

CHAPTER II

LITERATURE REVIEW

2.1 Chitin and Chitosan

Chitin is the second most abundant natural polymer in the world after cellulose. It is found in fungi, arthropods and exoskeletons of crustaceans (shrimp, crab and other shellfish); therefore chitin is a renewable resource. The structure of chitin is shown in Figure 2.1

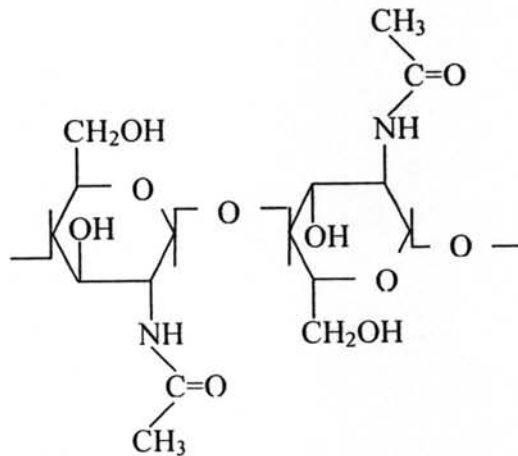


Figure 2.1 Structure of Chitin.

Chitin is a cellulose-like polysaccharide of β -linked 2-acetamido-2-deoxy-D-glucose residues, which exhibits various different properties from cellulose, whose hydroxyl groups in the C2 position are substituted with acetamide groups (-NH-CO-CH₃) in chitin. Similarly, chitosan is a linear polymer of a (1-4)-linked 2-amino-2-deoxy-D-glucopyranose, easily derived from chitin by a deacetylation process. Chitosan occurs naturally in some fungi but its occurrence is much less widespread than chitin. The structure of chitosan is shown in Figure 2.2

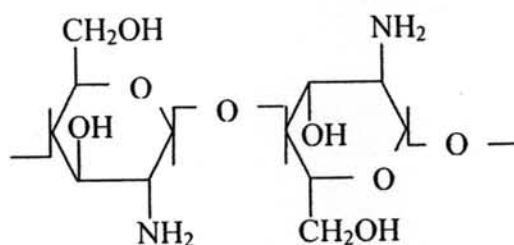


Figure 2.2 Structure of chitosan.

The deacetylation process is one of the main reactions carried out on chitin, most commonly by using aqueous alkali. The most frequently used alkali is NaOH. The extent of deacetylation is governed by the alkali concentration, temperature, time of reaction and particle size.

Most living tissues (e.g. skin, bone, hair), polysaccharide, polyanions, bacteria and fungi, enzymes and microbial cells are negatively charged. Therefore, chitosan possesses a wide range of useful properties. Specifically, it is a biocompatible, antibacterial and environmentally friendly polyelectrolyte, thus lending itself to a variety of applications such as water treatment, additives for cosmetics, textile treatment for antimicrobial activity and biomedical devices.

Chitosan can be used in many applications. It has been documented that chitosan confers considerable antibacterial activity against a broad spectrum of bacteria. (Harano & Nagano, 1989; Muzzarelli et al., 1990) Blending chitosan with cellulose by using trifluoroacetic acid as a solvent can increase its antibacterial ability. The treatment can produce membranes used as a wound dressing that can prevent a wound from excessive dehydration and infection. It was found that the number of colonies of all bacteria test (*E.Coli* and *S. Aureus*) decreased with an increase of chitosan concentration (Yu-Bey Wu, 2004). Chitosan blends can also be used as a filler to increase the strength of paper. Blending chitosan with poly(vinyl alcohol) (PVA) and starch, can improve the paper strength properties significantly without any additional treatment or curing (m. mucha, 1999). However, chitosan use is limited because it has limited solubility in water.

2.2 Cellulose

Cellulose is the most abundant polymeric material in nature that can be found in plant cell walls in combination with lignin and hemicellulose. It occurs naturally in almost pure form in cotton. It is the major constituent of paper; further processing can be performed to make cellophane and rayon, and more recently Modal, a textile derived from beech wood cellulose.

Cellulose is a linear polymer of β -(1-4)-D-glucopyranose unit. The similarity of cellulose and chitosan in primary structures suggests that they may be sufficiently similar to facilitate the formation of homogeneous composite films.

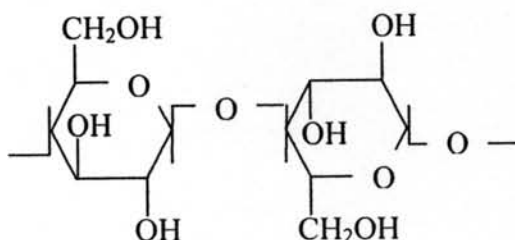


Figure 2.3 Structure of cellulose.

The fibers used in paper making are usually natural and composed of cellulose. They are bound together with large hydrogen bonding of hydroxyl groups on the glucose residues, holding the chains firmly together and contributing to their high tensile strength.

2.3 Antimicrobial

Antimicrobial indicates the ability to inhibit or kill microorganisms. This is a broad term that could mean effectiveness against just one type of organism or multiple types of organisms. The bacteria can be divided into 2 major types, gram-positive and gram-negative, which both have peptidoglycan cell walls. The difference between these two is based on the chemical and physical properties of their cell walls. The gram-negative bacteria are more dangerous as disease organisms because the outer membrane is often hidden by a capsule which becomes harder for the body to detect. The gram-positive have Teichoic acids which are negatively charged. Therefore these contribute to the negative charge of gram-positive cell walls.

The cell membrane is composed of protein and phospholipids. It has been proved that the targets of antimicrobial polymers are the acidic phospholipids. An antimicrobial polymer which has a cationic group would interact with the head groups of these molecules which are negatively charged. This will result in distorting the bilayer and altering the permeability of the cell membrane. The membrane damage will cause the leakage of low molecular weight cytoplasmic components such as potassium ions and activation of membrane bound enzymes

Polymeric quaternary ammonium compounds have received the most attention as biocide polymers. The quaternary ammonium groups are water-soluble and impart good antimicrobial activity to textiles (Chang-Woo Nam, 1999). Introducing quaternary ammonium groups into chitosan may produce a cationic antimicrobial polymer.

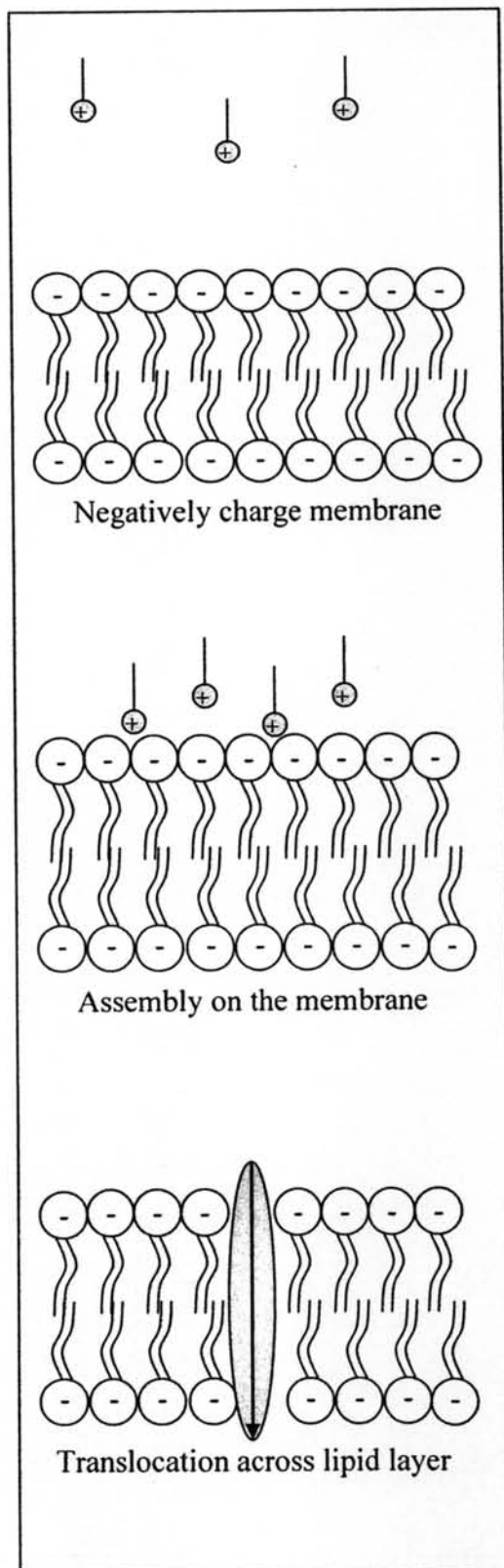


Figure 2.4 Antimicrobial mechanism of cationic polymer on bacterial membrane.
(P.Broxton, P.M. Woodcodk, 1984)

2.4 Modification of Chitosan

Chitosan and its derivatives are very attractive for medicine, pharmacy and biotechnology. Chitosan-based materials have many valuable bioactivities. Chitosan appears to be economically attractive because chitin, which is the source of chitosan, is the second most abundant biopolymer in nature.

Chitosan dissolves in water only in acidic conditions by the protonation of the amino groups and thus its antimicrobial activity is limited to acidic conditions. Therefore, introduction of quaternary ammonium salts onto the chitosan backbone is one of the best methods to enhance antimicrobial activity as well as its water solubility in neutral conditions.

GTMAC (glycidyltrimethylammonium chloride) was chosen as a quaternary reagent because of its ease of reaction with amino groups. The reaction between chitosan and GTMAC takes place in neutral aqueous conditions, in which the hydroxyl groups of chitosan are not sufficiently nucleophilic to induce ring opening of GTMAC, whereas the amino group of chitosan is nucleophilic enough to produce the ring opening.

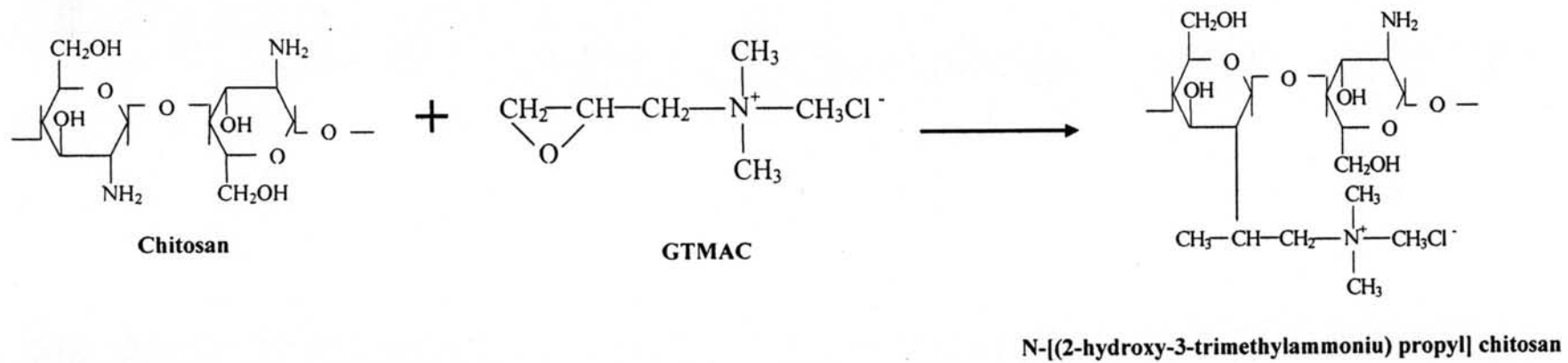


Figure 2.5 Modification reaction of chitosan with GTMAC.

2.5 Strength Properties

Interactions between any two particles involve both attractive and repulsive forces. The surface charge on fibers and fines is a complex function of the chemical composition of the fiber surface, its state of ionization, and the nature and amounts of additional substances adsorbed. For the simplest case, consider a suspension of fibers and fines that always take on a negative charge due to the ionization of surface carboxyl groups associated with hemicelluloses, oxidized cellulose and oxidized lignin.

The strength of paper is derived from the cooperative effects of hydrogen bonds (4-6 kcal/mol) or van der Waals forces (0.5-2 kcal/mol) acting at interfiber crossings. These bonds affect the distance between the separate crosslinking fibers. To improve this low strength a number of polymeric materials have been applied as additives. These polymers lodge between fibers and enhance the strength by increase the number of bonds between fibers or supplementing low-energy bonds by higher energy ionic (10-30 kcal/mol) or covalent (50-100 kcal/mol) interfiber linkages. (Alireza A. *et al*, 2006)

The dry-strength additive should (Mucha, M., 2006)

1. Be soluble in water-based systems for easy application with conventional papermaking systems.
2. Be substantive to cellulose so that retention is efficient.
3. Be compatible with the cellulose surface so that it does not disrupt conventional hydrogen bonding.
4. Be film-forming (of large enough Mw) to offer adhesive resistance to rupture.
5. Contain a functional group capable of ionic or covalent bonding with the paper fiber surface within the papermaking process.
6. Be nontoxic and perfectly natural(thus biodegradable) to conform with environmental regulations

Because of the negative charge of the fiber surface, cationic chitosan can be attached on the surface of fiber to reduce the space between fibers.

The dry strength of paper basically refers to the relative performance of the paper sheet when specific mechanical properties are tested, i.e., tensile, tear, etc., under normal dry conditions which the paper will be used. The main mechanism of attaining strength in paper is through the development of hydrogen bonds between the fibers in the sheet. The number of the hydrogen bonds formed will affect the strength of the bond between two fibers.

The bonding between fibers can be enhanced by two ways. The first is by refining, which can increase surface fibrillation and cell wall hydration (increases the flexibility of the fiber) both of which promote fiber conformability and increase the surface contact between fibers. The second means is to add a dry strength agent that will enhance and increase the number of bonds between adjacent fiber surfaces.

Dry strength additives are thought to act by several mechanisms. They build hydrogen bonds that naturally happen in the bonded area between two fibers. First, they will increase the number of hydrogen bonds that would naturally occur in the bonded area between two fibers. This is a chemical hydration of the fiber system. Refining hydrates the fiber, but in the process the fibers are generally weakened and shortened. This is the reason of decreasing in tear strength when the use of dry strength additives is present. Second mechanism involves improvement of the formation of the sheet. This provides more uniformly arrangement fiber-fiber-bonds. A third involves the improved web consolidation that occurs when dry strength agents enhance fines retention and sheet dewatering.

2.5.1 Tensile strength characteristics

2.5.1.1 Tensile strength

Tensile strength is the ratio of the maximum load paper can support without fracture when being stretched to the original area of a cross section of the paper. The unit of tensile strength is based on force per length (N/m).

Tensile index, reporting tensile force per unit basis weight corresponds in a better way with the practical importance of paper strength:

$$\text{Tensile strength} = \sigma_T^b = F_T/b \text{ [N/m]}$$

$$\text{Tensile index} = \sigma_T^l = F_T/bw \text{ [Nm/kg]}$$

where, F_T = breaking force [N]
 b = specimen width [m]
 w = basis weight [kg/m^2]

2.5.1.2 Tensile testing

The specimen for tensile testing should in most standards have a width of $b=15$ mm and a test length of $l=100$ mm. A sample is cut, conditioned and clamped (distance between parallel clamps, 100 mm), and the sample is loaded at a uniform straining rate until rupture. A large number of testing instruments are available, operating on horizontally or vertically oriented specimen.

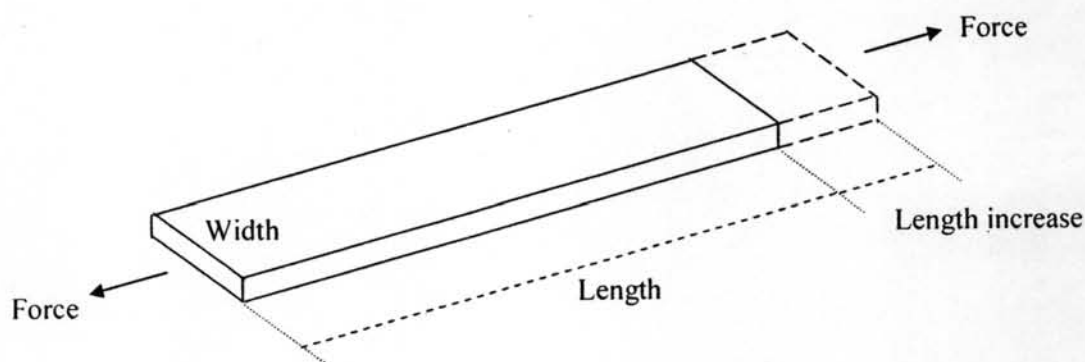
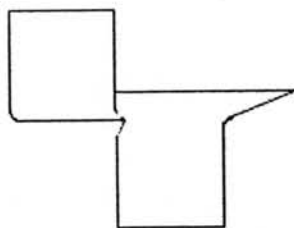


Figure 2.6 Test specimen for tensile testing.

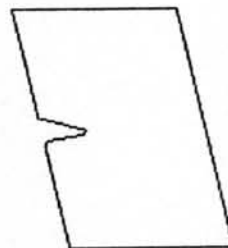
2.5.2 The tearing resistance

The most common tearing resistance test, the “Elmendorf” type, measures the force perpendicular to the plane of the paper required to tear one or multiple sheets of paper through a specified distance after the tear has been left.

In the Elmendorf tear, paper specimens of well-defined size are given an initial cut. After clamping the specimen in the pendulum instrument, the specimen is torn along a standardized distance, starting from the cut. The energy consumed during this tearing is measured, and average tearing force along the torn length is calculated and reported as the tearing resistance:



(a) Elmendorf tear



(b) In-plane tear

Figure 2.7 The working modes of the most commonly used Elmendorf tear test (a) and the less used (b).

The tearing index is calculated by normalizing the tearing resistance by the basis weight:

$$\text{Tear index} = T^w = T^b/w \text{ [Nm}^2\text{/kg]}$$

where, T^b = average tearing force [N]

w = basis weight [kg/m^2]