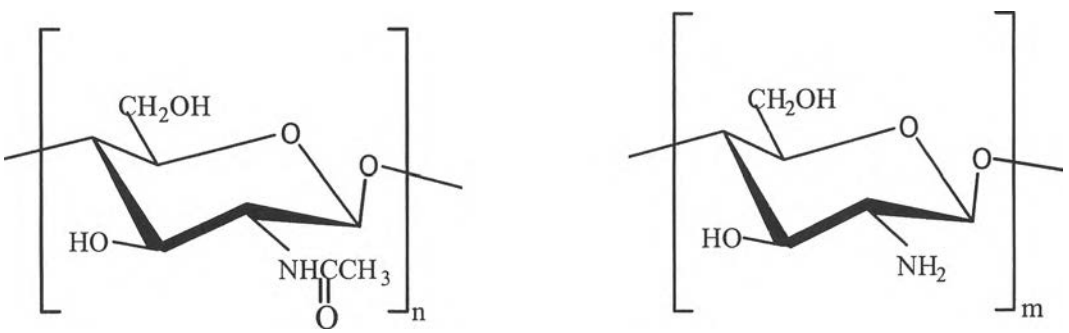
CHAPTER II
LITERATURE SURVEY

2.1 Chitin and Chitosan

Chitin is a natural occurring polysaccharide. It is found in bacterial cell walls, cuticle of insects, and the shells of crustaceans such as lobster, crabs or squids. The structure of chitin has an acetamide group substituted at the C-2 carbon position, resulting in mainly β-(1→4)-2-deoxy-D-glucopyranose structure units (Scheme 2.1 (a)). Since chitin has a limitation in solubility, chitosan, a derivative of chitin, is more attractive.

Chitosan (β-(1→4)-2-amino-2-deoxy-D-glucopyranose) (Scheme 2.1 (b)) is obtained by deacetylation of chitin. The amine group endows chitosan with a host of useful properties. Moreover, it is biopolymer, which make to be degraded by the action of enzymes from microorganisms and compatible to living tissues. As a result, chitosan is attractive for many applications such as biodegradable packaging, metal capture from wastewater, biomedical material, nutrition, and cosmetic (Kumar, 2000).



(a) (b)

Scheme 2.1 Chemical structures of (a) chitin and (b) chitosan.

2.2 Applications of Chitosan

Chitosan is recommended as useful functional material because this natural polymer has excellent properties such as biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. The important properties for some applications of chitosan have been reported as follows:

Chitosan has important applications in photography due to its resistance to abrasion, its optical characteristics, and film forming ability (Muzzarelli, 1997).

For cosmetic applications, chitosan has positive charge and high molecular weight that becomes a gel when added to the mixtures of alcohol and water. These materials are used in creams, shampoos, lotions, and permanent waving lotions (www.Biopolymer.com).

Since chitosan has the structure characteristics similar to glycosamino glycans, it could be considered as material for skin replacement (Sanford and Stinnes, 1991).

Due to the antitrombosic properties and the hemocompatibility of chitosan, the coating of the artificial blood vessel surface with a chitosan membrane could facilitate surgical treatment and provide successive adaptation of the artificial vessel to the human organism (Hirano and Noishiki, 1985).

The hydroxyl and amino groups endow chitosan with host of useful properties for ability to complex metal ions (Ratto *et al.*, 1996).

2.3 Limitation of Chitosan

Chitosan degrades before melting which is typical for polysaccharides. This makes it necessary to dissolve chitosan in order to conduct homogeneous reactions on this material. The solubility of chitosan is also important for the direct processing of chitosan into useful shaped objects, such as beads, films, and fibers, etc. Solvent systems for chitosan are aqueous acid solutions such as aqueous acetic acid and aqueous formic acid.

However, the application is limited by its low solubility in common organic solvents due to its rigid crystalline structure and high polarity (Zong *et al.*, 2000).

The key to any successful large-scale utilization of chitosan lies in the resolution of the intractability of chitosan. It would be desirable to design versatile synthetic routes for the formation of chitosan derivatives whose solubility and hydrophobicity could be tailored.

2.4 Chemical Modifications of Chitosan

Efficient procedures for the preparations of soluble chitosan derivatives have been established on the basis of chemical modifications. Solubility of chitosan derivatives in organic solvents is essential requirement for effecting fine molecular design leading to novel types of functional materials. The removal of the two hydrogen atoms of amino groups of chitosan and introduction of some hydrophobic nature by chemical modifications will cause destruction of chitosan's inherent crystalline structure and polarity. There are several researches that have been emphasized on chemical modification of the structure of chitosan.

Nishimura *et al.* (1991) prepared N-phthaloyl chitosan by the reaction of chitosan with phthalic anhydride in N, N-dimethylformamide (DMF) at 130°C. The modified chitosan obtained exhibited much improved solubility in common organic solvents such as DMF, N, N-dimethylacetamide, dimethyl sulfoxide, and pyridine.

Yalpani and Hall (1998) indicated that the attachment of carbohydrates to the 2-amino functions of chitosan transforms linear polymers into branched-chain polymers, which were soluble in both aqueous and organic solvents. This conversion can be achieved by reductive alkylation using sodium cyanoborohydride and any aldehydo or keto sugar, by Shiff base formation, or by amidation reactions using carboxylic acid or lactone derivatives. These procedures facilitate the chitosan derivatives exhibit a number of useful and uncommon properties in terms of their solution characteristics.

A simple and improved method of preparing highly soluble chitosan (half N-acetylated chitosan) was developed using a series of chitosan samples of low molecular weight, and the solubility of the half N-acetylated chitosan in water and organic solvents was investigated. To reduce the molecular weight, chitosan was treated with $NaBO_3$ under the condition that chitosan was homogeneously dissolved

in aqueous acetic acid. Chitosan was then N-acetylated with acetic anhydride under the condition that chitosan was homogeneously dissolved in aqueous acetic acid again. The result indicated that half N-acetylated chitosan had increased water solubility with decreasing molecular weight and good solubility in aqueous dimethylacetamide and dimethylsulfoxide (Kubota *et al.*, 2000).

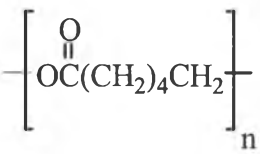
N-acyl chitosan had high susceptibility to lysosyme and showed more blood compatible properties than N-acetyl chitosan, in particular, N-hexanoyl chitosan was the most blood compatible (Lee *et al.*, 1995).

Novel N-acylchitosan fibers were obtained by treatment the filament surface of chitosan fiber with a series of carboxylic anhydrides in methanol at room temperature. Their filament tenacity and elongation values were little influenced by the N-acylation (Hirano *et al.*, 2000).

A series of acylated chitosan were synthesized by reacting chitosan with hexanoyl, decanoyl, and lauroyl chlorides and characterized the chemical and solid-state structures of acylated chitosan. These acylated chitosans exhibited an excellent solubility in organic solvents such as chloroform, benzene, pyridine, and THF. Transparent films were obtained from these solutions. The films are softer than chitosan and become more sticky and elastic at room temperature with increasing chain length of the acyl substituents (Zong *et al.*, 2000).

2.5 Poly(ε-caprolactone)

Poly(ε-caprolactone) (PCL) is a semicrystalline, biodegradable polymer belonging to aliphatic polyesters family (Scheme 2.2). The ester group is responsible for the chemical degradability of the polymer through hydrolysis. The chemical structure of PCL is the linear chain of methylene groups which imparts a hydrophobic nature that enhances its solubility in chlorinated, aromatic hydrocarbons solvents. PCL has a melting temperature of 59-64°C with a low glass transition temperature (-60°C) that gives PCL always in a rubbery state at room temperature.



Scheme 2.2 Chemical structure of poly(Ɛ-caprolactone).

2.6 Applications of PCL

The applications of PCL, a kind of biodegradable polymer with good biocompatibility and non-toxicity, have been focused on three major areas: agricultural, consumer goods packaging, and biomedical materials. Some of these have resulted in commercial products. Because of its specialized nature and greater unit value, the application as biomedical materials have been developed faster than the other two.

Bezwada *et al.* (1995) prepared the absorbable monofilament suture derived from a segmented copolymer of ε-caprolactone and glycolide (Monocryl® suture). The physical and biological properties of this suture were studied. The results reported that Monocryl® suture possessed the high tensile strength and good handling properties. This suture contained the soft segments of random copolymer of ε-caprolactone and glycolide which provide good handling characteristics and the hard segments of polyglycolide which provide high strength.

PCL is a suitable material for craiofacial bone repair, and a PCL matrix would benefit from reinforcement with long fibers such as phosphate fiber and bioabsorbable glass fiber. During bone remodelling, osteblasts will infiltrate into PCL matrix and allow the bone to form around the fibers, thus providing good implant bonding, maintaining biological, and mechanical integrity. Furthermore, the use of PCL as a matrix in long fiber composite material should give significant scope for tailoring of mechanical and degradation properties by varying the matrix molecular weight, the fibers orientation, and fraction. Corden *et al.* (1999) developed in-situ polymerization technique of PCL and used the long fiber reinforcement for producing implants for reconstructive facial surgery. The fibers

appeared to be well wetted and fully encapsulated within the PCL matrix. It was reported that this composite material should make it feasible to tailor the fiber fraction and matrix molecular weight to give a two-stage degradation.

PCL shows good biodegradability and biocompatibility. The materials, as matrix material of microparticles, can be decomposed into non-toxicity and low molecular weight species with release of the drug and then metabolized or absorbed by organism. Therefore, PCL is one of the widely used biodegradable polymers as drug microparticles. Chen *et al.* (2000) prepared PCL microparticles by emulsification-solvent evaporation technique and studied the degradation behaviour of the PCL microparticles with drug release. It was found that the degradation rate of PCL microparticles was enhanced in the presence of lipase enzyme. The degree of crystallinity of PCL microparticles increased with degradation, providing preferential degradation in amorphous domains of the PCL microparticles.

2.7 Blends of PCL with Various Polymers

Blending of PCL with various polymers has been attempted continuously. To provide a potential properties that could be benefit for different requirements.

A new family of biodegradable materials suitable for biomedical applications was prepared by means of blending of some available polyester to develop new biodegradable materials tailored for different requirements. Consequently, poly(β-hydroxybutyrate) (PHB)/PCL and poly(*d,l*-lactide) (PLA)/PCL blends were prepared and investigated the properties of these blends. As the DSC results indicated that PHB/PCL and PLA/PCL blends were immisible. The water content of PLA/PCL blends increased with the increased of PLA content in the blend, hence, the rate of hydrolysis increased (Zhang *et al.*, 1995).

Blending PCL with natural polymer seems to be an interesting way of tailored performance and economic advantage. Therefore, there have been various attempts to investigate these materials.

Koenig and Huang (1995) studied blend films of PCL/starch acetate derivatives (high-amylose corn starch (HA-CS), waxy corn starch granules, non-granular starch acetate derivatives). It was found that PCL/HA-CS blends were the

strongest, with 15% lower tensile strength and 50% higher modulus than pure PCL, for the blend with up to 25% HA-CS content. As a result of the small size of HA-CS granule (10 μm. diameter) it well dispersed in PCL matrix.

Averous *et al.* (2000) studied the different properties of wheat thermoplastic starch (TPS) and PCL blend which developed economically viable biodegradable materials. It was reported that the addition of PCL to TPS matrix allows overcoming the weakness of pure TPS (low resilience, high moisture sensitivity, and high shrinkage), even at low PCL concentration. Pure PCL has very high elongation at break. However, the elongation at break of TPS/PCL blend decreases inversely with PCL content because of phase separation between PCL and TPS.

Yang *et al.* (2000) prepared chitin/PCL blend and studied thermal properties and miscibility of the blend. Because of poor solubility of chitin, chitin/PCL blend was prepared by melt blending method. It was reported that chitin/PCL blend was immiscible at every ratio. To improve the miscibility, the *n*-butyrate (CB) was partially substituted to chitin in the blend. It was found that only interaction between CB-chitin and PCL at interfacial region was occurred but the glass transition temperature of the blend did not change.

Olabarrieta *et al.* (2001) prepared chitosan/PCL blend films by using solution casting technique and investigated the transport properties of the blend films. Before blending, chitosan solution was prepared by first dissolving 1% (w/w) of chitosan in water during high-speed stirring and adding 1% of acetic acid to the solution while PCL solution was prepared by dissolving 10% (w/w) of PCL in chloroform. It was found that at low PCL content, the oxygen permeability of blend films was decreased when the amount of chitosan increased. Moreover, the water vapour transmission rate of blend films was also determined. The results indicated that the water vapour transmission rate of blend films was decreased because of the decrease in swelling of chitosan matrix after blending with PCL content.

It is important to note that an alternative way of blending between chitosan and PCL by solution casting technique is chemical modification of chitosan which would improve chitosan's solubility in organic solvents and this would allow chitosan/PCL blend to be prepared by a more direct procedure. Therefore, the scope of this research is to modify the chemical structure of chitosan by hexanoyl reaction

and to study the effect of blend compositions of H-chitosan and PCL on morphology, thermal properties, crystalline structure, mechanical properties, and oxygen barrier property.