

**PREPARATION AND CHARACTERIZATION OF CELLULOSE-BASED
NANOPARTICLES AND HYDROGEL**

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the degree of Bachelor of Science with Honors in
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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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Preparation and Characterization of Cellulose-Based Nanoparticles and Hydrogel

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ABSTRACT

This project focuses on the synthesis and characterization of cellulose-based nanoparticles and hydrogel from three different sources. Preparation and modification of cellulose particles size required the dissolution of cellulose in suitable solvent systems. Two solvent systems, a solution mixture of 6% NaOH and 5% Thiourea, a 8.5% NaOH solution were used in the dissolution of cellulose samples. Differences in cellulose solubility for these two solvents systems were compared and changes in chemical structures of cellulose were characterized. Three main cellulose-based particles were prepared: regenerated cellulose, cross-linked cellulose and cellulose nanocrystallite. Regenerated celluloses were prepared by dialysis of cellulose suspensions against ultra-pure water for different time intervals. The regenerated cellulose appeared to form aggregation readily with increase in the dialysis duration. Meanwhile, cross-linked cellulose particles were synthesized in the water-in-oil emulsion using epichlorohydrin (ECH) as the cross-linker. Cellulose nanocrystallites were prepared by sulfuric acid hydrolysis. Preparation of cellulose nanocrystallites was strongly dependent on hydrolysis temperature and time. The particles sizes, morphology and chemical structures of these cellulose-based particles were characterized by SEM and FTIR. Though particles synthesized from different sources possessed very similar physical and chemical properties, they are distinctively different morphologically from their respective precursor materials.

Keywords: Cellulose, dissolution, dialysis, cross-linking, hydrolysis.

ABSTRAK

Projek ini berfokus pada penyediaan dan pencirian nanopartikel dan hidrogel selulosa daripada tiga sumber yang berlainan. Penyediaan dan perubahan terhadap saiz partikel memerlukan pemelarutan selulosa dalam larutan yang bersesuaian. Dua sistem larutan, 6% NaOH/ 5% Thiourea serta 8.5% NaOH telah digunakan dalam penyediaan larutan selulosa. Perbezaan dalam pemelarutan selulosa dalam dua sistem larutan ini telah dibandingkan dan perubahan dari segi struktur kimia telah diperhatikan. Tiga partikel selulosa yang utama telah disediakan: selulosa penghasilan semula, selulosa taut silang and nanocrystallite selulosa. Selulosa penghasilan semula disediakan melalui dialisis larutan selulosa terhadap air suling pada tempoh masa yang berlainan. Sementara itu, partikel selulosa juga dapat disintesis melalui taut-silang pengemulsian secara air-dalam-minyak dengan menggunakan epiklorohidrin (ECH) sebagai agent taut silang. Nanocrystallite selulosa juga dapat disediakan melalui hidrolisis dengan sulfurik asid. Penyediaan mikrocrystallite selulosa bergantung pada suhu dan masa hidrolisis. Saiz partikel, morfologi dan struktur kimia partikel selulosa telah dikaji. Walaupun partikel yang disintesis dari sumber berlainan menunjukkan sifat fizikal dan kimia yang hampir serupa, namun sifat-sifat ini amat berbeza daripada keadaan asalnya.

Kata kunci: Selulosa, pemelarutan, dialisis, taut-silang, hidrolisis.

CHAPTER 1

INTRODUCTION

The advancement in nanotechnology will fundamentally change the way materials and devices are produced. Most major governments around the world are investing heavily in nanotechnology and many see it as fueling the next Industrial Revolution. Discovery of the ability to liberate and obtain nanoscale building blocks with precisely controlled size and composition and assemble them into larger structures with unique properties and functions have indeed revolutionized segments of the materials manufacturing industry (Tang *et al.*, 2000).

Nanotechnology plays a major role in most of the economic sectors. Application of this technology allows the development of new critical enabling science with broad commercial potential, such as nanostructured materials, nanoscale-based manufacturing processes, and nanoelectronics. Nanotechnology takes advantages of assembly at the nanoscale level to produce lighter, stronger, and multifunctional materials. Materials with particles at the dimension range of 1 to 100 nanometer have special physical and chemical properties due to their finite small size (Tang *et al.*, 2000). Therefore, these nanomaterials offer a variety of potential applications, especially in the areas of chemistry, pharmacy, cosmetics, surface coating agents, textile sizing, paper coating, agriculture and biochemistry (Nakache, 2000). Nano-sized particles possess different properties from the bulk form due to their specific surface areas. The finely divided form can be in the order of a million to several

million times stronger than that of the bulk form of that substance (Otterstedt & Brandreth, 1998).

Moreover, innovative devices based on new principles and architectures are being produced, especially for the use of molecular/cluster manufacturing. New structures which are not previously observed in nature are achievable. It is expected that nanotechnology will soon have the most significant impact in traditional industries and leverage large amount of fundamental research to be carried out.

Recently, much emphasis have been made in exploiting cellulose nanotechnology. Many research and development investments in science and engineering are being made to determine the properties and characteristics of cellulose at nano-scale. In addition, much research also aims to develop technologies to manipulate cellulose self-assembly and multifunctionality within plants. Moreover, new cellulose technologies are also being developed to the point where industry can produce much more advanced and cost-competitive cellulose-based products (Wegner and Jones, 2006).

Cellulosic materials possess great potential to be utilized as nanomaterials. Besides being the most abundant biological raw materials, cellulose has nanofibrillar structure and can be self-assembled into well-defined architectures at multiple scales ranging form nanoscale to macroscale. Cellulose can be made multifunctional and self assembled to displace many non-renewable materials such as metals and ceramics. Cellulose nanotechnology can help in developing materials and structures that exhibit novel and significantly improved physical,

chemical and tribological properties. Such novel materials can even function more effectively due to their nanoscale size (Wegner and Jones, 2006).

In general, cellulose is the most abundant biopolymer which often acts as a sustainable source of materials for industrial processes (Mansfield and Meder, 2003). Though it is a renewable source, yet the potential applications of cellulose and cellulose products remain latent. This is due to the historical shift to petroleum-based polymers from the 1940s onward with more emphasis being put on petroleum-based products. Moreover, difficulties in modifying cellulose properties and limited number of common solvents that can readily dissolve cellulose also have led to the hesitation of exploiting the interesting properties of cellulose.

The use of cellulose particularly in the industrial process has recently gained much attention and emphasis. It is believed to be the potential sustainable source of raw materials, especially in pulp and paper production industries. In addition, the use of cellulose and its derivatives in a diverse array of other applications such as films, plastics, coatings, suspension agents and composites, continues to grow on the worldwide basis (Liu *et al.*, 2006). Cellulose also has many uses as anti-cake agent, emulsifier, stabilizer, dispersing agent, thickener and gelling agent due to its good water holding ability.

Since cellulose is a potential feedstock for various industries, more studies should be conducted to know its properties and characteristics for better utilization. Besides, more researches should also aim to preserve the environment by discovering potential uses of different cellulosic waste materials.

In this research project, cellulose nanoparticles were synthesized from three different cellulosic precursor materials: standard cellulose (Whatman CF11 Fibrous Cellulose Powder), synthetic cellulose (Filter paper Whatman No.1) and from lignocellulosic waste material (Sugarcane bagasse). All these cellulosic precursor materials will undergo some chemical and mechanical treatments for the preparation of cellulose-based nanoparticles and hydrogels. The physical and chemical properties of cellulose particles synthesized from three different sources were compared and studied.

CHAPTER TWO

LITERATURE REVIEW

Recently, there is growing concern on the uses of cellulose and its derivative. Cellulose is the major component of higher plant biomass. Cellulose is found in plants as microfibrils with 2-20 nm diameter and 100 - 40000 nm long. These form structurally strong framework in the cell walls. Moreover, cellulose is well known as the most abundant biopolymer in nature. It can be found either in crystalline or amorphous forms depending on its structures (Xu *et al.*, 2006).

Cellulose is homopolymer composed of (1-4)- β -D-glucopyranose units linked linearly by glycosidic bonds to form linear chains. The β -linked glucopyranose residues have fully equatorial conformation which stabilizes the chair structure and minimize its flexibility (Schult *et al.*, 2002; Ponpium *et al.*, 2000). In each constitutional anhydroglucose units, it consists of three reactive hydroxyl groups which play a major role during the preparation of various functional polymers (Orlando *et al.*, 2002).

This polysaccharide is an insoluble molecule consisting of between 2000-14000 residues. Each residue is oriented at 180° to the next with chain synthesise two residues at one time (Burchard, 1993). The parallel aligned linear chains are tightly linked by the hydrogen bond to form microfibrils (Liu *et al.*, 2006). The structure of cellulose is shown in the Figure 1 below.

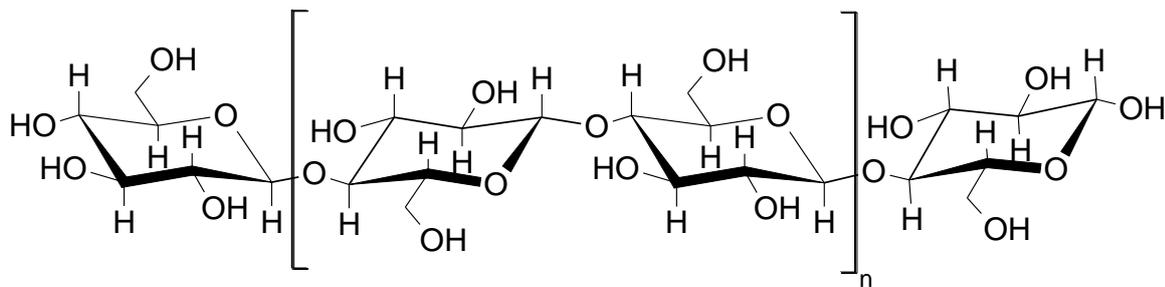


Figure 1 Structure of Cellulose

Most of the cellulose presented in higher plant biomass is known as native cellulose or Cellulose I. This cellulose is frequently found to coexist in cell wall structure together with amorphous cellulose. Cellulose I consists of two phases, I_{α} and I_{β} in varying proportions depending on its origin (Burchard, 1993). Cellulose I_{α} is the rarest form which exists only in some green algae and bacteria whilst Cellulose I_{β} is the most abundant form occurs in the microfibril of a wide range of species from higher plants to algae and tunicates (Liu *et al.*, 2006).

Though Cellulose I_{α} and Cellulose I_{β} have the same fiber repeat distance, they differ from each other in the way of sheet displacement. In cellulose I_{α} , the sheets stacks are linked by van der Waal's interaction and have a progressive shear running parallel to the chain axis. Meanwhile, cellulose I_{β} has the alternating shear (Burchard, 1993; Liu *et al.*, 2006). Cellulose I_{β} is found to be more stable than the cellulose I_{α} . They can be interconverted by bending during microfibril formation. Cellulose I_{α} can be converted to I_{β} by annealing at around 200°C in a number of different solvent media (Liu *et al.*, 2006).

Cellulose is known to have outstanding properties and a variety of useful applications. Starting with the dissolving pulp as raw material, cellulose is being converted by large scale industrial processing into cellulose derivatives such as ethers and ester and regenerated materials, for instance fibers, films, food casings, membranes and sponges (Fink *et al.*, 2001). Due to the presence of strong intra- and intermolecular hydrogen bonding which causes the insolubility of the natural polymer, chemical processing of cellulose is difficult.

Several researches have been done to study the properties of cellulose. One of the unique properties of cellulose is that it shows no variability in structure over its entire molecular weight range unlike other polysaccharides, for example hemicelluloses. Observed differences between cellulose samples originate mainly from differences in molecular weight distributions and supramolecular structure (Schult *et al.*, 2002). The variation of molecular weight distribution is notable since cellulose samples are being isolated from various raw materials. Besides, various processing conditions required to obtain high-purity cellulose from different raw materials also leads to the variation in molecular weight distribution.

Furthermore, cellulose is found to be insoluble molecule. Although individual strand of cellulose intrinsically shows neither hydrophilic nor hydrophobic properties, yet its tendency to form crystalline structure utilizing extensive intra- and intermolecular hydrogen bonding makes it completely insoluble in most of the normal aqueous solutions (Burchard, 1993; Fink *et al.*, 2001). Scientists have also discovered that the presence of intramolecular hydrogen bonds leads to large degree of inherent chain stiffness. Therefore, in order to lower the inherent chain stiffness by means of increasing the freedom of rotation around the glycosidic bond, these hydrogen bonds should be weakened (Schult *et al.*, 2002).

According to Burchard (1993), cellulose is found to be soluble in more exotic solvent. As cellulose is the most abundant naturally occurring polymer with great potential uses both in native and derivatized forms, there is undoubtedly a need for multiple solvents to provide a variety of processing routes. Many studies have been done on cellulose dissolution with the common theme of simplifying the multi-step and time consuming process required to prepare cellulose solutions in non-derivitizing solvents (Frey *et al.*, 2006). Moreover, the impetus for the continued search for solvents to dissolve cellulose also aims to obtain better-quality products (Fidale *et al.*, 2006).

The most common solvent used to dissolve and regenerated cellulose is NaOH. The aqueous NaOH system for dissolving cellulose have notable potential for fiber production and as medium for preparing cellulose derivatives, as well as for other scientific investigations. From the studies of Isogai and Atalla (1998), they had attempted to adapt this system for the studies of microcrystalline cellulose under optimum condition to obtain clear cellulose solution (Isogai, 1998). The presence of the hydroxyl ions can cause swelling of cellulose, hydrolysis of ester linkages and disruption of intermolecular hydrogen bonds between cellulose and hemicelluloses (Xu *et al.*, 2006; Ozturk *et al.*, 2006). Yet, the study showed that only microcrystalline celluloses with low degree of polymerization are soluble in NaOH by the freezing process. Fibrous celluloses of higher plant with higher degree of polymerization are found to be partially soluble even after swelling treatment (Isogai, 1998). Thus, more studies have to be done to obtain the clear cellulose solution.

Margaret *et al.* (1996) also have reported another unique solvent system for cellulose dissolution. By using ammonia/ammonium thiocyanate ($\text{NH}_3/\text{NH}_4\text{SCN}$) and analogous

solvent systems including hydrazine/salt, hydrazine hydrate/salt and ethylene diamine/salt solvent systems, dissolution of cellulose can be achieved by cycling the cellulose/solvent mixture through repeated freezing, thawing and mixing steps. Freeze thaw cycling process is found to disrupt the hydrogen bonding between and within cellulose chains. Successive cycling between -40 and 30°C transformed cellulose from the cellulose I crystal formation to cellulose II and then III amorphous. Once the cellulose was amorphous, dissolution in the solvent system occurred. Through this study, it has been found out that no activation step was required to form cellulose solution when sufficient mixing is employed (Frey *et al.*, 2006).

Studies of salt-cellulose solution also have been conducted by Jin *et al.*(2004). From the studies, Jin *et al.* (2004) discovered the formation of nanometer-sized cellulose hydrogels through controlled preparation conditions. Highly porous cellulose gel is formed by regeneration from aqueous calcium thiocyanate system (Fischer *et al.*, 2003). The hot solution of this salt is proven to be effective solvent of cellulose. The resulting salt-cellulose solution is found to undergo reversible sol-gel transition as the temperature of the solution decrease below 80°C (Jin *et al.*, 2004).

Other studies of producing cellulose solution using LiCl/DMAc also have gained much attention. Most of these solvent systems will later undergo acetylation process using acetylating agents such as acetic anhydride, acetyl chloride, ketene and acetic acid trifluoroacetic anhydride mixture to produce products with novel characteristic (Tosh *et al.*, 2000). For modification, the cellulose can either bring into the solution and then be regenerated, or it has to be modified chemically by derivatives. For maximum conversion of cellulose to its derivatives, the reaction has to be carried out in homogeneous medium

requiring suitable solvent system which is inert to cellulose but still can cause molecular dispersion (Frey *et al.*, 2006; Burchard, 2003).

Apart from the properties described above, cellulose also exhibits another significant characteristic in which cellulose is capable to imbibe and swell in water. Due to the presence of hydroxyl groups, cellulose can form inter- and intramolecular hydrogen bond with water molecules. Thus, cellulose fibers can retain a large amount of water. Yet, as the particles size of fiber was reduced from mechanical milling, the water retention capacity is also reduced (Altomare *et al.*, 1984; Chen *et al.*, 1984). Moreover, cellulose water retention capacity can be affected by the differences in microstructure of cellulose fibers obtained from different methods of extraction (Stephen, 1995). Presence of other hydrogen bonding ingredients, such as acids and sodium chloride also tends to interfere with bond sites available between fibers and water (Sanderson, 1981).

From the literature, most of the studies were carried out by using the standard cellulose powder to study the cellulose dissolution, characteristics and applications of the regenerated gel and cellulose composite. Fewer studies were being conducted on the cellulose extracted from the agriculture residues, such as crops and sugarcane. This may be due to the presence of other compounds which would lead to the decrease in cellulose purity.

Lignocellulosic materials consist of lignin and hemicelluloses bound to the cellulose. The presence of high amounts of lignin will affect the structure and properties of the fibers which later will lead to the decrease in the solubility of lignocellulosic materials (Liu *et al.*, 2006; Isogai, 1998). Moreover, fibers with high amount of lignins are coarse, stiff and

brownish in color. Besides, considerable research efforts also have been done on cleavage of intrachain linkages in hemicellulose and cellulose chains in lignocellulosic material.

In this study, one of the cellulose samples is obtained through extraction from the natural source, for instance sugarcane bagasse. Sugar bagasse has unique morphological heterogeneity. It consists of fiber bundles and other structural elements such as vessels, parenchyma, and epithelial cells (Xu *et al.*, 2006). Chemically, about 50% of the dry residue is found to be cellulose. Cellulose is linear homopolymer with para-crystalline structure stabilized by hydrogen bridges. Another 25% of dry residue is hemicellulose. Hemicelluloses are amorphous polymer consisting of various sugar units, for instance arabinose, galactose, glucose, and mannose arranged in different proportions and with different substituents. The remaining 25% is composed of lignin, minor amount of minerals, waxes and other compounds (Xu *et al.*, 2006; Liu *et al.*, 2006).

In order to extract the cellulose with higher purity, several pretreatments have to be done. Both chemical and mechanical methods had been applied to obtain fibers from the agriculture residue, for instance sugarcane bagasse. Chemical methods such as alkaline treatment were being used to produce pulp from sugarcane bagasse. Prior to alkaline treatment, solvent extraction was an important method conducted to remove the extractable fraction from the materials. This procedure may result in a more exposed cellulosic surface (Liu *et al.*, 2006).

Mechanical treatment such as steam explosion and ultrasonic irradiation can be used to separate fibers from sugarcane bagasse. It is also well-known that treatment of the

lignocellulosic materials with chlorite can remove almost all of the lignin and the following isolation of cellulose using alkali can be performed at room temperature (Adsul *et al.*, 2005; Singh *et al.*, 2005).

Much of the cellulose used in the industries undergo some crosslinking processes to obtain improved quality and desired properties for the products. Crosslinked cellulose products are of great commercial importance in the textile industry, where they are widely used for the production of wrinkle-resistant fabrics. In the pulp and paper industry, they are used to increase absorbance in disposable cellulose products such as diapers. They are also used as strengthening agents in paper industry (Roberts, 1996).

Crosslinked cellulose is normally produced by reacting bifunctional material that will covalently tie hydroxyl groups to neighboring cellulose chains. The most commonly used crosslinking agents have been formaldehyde and various derivatives of urea (Tesoro and Willard, 1961; Spence, 1987). Other materials, such as carboxylic acids which have actual or latent bifunctional reactive groups also act as crosslinking agents (Harsh and Gehrke, 1991; Bledzki *et al.*, 1996).

Currently, crosslinking reactions have been studied using succinic acid as crosslinking agents in the presence of nanometer TiO₂ catalyst under the irradiation of UV light. According to Chen and Wang (2006), carboxylic acid group of succinic acid can be photo-reduced to form aldehyde group. The crystalline structure of succinic acid adsorbed on nanometer TiO₂ particles can be altered under UV irradiation. The photo-reduction of succinic acid in the presence of nanometer titanium dioxide in water medium under UV irradiation can increase

the values of conductivity for the creation of free radicals (Wang *et al.*, 2002). Crosslinking reactions occur and involve two major reactions: reaction between aldehyde group of succinic acid and the hydroxyl group of cellulose and reaction between free radical of succinic acid and the free radical of cellulose (Chen and Wang, 2006).

In a recent study conducted by Wartell and Marshall (2005), crosslinking reactions are aimed to enhance the anion exchange properties. Lignocellulosic materials, for instance sugarcane bagasse are generally poor anion exchange resins. However, through introduction of quaternary ammonium groups, anion exchange properties can be improved. In this study, dimethyloldihydroxyethylene urea (DMDHEU) and choline chloride are used to crosslink and add cationic character to cellulose-containing fabrics.

DMDHEU acts as a crosslinking reagent between cellulose and choline chloride. Reaction between cellulose and DMDHEU and between DMDHEU and choline chloride occur through removal of water (dehydration) and formation of ether linkages among the primary alcoholic –OH groups on cellulose, DMDHEU and choline chloride (Wartell and Marshall, 2005).

These modified by-products can be used in wastewater treatment in removing metal ions, particularly chromate ion (Lee *et al.*, 1995). They demonstrated chromate ion adsorption that surpassed a cellulose-based anion exchange resin but was less than a synthetic, commercially available anion exchange resin. The manufacturing cost for the by-product-based resins is relatively lower compared to the market costs for the commercial products due

to the low cost of the starting materials and the reagents used for quaternization (Garg *et al.*, 2004).

Though much studies have been done on crosslinking reactions using different crosslinking agents, there have been no previous reports in literature that describe the size of the crosslinked cellulose and characterize it using different instruments. In this research project, crosslinking agents used is epichlorohydrin which is often used in modification of starch. It is speculated that by modification of the existing methods, cellulosic nanoparticles can also be produced.

Another significant study has been carried out recently based on polymer reinforcement with cellulose nanocrystalline fibrils. There has been an enormous increase in interest in producing composite materials with nanosized reinforcement, for instance nanocomposites. This enthusiasm is due to the extraordinary properties that these kinds of materials exhibit as a result of the nanometric size effect from the reinforcement. However, especially for continuous and large scale production, incorporating the reinforcement so that it is well dispersed and without agglomerates in a continuous matrix has proved quite problematic. Most efforts have focused on the production of nanocomposites with inorganic reinforcements, but organic materials have also been used (Orts *et al.*, 2005).

Cellulose whiskers have been separated from various sources such as wheat straw and tunicin and were used as reinforcements in polymer matrices. Incorporation of these nanosized elements into a polymeric matrix usually resulted in outstanding properties with respect to their conventional microcomposite counterparts. Using cellulose crystallites as

reinforcement in nanocomposite has led to numerous of advantages due to its remarkable reinforcing property (Shin & Exarhos, 2006).

Orts *et al.* (2005) reported that by dispersion of crystalline cellulose needles in a copolymer acrylate latex film, it can increase the dynamic storage modulus by more than three fold. The promise behind cellulose-derived composites lies in the fact that the axial Young's modulus of the basic cellulose crystalline microfibril is potentially stronger than steel and similar to Kelvar, having been reported as 137GPa (Wainwright *et al.*, 1982). However, no feasible method has been put forth to take full advantage of this remarkable stiffness. More research is needed to characterize the advantages of particular microfibril sources, comparing the effect of fiber source on surface properties, length, and their ability to interact within polymer matrices.