

CHAPTER I

INTRODUCTION

In the beginning of the twentieth, it was generally accepted that chitin and its derivatives are becoming increasingly more important in many fields. Especially in the biomedical field, they are particularly used for wound healing, tissue reconstruction and controlled drug delivery. The main advantage of chitin over other polymer is its biodegradability property. The advantage of biodegradable polymer is the disappearance of implanted foreign materials from the body as a result of their biodegradation. This is a marked contrast with non-biodegradable polymer with might elicit foreign-body reactions from the host's defense system during their long-term contact with a living structure. For medical applications, we need many kinds of biodegradable polymers that possess a variety of physical and chemical properties as well as biodegradation kinetics. Further requirements include minimal toxicity, low immunogenicity and tensile properties similar to uninjured tissue. Numerous materials have been evaluated in experimental models of repair, these include collagen (generally from bovine or porcine source), polylactide, polyglycolide, fibroin, fibronectin and chitin/chitosan.

In some instances a hard material with a high initial mechanical strength and a low degradation rate is required, while some surgical applications need soft materials with a high degradable rate. Most synthetic biodegradable polymers such as polyglycolide and polylactides have high strengths, while natural products such as collagen are low in mechanical strength but exhibit excellent cell adhesion. Chitin and its deacetylated product, chitosan are also very attractive biomaterials because both of them are crystallizable and have a high potentiality to provide materials of excellent mechanical properties (Tomihata and Ikada, 1997).

Theoretical Background

1.1 Chitin

Chitin is one of the most abundant polysaccharide polymers. It consists mainly of β - (1,4) - 2 - acetamido-2-deoxy-D-glucopyranose units (Rathke and Hudson, 1994). When the acetamide groups at the C₂ position are deacetylated to amino groups, it is called *deacetylated chitin or chitosan*. The chemical structure of chitin and chitosan is shown in Figure 1.1.

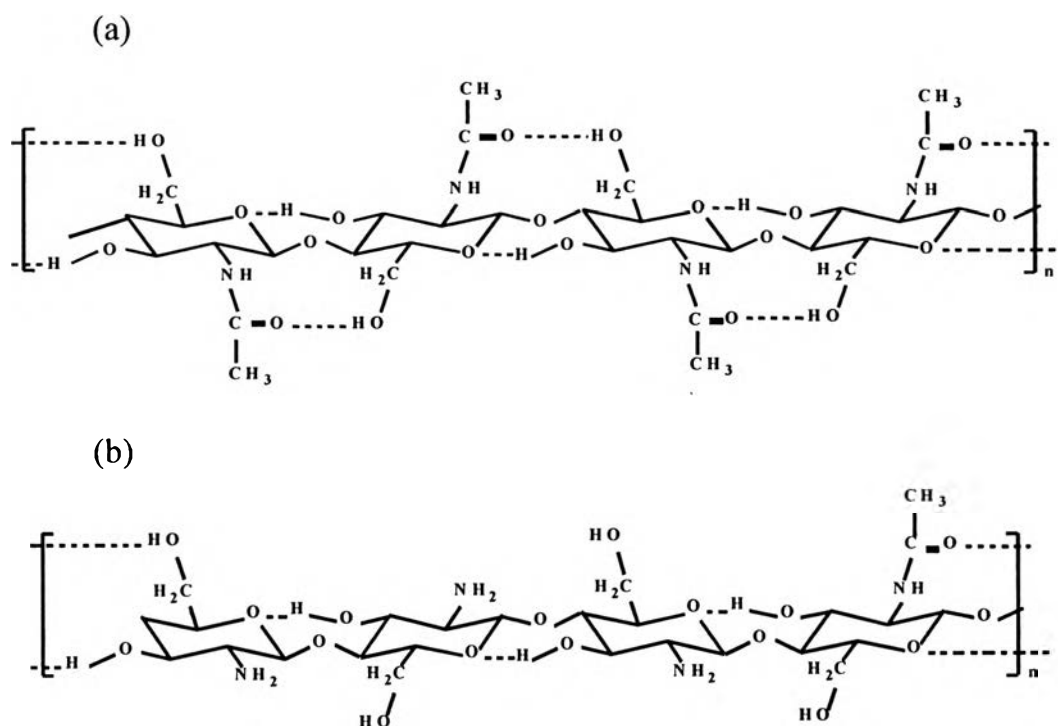


Figure 1.1 Chemical structures of (a) chitin and (b) chitosan.

Chitin was mostly found in the shell of crustaceans such as shrimp and crab shells. In addition, chitin acts as the structural polysaccharide in many lower organisms such as fungi. It is also found in bacterial cell walls and insect cuticles. Chitin, which isolated from crab and shrimp shells, have been

studied extensively owing to they are rich and easy to process. The wastes from seafood industries such as shrimp and crab containing 10-15% chitin is a readily available source of supply (Austin *et al.*, 1977). Since chitin is found together with protein and calcium carbonate in the exoskeleton of crustacean, deproteinization and demineralization processes are performed to remove protein and calcium carbonate from chitin, respectively (Mathur & Narang, 1990).

Chitin is known as a potential useful biomedical material for wound healing, artificial skin, suture, and drug carrier (Lee *et al.*, 1996). The unique properties of chitin such as biocompatibility, non-toxic, non-allergic and antifungal properties make it to be a promising polymer not only in the biomedical field but also in the other industrial areas as summarized in Table 1.1.

Table 1.1 Some applications of chitin-based materials.

Area	Application
Biomedical	Artificial skin (Kim <i>et al.</i> 1995) Absorbable surgical suture (Briane at al., 1992) Drug carrier (Briane at al., 1992)
Cosmetics	Skin-care product (Elizabeth, 1993) Hair stiffener (Elizabeth, 1993)
Environmental	Absorbent for waste-water treatment (Yang and Zall, 1984)
Biotechnology	Enzyme immobilization (Muzzarelli, 1980)
Food technology	Food additive (Elizabeth, 1993) Edible film (Elizabeth, 1993) Dietary supplement (Furda and Brine, 1990)
Paper and textile	Paper and fiber sizing (Muzzarelli, 1977) Polymeric dyeing (Muzzarelli, 1977)

Chitin can be prepared in various forms such as powder (Muzzareli, 1985), gel (Khor *et al.*, 1997; Bianchi *et al.*, 1997), fiber and film (Rathke and Hudson, 1994). The film forming property of chitin has been studied for many years, but it is not so popular as its deacetylated derivatives, chitosan. That is because chitin is insoluble in common organic solvents due to the strong intra- and inter- molecular hydrogen bonding, while chitosan could be dissolved in dilute acetic acid and is widely used in many applications (Rathke and Hudson, 1994). The chemical structure of chitosan is shown in Figure 1.2. However, in some applications, chitin is more favorable than chitosan. Especially in the field of biomedical application, chitin has an advantage in having biocompatibility better than chitosan because acetamide group of chitin is similar to the amide linkage of protein in living body (Muzzareli, 1985). Therefore, chitin is an attractive biopolymer for medical field.

Although chitin is difficult to dissolve in common organic solvents, it is reported that chitin could be dissolved in several solvent systems such as trichloroacetic acid/chloral hydrate/methylene chloride (Austin *et al.*, 1977), 5% LiCl/dimethylacetamide (DMAc) (Khor *et al.*, 1997; Bianchi *et al.*, 1997) 99% formic acid (Tomihata and Ikada, 1977; Kurita *et al.*, 1993; Kim *et al.*, 1996) and CaCl₂-saturated methanol (Tokura *et al.*, 1995). Kim *et al.* (1993) dissolved chitin in formic acid and cast a film from this solution. In dry state, the tensile strength and the elongation at break of chitin films were 5.2 MPa and 5%, respectively. It was found that chitin film was brittle and rarely elongated. However, the elongation at break of the film increased up to 20% in swollen state. Another solvent system for chitin is 5% LiCl/DMAc. This solvent is widely used for dissolving polysaccharide polymers such as chitin and cellulose. Aiba *et al.* (1985) prepared chitin film by dissolving chitin in 5% LiCl/DMAc and casting a film. The tensile strength of chitin film dissolved in this solvent system was 38 ± 4 MPa and the elongation at

break was in the range of 1.8 to 3.3% in dry state. In swollen state, the tensile strength decreased but the elongation at break increased up to 70%. In addition, Unitika Co (19886) reported several patents that used 5% LiCl/DMAc as solvent to prepare chitin film. However, it was indicated that chitin film is very rigid and brittle and it is not suitable for practical use. The mechanical properties of chitin film can be improved by blending with other natural (Bianchi *et al.*, 1995) or synthetic polymers (Lee *et al.* 1996). Among the large number of polymeric materials having potential suitable for blending with chitin, natural polymers are attractive due to their biocompatibility and biodegradability (Freddi *et al.*, 1995).

1.2 Cellulose

Cellulose is the most abundant polysaccharide found in the world. Cellulose has the same β -(1,4)-glycosidic linkages as chitin. Cellulose consists of β -(1,4)-D-glucopyranose units (Rathke and Hudson, 1994). Chemical structure of cellulose is showed in Figure 1.2. Like chitin, cellulose exhibits a strong tendency to form intra- and inter- molecular hydrogen bonding. It occurs throughout the plant world. However, much of the industrially utilized cellulose is derived from wood recovered by pulping. Cellulose is mainly used for the manufacture of paper, for which polymeric additives are also required. Other sources of cellulose are cotton and flax, which are widely used for clothing. Cotton linters, the short fibers cut from the cottonseeds, are widely used as a dissolving pulp for viscose rayon and cellulose acetate. Flax is used for linen and cigarette paper.

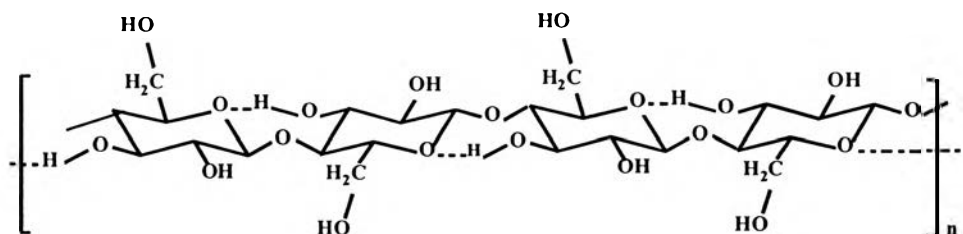


Figure 1.2 Chemical structure of cellulose.

The use of both cellulose and cellulose derivatives for the preparation of different kinds of biomaterials has been reported by various authors (Freddi *et al.*, 1995). Cellulose/chitosan blend has been extensively studied by Hasegawa *et al.* (1992), (1994) and Hosokawa *et al.* (1990) who had found that the combination of chitosan and cellulose resulted in the formation of strong, gas barrier, and water resistance films by only casting the material without any special treatment. The similarity of structures between chitosan and cellulose showed high compatibility when they are blended to prepare a film. Furthermore, the presence of cellulose could improve the tensile strength and elongation of the films because the formation of hydrogen bonding between chitosan and cellulose molecules.

The similar behaviors are expected to occur in the blend films of chitin and cellulose. Bianchi *et al.* (1995) studied the ternary phase diagram of cellulose and chitin in dimethylacetamide-LiCl. The intrinsic viscosities of the blend solutions at various chitin-cellulose ratios, as well as phase diagram behavior implied that chitin and cellulose have a good compatibility. There was some extent of hydrogen bonding formations between chitin and cellulose by characterization with FTIR. However, they studied only

confirmed that there were some existence of positive interactions between chitin and cellulose in the blend films.

The objectives of this work were to study the effect of blend compositions on mechanical properties, water absorption and oxygen permeability of chitin/cellulose blend films. For water absorption of the blend films, the effects of salt type, salt concentration and pH on the degree of swelling of the blend films were investigated.