

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Chitin

Toffey *et al.* (1995) converted chitin to chitosan by alkaline treatment. Since chitosan dissolved easily in acetic acid, the water-soluble ionic complex of chitosan and acetic acid is called chitosonium acetate. It can be cast a film. By heating, the chitosonium acetate film is converted into the water-insoluble chitin film.

Eugene *et al.* (1996) produced carboxymethylated chitin film in two-step process. The first step, chitin film was prepared from the solution of 0.5% chitin dissolving in 5%LiCl/DMAc. The second step, the dry chitin film was carboxymethylated. The property of this material is different from carboxymethyl-chitin. It can take up water but it is not soluble and retains a degree of rigidity. The degree of swelling of the carboxymethylated chitin film was higher than that of chitin film. Observation by SEM showed that the surface of chitin film appear rough. In contrast, a smooth surface was obtained for the film after carboxymethylation.

Bianchi *et al.* (1997) prepared chitin gel by heating the solution of chitin in 5% LiCl/DMAc. At the temperature higher than 90°C, the chitin gel was obtained. The sol-gel transition is reversible and its temperature depends on the polymer concentration and, to a lesser extent, on the molecular weight.

Laurent *et al.* (1997) studied the formation of N-acetyl chitosan gel. Chitosan, which degree of deacetylated below 30%, is prepared from chitin by N-deacetylation with alkaline. Increasing the temperature and the molecular

weight of chitosan influenced the formation of N-acetyl chitosan gels in an acetic acid-water-propanediol solution.

Tomihata and Ikada (1997) studied the biodegradable property of the films from chitin and its deacetylated derivatives. Chitin was deacetylated to various extents with NaOH solution to obtain partially and thoroughly deacetylated chitins. The maximum equilibrium water content (EWC) and the minimum tensile strength were observed for the films which was deacetylated between 0 and 68.8 %. As the degree of deacetylation became higher, the in vitro and in vivo degradation of their films occurred less rapidly without passing maximum and minimum.

## 2.2 Cellulose

Kawakami *et al.*(1982) reported the permeability (P) of cellulose nitrate (CN)/poly ethylene glycol (PEG) blend membrane for N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> as a function of film compositions. P for each gas had been found to almost constant or rather slightly decreased up to 20%wt of PEG which has molecular weight 300 (PEG-300) content and then increased appreciably with increasing fraction of PEG. The permeability ratio  $P_{N_2} / P_{O_2}$  increased with the fraction of PEG, while  $P_{CO_2} / P_{N_2}$  is practically constant. For the effect of molecular weight of PEG, P was larger when PEG had lower molecular weight.

Li *et al.*(1995) prepared the poly ethylene glycol(PEG) and cellulose acetate(CA) blend membrane. CA is one of the membrane materials applied to the separation of CO<sub>2</sub> from natural gas. It is inexpensive and highly qualified for the preparation of membrane. The membranes containing 10wt% PEG of low MW 200, 600, 2000 and 6000, and 10, 20, 30, 50, and 60 wt% of MW 2000 were prepared. The blend membrane, which contained 10%wt PEG 2000 exhibited higher permeability for CO<sub>2</sub> and higher

permeaselectivity for CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub> than those of blend membranes that contained 10%wtPEG of the MW range 200-6000. However, the blending of PEG 20,000 in the membrane resulted in decreasing of the selectivity coefficients of CO<sub>2</sub>/CH<sub>4</sub> values.

Striegel (1997) reported that dimethylacetamide (DMAc)/LiCl has become a favored solvent in the analysis of polysaccharides such as chitin, cellulose. They are essential to virtually all-biological systems and are also extremely important in the medical and pharmaceutical fields, as well as in the food pulp and paper, and textile industries. There are many applications of LiCl/DMAc solvent. For example, it used as the mobile phase in the gel permeation chromatography (GPC). LiCl/DMAc also used as the solvent for preparation many cellulose derivatives. For chitin, it could be dissolved in 5%LiCl/DMAc at room temperature.

Sjoholm *et al.* (1997) characterized the cellulosic residues from the dissolution of hardwood kraft pulps (HWKP) and softwood kraft pulps (SWKP) in LiCl/DMAc. In contrast to HWKP, SWKP are not completely soluble in LiCl/DMAc. Characterization of the undissolved fraction was made in order to obtain an understanding of reason for its limited solubility. For HWKP, it was found that the residue contains a higher relative amount of mannan, lignin and nitrogen. In contrast, in the SWKP, xylan seems to be easily dissolved and mainly amorphous structures were present in the residue.

Williamson *et al.* (1998) investigated the semi-interpenetrating networks (SIPNs) of poly (N,N-dimethyl acrylamide) (DMAm) containing chitin and cellulose by dissolving in 9%LiCl/N,N-dimethylacetamide (DMAc). DMAm has structural characteristic similar to DMAc and, therefore, is expected to dissolve completely in the presence of lithium chloride. The resulting SIPNs are optically transparent and exhibit a one-stage thermal degradation profile. The 25wt% cellulose DMAm SIPNs has a 6-fold higher storage modulus and lower equilibrium water content than

DMAm control system. The enhancement in mechanical stiffness was attributed to intimate molecular interaction and complexation between cellulose and DMAm.

In addition, Williamson *et al.* (1999) further studied the SIPNs of N,N-dimethylacrylamide(DMAm)–N,N-dimethylamino-ethylacrylamide (DMAEAm), or N,N-dimethylacrylamide(DMAm)-2-acrylamino-2-methyl-1-propanesulfonic acid (AMPS) contain chitin or cellulose. These were synthesized in 9%LiCl/DMAc. The SIPNs were formulated to contain (1, 2, or 5%w/w) cellulose and 0.8%w/w chitin. The swelling behavior of these materials was investigated as a function of pH (DAEAm-containing networks) or electrolyte concentration (AMPS-containing networks). The AMPS materials have higher equilibrium water content (EWC) than the DMAEAm materials, reflecting higher hydrophilicity. The pH swelling properties of the DMAEAm materials showed the maximum EWC values between pH = 4 and 5 due to the protonation of the tertiary amine with the chitin-containing material exhibited the largest EWC. All of the AMPS materials exhibited a decrease in EWC values with an increase in the concentration of added electrolyte.

### **2.3 Chitin blend with other polymers**

Shigehiro *et al.* (1995) studied the fixation of  $\text{CO}_3^{2-}$  ions dissolving in water-sphere on the surface of chitin, chitosan, and their derivatives and composite materials such as crab shell protein – chitin, silk fibroin – chitosan, silk fibroin – chitin, starch – chitosan, and starch - chitin. There were examined as mimetic model for the mineralization of  $\text{CO}_2$  in crab shell. The mineralization of  $\text{CO}_2$  is of important for preventing the green house effect on the earth, and for conserving the environment and eco-system. The result from ATR-FTIR indicated the participation of proteins in the mineralization

of  $\text{CO}_3^{2-}$  ions. The  $\text{Ca}^{2+}$  ions probably bound to the crab shell acidic proteins, and atmospheric  $\text{CO}_2$  ions are non-enzymatically or enzymatically adsorbed to form  $\text{CaCO}_3$ .

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 had good compatibility. There were some extent of hydrogen bonding formations between chitin and cellulose by characterization with FTIR.

Kim *et al.* (1995) prepared the semi-interpenetrating network (semi-IPN) hydrogel membranes of  $\beta$ -chitin and poly (ethylene glycol) (PEG) diacrylate macromer. PEG macromer and  $\beta$ -chitin dissolved in formic acid and was cast to prepare a film at various blend ratios. followed by subsequent crosslinking with 2,2-dimethoxy-2-phenylacetophenone by u.v. irradiation. photocrosslinked hydrogels. The  $\beta$ -chitin/PEG hydrogel membrane exhibited relatively high equilibrium water content in the range of 60-81%. All the crosslinked membranes revealed a remarkable decrease in crystallinity. Their glass transition temperatures increased as the  $\beta$ -chitin content increased. The tensile strength of the semi-IPNs in swollen state ranged between 1.35 and 2.41 MPa.

Lee *et al.* (1996) studied the mechanical properties of blend films of  $\beta$ -chitin and poly (vinyl alcohol) (PVA) at various blend compositions. It was found that the tensile strength of the blend films was greater than that of both homopolymers. Upon mixing with PVA, the elongation at break increased and the tensile strength decreased with the PVA content.

Miyashita *et al.* (1997) prepared chitin/poly (glycidyl methacrylate) (PGMA) composites, which were synthesized via bulk polymerization in a gel state of chitin impregnated with reactive GMA monomer. For the blend compositions which was higher PGMA content (chitin  $\leq$  20 wt %), it was

found that the chitin/PGMA composites gave a  $T_g$  value higher than that of PGMA homopolymer.

#### **2.4 Cellulose blend with other polymers**

Hosokawa *et al.* (1990) developed the composite film derived from chitosan and fine cellulosic fiber. The composite films were prepared in the ranges between 0 - 40%wt chitosan. The dry strength of the composite films increased with the chitosan content increased. On the other hand, the wet strength had a maximum point for the chitosan content 10-20%wt. A film composed of homogenized cellulose alone had no wet strength.

Hasegawa *et al.*(1992) studied the interaction between chitosan and cellulose in chitosan/cellulose blend films. The x-ray diffraction patterns showed the crystallinity of cellulose in the blend films decreased with an increase in chitosan content. Then, the presence of chitosan in the blend films prevented the crystallization of cellulose molecules. From Raman analysis, the blend films didn't show the different from pure chitosan and cellulose films. It assumed to be the same secondary structure were occurred in the blend films and pure films. The blend films had the maximum tensile strength and elongation at break at 30%cellulose content. These results suggested that there were some interaction between chitosan and cellulose molecules in the blend films.

In addition, Hasegawa *et al.* (1994) found that the chloral /dimethylformamide system also dissolved chitosan as well as cellulose. Therefore, they prepared chitosan/cellulose blend films in this solvent system. The tensile strength and Young's modulus of the blend films were greater than those calculated by adding the values of the two components according to the blend ratios. The maximum values of those properties were obtained at chitosan contents of 10-20%.