PREPARATION AND CHARACTERIZATION OF STARCH-BASED PARTICLES AND HYDROGELS FROM NATIVE SAGO STARCH

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Bachelor of Science with Honours
(Resource Chemistry)
2007
PREPARATION AND CHARACTERIZATION OF STARCH-BASED PARTICLES
AND HYDROGELS FROM NATIVE SAGO STARCH

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This project is submitted in partial fulfillment of the requirements for the degree of Bachelor
of Science with Honours
(Resource Chemistry)

Faculty of Resource Science and Technology
UNIVERSITY MALAYSIA SARAWAK
2007
DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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ACKNOWLEDGEMENT

First of all, I would like to acknowledge my supervisor Dr. Pang Suh Cern for his wisdom and careful guidance. His guidance and supports have helped me a lot to improve my final year project. Without his careful supervision, I would not have successfully completed my final year project.

I would also like to thank the master students in my labs for constantly advising and assisting throughout my project. Thanks are also addressed to all the lab assistants of Resource Chemistry Programme for helping me in the use of instruments and to solve problems encountered.

My appreciation is also extended to the Timber Research and technical Training Centre (TRTIC) for the permission to use their Scanning Electron Microscope (SEM). Special thanks are given to Mr. Lai and Mr. Voon who have helped me in acquiring the SEM and Optical Microscope images.

A huge thanks also addressed to my family for their support and encouragement and patience over this project and my entire degree course. This work would not have been possible without them and I am forever indebted to them.

Finally, I would like to express my appreciation to my course mates and all the lecturers who have giving me supports and helped me throughout my final year project.
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Preparation and Characterization of Starch-based Particles and Hydrogels from Native Sago Starch

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ABSTRACT

This project focuses on the synthesis and characterization of starch-based particles from native sago starch. Starch-based particles and hydrogel were synthesized through several methods which included the water-in-oil emulsion method using epichlorohydrin (ECH) as the cross-linker, and the regeneration method without using surfactants. These synthesis approaches involved dissolving starch in various solvent systems such as NaOH, NaOH-Thiourea mixture and aqueous dimethyl sulfoxide (DMSO). Macroporous starch gel sponge was prepared by the freeze-thaw method. These starch-based particles and hydrogel were being characterized with respect to their surface morphology, particle sizes and shape using Scanning Electron Microscope (SEM) and their chemical structures using Fourier Transformed Infra-Red Spectrometer (FTIR). Starch-based particles were observed to be of spherical or oval in shape and of much reduced granule size than native sago starch. Results of the FTIR showed that starch particles possessed very similar physical and chemical structures as their original precursor materials. As such, it was uncertain if nano-sized sago starch particles have been successfully formed through the cross-linking process. Further characterization using FESEM with higher resolution capability would be necessary for elucidating the effect of synthesis conditions on the morphological characteristics of starch particles and the microstructure of macroporous starch gel sponge.

Key words: starch-based particle, cross-linking, surfactant, macroporous sponge.

ABSTRAK


Kata kunci: partikel kanji, taut-silang, surfaktan, span makroporos
CHAPTER 1
INTRODUCTION

1.0 General Introduction:

Sago is the powdery starch made from the processed pith found inside the trunks of the Sago Palm *Metroxylon sagu* (McClatchey *et al.*, 2005). It is mainly being processed into flour, meal and pearl sago. It is found in Southeast Asia, Melanesia, and some islands in Micronesia and Polynesia. Growing up to 30 meters in height, the sago palm is found in tropical lowland forest and freshwater swamps, and can grow in a wide variety of soils. It is a fast-growing species.

Starch is a biocompatible, biodegradable, nontoxic polymer, existing in nature as the major storage polysaccharide in higher plants. It is found in nature as water-insoluble semicrystalline granules (Dziechciarek *et al.*, 2002). Native starches are a blend of two polyglucans, amylose and amylopectin. Amylose is the linear fraction consisting of α-D-glucose linked through α-(1-4) linkages and has a molecular weight of $10^5$-$10^6$ g/mol (Wesslen and Wesslen, 2002). Amylopectins, with molecular weights between $10^6$ and $10^7$ g/mol, are branched fractions containing short chains linking linear chains via α-(1-6) linkages.

Due to their biodegradable properties, starch and starch-based compounds are suitable candidates for use in paper, textile coatings and especially in plastics instead of using petroleum-based materials (Jansson and Jarnstrom, 2005). In the past 20 years, the production
and the use of plastics in the world have been enormously increased, worsening the problem of waste disposal. For examples, the used packaging materials, such as shopping bags, are still easily visible in the environment in many countries. So, biodegradable materials offer a possible alternative to the traditional non-biodegradable polymers. Among the biomaterials present today in market, those derived from renewable resources such as starch-based products are the most widespread and economic biomaterials (Avella et al., 2005). Moreover, polysaccharides including starch derivatives have been widely used in food and related industries to improve the textures and to increase viscosity and stabilization of products and/or to form a gel (Nishinari et al., 2006).

Additionally, starch is also being used in a broad range of applications as thickeners, stabilizer, gelling agent and as drug carrier (Schmidt et al., 2001; Jeffcoat et al., 2002; Lind et al., 2002). The potential of starch nanoparticles and microspheres as drug carriers has been extensively studied (Debuigne et al., 2001; Illum et al., 2001; Brigger et al., 2002).

However, in the past researches, problems were encountered while attempting to synthesize starch nanoparticles or microspheres (Ellis et al., 1998; Jane, 1995). For example, the range of functional properties of starch is restricted even for chemically modified starch with a high degree of substitution (Ellis et al., 1998; Jane, 1995). As a consequence of these limitations, it is not possible to form stable suspensions or to obtain colloidal systems from native starches. This is a disadvantage of starch for potential applications, such as, paper making, ink, coating, and pharmaceutical products (Soest et al., 2000).
Nevertheless, novel starch-based microspheres were successfully prepared, which behave as colloids in aqueous suspension (Soest et al., 1997). The synthesis is based on a combination of gelatinization and cross-linking performed in water-in-oil emulsions. The hydroxyl groups of the repeating glucose units of the starch chains, or other groups introduced chemically react with a cross-linking agent in an inverse emulsion (Soest et al., 1997; Jiugao and Jie, 1994). An extensive list of cross linkers is known for starch. Phosphoryl chloride, epichlorohydrin, and tri-sodium tri-metaphosphate are most commonly used.

Starch can also be made into hydrogel. Hydrogels are a broad class of hydrophilic materials formed by three-dimensional networks held together by covalent bond cross-links and weak cohesive forces in the form of hydrogen or ionic bonds. These cross-linked macromolecular structures are able to absorb large quantities of water and biological fluids without dissolution. Due to their high water content and special surface properties, hydrogels usually have good biocompatibility attributed to their ability to stimulate natural tissues. Since the pioneering work of Whichterle and Lim in 1960, hydrophilic hydrogels have been of great interest for biotechnological and biomedical applications (Hoffman, 2002; Peppas, 1986). In an attempt to develop starch-based hydrogels as the excipients in controlled drug release systems, epichlorohydrin, chloroethylamine hydrochloride, acetic anhydride and tri-metaphosphate were evaluated to cross-link starch (Ravenelle et al., 2002; Jerome et al., 2001; Ispas-Szabo et al., 2000; Shiflan et al., 2000).

On the other hand, Hamdi et al. (2001) described a water-in-oil emulsion technique for the production of microspheres by cross-linking soluble starch with epichlorohydrin, which is a very efficient divalent cross linking agent from starch. According to Shinoda and Takeda.
(1970), the addition of NaOH to the aqueous phase would result in the affinity of water for the hydrophilic head of surfactant leading to modifications of the surface tension at the water-organic phase interface. This resulted in the formation of unstable emulsion. More recently, Zhang and co-workers (2002) found that NaOH/urea and NaOH/thiourea aqueous solutions can dissolve cellulose directly and quickly. Both solvent systems are inexpensive and less toxic, and good cellulose fibers can be prepared using simple technology (Ruan et al., 2004; Cai et al., 2004; Chen et al., 2006). Due to the similarity in the structure between cellulose and starch, therefore, in this project study, a mixture of NaOH/thiourea will be used instead of NaOH to disperse the starch in order to reduce the instability of the emulsion.

In most applications, volume and conformation changes of starch particles are crucial since they determine, for example, the rheology of suspensions (Dickinson, 1992; Hunter, 1986; Makosko, 1994). Shape, size and structure of starch colloids, as well as their specific volume and swelling behavior, have had little study, thus far. Moreover, in the previous papers (Hamdi et al., 2001; Dziechciarek et al., 2002), only starch particles in the micro range were produced using the water-in-oil emulsion technique. The aim of this research is, therefore, not only to establish synthesis procedures for starch-based nanoparticles from stable emulsion but also to investigate both the physical and chemical properties of starch nanoparticles. In this research, sago starch was being used as the raw material because it is cheap and abundantly available locally.
CHAPTER 2
LITERATURE REVIEWS

Starch is a type of carbohydrate. Starch is the principle energy reserve in plants and is one of the most abundant carbohydrates in the biosphere. It is the food produced by photosynthesis in plants. Specifically, starch is a complex carbohydrate which is insoluble in water. This complex carbohydrate is made up of many glucose molecules linked together. Starch is deposited in the form of granules in almost all green plants and in various types of plant tissues and organs, e.g., leaves, roots, shoots, fruits, grains, and stems, notably in corn, potatoes, wheat, rice and sago. Illumination of the leaf in bright light causes the formation of starch granules in the chloroplast organelle and was demonstrated in the nineteenth century (Sachs, 1887). The presence of starch is readily observed by iodine staining of the tissues (Edwards and Walker, 1983) or by light and electron microscopy (Badenhuizen, 1969).

Starch, the generic name for the D-glucose storage polysaccharide in plants, consists of a mixture of two polysaccharides amylose and amylopectin (Van der Burgt et al., 2000). Specifically, starch is a natural occurring polysaccharide consisting of anhydroglucopyranose (Figure 1) residues linked together in two ways:

![Anhydroglucopyranose](image)

Figure 1: Anhydroglucopyranose
The most common one is the 1-4 glucoside link, which, when occurring exclusively, produces a linear chain-like molecule called amylose (Figure 2).

![Figure 2: The linear chain-like amylose.](image)

The second type of linkage is the 1-6 glycoside links, which, in conjunction with the 1-4 linkage, yields a branched structure called amylopectin (Figure 3), which forms the main constituent of starch (Avella et al., 2005). The proportion of amylose to amylopectin varies in starches from different plants.

![Figure 3: Amylopectin molecules](image)

Most starches used in industry usually contain between 20 to 30% amylose with the remainder being amylopectin (70-80%) and minor components (less than 1%) such as lipids.
and protein (Whistler et al., 1984). As an important class of complex polysaccharides, native starch, pure starch components including amylose, amylopectin and pullulan, as well as their derivatives are presently being used to prepare biodegradable hydrogels with technological applications in a large number of areas such as medicine, pharmacy, agriculture, biology, environmental remediation and protection (Park et al., 1993; Athawale and Lele, 2000; Lee and Mooney, 2001; Zhang and Chen, 2002). In particular, starch-based hydrogels are of interest for biomedical use due to their swellability in water, biocompatibility and biodegradability (Sinha and Kumria, 2001). Consequently, various approaches have been explored in the development of biodegradable starch-based hydrogels, for biomedical applications such as drug delivery carriers.

As for environmental remediation and protection, starches which are fully biodegradable in nature, are the sustainable polymeric materials of the future as synthetic polymers coming from oil become expensive and rare. They represent an almost inexhaustible resource of making a reality of the possibility of replacing oil-derived materials by biodegradable and biocompatible (compatible with living tissues) products. Therefore, the great potential of starch polysaccharides has been attracting a lot of interests from numerous industrial sectors, such as the paper industry, the textile industry, packaging, health, hygiene, the building industry and the transport sector.

In order for starch to be used in biomedical applications such as drug delivery carriers, it is crucial and of important pharmaceutical value if the starch-based particles were synthesized in the nano-sized range. Due to their nano-size, higher surface areas available on the starch particles were able to accommodate higher capacity loading of drugs. Thus, due to
this advantage and non-toxic nature of starch, attempts were extensively formulated to produce starch-based particles in nano-size (nanoparticle).

There is no standardized international definition of a nanoparticle, but one commonly accepted definition given in the recent report (Nanoscience, 2004) by The Royal Society and The Royal Academy of Engineering in the UK, is, ‘a particle that has one or more dimensions of the order of 100nm or less’. Novel properties that differentiate nanoparticles from the bulk materials typically develop at a critical length of under 100nm. Such novel properties are entirely dependent on the fact at nano-scale, the physical and chemical properties of nanoparticles are different from that of the bulk material.

In recent years, nanoparticles are becoming more significance and the technology of their production and uses is rapidly growing into an important industry. These materials have special physical and chemical properties due to their finite small size with dimension range of 1-100 nanometer (Tang et al., 2000). Therefore, they offer many potential applications in areas of chemistry, pharmacy, cosmetics, surface coating agents, textile sizing, paper coating, agriculture and biochemistry (Nakache, 2000). Nanoparticles possess different properties from the bulk form because the specific surface areas of the finely divided form can be on the order of a million to several million times greater than that of the bulk form of that substance (Otterstedt and Brandreth, 1998). Besides, nanoparticles as polymer additives may have high loading requirements compared to traditional additive (Schmidt and Malwitz, 2003).

Micro-sized or nano-sized starch based particles could be synthesized by cross-linking process. It is well known that covalent linkages between polymer chains can be established by
the reaction of functional groups with complementary reactivity. Therefore, biodegradable starch-based particles could be formed with cross-linking by condensation reactions due to the presence of specific functional groups (mainly –OH,) along the macromolecular chains of starch (Zhang et al., 2005). Cross-linked starches have long been used as food additives because of their safety and low cost (Gong et al., 2005). A few years ago, it was discovered that they also possess unique features that suggest their use as an excipient for the manufacture of controlled release solid oral dosage forms of drugs. It was also found that drug release rate increases with increasing cross-linking degree of polymer (Lenaerts et al., 1991; Lenaerts et al., 1998). Thus the efficiency of the drug is improved and its toxicity may be controlled.

Hamdi et al. (2000) reported the use of water-in-oil emulsions for the preparation of starch microspheres by cross-linking starch molecules using epichlorohydrin. It was reported that the stirring rate during the emulsification step was crucial for controlling the particles size. The influence of emulsification stirring rate before and during cross linking on the size of the starch particles formed have been studied (Hamdi et al., 2001). The aqueous phase was added under varying stirring rates to the organic phase before adding the cross linking agent (emulsification step). After that, the cross linking reaction was made under mechanical stirring (cross-linking step). The results showed that, an increase in the stirring rate during the emulsification step resulted in a decrease in the mean diameter and in the narrowing of the starch particles size distributions. Mean diameters ranged from 138 to 3.6 μm for stirring rates ranging from 600-24 000 rpm (Hamdi et al., 2001). Broad distributions were obtained for 600 and 1800 rpm, whereas almost monodisperse populations were observed when the stirring rate
was 24 000 rpm (Hamdi et al., 2001). Interestingly, very small particles (4 μm in the swollen state) could be obtained when the stirring rate during the emulsification state was 24 000 rpm.

However, the stirring rate during the cross linking step has almost no influence on the final size of the microspheres. The mean diameter of microspheres remained practically constant when the stirring rate was varied from 600 to 1800 rpm, suggesting that addition of cross linker in the medium was able to immediately rigidify the starch-containing water droplets in the emulsion and to prevent them from coalescence and aggregation. As shown in many studies (Ishizaka et al., 1981; Reddy et al., 1990; Sandraps and Moes, 1993), the inverse relationship between the size of the particles and the stirring rate during the emulsification step is due to the mechanical breaking up of the aqueous phase into smaller sized droplets.

As shown by the absence of effect of the stirring rate after the addition of cross linker, it was likely that the cross-linking of starch prevented the coalescence of the droplets. Therefore, it was only necessary to keep in suspension the droplets already formed during the cross-linking process until the hardening of these droplets by covalent cross-linking and the formation of the final microsphere.

Additionally, a high organic to aqueous phase ratio and the present of the surfactant agent helped to prevent the coalescence of the droplets during the formation of the particles. The effect of the organic to aqueous phase ratio on the diameter of the particles size has been studied by Hamdi et al. (2001). It has been observed that the mean diameter decreased when the organic to aqueous phase ratio was increased. The mean diameter (±SD) ranged from 4 ± 0.5 μm for a 12/1 ratio to 60 ± 6.3 μm for a 1/1 ratio (Hamdi et al., 2001). The increase in the
mean diameter is a result of the coalescence of droplets due to the probability of a collision between two or more droplets.

It was also reported that in the absence of surfactants, the preparation of the particles was not successful and resulted in aggregation (Hamdi et al., 2001). In order to eliminate these aggregates, it was necessary to add a minimal surfactant concentration of 0.5%. the effect of the surfactant concentration (ranging from 0.5-5%) on the diameter and the size distribution of the starch microspheres prepared at emulsification stirring rate of 9500 rpm has been determined (Hamdi et al., 2001). An increase in the surfactant concentration resulted a slight decrease in the mean diameter of the particles, whilst a narrowing of the size distributions was observed.

On the other hand, the cross-linker/starch molar ratio did not affect the mean diameter of the swollen starch particles, whilst the swelling volume degree of the particles could be considerably altered. An increase in the crosslinker/starch ratio reduced the ability of the particles to swell. In other words, the swelling degree had decreased. Thus, the rheological properties of starch can be controlled.

However, one of the major disadvantages in water-in-oil emulsion method is lack of stability in the emulsion formed. According to Shinoda and Takeda (1970), the addition of NaOH to the aqueous phase of starch solution would result in the affinity of water for the hydrophilic head of surfactant leading to modifications of the surface tension at the water-organic phase interface. Thus, different solvent systems were investigated which would result in the formation of stable water-in-oil emulsion. It was proposed that mixture solvent system
of NaOH/thiourea (Jin et al., 2007) would reduce the affinity of water for the hydrophilic head of surfactant and lead to formation of stable emulsion.

According to Jin et al. (2007), untreated or nonactivated cellulose can be dissolved directly and quickly in NaOH/thiourea or NaOH/urea aqueous solution. The solvent systems are of low toxicity and possess higher solubility capacity for cellulose compared NaOH aqueous solutions. The mechanism for dissolution of cellulose in the novel solvent was investigated by SEM, WXRD, and $^{13}$C NMR. The results show that single components of this solvent system cannot dissolve untreated cellulose, implying that interactions between NaOH and urea, and NaOH and thiourea play an important role in improving the dissolution of cellulose. Moreover, $^{13}$C NMR spectra proved that NaOH, thiourea, and urea were bound to cellulose molecules, which brings cellulose molecules into the aqueous solution to a greater extent and prevents cellulose macromolecules from associating. Due to the great dissolution power of NaOH/thiourea aqueous solution to dissolve cellulose, this solvent system was implied in this study since starch possesses very similar structure to cellulose. Moreover, this simple technology is cheap and environmentally friendly, and is a promising method for substitution of the viscose technology that involves hazardous byproducts.

Apart from synthesizing starch-based nanoparticles from water-in-oil emulsion method, nano-size starch particles can also be prepared without using surfactants (Lawton Jr. et al., 2004). In this method, starch was dissolved in 90% aqueous dimethyl sulfoxide and filtered. The filtered 1% starch solution was dialyzed against absolute ethanol using dialysis membrane having a molecular weight cut off of 6,000-8,000. The precipitated starch particles were centrifuged to separate them from the ethanol and then were critical point dried using
carbon dioxide. The dried starch particles were in the size range of 200 to 300 nm, which are slightly greater than what is generally classified as nano-particles.

On the other hand, materials with ordered multimodal pore size distribution have attracted much attention recently because they combine the benefits of high surface area micro- and mesoporosity with the accessible diffusion pathways of macroporous networks. Starch sponges with high internal porosities were prepared by a novel method that involved the freezing and thawing of starch gels (Zhang et al., 2002). The sponges consisted of intact 3D bicontinuous macroporous networks with pore sizes that were dependent on the starch concentration used. Because the pore size distribution in the starch gel primarily depends on the starch content, starch sponges with varying macroporosities can therefore be prepared by changing the starch concentration. Thus, the porosity can be used to load drugs for application in drug delivery system.

The use of starch to produce macroporous sponge has several advantages. Starch is readily available, inexpensive, and easy to process. Therefore, the synthesis method has the advantages of being facile, low-cost, environmentally benign and amenable to scale-up.
CHAPTER 3
MATERIALS AND METHODS

3.1 Materials

Native sago starch was purchased from a local supermarket in Samarahan, Sarawak and was used in the preparation of hydrophilic phase. Sodium hydroxide (NaOH), thiourea and cyclohexane of reagent grade were used as delivered without further purification. Epichlorohydrin (ECH) was used as the cross-linking agent and sorbitan monooleate (Span 60) was used as the emulsifier. Cyclohexane was used as the organic phase, acetic acid was used as the emulsion destroyer to separate the hydrophilic phase and the organic phase, and ethanol was used to purify starch particles during centrifugation steps. Furthermore, aqueous dimethyl sulfoxide (DMSO) was used as the solvent for dissolving the sago starch in the alternative synthesis approach.

3.2 Methods

3.2.1 Dissolution of native sago starch.

The aqueous phase was prepared by dispersing native sago starch in sodium hydroxide solution under magnetic stirring. According to method reported by Dziechciarek et al. (2002), 20g of sago starch was dispersed in a beaker containing 100g of 0.25M NaOH solution. The suspension was stirred by magnetic stirrer at temperature around 40-50°C until all the starch was dissolved.