonly used nowadays (Kalia *et al.*, 2000). In agricultural sector, especially industrial greenhouses and nurseries, they contribute as major users of plastic-based tools because it is convenient and cheaper. Problems arise when these plastics become their major waste and give harm to environment. Because of the concern towards pollution issue, the biodegradable plastic or known as bioplastic, was introduced to overcome plastic waste as it is easily biodegradable back to nature in a short period of time (Mathers *et al.*, 2014).

Bioplastic made from starch becomes widely known nowadays and several studies had been conduct by researchers to expand its uses and utility. Starch is widely picked as a material for bioplastic because it is inexpensive and easy to obtain. Besides, it is natural form because it derived from plant and that will make the bioplastic more degradable. Starch is a versatile product as it has many uses besides making bioplastic such as fillers, binders, disintegrants, lubricants in tablet formulation super-absorbent products, flocculants in the purification of water, textiles, cosmetics, agrochemicals, and constructions (Izuagie *et al.*, 2012). Hence, starch is also convenient as a raw material for modification especially chemical modification.

According to Hemsri *et al.* (2015), water absorption of polymer in bioplastic tend to be the crucial properties to evaluate its stability on water that affecting their long term performance. The bioplastic that contain chemically modified starch will either have the hydrophobic nature or hydrophilic nature in their final products. Nashed *et al.* (2003) and Gáspár *et al.* (2005) stated that hydrophilic nature of glycerol will tend to bind more water during starch gelatinization process, hence it will limit the long term stability of the bioplastic. This cause is to presence of polar amino acid and resulting in a high degree of water absorption.

Chemical modification is done onto starch to improve its native properties, either physical or chemical properties, to produce a value added end-products. Usually it provides a greater strength, better quality of product and is highly functional (Satin, 2006). For this research, grafting copolymerization method is used to enhance the characteristics of starch. It is important to do chemical modification to starch before working on bioplastic production to review its advantages or weaknesses of starch.

1.2 Justification

The main interest of this study was to conduct modification of starch before applying it into bioplastic. Graft copolymerization method is chosen for the chemical modification of starch, by which it is a method of adding a new and desirable properties to starch without drastically affecting the basic properties of starch uses. Modification of starch through this method improves the properties of natural starch itself. Starch is chosen as main raw material in this study simply because it is renewable and biodegradable with agriculturally derived biopolymer. Besides, their native natures provide mechanical strength to plants which make them fit for various applications (Pathania *et al.*, 2012).

Since starch itself has high hydrophilicity nature and less soluble, it is subjected to various types of modification to enhance its favourable outcome. Lewicka *et al.* (2015) stated that the reactivity of starch was affected by the grain size of starch thus the larger grain size will increase its modification susceptibility. Besides, the shape of grains such as either spherical or crystalline also would be effected by it as well. This will cause the external factors have an easy access on them during modification. Abbott *et al.* (2014) conducted a study that the starch modified bioplastic has nearly similar properties equivalent to traditional petroleum-based plastic. The improvement observed are such as the plasticisation process, flexibility, mouldable, recyclable and biodegradable.

Since starch itself has drawbacks such as high brittleness and possess high concentration of water solubility, adding additive such as plasticizer could modify its polymer arrangement by de-structuring the starch chain as the result from breakage of semi crystalline structure of starch (Ramirez *et al.*, 2011). The common plasticizer uses was glycerol, which is having a properties of increasing the mobility and mechanical properties of modified starch. According to Munthoub and Wan (2011), even though the addition of glycerol strengthen the tensile properties of composite, the water absorption content was increased due to the nature hygroscopic properties of glycerol itself that keep in absorbing more water. To overcome this problem, chemical modification is adopted by using graft copolymerization method onto starch before producing bioplastic.

After producing bioplastic, it was tested with various analytical equipments such as FTIR, TGA, XRD and SEM to study its properties. Besides, using those instrumentations too will give some knowledge on the changes in polymer structure or the contents of starch after chemically modified. The purpose of the testing is to examine the changes in chemical compound of modified starch as well as to identify its properties and characteristics before and after producing the bioplastic.

1.3 Objectives

In this study, there were three main objectives which are listed below:

a. To determine the optimum percentage of potassium persulfate (0.2%, 0.4%, 0.6%, 0.8% and 1.0%) in graft copolymerization process.
b. To determine the absorbency rate of three different grafted starches (potato starch, cassava starch and corn starch).
c. To evaluate the relationship between bioplastic of hydrolysed starch to bioplastic of native starch at five different ratios (0:100, 30:70, 50:50, 70:30 and 100:0) of potato-based bioplastic, cassava-based bioplastic and corn-based bioplastic.

CHAPTER 2

LITERATURE REVIEW

2.1 Bioplastics

Bioplastic comprises a range of materials with differing properties and these days it is used in a growing number of markets, including the packaging, consumer electronics, toys, furniture, handheld devices, fibres and automotive sectors. Bioplastic defined as a plastic that is made by a part of or the whole polymers that are derived from biological sources such as plant starch or cellulose from trees that able to biodegrade easily compared to typical petroleum-based plastics (Chen, 2014). Generally, bioplastics can be described as biobased and biodegradable. Biobased means that the products are partly derived from biomass while biodegradable means the process of biodegradation that involve chemical process by which the microorganisms that available in surrounding environment convert the products into natural substances such as carbon dioxide and compost.

Basically, bioplastic was made by converting the sugar present in plants into plastic. In general, it contains one or more biopolymers (polysaccharides, protein, peptide, etc.) as essential components, plasticizers, and other additives. According to Song *et al.* (2009), bioplastic made from plant carbohydrate such as corn, soy, wheat and cottonseed, show some advantages in terms of its biodegradability, abundant resources, low cost and suitable properties as well. Those natural