UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERISATION OF POLYSTYRENE GRAFTED SAGO STARCH

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PREPARATION AND CHARACTERISATION OF POLYSTYRENE GRAFTED SAGO STARCH

By

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Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Science and Environment Studies, Universiti Putra Malaysia

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DEDICATION

To my husband, Vengidesh, whose patience, support and

companionship have facilitated my work and made my life enjoyable.

And also my beloved father, mother, brothers, sister and friends

for their love and encouragement.

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TABLE OF CONTENTS

APPENDIX

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

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

PREPARATION AND CHARACTERISATION OF POLYSTYRENE GRAFTED SAGO STARCH

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May 1999

Chairman: **Associate Professor Wan Md. Zin Wan Yunus, Ph.D.**

Faculty: **Science and Environmental Studies**

Styrene grafting onto sago starch was carried out by using ceric ammonium nitrate (CAN) as a redox initiator. The parameters affecting the grafting reaction were investigated and the optimum conditions obtained are as follows: temperature, 50°C; nitric acid concentration, 0.01M; amount of styrene, 0.35 mol; amount of CAN, 16.8×10^{-4} mol and reaction period, 2h. Percentages of grafting and grafting efficiency under the optimum condition were 53.92% and 73.21%, respectively. Reactions in the presence of nitrogen gas resulted in higher percentages of grafting and grafting efficiency.

FTIR spectra analysis of the grafted chain and polystyrene was identical indicating that styrene was successfully grafted onto sago starch. TGA thermograms, DSC curves and SEM photographs of sago starch-g-poly(styrene) and the original polymers (sago starch and polystyrene) were different which suggested that styrene was grafted onto sago starch. The bio-degradability study using α-amylase showed that the rate of degradation of gelatinised sago starch was higher than that of sago starch-g-poly(styrene). The highest rate of degradation of sago starch-g-poly(styrene) was obtained at 50 ppm of α-amylase concentration. Viscosity measurements showed that the intrinsic viscosity and the average molecular weight (M_v) increased with the increase in the percentage of grafted polystyrene. The M_v of the various percentages of grafted polystyrene were in the order of 10^4 . The results obtained from the swelling of sago starch-g-poly(styrene) in polar and non polar solvents showed that the percentage of swelling at equilibrium and the swelling rate coefficient decreased in the following order: DMSO > water > acetone > cyclohexanone $\approx$ $CHCl_3$ > toluene $\approx$ CCl_4. Diffusions of the solvents onto the polymers were found to be of a Fickian only for DMSO.

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

PENYEDIAAN DAN PENCIRIAN KOPOLIMER KANJI SAGO-POLISTIRENA

Oleh

PUSHPAMALAR A/P JANARTHANAN

Mei 1999

Pengerusi: **Profesor Madya Wan Md. Zin Wan Yunus, Ph.D.**

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Kajian bagi pengkopolimeran cangkuk stirena ke atas kanji sagu telah dibuat dengan menggunakan serium ammonium nitrat (SAN) sebagai pemula tindak balas redoks. Parameter-parameter yang memberi kesan ke atas pengkopolimeran telah dikaji dan keadaan optimum tindak balas yang diperolehi adalah seperti berikut : suhu tindak balas, 50°C; kepekatan asid nitrik, 0.01 M; amaun stirena, 0.35 mol; amaun SAN, 16.8×10^{-4} mol dan masa tindak balas, 2 jam. Peratus-peratus pengkopolimeran cangkuk dan kecekapan pengkopolimeran cangkuk di bawah keadaan optimum adalah masing-masing 53.92% dan 73.21%. Tindak balas dengan kehadiran gas nitrogen menghasilkan peratus-peratus pengkopolimeran cangkuk dan kecekapan pengkopolimeran cangkuk adalah lebih tinggi.

Analisis spektra daripada spektrofotometer inframerah untuk polistirena yang dicangkuk adalah sama dengan polistirena piawai. Ini

menunjukkan bahawa stirena berjaya dicangkukkan ke atas kanji sagu. Termogram-termogram daripada termogravimetri, keluk-keluk daripada kalorimetri pengimbasan pembezaan dan gambar-gambar daripada elektron mikroskop untuk kopolimer kanji sagu-polistirena dan polimer permulaan (kanji sagu) adalah berbeza. Ini juga mencadangkan bahawa stirena telah dicangkukkan ke atas kanji sagu.

Kajian mengenai penguraian secara biologi dengan menggunakan α-amilase menunjukkan bahawa kadar penguraian untuk kanji sagu yang telah digelatinkan adalah lebih tinggi daripada kopolimer kanji sagu-polistirena. Kadar penguraian yang paling tinggi bagi kopolimer kanji sagu-polistirena diperolehi dengan menggunakan α-amilase pada kepekatan 50 ppm. Pengukuran kelikatan larutan cair menunjukkan kelikatan intrinsik dan purata jisim molekul (M_v) meningkat dengan meningkatnya peratus polistirena yang dicangkuk. Purata jisim molekul untuk pelbagai peratus polistirena yang dicangkuk adalah dalam urutan 10^4. Keputusan kajian pengembungan kopolimer kanji sagu-polistirena di dalam plarut-pelarut berkutub dan tak berkutub menunjukkan bahawa peratus pengembungan pada keseimbangan dan pemalar kadar pengembungan menurun secara berikut: DMSO > air > acetone > cyclohexanone $\approx$ $CHCl_3$ > toulena $\approx$ CCl_4. Pembauran pelarut ke dalam kopolimer kanji sagu-polistirena adalah secara Fickian hanya bagi DMSO.

CHAPTER I

INTRODUCTION

Starch

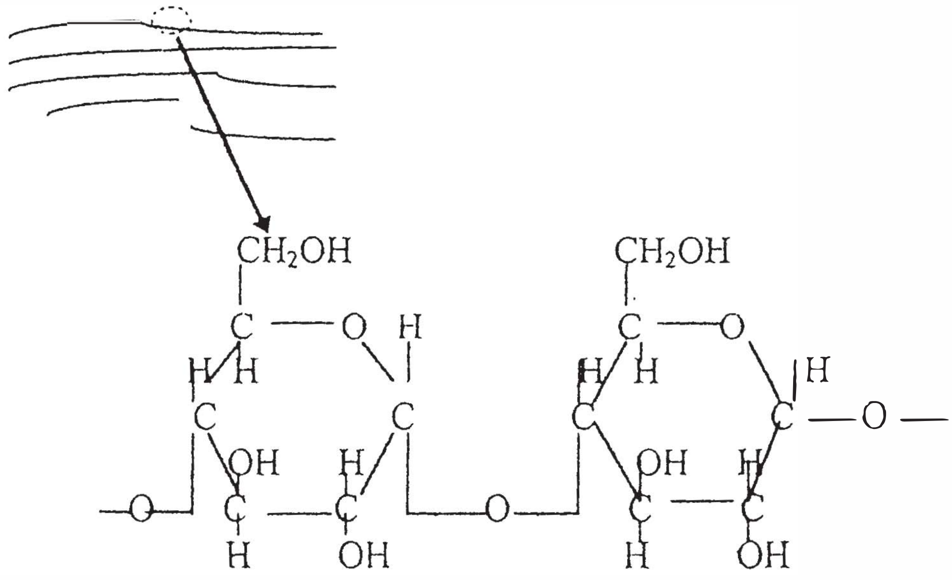
Starch is one of the cheapest, bio-degradable and most readily available of all renewable natural polymers exists in plants. It is anhydrous D-glucose consisting of mixture of amylose and amylopectin as shown in Figure 1. Amylose is a linear polymer of molecular weight between one thousand and one million and made up of several hundred glucose units linked by α 1-4 glycosidic linkages. Amylopectin is a branched polymer of glucose units of α 1-6 glycosidic linkages at the branching points and α 1-4 glycosidic linkages in the linear region. The molecular weight of amylopectin can run into several millions. Starch is not truly thermoplastic like most synthetic polymers. However, it can be melted and flow at high temperatures under pressure and shear. If the mechanical shear becomes too high then starch will degrade to form products with low molecular weight. Addition of water or other plasticisers enables starch to flow under milder conditions and reduces degradation considerably (Wurzburg, 1989). Starch has both the crystal and amorphous structures (Gao *et al.*, 1994). Because of their crystallinity, most starch granules show a Maltese crosses when observed under polarized light. Native starch granules have a crystallinity range from 15 to 45%. The granule appears to be made up of alternating semi-crystalline and crystalline shells which are between 120 and 420 nm thick. Solid state ^{13}H NMR analysis shows that the level of helical order in the starch granules is significantly greater than the extent of crystalline order. Consequently, it appears that much of amylopectin in semi-crystalline shells is in the double helical form, although it is not crystalline (Gallant *et al.*, 1997).

The properties of starch can be significantly improved by blending it with synthetic polymers. However, most of the synthetic polymers are immiscible with starch at the molecular level which leads to the poor performance of these blends. In order to overcome this drawback, graft copolymerisation of vinyl monomers on the starch backbone is used to modify starch (Vaidya *et al.*, 1995). A review of the literature indicates that although the grafting of starch with synthetic monomers has been known for 30 years, very few processes have led to full-scale commercialisation.

Sago Starch

Sago starch has been known to exist for 400 years and produced from sago palm plants. There are two main species of sago palm:

AMYLOSE- linked through α - D- (1→4) glucosidic bonds



AMYLOPECTIN → α - D- (1 → 4) glucosidic bond
→ branch linked α - D (1 → 6) glucosidic bond.

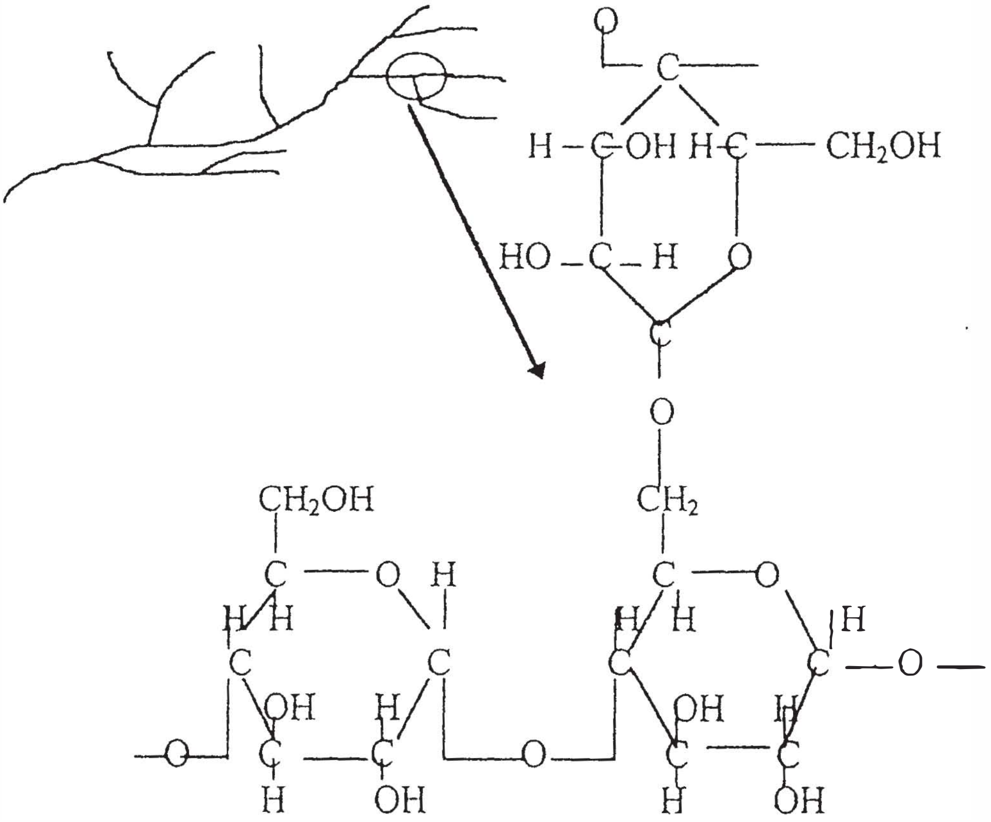


Figure 1 : Chemical Structure of Starch

Metroxylon rumphii with the thorny main stem and *Metroxylon sagu Rottbboll* with thornless main stem (Jeffrey, 1986). Sago starch studied by the scanning electron microscope are deformed prolate ellipsoidal shape particles which are larger than those of maize and tapioca (Griffin, 1977). In 1941, Thomas Schoch showed that sago starch consists of 27% amylose and 73% amylopectin (Wurzburg, 1989). Quality characteristics of sago starch depend on interrelated factors such as raw material, mode of transport, supply and quality of water, method and efficiency of the extraction and purification processes (Jeffrey, 1986).

Polymer

Polymers are large molecules made up by the repetition of small, simple chemical units. The essential requirement for a small molecule to qualify as a monomer is the possession of two or more bonding sites. It is produced through a process known as polymerisation in which the monomer molecules react chemically to form a linear chain by covalent bond. The polymerisation techniques are classified as addition and condensation polymerisations. Linear chain polymers composed of chemically identical monomers called homopolymers. The polymers incorporating two or more chemically different types of monomers onto the chain are called copolymers.

The copolymer structure can be divided in random, alternating, block or graft copolymers. When two different monomers in a copolymer are distributed at random throughout the chain, the polymer is called a random copolymer. If the units of two monomers are distributed alternatively throughout the chain, this polymer is called alternating copolymer. Polymers containing long stretches of two or more monomers linked together by chemical valences in one single chain is called block copolymers. A graft copolymer is a branched block arrangement in which the polymer structure consisting of one polymer with another polymer branched to it (Billmeyer, 1984 ; Hiemenz, 1984).

Graft Polymerisation

Graft copolymerisation is a well known method to modify the chemical and physical properties of polymers. Graft copolymerisation results from the formation of an active site at a point on a polymer molecule back bone and exposure to a second monomer. Most of the graft copolymers are formed by free radical polymerisation using chemical or radiation methods. The radiation method is carried out by irradiating the polymer using gamma or ultraviolet radiations. The chemical method is through the formation of free radicals, cations and anions by a suitable chemical reaction. Starch graft copolymers are becoming important because of their potential application in industry. The wide range of available vinyl and other monomers suggests that grafting is a powerful method for producing modification in starch properties and enlarging the range of utilization (Athawale and Rathi, 1997a).

Acidic and Enzymatic Degradation of Starch

Starch is a bio-degradable natural polymer. It degrades when the enzyme or acid molecule attacks the starch back bone. Enzymatic and acidic attacks of starch are similar since they both involve hydrolysis of the bonds in the starch. In both processes the semi-crystallinity of the granules are more easily and rapidly hydrolysed than the crystalline layers. The size of the acid molecule is smaller than the enzyme which allows the acidic the attack to occur on a finer scale than the enzymatic attack. The acid degradation is affected by the acid concentration, temperature and the presence of alcohols. Prolonged exposure to acid molecules will allow the acid molecules to penetrate through even the crystalline regions of the granule and act on the α-1,6 bonds of the amylopectin molecules in the starch (Cui and Oates, 1997).

During the enzymatic attack the less crystalline part of the starch granules is easily digested than the hard crystalline part. Pits are formed randomly all over the granule surface and combined to form canals which will enlarge and merge (Gallant *et at.*, 1997). Alpha amylase from a new source (*Aspergillus fumigatus*) has been shown to have a different pattern of degradation. It forms pores at the surface of the granules even with the resistant starches (Gallant *et al*., 1997).

Swelling

Studies on the diffusion of polar and non polar solvents in swellable polymeric systems have received considerable attention because of the important applications of biomedical, pharmaceutical, environmental and agriculture engineering. In a swelling process it is necessary to take into account the force of friction. When the polymer is swelling in a solution from the dry state, it takes time for a network to swell from the surface to the core. The swelling processes consist of the interaction with the solvent and the polymer, followed by the solvent penetration inside the network which induces a polymer swelling (Budtova, 1997). The percentage of swelling (%S) can be calculated from the following relation:

$$\%S = [(m_t - m_o) / m_o] \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where m_t is the mass of swollen polymer at time t, and m_o is the initial mass of the swollen polymer.

Objectives of the Study

The objectives of this study are as follows :

1. To prepare the grafting of styrene onto sago starch by using ceric ammonium nitrate as the initiator and to study the effecting reaction parameters to obtain an optimum condition which leads to maximum grafting.

2. To characterise sago starch-g-poly(styrene) by Fourier Transform Infrared Spectroscopy, Thermogravimetry, Differential Scanning Calorimetry and Scanning Electron Microscopy.

3. To investigate the bio-degradability of the polystyrene grafted sago starch and gelatinised sago starch by using α-amylase as the enzyme.

4. To study the swelling behavior of polystyrene grafted sago starch in various types of solvent to determine the swelling at equilibrium and the nature of diffusion of the solvents on the grafted copolymer.

5. To carry out viscosity measurements for various percentages of grafted polystyrene to determine the average molecular weight.

CHAPTER II

LITERATURE REVIEW

Grafting Copolymerisation of Synthetic Monomers onto Natural Polymers

The modification of natural polymers is a promising method for the preparation of new materials. This enables one to introduce special properties and enlarge the field of the potential applications of those biopolymers of abundance. Among the diverse modifications that are possible to achieve, grafting of synthetic polymers is a convenient method (Yazdani-Pedram and Retuert, 1997).

Grafting Vinyl Monomers onto Wool Fibres

Chemical modification of wool through graft copolymerisation of vinyl monomers can be effective in improving some of the fibre properties. Grafting of vinyl monomers was achieved by free radical initiation mechanism. Free radical can be produced by both chemical and physical methods, including the use of redox systems, oxidizing agents, low and high energy radiation. The monomer may interact with free radical sites