CHAPTER II
LITERATURE REVIEW

2.1 Fiber and Fiber Production

Fibers are defined as units of matter characterized by flexibility, fineness, and a high ratio of length to thickness (Morton and Hearle, 1975).

Fibers can be classified based on the generation process into two categories: 1) natural fiber and 2) man-made fiber (Cook, 1984a; Corbman, 1987; Nakamura, 2000). The natural fibers are those occur in nature in a ready-made fibrous form, for example, cotton, silk, wool, and flax. On the other side, the man-made fibers are produced by man from something which might be either the naturally occurring polymers or synthetic polymers that was not previously in a suitable fibrous form (Cook, 1984a).

Man-made fibers can be sub-divided into two distinct groups: 1) synthetic fiber and 2) natural polymer fiber, according to the source of the fiber-forming substances from which they are made (Cook, 1984a).

The synthetic fibers are those made from simple chemicals such as those derived from coal or oil. These chemicals are polymerized into materials capable of forming fibers, and then manipulated into a fibrous from, entirely by man.

The natural polymer fibers, on the other hand, are those in which the fiber-forming substances has been generated by nature. In these natural polymer fibers, nature, which can possibly be both plants and animals, has created a substance capable of taking on a fibrous form. Then, man has only taken a further step by manipulating this substance into a fiber. Examples of the natural polymers that can be used as raw materials for making fibers are proteins and polysaccharides.

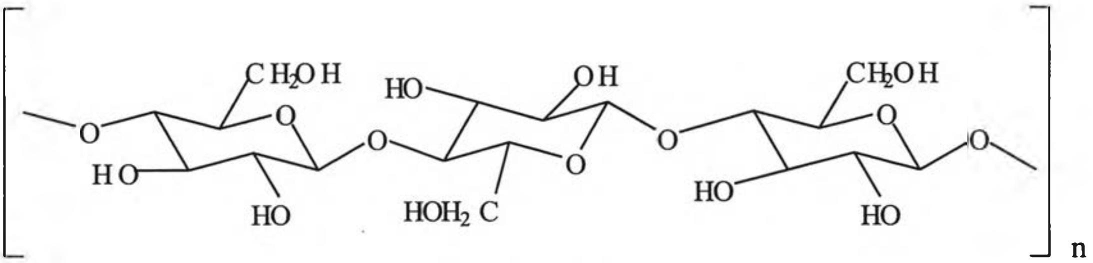
The production of man-made fibers is described as 'fiber spinning'. The first step of fiber spinning process is to change the fiber-forming substance from its raw state, which is usually in a solid form, into a liquid or semi-liquid state. This can be achieved either by dissolving the material in high concentration in a solvent that does not degrade the polymer or by melting it with heat and shear. The liquid containing the fiber-forming material is then filtered and extruded under pressure out of spinneret, a specific device containing very small holes, to be formed in endless, fine jets of liquid. From this point on, to solidify the extruded liquid jets as filaments, several ways might be applied, and thus fiber spinning process can be classified into three main types: melt spinning, dry spinning, and wet spinning. When the fiber-forming material is rendered liquid by heating it until it melts, extruded through spinneret, and then solidified by being cooled down from its molten state, the process is called melt spinning. In dry spinning, the fiber-forming substance is dissolved in a solvent and then solidified by evaporating the solvent after passing through the spinneret. In the wet system, the solution of fiber-forming material is extruded into a fluid which either extracts the solvent from the filaments or enters into a chemical reaction causing the original polymer to be recovered (Walczak, 1977; Cook, 1984b; Rathke and Hudson, 1994; Knaul and Creber, 1997b).

The wet spinning technique, in spite of its low productivity as comparing to melt or dry spinning process, is the most suitable technique for the production of fibers from polysaccharide materials of which high melting temperature resulted from a large amount of hydrogen bonds in their molecules.

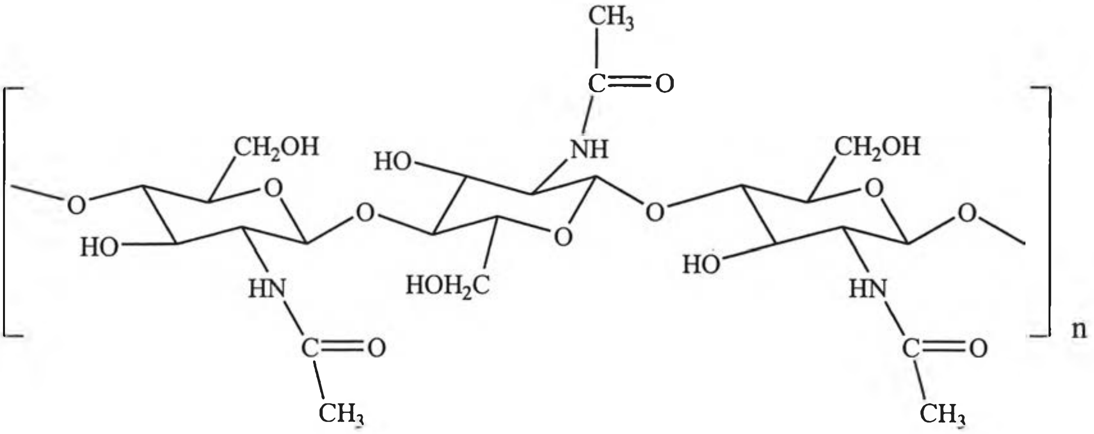
Polysaccharides, a kind of natural polymer, have received considerable attention across a broad range of fields because they are not only naturally abundant, but also nontoxic and biodegradable (Li *et al.*, 1992). While cellulose is the most abundant renewable polysaccharide known, chitin, which has a very similar molecular structure to cellulose, is considered to be in the second rank (Knaul *et al.*, 1999a) with an annual production of 10^{10} to 10^{11} tons per year (Felse, P.A. and Panda, T., 1999).

2.2 Chitin and Chitosan

As can be seen in Figure 2.1, chitin has the same backbone as cellulose which consists of β-(1,4)-D-glucopyranose units, but the 2-hydroxy group has been replaced by an acetamide group, resulting in mainly β-(1,4)-2-acetamido-2-deoxy-D-glucopyranose structural units. That is why chitin is often considered as a cellulose derivative although it does not occur in organisms producing cellulose (Rathke and Hudson, 1994).



(a) Cellulose



(b) Chitin

Figure 2.1 Chemical structures of cellulose and chitin.

Whereas cellulose can be obtained from wood and pulp products (Knaul *et al.*, 1999a), chitin is found in mushrooms, yeasts, and especially the hard outer shells of crustaceans and the cuticles of insects in which about 50–80% of the organic compounds consists of chitin (Li *et al.*, 1992). At present, most commercially available chitin is extracted from the shells of crustaceans such as lobsters and crabs, which contain as much as 20–50% chitin (Rathke and Hudson, 1994). Various methods have been studied and developed to achieve chitin from crustacean shell waste as reviewed by No and Meyers (1997). Typically, the extraction can be completed in three steps: 1) deproteinization in 1–10% NaOH solution at 65–100°C for 0.5–6 hours, 2) demineralization in dilute hydrochloric acid (HCl) at room temperature for 30 minutes to over 2 days, and 3) decoloration in various reagents like ethanol, ether, and sodium hypochlorite solution. The former two steps can be conducted in a reverse order. Demineralization in a cold 2% aqueous HCl followed by deproteinization in a hot 5% (w/w) aqueous NaOH, for example, gives chitin with an average degree of *N*-deacetylation of 50% (Knaul *et al.*, 1999a).

Chitosan, a group of polymers deacetylated from chitin (Li *et al.*, 1992), was first discovered in 1859 by Rouget who found that, after chitin is boiled in a very concentrated potassium hydroxide (KOH) solution, the product becomes soluble in organic acids (Muzzarelli, 1977). Currently, chitosan is generally prepared by treatment of chitin with 40–50% NaOH or KOH solution at high temperature (100°C or higher) (No and Meyers, 1997). As a result of such treatment, acetamido groups adjacent to *cis* related hydroxyl groups may undergo *N*-deacetylation (Muzzarelli, 1977). However, to achieve a completion of *N*-deacetylation of chitin is almost impossible even under harsh treatment (Li *et al.*, 1992), chitosan is a copolymer with the main repeating units of (1,4)-linked 2-amino-2-deoxy-β-D-glucopyranose and some units of (1,4)-linked 2-acetamido-2-deoxy-β-D-glucopyranose (Knaul *et al.*, 1999a). Figure 2.2 represents a segment of chitosan.

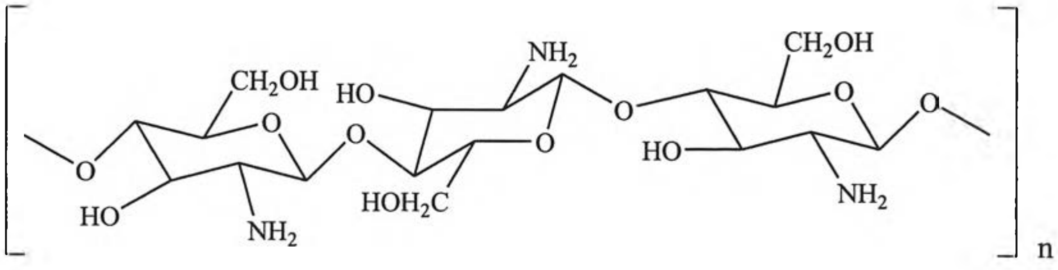


Figure 2.2 Chemical structure of chitosan.

The degree of *N*-deacetylation, which is usually expressed as a percentage to represent the average number of *D*-glucosamine units per 100 monomers (Sabnis and Block, 1997), is one of the important parameters that has a remarkable effect on the solubility and solution properties of chitin and chitosan (Rathke and Hudson, 1994). The term chitosan is usually referred to chitin when it is highly deacetylated enough to become soluble in dilute aqueous acidic systems (e.g., 1-10% by volume aqueous acetic acid) (Knaul *et al.*, 1999b). Otherwise, most publications use the term chitosan when the degree of deacetylation is more than 70% (Li *et al.*, 1992).

Although chitosan is easily soluble in most aqueous organic acid solutions, e.g. formic, acetic, 10% citric, pyruvic, and lactic acids (Rathke and Hudson, 1994) as a result of the basicity of the primary amine groups in its molecule (East and Qin, 1993), it is insoluble in water, alkali, and organic solvents (Li *et al.*, 1992) such as methanol, absolute ethanol, and acetone.

Interestingly, for the reason that the amino group is protonated at low pH (Zhang *et al.*, 2001), chitosan is a cationic polyelectrolyte which can interact with negatively charged substances like proteins, solids, dyes, and polymers. On the other hand, the nitrogen in the amino group of its molecule acts as an electron donor which can also interact with positively charged metal ions such as copper, lead, mercury, and uranium (Li *et al.*, 1992).

Various methods for determination of the degree of deacetylation and molecular weight, viscosity and solubility, and coagulating ability of chitosan are summarized by Li *et al.* (1992) as shown in Table 2.1.

Table 2.1 Physicochemical properties of chitosan (Li *et al.*, 1992)

Property	Comments
Degree of deacetylation	Determined by UV spectrophotometry, dye adsorption, IR spectrometry, metachromatic titration, and gas chromatography
Molecular weight	Determined by chromatography, light scattering, and viscometry
Viscosity	Affected by ionic strength, deacetylation time, molecular weight, and concentration
Solubility	Usually dissolved when pH < 6 but also affected by solvent mixing, deacetylation, solvation, and chemical modification
Coagulating ability	Binding for metal ions, anionic polymers, amino acids, proteins, DNA, cells, dyes, and solids

The industrial production and use of chitosan has been growing continuously since the 1970s when the major applications of chitosan were focused on sludge dewatering, food processing, and metal ion chelation. At present, anyway, it tends to be used to produce higher value products such as cosmetics, drug carriers, food additives, semipermeable membranes, and pharmaceutics (Li *et al.*, 1992). Moreover, as being one of the good fiber forming materials, some of the applications of chitosan fibers have included manufacture of wound-dressings, sanitary fibrous materials, surgical treads, artificial limbs, textile materials for waste water treatment, or fibrous carriers for bioactive substances (Struszczyk, 1997).

2.3 Preparation of Chitosan Fibers

The presence of microfibrils suggests that chitin and also its derivative, chitosan, have characteristics which make them a good candidate for fiber spinning. To fabricate chitin or chitosan fibers, extraneous material such as calcium carbonate and proteins which encase the microfibrils must be suitably removed from the raw polymer (Rathke and Hudson, 1994). Although the production of fiber is attractive for both chitin and chitosan, there are two main advantages of chitosan over chitin (Knaul *et al.*, 1999a). One is that chitosan is easily soluble in relatively convenient solvents like 1–10% (v/v) aqueous acetic acid. Another is that the presence of the free amine group not only renders a polyelectrolytic effect to the polymer backbone, but also presents an active site upon which many chemical reactions may be applied.

Chitosan degrades before melting, which is the characteristic for most polysaccharides with extensive hydrogen bonding. Therefore, wet spinning process is a typical method to prepare fibers from chitosan. This process involves dissolution of about 3–10% of the polymer in its bulk form, usually powder or flake, in solvents such as 2–10% (v/v) aqueous acetic acid to form a dope solution. The dope is then extruded as a liquid jet through a spinneret. The liquid jet may be immersed directly into a coagulation bath in which the spinneret is submerged; otherwise, it can go through an inert gas gap first—known as the dry-jet wet spinning technique. During travelling along the coagulation bath, the solvent is drawn off and the chitosan solution is precipitated in fiber form. Then, the chitosan fibers are led into a washing aqueous bath, dewatered in an alcohol containing bath and dried (Rathke and Hudson, 1994; Struszczyk, 1997; Knaul *et al.*, 1999b). In addition, other intermediate steps such as drawing, crosslinking, and dyeing may also be incorporated into the process (Knaul *et al.*, 1998).

Tokura *et al.* (1987) prepared and investigated some properties of various deacetylated chitin fibers. Chitin with the degree of deacetylation of less than 50% was dissolved in 3% dichloroacetic acid to give a concentration of 5% while chitin with the degree of deacetylation of higher than 50% was dissolved in 2–4% acetic acid to give a concentration of 4–7%. Three types of coagulants were applied: 1) copper–ammonia coagulant, 2) alcoholic sodium hydroxide solution, and 3) acidic coagulant (copper sulfate–sulfuric acid). It was found that the rough surface appeared on the fiber by the copper coagulant instead of the smooth surface by alcoholic coagulant, and the surface of fiber prepared by acidic coagulant was very close to that of alcoholic alkaline fiber. Furthermore, they suggested that the fiber could be useful in various fields because of its high tensile strength similar to that of rayon fiber and its multifunctionalities.

East and Qin (1993) proposed the production of chitosan fiber and regenerated chitin fiber by wet spinning of 5% (w/v) chitosan in 2% (v/v) aqueous acetic acid into a coagulation bath containing dilute NaOH aqueous solution. The maximum tenacity that could be reached for chitosan fiber is 24 cN/tex. After that, the regenerated chitin fiber was obtained by treatment of the chitosan fiber with a solution of acetic anhydride in methanol. It was found that the acetylation reaction could improve thermal stability and tensile strength of fibers.

Struszczyk (1997) produced chitosan fibers by using the coagulation and regeneration bath containing an aqueous alkali solution with the concentration ranging between 0.5 and 20%, the washing bath containing warm water of 30°C, the stretching ratio of 10–100%, and the spinning rate of 10–50 m/min. After dewatering in the alcohol bath and drying, the chitosan fibers obtained have some typical properties as shown in Table 2.2

Table 2.2 Some properties of chitosan fibers produced by Struszczyk (1997)

Property	Value
Titer (dtex)	1.5–3.0
Tenacity in standard conditions (Cn/tex)	10–15
Tenacity in wet conditions (cN/tex)	3–7
Loop tenacity (cN/tex)	3–7
Elongation in standard conditions (%)	10–20
Water retention value (%)	≤250

In order to assure that the individual filaments in the wound yarn are well separated and not stuck together, the drying step is also necessary to the spinning process. In 1998, Knaul *et al.* (1998) studied the improvements in the drying process for wet-spun chitosan fibers prepared from a 6% by weight chitosan in 3% by volume acetic acid solution to achieve the well separation of the individual filaments. Various drying techniques including direct heat, heated chrome rollers, forced air, and six different chemical drying agents which were acetone, methanol, ethanol, isopropanol, acetone/methanol, and acetone/isopropanol, were investigated. The optimum drying of the chitosan yarn was found to be provided by a methanol dry bath. The obtained filaments have low moisture content and are easily separated from each other. In addition, they have smaller diameter, superior surface smoothness and mechanical properties than fibers dried using other techniques involved in their study.

In 1999 also, Hirano *et al.* (1999) reported nine spinning conditions for the preparation of chitosan staple fibers. In this study, they made use of three types of solvents for chitosan: 1) aqueous 2% acetic acid – methanol, 2) aqueous 2% acetic acid, and 3) aqueous 2% oxalic acid. Furthermore, two types of coagulants: 1) aqueous 10% NaOH–30% sodium acetate and 2) aqueous 10% NaOH–30% sodium sulfate were applied. It was found that the dilution of the viscous chitosan solution with methanol remarkably reduced the viscosity and gave a chitosan solution in a homogenous molecular distribution at a proper viscosity for spinning.

Besides the use of strong alkali- or heavy metal-containing coagulation bath (Tokura *et al.*, 1987), which was considered to be unfavorable on the environmental or biomedical aspects, Tokura and Tamura (2002) has developed another type of coagulant, calcium chloride saturated aqueous alcohol. Chitosan dope was extruded into the first coagulation bath containing calcium chloride saturated 50% aqueous ethanol and followed by the second bath containing 50% aqueous ethanol for washing. Coagulation was explained to occur through the chelation of calcium ion between amino groups of chitosan. Moreover, it was claimed that the removal of alcohol and calcium ion from the regenerated chitosan fiber was so easy, compared to other reported regeneration conditions, due to high solubility of calcium chloride in water or methanol.

2.4 Crosslinked Chitosan Fibers

A key deficiency of chitosan fibers has been their poor tensile strengths as a result of the copolymeric structure of partially deacetylated chitosan (Knaul *et al.*, 1999b), consisting of *D*-glucosamine and *N*-acetyl-*D*-glucosamine units. To improve the mechanical properties of chitosan fiber, either of the following two methods might be used. One is a physical approach or known as fiber drawing or stretching. Another is a chemical approach by reaction with another compound, for example crosslinking, which involves the post-spinning treatment of the spun fiber (Knaul *et al.*, 1999b).

In 1992, Wei *et al.* (1992) used epiclorohydrin as a crosslinking agent for chitosan fiber. With increasing reaction time, temperature, and concentration of the crosslinker, the wet mechanical properties of the crosslinked chitosan fiber were increased significantly. However, dry mechanical properties were slightly increased or even decreased in some cases. Elongation at break of the fiber in both dry and wet state remained constant or decreased under all reaction conditions.

Knaul *et al.* (1999a) discussed improvements in dry mechanical properties through the post-spinning application of glyoxal and glutaraldehyde as crosslinking agents in 1999. FTIR data suggested that some interaction is occurring between the glutaraldehyde or glyoxal and the amine group on the chitosan backbone. The strength of the fiber was improved up to a point and then decreased by crosslinking with glutaraldehyde or stayed constant in the case of glyoxal. The elongation at break of the crosslinked fibers was extensively decreased by both types of dialdehyde. However, due to the relative toxicity of most aldehydes, Knaul *et al.* (1999b) also proposed the use of two types of buffered solutions based on potassium dihydrogen phosphate and potassium hydrogen phthalate as crosslinking agents in the same year. The results showed the improvement in the strength of fiber with the highest dry mechanical properties resulted from solutions containing phthalate ions at pH between 4.5–5.5, and from solutions containing phosphate ions at pH 5.4. The authors explained that a crosslinked network might be set up whereby the phosphate ions or the phthalate ions establish bridges in between the free amine groups on the chitosan molecules. In contrast with dialdehydes, the elongation at break of the crosslinked fiber was increased in this case.

Besides the conventional wet spinning, in 2000, Denkbaş *et al.* (2000) proposed the preparation of crosslinked chitosan scaffold loaded with an active agent, 5-fluorouracil (5-FU), by using a modified wet spinning technique. Chitosan dissolved in 5% (v/v) aqueous acetic acid with the addition of 5-FU (1.0–5.0 mg/ml acetic acid) was used as a spinning solution which was then precipitated in the precipitation medium composed of ethyl alcohol and crosslinker—glutaraldehyde.

2.5 Citrate-Crosslinked Chitosan

As citric acid was expected to react with hydroxyl or amino groups in chitosan to form ester crosslinking or an inter-ionic attraction (Chung *et al.*, 1998), crosslinking of chitosan with citric acid or citrate salt has been reported in various forms.

In 2001, Shu *et al.* (2001) prepared a pH-sensitive citrate-crosslinked chitosan film for drug controlled release by simply dipping chitosan film into sodium citrate solution. No tensile data or other mechanical properties were shown in this study except swelling and drug release characteristics of the film. The authors also mentioned that the electrostatic interaction between sodium citrate and chitosan was found in their previous works (Shu and Zhu, 2000; Shu and Zhu, 2001) in which citrate-crosslinked chitosan beads or microspheres were prepared.

In 2002, Shu and Zhu (2002) prepared citrate-crosslinked chitosan bead together with other two anionic crosslinkers, sulfate and tripolyphosphate (TPP). SEM micrographs showed a smooth surface appeared on sulfate- and citrate-crosslinked chitosan beads. Moreover, the results from cross-sectional analysis indicated that the crosslinking process of sulfate and citrate to chitosan was much faster than that of TTP. The authors suggested that this is due to the smaller molecular size of sulfate and citrate than that of TTP.

Effect of citric acid on chitosan was also observed in the preparation of chitosan film using various types of acid conducted by Begin and Van Calsteren (1999). From the result, it was found that chitosan films prepared from hydrochloric, formic, and acetic acids were hard and brittle, whereas those from lactic and citric acids were soft and could be stretched.