UNIVERSITI PUTRA MALAYSIA

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

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FS 2008 29

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By

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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

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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:

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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:

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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 institutions.

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SARADA BINTI IDRIS

Date: 25 April 2008

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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.