CHAPTER II
LITERATURE SURVEY

Chitin and chitosan are industrially produced in the United States of America, Germany, Canada, France and in Japan. Crustacea, mainly crabs, shrimps, prawns and krills, are very abundant all over the world and a limited part of these resources is being exploited by the marine food industry which produces crab meal, proteins, and shell wastes. The regions of the world where crustacea are abundant include the United States of America, India, Malaysia, Philippines, South Africa, Mexico and Thailand. The wet waste which can be a chitin resource in Thailand increased from 60,000 tons a year in 1968 to 110,000 tons a year in 1976 (Hattis and Murray, 1976). It is estimated that more than billion tons of this material is now produced annually, mainly by sea animals. It comprises a sizable portion of the organic exoskeletion of these invertebrates. Although they have a short life span, these animals have enormous regeneration capacity. They can, therefore, produce huge quantities of this biomass. The production of chitin is possible as a secondary activity of the marine food industry.

2.1 Chitin, the Source and the Structure

Chitin consists of β-1,4-linked-2-acetamido-2-deoxy-D-glucose (GlcNAc) residues, and is the second most abundant naturally occurring polymer found in the cell walls of fungi and in the exoskeletons of crustacea.

Large amount of chitin-containing biomass exists today in the form of shellfish, shrimp, crabs or krill shells (Muzzarelli, 1977).

Most chitins can be classified into three forms, α-form, β-form, and γ-form. All these structures have the same helical conformation and differ simply in the mode of packing of adjacent chains (Rudall, 1967).

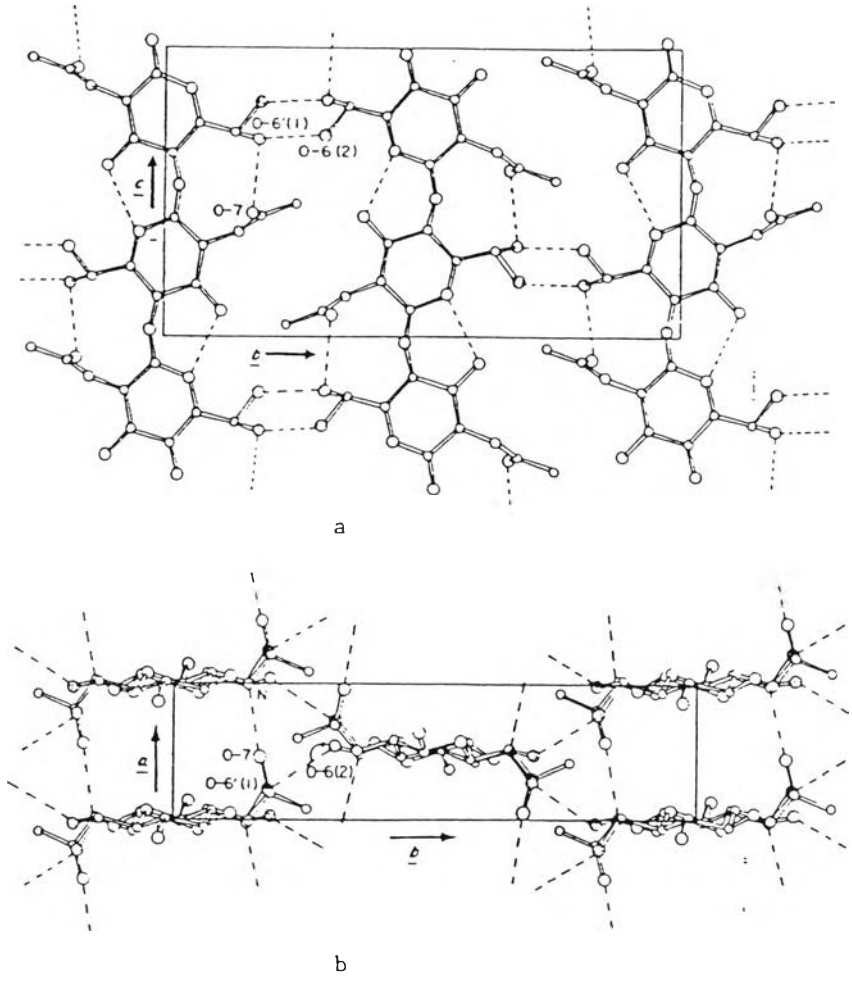

Figure 2.1 Structure of α chitin (a) *bc* projection; (b) *ab* projection (Minke and Blackwell, 1978).

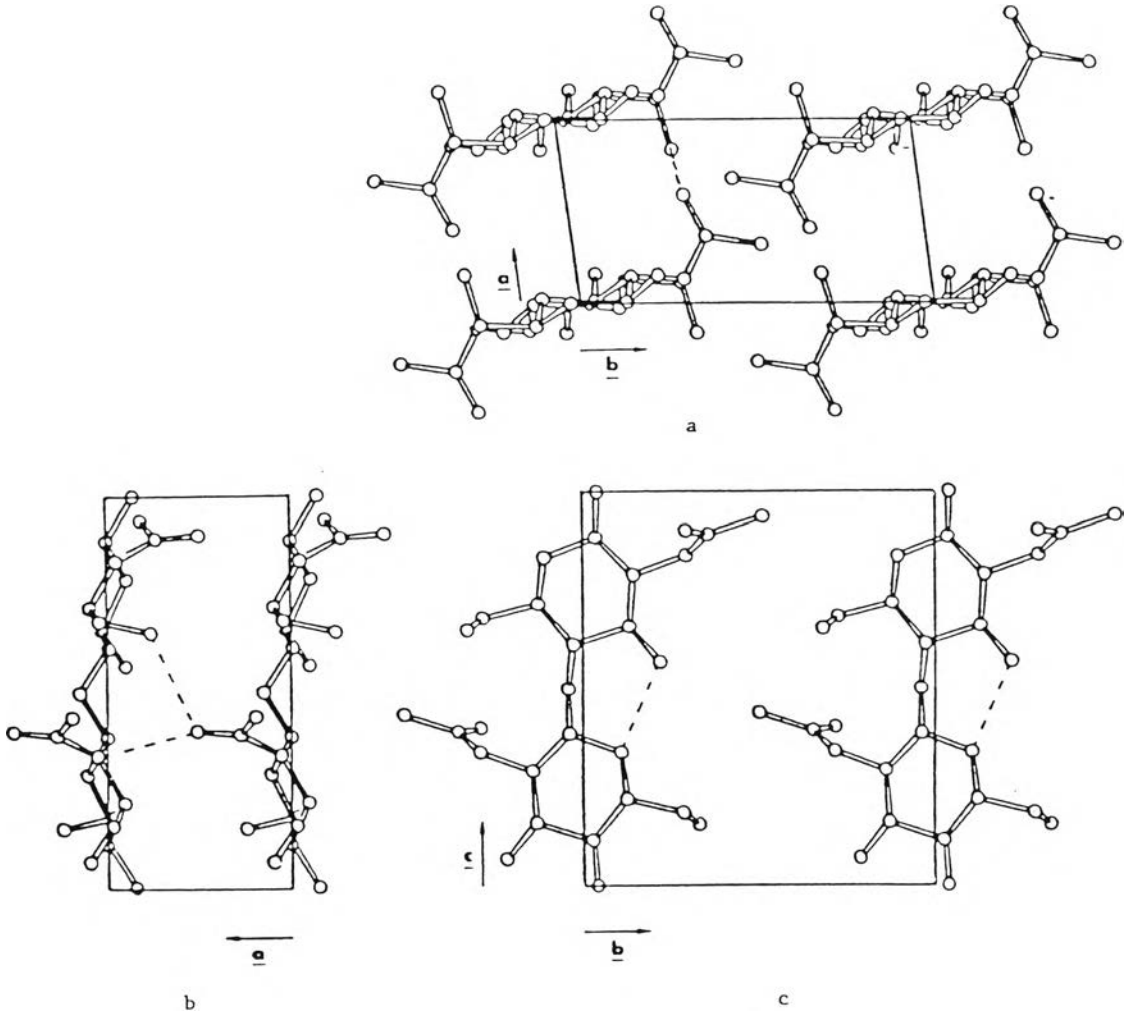

Figure 2.2 Structure of anhydrous β chitin (a) *ab* projection; (b) *ac* projection; (c) *bc* projection (Lotmar and Picken, 1950).

The α– and β– chitins can be distinguished by their hydrogen bonding network. As a result, differences can be observed by infrared spectroscopy in the frequencies of amide I mode in the region of 1660-1620 cm^{-1}. The α–chitin shows a doublet at 1656 and 1621 cm^{-1} while β–chitin shows a singlet at 1631 cm^{-1} (Rudall, 1963).

Chitin has a structure similar to that of cellulose, i.e., the OH group of each glucose unit in cellulose is substituted by an acetamide group ($NHCOCH_3$) to form the chitin chain.

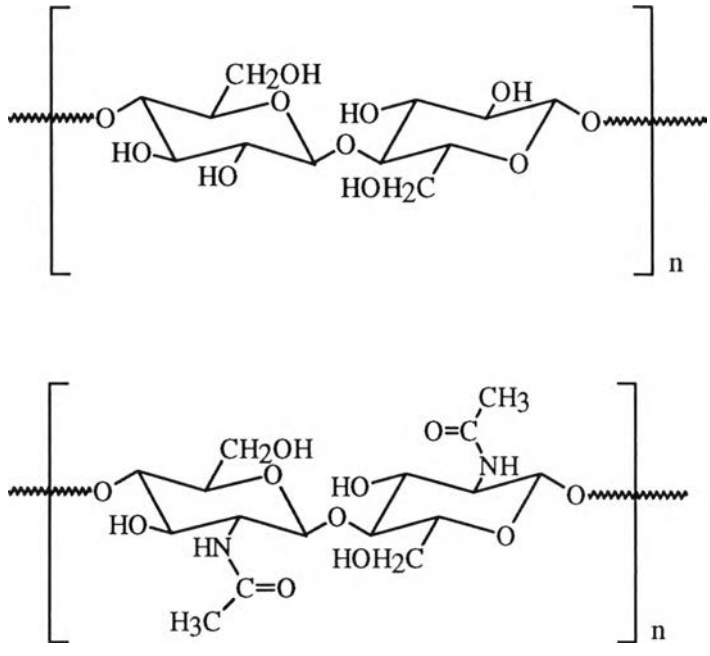

Figure 2.3 Chemical structure of (a) cellulose; (b) chitin.

In nature, chitin is covalently bonded to proteins which serve to link the chitin to carbohydrates (Brine and Austine, 1981). Chitin may also be associated tightly with inorganic salts, such as calcuium carbonate, and lipids including pigments in the shells of crustacea. In plants, chitin serves as an alternative to cellulose while in animals it alternates for collagen. The structure of chitin was clarified on the basis of its chemical and enzymatic hydrolysis for eliminating inorganic salts and protein in 1930 by Zechmeister and Toth. It was found that enzymatic hydrolysis by chitinase, which was established as a method for chitin biosynthesis, produced 2-acetamido-2-deoxyglucose (Figure 2.4e) (Karrer and Hoffman, 1929).

2.2 The Purification by Chemical Treatment Process

It is known that chitin can be purified by chemical treatments of natural biocomposite resources. Chitin was described for the first time by Braconnot (1811), in the pursuit of the research on mushrooms. The mushroom was treated with diluted warm alkali and although possibly slightly contaminated with proteins, chitin was isolated successfully.

Chitin is insoluble in common solvents. Practical dissolution can be achieved in N,N-dimethylacetamide containing 5% lithium chloride (Muzzarelli, 1977). Hexafluoroisopropanol and hexafluoroacetone are also good solvents for chitin as reported by Capozza (1995). Austin (1975) found that chloroalcohols in conjunction with aqueous solutions of mineral acids or with certain organic acids are effective systems for dissolving chitin.

Hirano et al. (1974) proposed a chemical treatment to purify chitin from exoskeleton shells. Sodium hydroxide was applied to dissociate the protein matrices followed by extraction with hydrochloric acid to remove inorganic salts of $CaCO_3$ and $Ca_3(PO_4)_2$. The treatments were required to be conducted at low temperature to minimize deacetylation and degradation of the chitin. Nevertheless, approximately 15% deacetylation was found to occur (Sanford and Hutchings, 1987). Chitin can be recovered and collected as a flaked material.

The complete hydrolysis of chitin can be achieved in nearly equimolar amounts of acetic acid to yield a homopolymer of acetylated glucosamine 2-deoxy-2-aminoglucose (Figure 2.4c). In basic conditions, chitin is known to be further deacetylated extensively to form a copolymer of 2-deoxy-2-aminoglucose and 2-acetamido-2-deoxyglucosamine which is known as chitosan, as named by Hoppe-Seyler (1894).

Chitosan was evidently first discovered by Rouget (1859). It was found that chitin which was boiled in a very concentrated potassium hydroxide solution became soluble in organic acids.

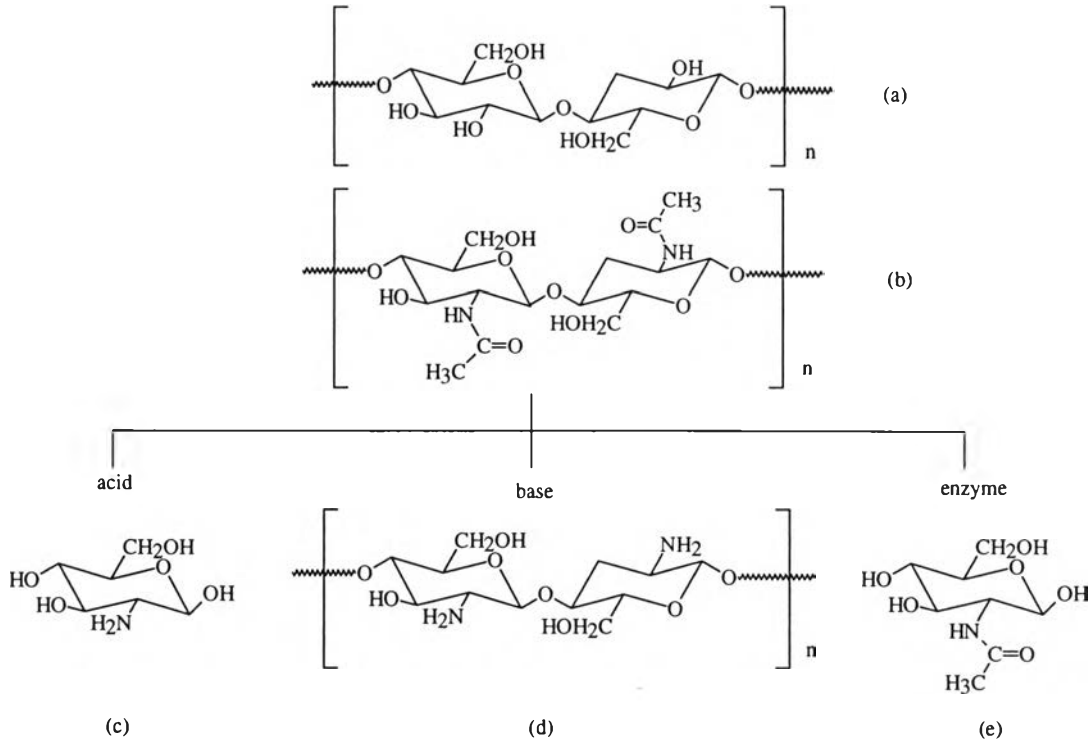

Figure 2.4 Structural relationships between (a) cellulose; (b) chitin; (d) chitosan; (c,e) the hydrolysis of chitin.

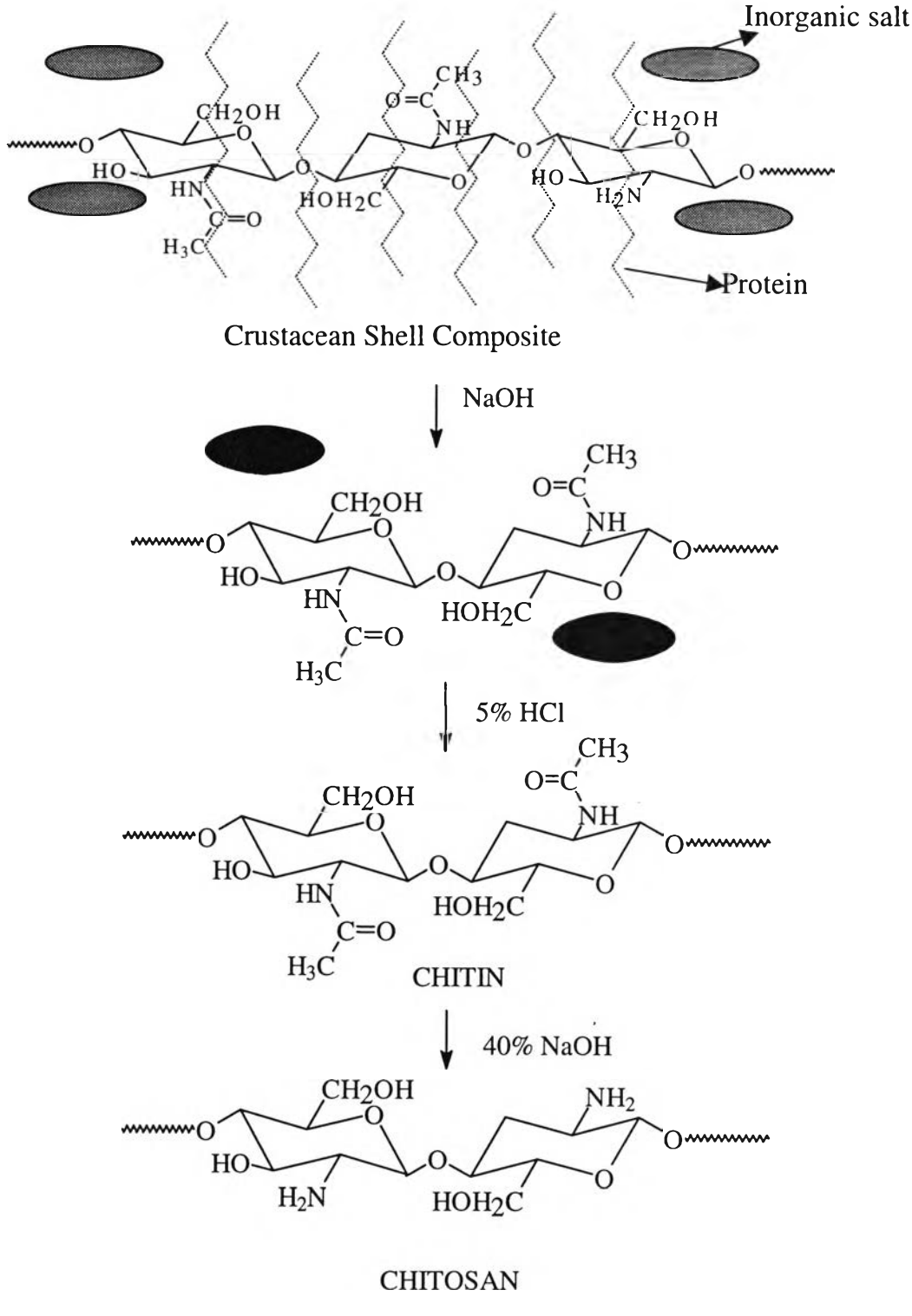

Figure 2.5 Isolation of chitin and chitosan.

2.3 Chitosan, the Most Important Chitin Derivative

Generally, chitin is a copolymer of N-acetylglucosamine and glucosamine. Chitin shows less than 7% nitrogen content. However, when the deacetylation of acetamide group progresses, giving the glucosamine unit to be significant in the main chain of polysaccharide to provide a nitrogen content exceeding 7%, the copolymer is called chitosan (Muzzarelli, 1977). The properties of chitosan are somewhat different from that of chitin which can be led to various derivatives and provide the possibilities for novel applications which cannot be achieved easily for chitin itself.

Chitosan is prepared by treating chitin with concentrated sodium hydroxide in the presence of $NaBH_4$ to minimize chain scission. The degree of deacetylation can be controlled by the reaction conditions.

Chitosan, though insoluble in water, can be dissolved in aqueous organic acids, e.g., acetic acid and formic acid as well as some inorganic acids, to give viscous chitosan solutions. The solvation of chitosan can be explained by the fact that amino groups in chitosan are fully protonated at low pH (such as pH 3). As a result, the polymer chains which are positively charged, dissociate in solution. In the protonated form, chitosan exhibits a high charge density and is effective in interacting with negatively charged biomolecules and chemical reagents. Here, chitosan can undergo via various organic chemical reactions at the position of the C-6 carbon, the primary alcohol group and at the C-2 carbon, the amino group. Thus, it is known that most chitin derivatives are achieved from the chitosan precursor.

2.4 The Properties of Chitosan

Though chitin is known as a biopolymer and a biocompatible material, the application of chitin is limited owing to its limited processing ability. Recently, interest has focused on chitosan due to a number of unique properties including :

1. Biocompatibility
2. Non-toxicity, its degradation products are natural metabolites
3. Water absorption ability
4. Beads, film, fiber or membrane formation ability
5. Selectivity in binding with metal ions
6. Ease of chemical modification

2.5 The Common Uses and Potential Applications of Chitosan

Currently, chitin and chitosan are manufactured commercially in large scale from the shell of crustaceans. The vast amount of shellfish waste today make studies on the applications of this biomaterial extensively attractive.

1. Water and Effluent Treatment (Davidson, 1980). Since most colloidal impurities in water carry a negative charge, cationic coagulants are generally used for treatment of water in industrial effluents.
2. Manufacture of Paper (Whistler et al., 1973). Chitosan is now being used in the paper industry as a wet-strength additive. Paper produced in the presence of chitosan is of higher dry, wet strength, and has a smoother surface for quality printing. Chitosan is used in the production of paper towels and sanitary napkins and also packaging paper and paper boards.
3. Medical and Pharmaceutical Applications. Owing to the biocompatilbility of chitosan, some of the unique and interesting applications in these fields

such as artificial kidney skin (Hirono, Tobetto, and Noishiki, 1981; Chandy and Sharma, 1987), surgical sutures (Chhapgar, 1987), optical applications, e.g., contact lenses (Mathur, 1988), artificial biomembrane for encapsulation of enzymes and cells (Stanley, 1973), chromatographic media (Imoto and Yagashita, 1973), etc.

4. Applications in the Textile Industry (Phadnis et al., 1987). Textile fibers having a poor affinity for dyes, e.g., nylons and glass fibers can be modified by blending or surface-coating with chitin or chitosan. This makes fibers more receptive to dyeing with reactive acids. A chitin-chitosan blend can also be used as print-paste thickener for cationic (basic) and direct dyes and resist-style printings. In addition to increasing dry fastness, it also improves the strength of the fiber and imparts a much-desired antistatic property to the synthetic fiber.
5. Applications in the Cosmetic Industry (Gross, Konrad and Mager, 1983). The first application of chitosan in cosmetics was reported by the Fine Cosmetics Co. of Japan in 1986 for hair-care products. The application takes advantage of the high-performance film-forming and moisture-holding properties of chitosan. The product obtained by the hyperchlorite oxidation of chitin, has cosmetic properties similar to the rare natural polysaccharide, hyaluronic acid (HLA). The only structural differences between HLA and chitin is the presence of a carboxylic group in position 6 of the hexose unit in the hyaluronic acid, in place of a $-CH_2OH$ group in chitin.
6. Applications in the Food Industry (Phadnis et al., 1987). Chitin and chitosan are nontoxic. They promote the growth of favorable bacteria in the stomachs of cattle and poultry and enable them to digest the highly nutrient.
7. Applications in Photography (Mathur et al., 1988). In color photography, chitosan has been used as a fixing agent for acid dyes in gelatin.

2.6 Chemical Modification of Chitin and Chitosan

Hirano et al. (1976) investigated the selective N-acylation of chitosan by treatment of a solution in aqueous, methanolic acetic acid with carboxylic anhydrides at room temperature. The obtained N-acylchitosans were found to be effective as a selective aggregation for specific cancer cell.

Nishi et al. (1981) reported the preparation of hexanoyl, decanoyl, and dodecanoylchitin which were achieved by using acyl cholride in methanesulfonic acid. The introduction of an alkyl chain into a chitin molecule was proven to proceed more easily when the aliphatic chain of acyl chloride was shorter because of the small steric hindrance.

Grant et al. (1988) studied water-soluble derivatives of chitosan. The butyrylation of chitosan of various degree of acetylation yielded water and methanol soluble derivatives. After sovent removal, the derivatives afforded tough clear flexible films.

Terbojevich et al. (1988) studied homogenous phase synthesis of chitin derivatives. Derivatization reactions were reported for chitin dissolved in dimethylacetamide-5%LiCl with acid chloride or anhydride, yielding esters soluble in organic and in aqueous media.

Yalpani et al. (1991) investigated the synthesis of biopolymer-chitosan conjugates. Low molecular weight poly(3-hydroxyalkanoate) (PHA) was attached via amidation yielding novel types of branced conjugates.

Kurita et al. (1992) investigated the tosylation of chitin to prepare tosylchitin as a precursor for facile chemical modification. The obtained tosylchitin efficiently underwent reactions such as acetylation and iodination to fully acetyled tosylchitin and iodochitin. Furthermore, iodochitin was evaluated as a precursor for graft copolymerization of styrene both by cationic and a free-radical mechanisms. Though the grafting percentages were not high in the radical graft copolymerization, a small amount of homopolystyrene

could be achieved. The resulting chitin-*graft*-polystyrene was proven to be more soluble or swellable in organic solvents.

2.7 Chitin-Chitosan for Biodegradable-Biodecomposible Polymer

Recent efforts have demonstrated the feasibility of using chitin as a biodegradable compounding agent for polymer blends.

Jin Xu et al. (1996) studied chitosan film acylation and effects of biodegradability. Chitosan films were acylated under heterogenous conditions in methanol and hexanoic anhydride and found that the modified chitosan appeared biodegradable when exposed to mesophilic marine and soil environments.

Laham et al. (1995) reported that for polyethylene-chitin and polyetylene-chitosan blends containing 90% polyethylene, substantial weight loss of the chitosan (73%) and chitin (85%) components was found after 6 months incubations in soil environments. Also, it has been demonstrated that chitosan was degeaded by chitosanases produced by microbial genera such as *Arthrobacter*, *Bacillus*, *Streptomyces*, *Aspergillus*, and *Penicilium* which are found widely in ecosystems.

2.8 The Scope of the Present Work

Recently, chitin and chitosan have attracted interest as a blending agent for biodegradable plastics. Unfortunately, chitin and chitosan, owing to their structures, have high hydrogen bonding between polymer chains. Thus, the miscibility between chitin and chitosan and polymer matrices is one of the main problems for blending. However, the utility of chitin as a reinforcing

agent for thermoplastics has not been extensively investigated. Recent efforts have demonstated the feasibility of using chitin as a biodegradable compounding agent for polymer blends. Chitin has been used as a blending agent with natural polymers such as albumin, cellulose and silk fibroin, and synthetic polymers such as poly(vinyl alcohol) (Nakatsuka and Andrady, 1992), poly(vinylpyrrolidone), poly(ethylene glycol) (Kim et al., 1995), and poly(ethylene) (Laham, 1995). The biodegradation characteristics of chitin-polymer blends have recently been studied.

The purpose of this research will be to systematically explore the utility of chitin and chemically modified chitin as biodegradable reinforcing agents in commercially important thermoplastics such as polyethylene (PE), polypropylene (PP), and poly(ethylene terephthalate) (PET). Considerable work has been invested in the introduction of other polysaccharides such as starch into polyolefins in order to provide improvement in properties such as dimensional stability, as well as to provide the biodegradability (Greizerstein et al., 1991). The potential to prepare new polymer compounds with biological degradability, as well as to explore the utility of a naturally occuring polymer in a technologically important application, provides considerable motivation for the pursuit and eventual commercial potential of this research. Therefore, in this work, chitosan is chemically changed into tosylchitosan though the tosylation. These functionalized precursors can be modified with stearic acid to promote stearyl group onto their structure which is expected to promote compatibility with thermoplastic matrices.

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