



## CHAPTER I

### INTRODUCTION

Fibers, units of matter characterized by flexibility, fineness, and a high ratio of length to thickness (Morton and Hearle, 1975), are widely produced from many sorts of raw materials both by nature (natural fibers) and mankind (man-made fibers) (Cook, 1984a). They have been widely used for thousands of years for various purposes such as textile applications, reinforcing materials, biotechnology, and medical applications. To obtain man-made fibers, a process called 'fiber spinning' is required. Generally, fiber spinning techniques can be classified into three main types: 1) wet spinning, 2) dry spinning, and 3) melt spinning (Cook, 1984b).

Although the wet spinning technique is the oldest method of fiber spinning and cannot be competitive in view of productivity with the melt or dry spinning processes, it is the most suitable technique for the production of fibers from polysaccharide materials such as cellulose and its derivatives. Such polymeric materials contain ring structures and a large amount of hydrogen bonds in their molecules; therefore, they have such high melting temperatures that cause them to degrade before melting and the difficulty of solubilization. As a result, it is not suitable to fabricate fibers from this kind of materials by using melt or dry spinning method.

Besides cellulose, chitin and chitosan are other examples of polysaccharides receiving much attention. Chitin is found in many kinds of living things: arthropods (marine invertebrates and insects), fungi, and yeasts (Muzzarelli, 1977). Commercially, it is mostly produced from crustacean shells, especially crab shells, shrimp shells, and prawn wastes, which are abundantly available from seafood industries. Much interest has been paid on chitin and chitosan because of their good biocompatibility, biodegradability (East and Qin, 1993), miscellaneous biofunctional properties (Hirano, 1992), and variety of applications: biomedical applications, biotechnology, environment and pollution control, etc. (Felse and Panda, 1999).

Since the major problem of chitin is the difficulty to find a mild solvent and most of the solvents that can dissolve chitin are not convenient to use and may cause

the degradation to occur (East and Qin, 1993), another interesting material is its *N*-deacetylated product, chitosan.

Chitosan is a copolymer consisting of glucosamine and *N*-acetyl glucosamine units. Due to the formation of viscous solutions as a result of a high molecular weight (Zheng *et al.*, 2001), chitosan can be made into fibers by wet spinning. Chitosan dissolved in aqueous acidic solution is solidified by passing into aqueous alkaline coagulation bath (East and Qin, 1993). Examples of coagulants that can be used to coagulate chitosan are concentrated ammonia solution containing copper sulfate (Tokura *et al.*, 1987), aqueous sodium hydroxide (NaOH) solution containing methanol (Urbanczyk, 1997), aqueous solution of ethylene glycol containing NaOH (Shigemasa and Minami, 1995), aqueous NaOH solution (Struszczyk *et al.*, 1992; Struszczyk *et al.*, 1994; East and Qin, 1993; East *et al.*, 1989; Wei and Hudson, 1994; Lipp-Symonowicz and Kowalska, 1994; Knaul and Creber, 1997a), and aqueous NaOH solution containing sodium sulfate or sodium acetate (Hirano *et al.*, 1999).

Since a key deficiency of chitosan fibers is their poor tensile strength as a result of the copolymeric structure of partially deacetylated chitosan, this tends to limit chitosan's use as a fiber unless the polymer is blended with other polymers or crosslinked to increase its toughness and/or plasticised to increase its flexibility (Knaul *et al.*, 1999a; Knaul *et al.*, 1999b; Molloy and Yoriya, 2002). Combination of chitosan with other natural or synthetic polymeric materials was widely investigated, for example, gellan gum (Amaike *et al.*, 1998), silk fibroin (Park *et al.*, 2000), collagen (Hirano *et al.*, 2000), cellulose (Nousiainen *et al.*, 2000), poly(propylene glycol) (Sun *et al.*, 2000), poly(vinyl alcohol) (Zheng *et al.*, 2001), polyacrylonitrile (Min and Kim, 2002), and alginate (Tamura *et al.*, 2002b).

Knaul *et al.* (1999a) discussed improvements in dry mechanical properties through the post-spinning application of glyoxal and glutaraldehyde as crosslinking agents by immersing the spun chitosan fibers in aqueous solution of glyoxal or glutaraldehyde. However, due to the relative toxicity of most aldehydes, following the same two-step method (spinning and then crosslinking), 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.

Moreover, citric acid is also expected to react with hydroxyl or amino groups in chitosan to form ester crosslinking or an inter-ionic attraction (Chung *et al.*, 1998). Thus, crosslinking of chitosan with citric acid or citrate salt has been reported, usually in chitosan microspheres, beads, films, or membranes (Shu and Zhu, 2001; Shu and Zhu, 2002; Park *et al.*, 2001; Zhou *et al.*, 2001).

Adopted from these concepts, citric acid would probably be applied to either part of the spinning process, and thus one-step procedure for the preparation of crosslinked chitosan fiber might be achieved. Therefore, the objective of this research work was to study the possibility to prepare a citrate-crosslinked chitosan fiber by the addition of citric acid to the spinning solution or the first coagulation bath and investigate the effect of citrate-crosslinking on mechanical properties of chitosan fiber.