UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF SAGO STARCH ESTERS AND THEIR BLENDS WITH POLY(VINYL CHLORIDE)

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SYNTHESIS AND CHARACTERIZATION OF SAGO STARCH ESTERS AND THEIR BLENDS WITH POLY(VINYL CHLORIDE)

By

SEE YAW KOON

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

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To my beloved parent, wife and daughter, for their support
and patience with this thesis.
To my sister and brother in law;
to my niece and bother, and to all the others.

See Y. K.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
fulfilment of the requirement for the degree of Master of Science

SYNTHESIS AND CHARACTERIZATION OF SAGO STARCH ESTERS AND THEIR BLENDS WITH POLY(VINYL CHLORIDE)

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Chairman: Professor Dzulkefly Kuang Abdullah, PhD

Faculty: Science

Esterifying of palm oil based oleochemicals like hexanoyl, octanoyl and lauroyl chloride onto dried sago starch by using formic acid as an initiator had been studied in the absence of an organic solvent. A stream of nitrogen gas had been used to eliminate the hydrochloric acid produced by the reaction. The optimum conditions in esterifying of starch hexanoate, starch octanoate and starch lauroate had been studied based on the highest percentage of the recuperation yield. About 89% of starch hexanoate, 86% of starch octanoate and 80% of starch lauraote were obtained under optimized conditions with the degree of substitution (DS) of 1.3, 1.2 and 1.2 respectively. Esterification was evidenced by the presence of ester carbonyl peak in Fourier transform infrared (FT-IR) and ^{1}H nuclear magnetic resonance (^{1}H-NMR). The ester group was found to act like an internal plasticizer because of the reduction of hydrogen bonds between the starch molecules. The DS of starch esters was determined by elemental analysis. The TGA had shown that the prepared starch esters had higher thermal stability than native starch and increased with the increasing of side-chain length and DS.

The DSC thermograms of esterified sago starch showed the depression of glass transition temperature (T_g) from shorter side-chain length starch ester (starch hexanoate, 85 ^{o}C) to longer side-chain length starch ester (starch lauroate, 36 ^{o}C).The mechanical properties of starch esters were determined. Starch lauroate with the longest side chain length had measurable tensile strength (11.6 ± 0.5 MPa) and elongation at break (2.4 ± 0.3 %) properties compared to starch hexanoate, starch octanoate and native starch. Tensile strength and elongation at break depended on the side-chain length and the DS.

Starch hexanoate, starch octanoate and starch lauroate were blended with poly(vinly chloride) (PVC) at various proportions by using conventional solvent-casting technique. The FT-IR analysis showed that there were no intermolecular interactions between starch esters and PVC in room temperature. Thermal and mechanical properties, water absorption and biodegradation were investigated as a function of blend composition. The existence of starch esters had enhanced the thermal properties of PVC and increased with the increasing of starch ester content. For all blends, the mechanical properties (tensile strength and elongation at break) retained satisfactory up to 20 wt % for starch ester content. The higher the content of starch esters was the greater the decreased of mechanical properties. The blends had shown a minimal water uptake (< 4 wt %) even at the highest starch ester content (70%). The extent of their biodegradability, after exposure to sludge, was assessed by weight loss measurements. It was found that the blends were biodegradable, and the biodegradation rate decreased with increasing DS.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN ESTER KANJI SAGU DAN CAMPURANNYA DENGAN POLI(VINIL KLORIDA)

Oleh

SEE YAW KOON

Februari 2007

Pengerusi: **Profesor Dzulkefly Kuang Abdullah, PhD**

Fakulti: **Sains**

Mengester oleokimia asas minyak sawit seperti heksanoil, octanoil dan lauroil klorida keatas kanji sagu yang kering dengan menggunakan asid formik sebagai pemula telah dikaji dalam ketidakhadiran sebarang larutan organik. Satu aliran gas nitrogen telah diguna untuk menyingkir asid hidroklorik yang terhasil oleh tindak balas. Keadaan-keadaan optimum dalam mengester kanji heksanoat, kanji oktanoat dan kanji lauroat telah dikaji berdasarkan kepada peratusan hasil pemulihan yang tertinggi. Kira-kira 89% kanji heksanoat, 86% kanji octanoat and 80% kanji lauroat telah diperolehi di bawah keadaan-keadaan teroptimum dengan darjah penggantian (DS) 1.3, 1.2 and 1.2 masing-masing. Pengesteran telah terbukti oleh kehadiran puncak karbonil ester dalam inframerah Fourier Transform (FT-IR) dan ^{1}H resonan magnetik nuklear (^{1}H-NMR). Kumpulan ester telah dijumpai bertindak selaku bahan plastik dalaman sebab ia mengurangkan ikatan hidrogen antara molekul kanji. DS ester kanji telah ditentukan dengan analisis pengunsuran. TGA telah menunjukkan bahawa ester-ester kanji yang tersedia mempunyai kestabilan terma yang lebih tinggi daripada kanji semula jadi dan meningkat dengan peningkatan kepanjangan rantai sisi dan DS. Termogram DSC bagi kanji sagu yang terester menunjuk penurunan suhu peralihan kaca (T_g) dari ester kanji yang lebih pendek rantai sisi (kanji heksanoat, 85 ^oC) kepada ester kanji yang lebih pangjang rantai sisi (kanji lauroat, 36 ^oC) . Sifat-sifat mekanikal ester-ester kanji telah ditentu. Kanji lauroat dengan kepanjangan rantai sisi yang terpanjang mempunyai sifat-sifat kekuatan tegangan (11.6 ± 0.5 %) dan perpanjangan pada putus (2.4 ± 0.3 %) yang boleh diukur berbanding dengan kanji hexanoat, kanji octanoat dan kanji asal. Kekuatan tegangan dan perpanjangan pada putus bergantung kepada kepanjangan rantai sisi dan DS.

Kanji heksanoat, kanji oktanoat dan kanji lauroat telah dicampur dengan poli(vinil klorida) (PVC) pada pelbagai nisbah dengan menggunakan teknik pembalutan larutan yang biasa. Analysis FT-IR menunjukkan bahawa tiada interaksi antara molekul di antara ester kanji dan PVC dalam suhu bilik. Sifat-sifat terma dan mekanikal, penyerapan air, dan biodegradasi telah dikaji sebagai fungsi komposisi campuran. Kehadiran ester kanji telah menambah sifat-sifat terma PVC dan meningkat dengan peningkatan kandungan ester kanji. Bagi semua campuran, sifat-sifat mekanikal (kekuatan tegangan dan perpanjangan pada putus) adalah kekal sehingga 20 wt % kandungan ester kanji. Semakin tinggi kandungan ester-ester kanji, semakin kurang sifat-sifat mekanikalnya. Campuran-campuran telah menunjukkan pengambilan air yang minimal (< 4 wt %) walaupun pada kandungan ester kanji yang tertinggi (70%). Takat kebolehdegradasinya, selepas dedahkan kepada lumpur, telah dinilai dengan

pengukuran kehilangan berat. Adalah didapati bahawa campuran-campuran adalah boleh dibiodegradasi, dan kadar biodegradasi berkurangan dengan peningkatan DS.

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I certify that an Examination Committee has met on 13rd February 2007 to conduct the final examination of See Yaw Koon on his Master of Science thesis entitled “Synthesis and Characterization of Sago Starch Esters and Their Blends with Poly(Vinyl Chloride)” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Md. Jelas Haron, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Zaizi Desa, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohamad Zaki Ab. Rahman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Hamdan bin Suhaimi, PhD
Professor
Faculty of Science and Technology
Universiti Malaysia Terengganu
(External Examiner)

HASANAH MOHD GHAZALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

Dzulkefly Kuang bin Abdullah, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Anuar bin Kassim, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Abdul Halim bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

AINI IDERIS, PhD
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 14 JUNE 2007

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

SEE YAW KOON

Date: 31 August 2007

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LIST OF ABBREVIATIONS

ASTM	The American Society for Testing and Materials
CPKO	Crude palm kernel oil
CPO	Crude palm oil
DS	Degree of substitution
DSC	Differential Scanning Calorimeter
DMSO	Dimethyl sulfoxide
EDC	Ethylene dichloride
et al.	et alia (and others)
FT-IR	Fourier Transform Infrared
GPa	Giga pascal
ha	Hectare
HCl	Hydrochloric acid
LDPE	Low density polyethylene
Mpa	Mega pascal
M_{res}	Residual mass
NMR	Nuclear Magnetic Resonance
psi	Pounds per square inch
PVC	Poly(vinly chloride)
spp.	Species (more than one)
t	Time
T	Temperature
T_d	Decomposition temperature

T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T_m	Melt transition temperature
T_o	Oxidation temperature
VC	Vinyl chloride
wt %	Percentage of weight
>	More than
<	Less than

CHAPTER 1

INTRODUCTION

1.1 General Review

Today, plastic industries are concerning about the biodegradability of their petroleum-based products before bring them to the market place. Virtually no synthetic plastic is totally biodegradable. It is highly resistant to microbial attack and is the major cause of the environmental problems. Replacement of synthetic plastics with materials from agro resources, especially starch, is attractive because of providing biodegradation properties.

However, starch by itself is unsuitable for most uses as a plastic because of its poor physical and chemical properties. Some approaches to overcoming these problems include physical and chemical modifications. For example, long chain esters of starch with high degree of substitution (DS) from chemical modification have interesting thermoplastic properties (Aburto et al., 1999a).

Actually, utilization of modified starch in the plastics industry is not new. Interest in the preparation of chemically or physically modified starches remains high (Aburto et al., 1999a; Kiatamjornwong et al., 2001; Sang and Lim, 1998) despite the fact that the vast majority of commercially available modified starches today are based on the work carried out in the 1940s and 1950s (Fang et al., 2002).

1.2 Justification of the Study

Biodegradable plastics offer a solution to the growing disposal problem of petroleum-based plastics. The greatest part of the plastic waste derived from packaging and building constructions for which recycling are neither practical nor economical. The choices for dealing with this waste are limited as incineration of plastic polymers results in the generation of toxic emissions; the only viable solution is to bury the material in landfills. However, this approach is also limited because of the resistant nature of plastic to biological degradation. So, the productions of biodegradable starch plastics are desirable.

Substitution of petroleum based plastics with starch plastic would permit us to conserve our petrochemical resources and to find out new non-food uses for starch. Starch is inexpensive, abundance and is produced in greater quantities than current market demand (Shogren et al., 1993).

Biodegradable starch plastics can be prepared in numerous ways include chemical and physical means. One of the chemical modifications is esterification. Lipophilic substitution of hydroxyl groups of starch with alkyl groups in organic solvent medium has produced starch ester. High degree substitution of starch esters behaves as thermoplastic properties, but their high