UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF ELECTRON BEAM-IRRADIATED SAGO STARCH-POLYVINYL ALCOHOL BLEND FILMS

SARADA BINTI IDRIS

CHARACTERIZATION OF ELECTRON BEAM-IRRADIATED SAGO STARCH-POLYVINYL ALCOHOL BLEND FILMS

By

SARADA BINTI IDRIS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,

In Fulfilment of the Requirements for the Degree of Master of Science

November 2007

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

CHARACTERIZATION OF RADIATION MODIFIED SAGO-POLYVINYL ALCOHOL BLENDS FILMS

By

SARADA BINTI IDRIS

November 2007

Chairman : Professor Dzulkefly Kuang bin Abdullah, PhD

Faculty : Science

Blends from sago starch, poly (vinyl alcohol)(PVA) and distilled water have been prepared and subjected to electron beam irradiation with doses ranging from 10 to 40 kGy to form hydrogels. The hydrogels were then cooled in refrigerator overnight to remove trapped bubbles formed during irradiation reaction. Films were subsequently produced by drying hydrogels in an oven. The characteristic of the irradiated blends and films were then determined. Poly (vinyl alcohol) solution was found to be viscous obviously after irradiation indicated the formation of irradiation induced crosslinking. Radiation degradation of sago starch solution was confirmed by observing the viscosity of the solution which was lowered after irradiation. The gel content of irradiated films was increased compared to unirradiated. Crosslinking/grafting had occurred in the blends at optimum dose of 20 kGy. The gel content of poly (vinyl alcohol) film was maximum at 30 kGy. Above 30 kGy, over crosslinking occurred as the film was shrunk to the smaller size. Melting temperature of PVA film as determined by Differential

Scanning Calorimetry decreased with increasing irradiation dose. This indicate that cross linking had lowered the melting point of PVA film. The existence of only one peak of melting temperature by Thermo Gravimetric Analysis revealed the compatibility of the blends. Scanning Electron Miscroscopy studies on the surface morphology and freeze fracture revealed more evidence of the radiation induced crosslinking and grafting of the blends. Studies also done on effect of sago and PVA contents of the blend, addition and types of plastisizers added and irradiation dose on the quality of the film produced. Results show that irradiation has improved the tensile strength but elongation at break was slightly reduced for blends S25/P75, S50/P50 and S75/P25.

The biodegradability of sago, PVA and blends films was studied by monitoring its weight loss for 6 months. Sago starch film was totally degraded in the first month of burial period but PVA film remain un intact for the last six months. Incorporating sago starch to the blend sago-PVA improved the weight loss up to 60% in six months.

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

PENCIRIAN FILEM YANG DISEDIAKAN DARI SINARAN MODIFIKASI ADUNAN KANJI SAGU- PVA

Oleh

SARADA BINTI IDRIS

November 2007

Pengerusi : Professor Dzulkefly Kuang bin Abdullah, PhD

Fakulti : Sains

Adunan daripada kanji sagu, poli vinil alkohol dan air suling telah disediakan dan dikenakan sinaran alur elektron dengan dos sinaran diantara 10 hingga 40 kGy untuk menghasilkan hidrogel. Hidrogel yang terhasil kemudian disejukkan di dalam peti penyejuk semalaman untuk menghilangkan buih terperangkap yang terbentuk semasa tindak balas sinaran. Filem kemudian dihasilkan dengan mengeringkan hidrogel di dalam oven. Ciri-ciri adunan selepas sinaran serta filem yang terhasil kemudian ditentukan. Larutan poli vinil alcohol didapati lebih pekat(kental) sebaik selepas dikenakan sinaran menunjukkan telah berlaku tautsilang disebabkan oleh kesan sinaran. Degradasi oleh tindak balas sinaran bagi larutan kanji sagu telah dibuktikan dengan mengkaji kesan kepekatan larutan yang berkurang selepas dikenakan sinaran. Peratus kandungan gel bagi filem-filem yang dikenakan sinaran adalah tinggi berbanding

sebelum sinaran dan semakin meningkat sehingga dos sinaran optimum iaitu pada 20 kGy menunjukkan bahawa taut silang atau cangkukan telah berlaku di dalam adunan yang dikenakan sinaran. Kandungan gel bagi filem poli vinil alkohol direkodkan maksimum pada dos 30 kGy, tetapi ia boleh dikategorikan sebagai taut silang berlebihan dimana filem yang terhasil adalah mengecil kepada saiz yang lebih kecil iaitu pada dos 30 kGy dan ke atas. Suhu melebur bagi filem filem PVA yang diperolehi dari Kalorimetri Perbezaan Imbasan berkurang dengan penambahan dos sinaran. Ini menunjukkan bahawa berlaku tindak balas taut silang di antara molekul-molekul PVA. Kewujudan hanya satu puncak pada suhu melebur oleh Analisis Thermo Gravimetrik mendedahkan tentang keserasian adunan. Mikroskopi Imbasan Elektron bagi morfologi permukaan dan keratan rentas adunan filem mendedahkan lebih bukti mengenai kewujudan taut silang dan cangkukan oleh tindak balas sinaran. Kajian mengenai kesan kandungan kanji sagu dan PVA di dalam adunan, penambahan dan jenis bahan pemplastik serta dos sinaran terhadap kualiti filem juga dibuat dalam penyelidikan ini. Keputusan menunjukkan bahawa kesan sinaran yang dikenakan telah memberikan kekuatan regangan yang lebih baik tetapi nilai pemanjangan filem agak berkurang untuk kesemua adunan S25/P75, S50/P50 adan S75/P25.

Penguraian kanji sagu, PVA serta adunan telah dibuat dengan memerhatikan pengurangan berat selama 6 bulan. Filem kanji sagu adalah terurai sepenuhnya pada bulan yang pertama tempoh penanaman tetapi filem PVA adalah tidak terjejas dalam masa 6 bulan. Kemasukan kanji sagu kedalam adunan telah membaiki kehilangan berat kepada 60% dalam masa 6 bulan.

ACKNOWLEDGEMENTS

I would like to express my thankfulness to Almighty God for giving me an opportunity to finish this study. Also, I would like to express my sincere gratitude to my supervisors, Professor Dr. Dzulkefly Kuang bin Abdullah, the chairman of my Supervisory Committee, Professor Dr. Wan Md. Zin Wan Yunus, for their guidance, advice and most of all their patience for me to complete this project. My deepest appreciation goes to Dr. Zulkafli bin Ghazali and Dr. Kamaruddin Hashim, for their scientific guidance during these years, for always finding time for my problems, for sharing their scientific experience, support and supervision.

I thank the technical assistants from Radiation Processing Technology Division of Malaysian Institute for Nuclear Technology Research (MINT) for their significant technical assistance. My appreciation goes to my friends, especially Rida and Nora for their understanding and wonderful support.

I warmly thank my parents, my brothers and sisters for always offering a helping hand when needed.

Most of all I thank Nusi for his love, encouragement and most valuable support and my dear children, Izz Mirza, Izzan Mirza and Irdina Zahra for an abundance of joyful moments.

I certify that an Examination Committee has met on 19 November 2007 to conduct the final examination of Sarada binti Idris on her Master of Science thesis entitled "Characterization of Film Prepared from Radiation Modified Sago" 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:

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

Nor Azowa Ibrahim, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Faujan Haji Ahmad, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Ibrahim Baba, PhD
Professor
Faculty Science & Technology
Universiti Kebangsaan Malaysia
(External Examiner)

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

Date:

This thesis was 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 were as follows:

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

Wan Md Zin Wan Yunus, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Zulkafli Ghazali, PhD
Malaysian Institute for Nuclear Technology Research (MINT)
(Member)

Kamaruddin Hashim, PhD
Malaysian Institute for Nuclear Technology Research (MINT)
(Member)

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

Date: 8 May 2008

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 institutions.

_____

SARADA BINTI IDRIS

Date: 25 April 2008

TABLE OF CONTENTS

		Page
ABSTRACT		ii
ABSTRAK		iv
ACKNOWLEDGEMENTS		vi
APPROVAL		vii
DECLARATION FORM		ix
LIST OF TABLES		xii
LIST OF FIGURES		xiii
LIST OF ABBREVIATIONS		xvii
CHAPTER		
I	**INTRODUCTION**	1
	Introduction	1
	Objectives of the Study	3
II	**LITERATURE REVIEW**	4
	Biodegradable Plastic	4
	Biodegradable Starch Based Polymers	6
	Production of Biodegradable Plastics	6
	Solution Casting	7
	Extrusion Blending	7
	Properties of Starch Films	8
	Applications of Starch Films	9
	Biodegradability of Starch Plastics	10
	Biodegradable Film Composition	11
	Starch	11
	Properties of Starch	15
	Sago Starch	16
	Polyvinyl Alcohol	20
	Factors Affecting of Biodegradable Films	22
	Starch Retrogradation	22
	Influence of Crosslinking Agent	22
	Crosslinking of Polymer Through Irradiation	24
	Radiation Processing	24
	Influence of Amylose/Amylopectin Content	35
	Influence of Plastisizer	36
III	**MATERIALS AND METHODS**	39
	Materials	39

	Methodology	39
	Formation of Films by Irradiation Technique	40
	Gel Content Determination	41
	Relative Viscosity	41
	Swelling Test	42
	Differential Scanning calorimetry	42
	Thermogravimetry Analysis	42
	Mechanical Properties	
43	Scanning Electron Microscopy	
43		
	Biodegradability Test	44
IV	**RESULTS AND DISCUSSION**	45
	Effect of Irradiation Dose on Sago-PVA Blends	45
	Effect of Irradiation Dose on Crosslinking of Sago-PVA Blends	49
	Effect of Sago Content and Radiation Dose on Gel Content of Sago-PVA Blends	51
	Effect of Irradiation on the Viscosity of Blends and Pure samples	55
	Swelling Test	59
	Melting Temperature	64
	Thermogravimetry Analysis	70
	Mechanical Properties	77
	Scanning Electron Microscopy	85
	Biodegradability Test	95
V	**CONCLUSIONS**	103
REFERENCES		106
APPENDICES		116
VITAE		120

LIST OF TABLES

Table		Page
1	Characteristic of Sago Starch	19
2	Advances in Radiation Chemistry of Polymers	26
3	Spur Reactions in Aqueous Solution	33
4	Visual Inspection of sago Starch, PVA and Sago-PVA Blends After Subjected to Electron Beam Irradiation	48
5	Relative Viscosity Data for Sago Starch, PVA and Blend of sago-PVA	58
6	Thermal Decomposition Data for Non-irradiated Sago Starch, PVA, Blends Sago-PVA, Sago-PVA-Glycerol, 10 and 40 kGy Blend Sago-PVA	71
7	Tensile Strength and Elongation at Break Data for Blends Sago Starch-PVA of Non-Irradiated and Irradiated Films (10, 15 and 20 kGy)	78

LIST OF FIGURES

Figure		Page
1	Characteristic of Amylose and Amylopectin	13
2	Schematic Representation of the Cluster Model of Amylopectin Constituting matrix of the Starch Granule	14
3	Repeating Unit of Polyvinyl Alcohol	21
4	Comparison between Crosslinking of Solid Polymer and Crosslinking of Polymer in the Presense of water	32
5	Molecular Structure of a) Glycerol and b) Sorbitol	38
6	Influence if Irradiation Dose on the Gel Content of Sago Starch, PVA, Blend Sago-PVA and Sago-PVA-Glycerol (spg)	50
7	Influence of Irradiation Dose and Ratio of Sago Starch:PVA on the Gel Content	52
8	Influence of Irradiation Dose and Plastisizers on the Gel Content: SP(Sago-PVA), SPG(Sago-PVA-Glycerol), SPS(Sago-PVA-Sorbitol) and SPPG(sago-PVA-Propylene Glycol)	54
9	Relative Viscosity of Sago 5%, PVA5% and Sago 5%-PVA 5% Blends (50:50) Irradiated at 0, 10 and 40 kGy Doses	56
10	Influence of Irradiation Dose to the Swelling of Sago Starch, PVA, Sago-PVA Blends	60
11	Influence of Irradiation Dose to the Swelling of Sago-PVA Blends	62

12	Influence of Irradiation Dose and Plastisizers on the Swelling Properties: SP(Sago-PVA), SPG(Sago-PVA-Glycerol), SPS(Sago-PVA-Sorbitol) and SPPG(sago-PVA-Propylene Glycol)	63
13	DSC Thermograms of PVA Films of Non-irradiated, 10, 20, 30 and 40 kGy	65
14	DSC Thermograms of Sago-PVA Blend Films of Non-irradiated, 10, 20 and 30 kGy	67
15	DSC Thermograms of Sago-PVA-Glycerol Blend Films of Non-irradiated, 10, 20, 30 and 40 kGy	69
16	TGA and DTG Thermograms of Non-irradiated sago Starch Film	72
17	TGA and DTG Thermograms of Non-irradiated PVA Film	72
18	TGA and DTG Thermograms of Non-irradiated Sago-PVA Blends Film	74
19	TGA and DTG Thermograms of Non-irradiated Sago-PVA-Glycerol Blends Film	74
20	TGA and DTG Thermograms of 10 kGy Irradiated Sago-PVA Blends Film	75
21	TGA and DTG Thermograms of 40 kGy Irradiated Sago-PVA Blends Film	75
22	Tensile Strength and Elongation at Break of 15 kGy Irradiated Blends Film	80
23	Tensile Strength and Elongation at Break of Non-irradiated Blends Film	81
24	Tensile Strength of 0-20 kGy Irradiated Films with	82

	Different Plastisizers	
25	Elongation at Break of 0-20 kGy Irradiated Films with Different Plastisizers	83
26	SEM-micrograph for Film Surface of Non-irradiated Sago Starch	86
27	SEM-micrograph for Cross Section of Non-irradiated Sago Starch	86
28	SEM-micrograph for Film Surface of Non-irradiated PVA	87
29	SEM-micrograph for Cross Section of Non-irradiated PVA	87
30	SEM –micrograph for Film Surface of 10 kGy Irradiated PVA	88
31	SEM –micrograph for Cross Section of 10 kGy Irradiated PVA	88
32	SEM-micrograph for Non-irradiated Sago-PVA Film (Film Surface)	89
33	SEM-micrograph for Non-irradiated Sago-PVA Film (Cross-section)	89
34	SEM-micrograph for 10 kGy Irradiated Sago-PVA Film (Film Surface)	90
35	SEM-micrograph for 10 kGy Irradiated Sago-PVA Film (Cross-section)	90
36	SEM-micrograph for Non-irradiated Sago-PVA-Glycerol Film (Film Surface)	93
37	SEM-micrograph for Non-irradiated Sago-PVA-Glycerol Film (Cross-section)	93
38	SEM-micrograph for 10 kGy Irradiated Sago-PVA-Glycerol Film (Film Surface)	94
39	SEM-micrograph for 10 kGy Irradiated Sago-PVA-Glycerol Film (Cross-section)	94

40 Percentage of weight loss of non-irradiated sago starch, PVA and blend sago-PVA films against time 97

40 Percentage of weight loss of 10 kGy irradiated sago starch, PVA and blend sago-PVA films against time 98

41 Percentage of weight loss of non-irradiated sago-PVA blends films with addition of plastisizers 101

42 Percentage of weight loss of 10 kGy irradiated blend sago-PVA films with addition of plastisizers 102

LIST OF ABBREVIATIONS

PVA	Poly (Vinyl alcohol)
SPG	Sago-PVA-Glycerol Blends
SPPg	Sago-PVA-Propylene Glycol Blends
SPS	Sago-PVA-Sorbitol Blends
CMC	Carboxyl Methyl Cellulose

CHAPTER I

INTRODUCTION

Sago palm (Metroxylon Spp) is one of the important starch crops in Malaysia that is potentially be developed as carbohydrate sources, industry raw material and other economic activities. Sago palm trees grow in swampy area or marginal land where others produced carbohydrate could not grow. Currently sago starch is used both in the food industries as in production of high fructrose syrup, glucose and monosodium glutamate (MSG), making of noodle, caramel, sago pearl, crackers and bread and in non-food industries as in the making of non-toxic paper glue.

Since the 1970s, starch has been incorporated to varying extents into plastics in an effort to develop a biodegradable alternative to petroleum-based commodity plastics which are discarded in landfills and place a strain on the non-renewable resources from which they originate. Some starch plastics have been labeled as biodegradable when they, in fact, had a very small content (as low as 5%) which was the only part of the plastics that biodegraded. For starch plastics to be biodegradable, their properties will have to be at least comparable to those of traditional plastics and, for cost-effectiveness, it must be possible to produce them using the conventional techniques used for production of commodity plastics. (Meadows, 1998)

Most of the raw material used in the plastic packaging products are derived from petroleum based material. Among them are polypropylene (PP), polyethylene (PE) and nylon which is not environmental friendly. These petroleum based products will not able to degrade biologically and mostly disposed off as garbage in landfill disposal areas. Incineration of these material poses other environmental and health related issues as a result of release of flue gases (NO_X and SO_X) as well as dioxin, the by-products from the process.

Some of these materials are treated and recycled, however, the remaining plastic waste remains and contaminate the environmental and affect the ecology equilibrium and ultimately our well being and livelihood. Interest in biodegradable packaging has increased significantly in recent years due to many factors, including rapidly diminishing landfill space, concern over future oil prices for the manufacture of synthetic plastic packaging, public awareness of environmental issues, damage to marine life due to discarded plastics and the development of new technologies for alternative degradable packaging materials.

This study aims to relate a biodegradable sago starch blend film composition, to a radiation cross-linkable sago starch blend films, prepared from sago starch, polyvinyl alcohol and plastisizers. This water soluble film is useful as application of detergent sachet, embroidery backing film, hospital laundry and other application that requires soluble and biodegradable films.

The objectives of the study are ,

1. To produce films from blends of sago starch, polyvinyl alcohol and plastisizers through irradiation technique (electron beam).
2. To study the effects of irradiation dose on sago starch, polyvinyl alcohol and the blends, and evaluate the conditions of crosslinking or degradation by gel content measurement.
3. To study the swelling, viscosity, biodegradability and mechanical properties of the sago starch, polyvinyl alcohol and the blends films.
4. To characterize the non-irradiated and irradiated films by Differential Scanning Calorimetry (DSC), Thermogravimetry Analysis (TGA) and Scanning electron Microscopy (SEM).

CHAPTER II

LITERATURE REVIEW

Biodegradable Plastics

The disposal of plastics in an ecologically sound manner has resulted in the evolution of two new growth industries named Recyclable Plastics and Biodegradable Plastics. Biodegradable plastics are targeted towards single-use, disposable packaging, consumer goods, disposable nonwovens, coating for paper and paperboard as well as some non-packaging markets. The growth of composting as an ecologically sound waste management approach supports the need for biodegradable plastics in the market place. Polyesters such as poly(ε-caprolactone), poly(lactic acid), poly (hydroxybutyrate-co-hydroxyvalerate), thermoplastic starch and modified starch formulations, poly (vinyl alcohol), protein polymers, are examples of biodegradable polymeric materials being introduced into the market (Narayan, 1993).

The biodegradability of plastics is dependent on the chemical structure of the material and on the constitution of the final product, not just on the raw materials used for its production. Therefore, biodegradable plastics can be based on natural and synthetic resins. Natural biodegradable plastics are based primarily on renewable resources (such as starch) and can be either naturally produced or synthesized from renewable resources. Non-renewable synthetic biodegradable plastics are petroleum based. As

any marketable plastic product must meet the performance requirements of its intended function, many natural biodegradable plastics are blended with synthetic polymers to produce plastics which meet these functional requirements.

Biodegradable Starch Based Polymers

Combining a biodegradable polymer (starch, protein or lipids) and a petroleum polymer raises the issue of how biodegradation will proceed in the environment. Biological material can be metabolized by certain bacterium, whereas the petroleum polymer does not biodegrade but disintegrates. The presence of plasticizers, processing aids, stabilizers and other additives are other factors that determine overall biodegradability of the product (Koelsch and Labuza, 1991)

Production of biodegradable plastics

Use of granular starch as filler in plastics began with the work of Griffin in the 1970's. Starch-containing polyethylene films and other consumer items based on this technology are currently being marketed. Since whole starch granules are used in this technology, the level of starch addition is generally limited to about 10% or less, by weight **(**Shogren *et al*., 1993**).**

In the past few decades, there has been a marked advance in the development of biodegradable plastics from renewable resources, especially for those derived from

starch-based materials. The goal of this development is to obtain biodegradable plastics that perform as well as traditional plastics when in use and which completely biodegrade at disposal. Several starch-based plastics have been introduced into the market, and are used in some applications now. The type of starch and synthetic polymer as well as their relative proportions in the blends influence the properties of the resulting plastics (Sriroth and Sangseethong, 2005).

Engineering of biodegradable plastic material requires knowledge of the processing and material properties of the polymers. If the properties of the native biopolymer are not identical to the required one, or if the polymer by nature is not thermoplastic, a certain modification of the polymer must take place. In my study, the processing of biodegradable plastic film used the basic simple casting followed by irradiation of solution by electron beam to initiate cross-linking.

Solution casting

Jayasekara *et al*., 2004 studied the production of solution cast chitosan – poly vinyl alcohol blended films. The hydrophilic nature of the film surfaces was altered by surface modification with the biopolymer chitosan. Chitosan was chosen to tender the surface more hydrophobic and thus more amenable to examination.

Film-forming properties of corn zein have been extensively studied by many researchers. The films obtained by drying of alcoholic aqueous dispersion are not water

soluble but are relatively brilliant and grease resistant. Films and coating based on zein are, for instance, used to preserve fresh food, to retain enriching vitamins, and for controlled release of medically active compounds. These films are used to protect dry or dried fruits and frozen or intermediate moisture foods. Aqueous dispersions of zein are commercially available. Starch and zein mixtures have been investigated for manufacturing of biodegradable plastics (Jane, 1995).

Films and water soluble bags have been fabricated from peanut proteins by collecting the lipoproteic skin formed after boiling peanut milk, in a manner similar to film formation on soy milk surface. Biodegradable films based on cottonseed proteins, obtained from a film forming solution treated with various crosslinking agents, have been studied and developed by Marquie *et al*. (1997).

Extrusion Blending

In the last 10 years, various researchers focused on reactive blending of starch and synthetic polymers in twin screw extruders and injection molded samples. The blending of corn starch and ethylene-propylene-g-maleic anhydride (EPMA) and modified polystyrene with maleic anhydride (SMA) was studied by Vaidya *et al*., (1995). They found that the torque generated during the blending was higher for the blends of anhydride functional polymers than for the blends of corresponding nonfunctional polymers.