

UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF BIOPLOYMERS PRODUCED FROM DIFFERENT BLENDS OF CHEMICALLY MODIFIED STARCH AND NATURAL RUBBER LATEX

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of Requirements for the Degree of Master of Science

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CHARACTERIZATION OF BIOPLOYMERS PRODUCED FROM DIFFERENT BLENDS OF CHEMICALLY MODIFIED STARCH AND NATURAL RUBBER LATEX

By

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Development of biodegradable polymers from absolute environmental friendly materials has attracted increasing research interest due to public awareness of waste disposal problems with low degradable conventional plastic. In this study, starch and natural rubber latex which abundant, were assessed for their potential in making biodegradable polymers. Sago starch and rice starch with low and high amylose and chemically modified contents were chosen via acetylation and hydroxypropylation. Starches with and without chemical treatments were gelatinized and later casted with natural rubber latex in the following ratios 100.00/0.00, 99.75/1.25, 98.50/2.50, 95.00/5.00, 90.00/10.00 and 80.00/20.00 wt/wt, for preparing biopolymer films using solution spreading technique. The products were evaluated according to their water absorption, mechanical, thermal, morphological and biodegradable properties.

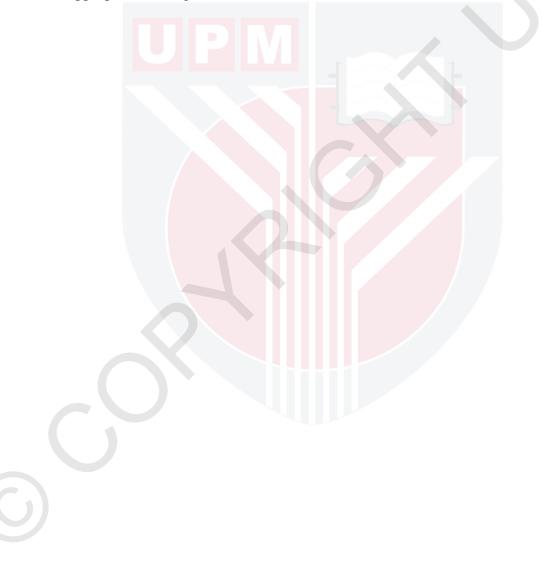


Level of substitution showed that starches were successfully chemical modified. Acetylation of sago, LAR and HAR gave result of DS 1.05, 1.35 and 1.30 respectively. Hydroxypropylation of sago, LAR and HAR gave result of MS 0.13, 0.27 and 0.31 respectively. FTIR (Fourier Transform Infrared) analysis proved that acetyl and hydroxypropyl groups were successfully substituted into the starch macrostructures after the chemical substitutions. These substitutions improved starch water solubility and their compatibility with natural rubber latex in the film fabricating process via solution casting.

Modifications of starches by either acetylation or hydroxypropylation increase water absorption ability of product films about 2 to 5 times higher compare to native starch product films. In terms of compatibility with natural rubber latex, high amylose rice, native and acetylated sago starch proved to be compatible and had good adhesion with natural rubber latex through SEM result. However, both modification modes did not exhibit differences trend in their thermal profile. Sago starch and rice starch product films showed similar trend of thermal and mechanical properties. Product films formulated from sago starch absorbed less water as compared to rice starch. Native sago starch product film showed 110% in water absorption capacity. However, native LAR and HAR product films showed 190 and 300% in water absorption capacity. Water absorption capacity of all type of biopolymer was able to reduce up to 95% when addition of natural rubber latex concentration reached 20%. Addition of natural rubber latex delayed biodegradable threshold of product films, but they were still completely biodegradable in the natural environment. Product films with less than 2.5% natural rubber content was totally biodegraded within 2 to 6 weeks. However, as concentration of natural rubber latex increase to 20%, biodegradability of the film still achieved 50% within 12 weeks. Product films with high natural

rubber latex content exhibit high melting temperatures, inhibited the absorption of water and increased elongation at break.

From the analysis of product films, it can be concluded that the ratio of the starch to natural rubber latex, selection of chemical substitution modes and types of starch played an important role in determining characteristics of final product blends. Biopolymer films with desirable properties can be fabricated by choosing an appropriate casting formulation.



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PENCIRIAN BIOPOLIMER YANG DIHASILKAN DARIPADA ADUNAN KANJI MODIFIKASI KIMIA DAN LATEKS GETAH ASLI

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Pembangunan polimer biodegradasi daripada bahan-bahan yang penuh mesra alam telah menarik minat perkembangan penyelidikan kerana kesedaran orang ramai terhadap masalah pembuangan sisa polimer yang mengandungi polimer-polimer biasa yang tidak mudah reput. Dalam penyelidikan ini, kanji dan getah yang mudah didapati di tempatan telah diujikaji tentang potensi dalam menghasilkan polimer yang dapat biodegradasi. Kanji sago dan beras yang mengandungi amilose tinggi dan amilose rendah telah dipilih dan dimodifikasi melalui kaedah kimia iaitu asetilasi dan hidroksipropilasi. Kanji semulajadi dan kanji yang dimodifikasi telah digelatinasi dan dijadikan biopolymer filem bersama getah berdasarkan nisbah kanji kepada getah 100.00/0.00, 99.75/1.25, 98.50/2.50, 95.00/5.00, 90.00/10.00 dan 80.00/20.00. Polimer yang dihasilkan telah dianalisis melalui ujian-ujian seperti penyerapan air, mekanikal, morfologi, profil termal dan biodegradasi.

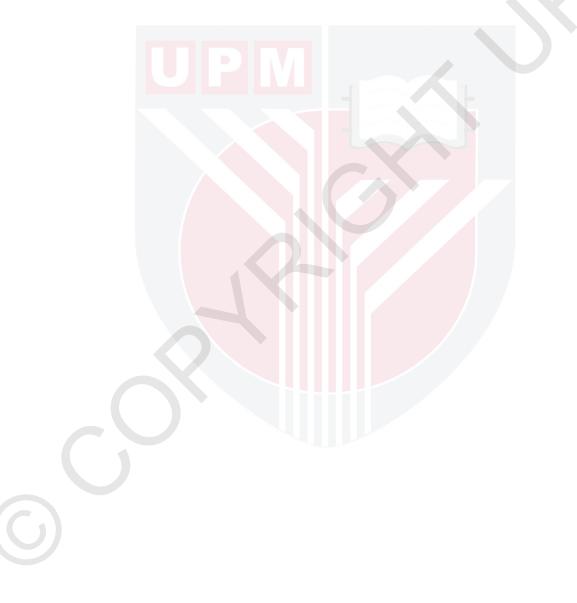
Keputusan tahap penggantian menunjukkan bahawa kanji telah berjaya dimodifikasi secara kimia. Asetilasi bagi kanji sago, LAR dan HAR masing masing menghasilkan DS sebanyak 1.05, 1.35 dan 1.30. Hidroksipropilasi bagi kanji sago, LAR dan HAR

masing masing menghasilkan MS sebanyak 0.13, 0.27 dan 0.31. Analisis FTIR (Fourier Transform Infrared) telah membuktikan bahawa kumpulan berfungsi, asetil dan hidroksipropil telah berjaya digantikan ke dalam makrostruktur kanji selepas rawatan-rawatan kimia berkenaan. Proses penggantian ini berjaya meningkatkan keterlarutan air kanji dan kesesuaiannya bersama getah dalam penghasilan produk filem melalui proses pengkasan larutan.

Modifikasi kanji sama ada secara asetilasi atau hidroksipropilasi telah meningkatkan daya penyerapan air filem sebanyak 2 hingga 5 kali ganda berbanding dengan filem daripada kanji tanpa modifikasi.. Dari segi kesesuaian kanji dengan getah, keputusan SEM menunjukkan kanji HAR, kanji sago dan kanji sago yang dimodifikasi secara asetilasi adalah dibuktikan lebih sesuai. Walau bagaimanapun, kedua-dua mod modifikasi tidak menunjukkan perubahan ketara dari segi sifat termal. Produkproduk filem yang dihasilkan daripada kanji sago dan beras bersifat serupa dari segi termal dan mekanikal. Biopolimer-biopolimer yang diperbuat daripada kanji sago menunjukkan daya penyerapan air yang rendah berbanding dengan kanji beras. Biopolimer diperbuat daripada kanji sago menunjukkan daya penyerapan air sebanyak 110%, manakala biopolimer diperbuat daripada kanji LAR dan HAR masing-masing menunjukkan daya penyerapan air sebanyak 190% dan 300%. Penambahan getah dalam penghasilan biopolymer melambatkan proses biodegradasi, tetapi biopolymer tersebut masih dapat direput dengan sepenuhnya dalam alam semula jadi. Biopolimer yang mengandungi kandungan getah yang serendah 2.5% memerlukan masa sebanyak 2 higga 6 minggu untuk biodegradasi. Apabila kandungan getah ditingkatkan ke 20%, biopolimer masih dapat direputkan sebayank 50% dalam masa 12 minggu. Polimer yang mengandungi kandungan getah yang

tinggi menunjukkan takat lebur yang tinggi, penyerapan air yang rendah dan daya tarikan yang tinggi.

Analisis telah menunjukkan bahawa nisbah kanji kepada getah, bentuk modifikasi dan jenis kanji merupakan faktor-faktor utama dalam menghasilkan biopolimer. Filem-filem biopolimer dengan sifat-sifat yang diperlukan dapat disediakan dengan memilih sesuatu formulasi tebaran yang sesuai.



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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

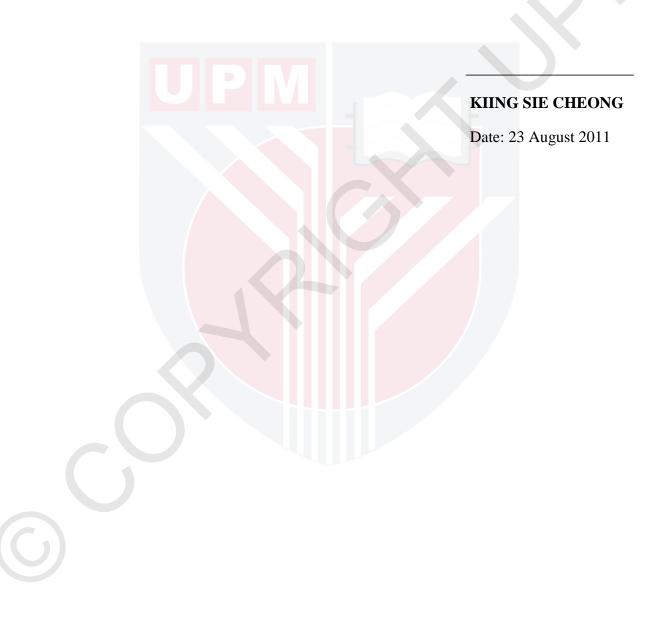


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LIST OF ABBREVIATIONS

AS	-	Acetylated Sago
FTIR	-	Fourier Transform Infrared
g	-	Gram
h	-	Hour
HAR	-	High Amylose Rice
HCL	-	Hydrochloric Acid
HHAR		Hydroxypropylated High Amylose Rice
HLAR		Hydroxypropylated Low Amylose Rice
H ₂ SO ₄	-	Sulphuric Acid
HS	-	Hydroxypropylated Sago
КОН	-	Potassium Hydroxide
LAR	-)	Low Amylose Rice
LDPE		Low Density Polyethylene
min	, -	Minute
М	-	Molarity
mg	-	Miligram
mL	_	Mililiter
Ν	-	Normality
NS	-	Native Sago
NaOH	-	Sodium Hydroxide
NHAR	-	Native High Amylose Rice
NLAR	-	Native Low Amylose Rice
NRL	-	Natural Rubber Latex

Na ₂ SO ₄	-	Sodium Sulphate
$Na_2S_2O_5$	-	Sodium Disulphite
NS	-	Native Sago
SEM	-	Scanning Electron Microscope
Tg	-	Glass Transition Temperature
T _m	-	Melting Temperature
°C	-	Degree Celcius
%	Ņ	Percentage

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CHAPTER 1

INTRODUCTION

In recent years, there has been increasing public awareness about environmental pollution due to disposal of non-degradable plastics. Modern plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) are mechanically strong, inexpensive, easily processed, and durable. These materials with high durability create environmental problems once they enter the waste streams. As an alternative, biodegradable material which can undergo natural biodegradation process has attracted the attention of the scientific world. Many types of synthetic biopolymers such as poly (Ecaprolactone) (PCL), Polylactic acid (PLA), and polyvinyl alcohol (PVA) (Guohua et al., 2006; Jang et al., 2007; Rosa et al., 2005) have been investigated to substitute petroleum based polymers. The advantages of synthetic biopolymers are obvious, including predictable properties, batch-to-batch uniformity and can be tailored easily (Lu et al., 2009). However, cost of manufacturing is a burden to introduce them for common applications. Natural biopolymers which are inherently biodegradable have gained much focus nowadays due to their potential to replace synthetic biopolymers. Starch, cellulose and chitosan are popular renewable and abundant natural biopolymers for making biodegradable polymers. Wu (2003) has evaluated the possibility of making a fully or partially biodegradable film from natural biopolymer, either alone or combined with synthetic polymers. Among them, starch is the most attractive source due to low cost, easy availability and high production (Miladinov and Hanna, 2001).

Starch comprises of mainly two macromolecules, known as amylose and amylopectin. Amylose is a linear polymer linked by α -1,4 glycosidic bonds while, amylopectin is a branched polymer consisting of short linear α -1,4 polymer chains linked to each other by α -1,6 linkages (Carvalho *et al.*, 2003). Starch films can be prepared from native starch or its components, amylose and amylopectin (Myllarinen et al., 2002), through various techniques such as thermoplastic processing and solution casting. The film products rich in amylose or amylopectin are reported to have many properties (Paes et al., 2008). Starches with high amylose give stronger films while the branched structure of amylopectin generally leads to films with different mechanical properties, such as lower tensile stress. However, starch-based film has not been extensively utilized especially as packaging material due to weak mechanical properties and water sensitivity (Guan et al., 2005). Starch based products will swell and deform when exposed to moisture. Hence, starches must be treated to improve their weak native properties either by physical or chemical means, and/or incorporating other materials into their crystalline structure (Rouilly et al., 2004).

Chemical modification is one of the alternative ways to enhance native starch properties by introducing new functional groups into the starch molecule either through chemical derivations (etherification, esterification, cross-linking and grafting) or decomposition reactions such as acid or enzymatic hydrolysis and oxidation (Lopez *et al.*, 2008). Chemical treatments change the functional groups on starch molecules and thus alter their properties. Chemical derivations have long been studied as a way to solve this problem and to produce waterproof materials (Fringant *et al.*, 1998). Several studies on the use of modified starches for instance, starch ester (Guan *et al.*, 2005; Copinet *et al.*, 2001; Guan and Hanna, 2004) and starch ether (Kim, 2003; Guohua *et al.*, 2006) in producing biodegradable films have been reported. Chemical modifications will also reduce the likelihood of retrogradation, allowing the starch to remain "shelf stable" for extended periods. Liu *et al.* (2007) had reported that the retrogradation process affects the mechanical properties of starch-based plastics significantly.

Mechanical properties are important in polymer study. Biodegradable polymer with 100% starch inhibits high brittleness as compared to those of synthetic polymers. This mechanical weakness limits their extensive application. Much work has been carried out to overcome this drawback, including incorporation of filler, like glycerol which can reduce the brittleness of starch based polymers (Myllarinen *et al.*, 2002). Several literatures have reported on blending of starch based polymers with high performance synthetic polymers to yield strong films (Koenig and Huang, 1995; Kim, 2003; Wu, 2003; Nakason *et al.*, 2005). There were a few studies on the use of rubber in starch polymer blends (Arvanitoyannis *et al.*, 1997; Rouilly *et al.*, 2004; Wu *et al.*, 2004; Nakason *et al.*, 2005), but the properties of starch/rubber blends depend on many factors, among which the most important ones are dispersion level, interfacial strength, and type of starch. However, there is no information about biopolymers prepared from chemically modified starch and natural rubber latex blends.

In this study, starch from sago and local Sarawak rice cultivars with high and low amylose contents were chosen. Amylose content is an important factor in the choice of potential starch sources, as it affects the mechanical properties and biodegradability of polymer products (Lourdin *et al.*, 1995). All starches were chemically modified through acetylation and hydroxypropylation, blended with natural rubber latex and casted into product films. All final polymer films were tested for their water absorption capacity, mechanical properties, thermal profile, morphology and biodegradability.

The main objective of this study was to produce biodegradable polymers from chemically modified sago and rice starches blends containing natural rubber latex. The study could be divided into three specific objectives. They were to:

- (a) prepare acetylated and hydroxypropylated starch for the production of biodegradable biopolymers
- (b) identify or determine the optimal blending compositions between chemically modified starches and the natural rubber latex.
- (c) determine chemical and physical properties of the prepared polymer films.

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