

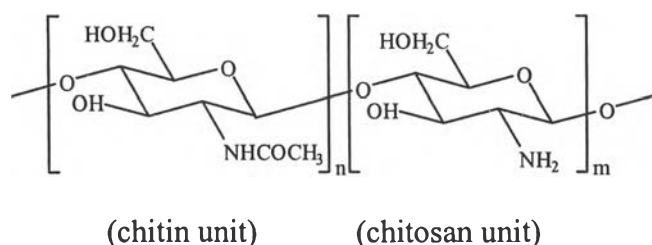


CHAPTER II LITERATURE REVIEW

2.1 Chitin-Chitosan: Specific Properties and Potential Applications

Chitin is the second most plentiful organic resource on the earth next to cellulose, presenting in marine invertebrates, insects, fungi and yeasts. Chitin is a homopolymer of 2-acetamido-2-deoxy- β -D-glucopyranose. Acetyl group can be removed by methods such as heterogeneous alkaline hydrolysis and thermomechanical technology to obtain a derivative of chitosan. Chitosan, 2-amino-2-deoxy- β -D-glucopyranose which shows significant property about solubility in acidic solvent. In general, chitin and chitosan are existed as a copolymer (Scheme I).

Scheme I



The basic chemical structure of chitin-chitosan is a polysaccharide chain having two hydroxyl groups at C-3 and C-6 positions. Basically, the hydroxyl and amino groups of chitin-chitosan act as a crosslinkable site which can be applied to many applications such as membrane, gel and beads. Moreover, the amino group in chitosan can be protonated to be cationic polymer, which is considered to be effective for binding with metal ions. The glucopyranose ring is nontoxic and biocompatible meet the requirements for medical field. Chitin-chitosan is a unique polysaccharide due to the nitrogen atom of acetamide and amino group at C-2 position. Therefore, chitin-chitosan is not only attractive in terms of bioactivity

(Kurita *et al.*, 1997), biocompatibility (Singh *et al.*, 1994), biodegradability (Mark *et al.*, 1985) and nontoxicity (Chandy *et al.*, 1992) but also the possibility for chemical modification (Goosen, 1997).

2.2 Limitations

For more than three decades, the many approaches to modify chitin-chitosan based on its unique properties have been presented. Recently, various chitin-chitosan derivatives are proposed to develop value-added products which never been achieved in natural one. However, by considering the chemical structure, chitin-chitosan is known for the high molecular weight, and strong inter and intramolecular hydrogen bonding (Figure 2.1). The limitation in chemical reaction such as heterogeneous reaction and non-quantitative reaction is the main problem to overcome and makes the chemically modified chitin-chitosan product be not available in the market.

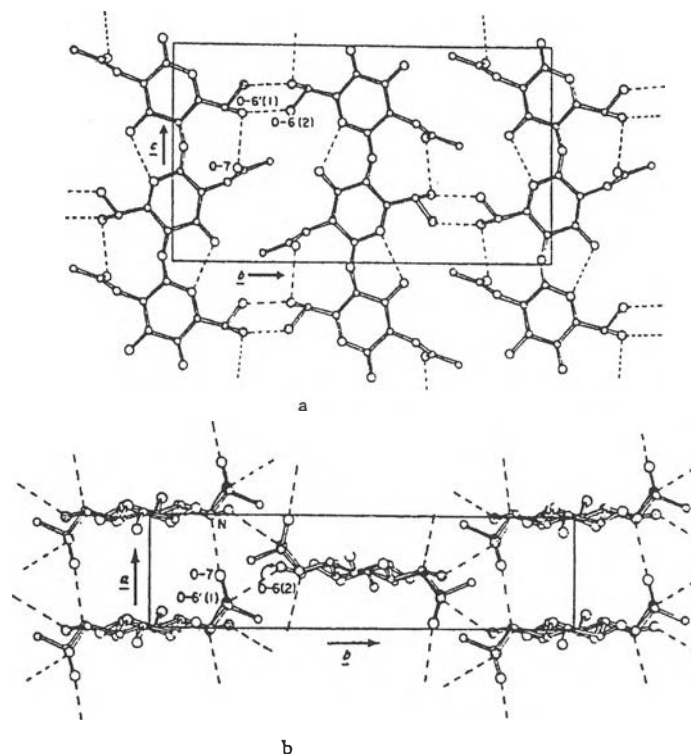


Figure 2.1 Structure of α -chitin; (a) bc projection, and (b) ab projection (Minke and Blackwell, 1978).

2.3 Approaches to Overcome Limitations

Due to the strong inter and intramolecular hydrogen bond networks, chitin-chitosan cannot be dissolved in most organic solvents and water. For example, the solvent for chitin is lithium chloride saturated methanol, whereas for chitosan is acids. In order to overcome this limitation, the breaking of crystalline structure of chitosan is the main point to be done which can be achieved by (i) the hydrophobic/hydrophilic functionalization of chitosan chain and (ii) chain scission.

In the case of (i) Kurita (1991) converted insoluble chitin-chitosan into organosoluble derivatives such as N-phthaloylated chitosan by the reaction between chitosan and phthalic anhydride. The product showed the solubility in dimethyl sulfoxide. Tokura (1981) proposed water-soluble derivatives such as carboxymethyl chitin (CM-chitin) as well as CM-chitosan. Although we can obtain organic solvent and water soluble derivatives, those compounds obtained might need the careful purification steps whereas the structure of chitosan has been changed. In addition, some derivatives contain bio-incompatible group to use in further step.

In the case of (ii) typically, chain scission can be achieved by 3 main methods, i.e. enzymatic hydrolysis, photoirradiation, and chemical treatment. Enzymatic hydrolysis is an attractive method because of the mild reaction conditions and high specific cleavage. For example, endochitinase performs the chain scission of chitin at the β -(1,4) glycosidic linkage of N-acetylglucosamine within the chain, whereas exochitinase exhibits the cleavage at the end of the chain. However, this method requires many steps in the enzyme preparation process. Mekkriengkrai (2000) used chitinase, *Staphylococcus species* strain TU005(E) to degrade chitosan. The experimental results showed that oligochitosan was one-third of the starting chitosan. Photoirradiation is an approach to apply the high radiation energy with a large scale production whereas no purification step is required. Yoksan *et al.* (2001) studied on the optimum γ -ray irradiation condition at 25 kGy to obtain 75% chain degradation with limited crosslinking or changes in structure. The reduction of molecular weight reached a steady state of 10^5 gms/mole when the starting molecular weight is above 7×10^5 gms/mole. Allan *et al.* (1997) reported the depolymerization

of chitosan by the action of HONO for producing chito-oligosaccharides at a desired molecular size. The results showed that the rate of depolymerization depends on the concentration of nitrous acid, glucosamine moieties, and Arrhenius temperature, whereas the molecular weight and concentration of catalyst do not affect to the rate of depolymerization. Samakrat (2002) prepared water soluble low molecular weight chitosan by using hydrochloric acid. Degree of deacetylation is increased significantly to nearly 100% after hydrolysis time for 3 hours and the product obtained from the hydrolysis time above 9 hours performs the water-soluble property. Here, the short chain molecules of chitosan can be obtained and the solubility is expected to improve. However, the chain degradation brings the polydispersity of the chains and in most cases the crystalline part still remains. In addition, if the chain degradation is not proceeded upto oligomer level, it is found that the solvents used for low molecular weight ones are the same as chitosan starting materials.

2.4 Chitin-Chitosan Chemical Modification for Value-Added Product

Since the reactive amino as well as primary and secondary hydroxyl groups in chitin-chitosan are ready for chemical reaction. Accordingly, many efforts have been paid to chemical modifications of chitin-chitosan not only to improve the solubility and overcome the rigid structure but also to achieve the property that never be obtained in the original polymer. Considering the chemical structure, chitin-chitosan can react with other reactive functional groups, for instance acid chloride, aldehyde, alkyl halide and carboxylic acid or it can undergo crosslinking, esterification, etherification and graft copolymerization reactions (Hun, 1992).

Poly(ethylene glycol) has many advantages such as solubility in aqueous and organic solvents, metal complexing ability, biological compatibility, ease of chemical modification and cost effective. Therefore, many studies have been paid to the modification of chitin-chitosan with high molecular weight poly(ethylene glycol).

Ouchi *et al.*, (1998) prepared a highly water-soluble chitosan derivatives which have a low degree of substitution by using poly(ethylene glycol) grafted chitosan (PEG-g-Chitosan). The results showed that the aggregation properties in

aqueous solution of PEG-g-Chitosans solution are different depending upon the degree of introduction of PEG in aqueous solution. The PEG-g-Chitosan aggregates could also uptake N-phenyl-1-naphthylamine (PNA) in neutral conditions. Kurita *et al.*, (1999) synthesized comb-shaped chitosan derivatives having oligo(ethylene glycol) side chains by the reductive alkylation technique. The products have high affinity for organic solvents as well as water and significant adsorption activity toward metal cations.

2.5 Inclusion Properties to Chitosan Molecules

During the past few years, biosorption or sorption to material of biological origin has been recognized as an emerging technique for the depollution of metal-ion polluted streams (Volesky and Holan., 1995). Chitosan is a biopolymer with high proportion of amino groups, and has specific property to provide lone pair electrons for metal complexation. As a result, this natural polymer exhibits novel binding properties for metal ions such as mercury, cadmium and chromium.

Nair and Madhavan (1984) and Peniche-Covas *et al.*, (1987) studied on the removal of mercury from solutions, and the adsorption kinetics of mercuric ion by using chitosan. The results showed that the adsorption efficiency of Hg^+ by chitosan depends on the treatment period, the particle size, the initial concentration of Hg^+ and the quantity of chitosan.

Maruca *et al.*, (1982) used chitosan flakes of 0.4-4 mm for the removal of Cr^{3+} from wastewater. The results showed that the adsorption capacity increased by decreasing the flake sizes. This implied that metal ions were preferably adsorbed on the outer surface of chitosan in the removal of Cr^{3+} from the wastewater. McKay *et al.*, (1989) studied the effect of temperature on the removal of Cu^{2+} , Hg^{2+} , Ni^{2+} and Zn^{2+} by chitosan. However many researchers paid an attention on the chemical modification in order to improve inclusion properties of chitin-chitosan for various advanced applications. One of the potential value-added products is the adding of some supramolecules such as crown ether, cyclodextrin, and calixarene on chitin-chitosan chain in order to increase the potential adsorption property for metal ions or inclusion property for neutral molecules.

Peng *et al.*, (1998) synthesized crosslinked-crown ethers by the reaction of crosslinked chitosan with 4'-formyl benzo-15-crown-5 and 4'-formyl benzo-18-crown-6. The experimental results showed that they have not only good adsorption capacity for Ag^+ and Pd^{2+} but also high selectivity for the adsorption of Ag^+ or Pd^{2+} with the coexistence of Pb^{2+} and Cr^{3+} .

Tan *et al.*, (1999) synthesized crosslinked chitosan dibenzo-16-crown-5 acetate crown ether and crosslinked chitosan 3,5-di-tert-butyl dibenzo-14-crown-4 diacetate crown ether, which could be used in hazardous aqueous waste remediation as toxic metal-binding agents. Experimental results showed that the two crosslinked chitosan derivatives does not only show adsorption capability for Pb^{2+} and Cu^{2+} but also high selectivity for Pb^{2+} and Cu^{2+} in the coexistence of Ni^{2+} .

Yang *et al.*, (2000) prepared synthesized mesocyclic diamine-grafted chitosan-crown ether by using mesocyclic diamine crown ether as the grafting agent. The product has high selectivity for the adsorption of Cu^{2+} in the presence of Pb^{2+} , Cu^{2+} and Cd^{2+} , and its adsorption selectivity was better than that of chitosan.

Yang and Yuan, (2001) studied on static adsorption properties of chitosan hydroxyl azacrown ether for Ag^+ , Cd^{2+} , Pd^{2+} and Cr^{3+} . The derivative was synthesized by reaction of hydroxyl azacrown ether with epoxy-activated chitosan, and exhibits good adsorption capacity and high selectivity for Ag^+ in the coexistence of Pb^{2+} and Cd^{2+} .

Wan *et al.*, (2002) investigated the adsorption capacity and selectivity of N-benzylidene chitosan (CTB), chitosan-dibenzo-18-crown-6 crown ether bearing Schiff-base group (CTBD) and chitosan-dibenzo-18-crown-6 crown ether (CTSD) for Ag^+ , Cu^{2+} , Pb^{2+} and Ni^{2+} . The results showed that CTBD has better adsorption properties and higher selectivity for metal ions than CTSD.

Tanida *et al.*, (1998) proposed a convenient method for introducing a β -cyclodextrin residue into high molecular weight chitosan by using amination as a key reaction. The experimental results showed that the product possesses an inclusion ability with *p*-nitrophenolate and it would be useful in cosmetic or pharmaceutical industries.

An α -cyclodextrin-linked chitosan derivative was prepared via reductive amination proposed by Tujima *et al.*, (1998). The product showed an inclusion formation with *p*-nitrophenolate which would be useful in cosmetic and pharmaceutical industries.

Considering supramolecular specific properties, it can be concluded that most of the approaches for chitosan are from the functionalization of chitosan with macrocyclic unit. In other words, the ionic interaction ability is achieved mainly from the conjugated macrocyclic itself. Here, we proposed a supramolecular structured chitosan generated from a linear ethylene glycol chain where the pseudocyclic cavity for ionic interaction is expected. Yamagishi *et al.*, (1996) reported that the ethylene glycol chain attached onto phenolic resin performs host-guest property to entrap metal ion via the pseudocyclic crown ether-like structure of ethylene glycol chain.

2.6 The Scope of The Present Work

The present work stands on the viewpoint to functionalize chitosan with simple functional group as polyethylene glycol, which can induce molecular recognition onto chitosan chain. The present work will concentrate on the inclusion phenomena to clarify supramolecular structure of chitosan-PEG.