CHAPTER II

LITERATURE REVIEW

Cellulose is the most plentiful biological macromolecule on earth. It is a major constituent of most land plants and it is an important commercial raw material for textile industry. Cellulose is a linear polymer of carbons 1 and 4 linked β-D glucose residues (Figure 2.1) and its degree of polymerization varies with sources. In native cellulose, polymer chains are aligned to form fibers with high crystallinity. The fibers are mechanically strong and are resistant to both chemical and enzymatic attacks. Cellulose found in the plant cell wall is usually embedded in lignin and hemicellulose matrix. It also can be found in the cell wall of algae and some bacterial producing cellulose. Examples of native cellulose are cotton, ramie, and algae cellulose. Each of them is an intimate mixture of crystalline and amorphous regions.

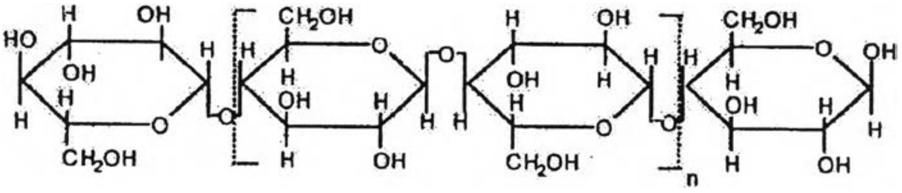

Figure 2.1 Chemical structure of cellulose.(1)

It is widely known that cellulose has four polymorphs, cellulose I, cellulose II, cellulose III and cellulose IV (Figure 2.2) and they can be distinguished by X-ray diffraction technique (Figure 2.3).

Cellulose I is a native form of cellulose. Cellulose II is easily obtained by the mercerization or regeneration of cellulose with caustic soda.(2-5) Cellulose III is prepared by a treatment of cellulose with liquid ammonia or organic amines followed by a dry-air evaporation of the chemical. Cellulose IV is prepared by a heat treatment of cellulose with glycerol.(3, 5-7)

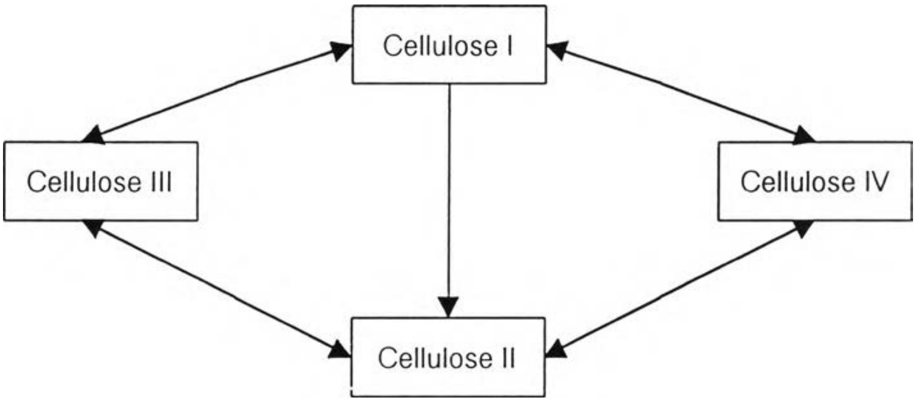

Figure 2.2 Cellulose polymorphs and their transition possibilities.

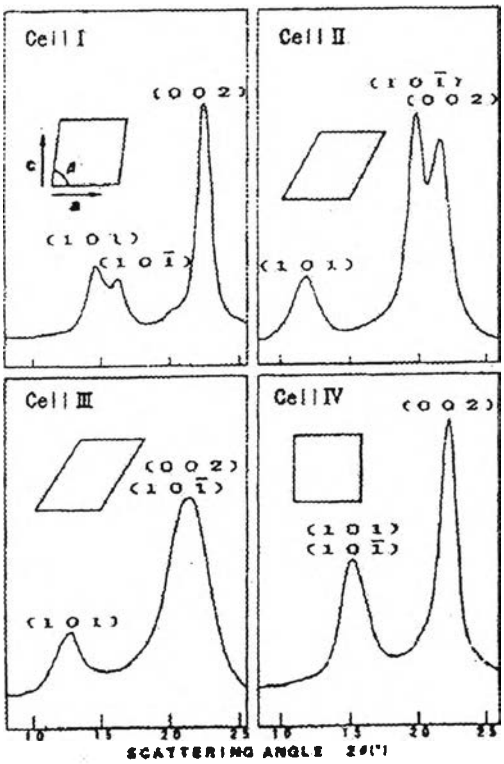

Figure 2.3 Equatorial X-ray diffractograms of four cellulose polymorphs, together with projections to the ac plane along the fiber axis of each unit cell.(8)

2.1 CELLULOSE I

2.1.1 Sources of Cellulose I

Cellulose I or native cellulose is mainly derived from plants such as cotton, ramie, flax etc. The amount of cellulose in the fibers varies according to fiber sources and it is generally associated with other materials such as water, wax, pectin, lignin and mineral substances. Cellulose I also presents in bacteria, fungi and algae. Native cellulose obtained from bacteria and algae are called *Acetobacter xylinum* and *Valonia ventricosa*, respectively.

All native celluloses are a mixture of two crystalline modifications with different properties. One is cellulose I_α and the other is cellulose I_β. Results from nuclear magnetic resonance suggest that cellulose I_α is dominant in celluloses from lower plants such as *Valonia ventricosa* and from bacterial celluloses such as *Acetobacter xylinum.* While cellulose I_β is dominant in celluloses from higher plants such as cotton and ramie.(7, 9)

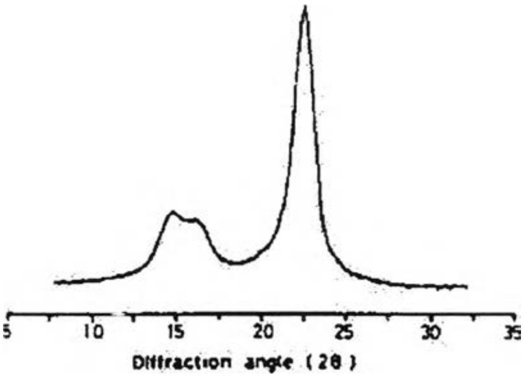

Figure 2.4 X-ray diffractograms of cellulose I.(3)

Native celluloses from a wide variety of sources give similar X-ray diffraction patterns (Figure 2.4). X-ray diffraction analysis reveals that although there are clear differences in perfection and angular orientation of the crystallites among native cellulose samples, but the chief diffraction maxima are in essentially the same positions and they have the same proportions of intensity. This common pattern comes from a structure that is referred to as cellulose I.(7)

2.1.2 Molecular Structure of Cellulose I

The molecular structure of native cellulose or cellulose I was first studied on ramie by x-ray diffraction analysis and reported by Meyer and Misch in 1937.(10) They found that the unit cell was monoclinic arrangement containing two cellulose chains pass through the unit cell, and suggested that the chains had two-foid screw symmetry. The unit cell parameters was $a = 8.35^{\circ}A$, $b = 10.30^{\circ}A$, $c = 7.90^{\circ}A$ and $\beta = 84.00$ (Figure 2.5)

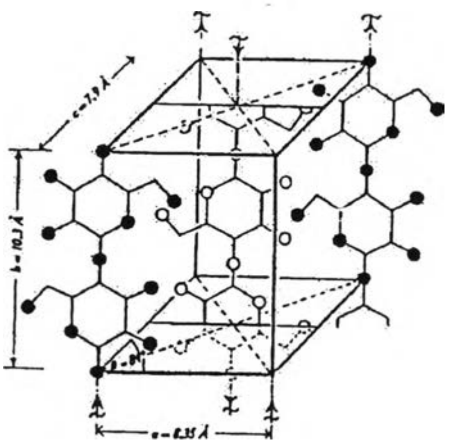

Figure 2. 5 Unit cell of cellulose I.(10)

Sarko and Muggli (5) studied the crystal structure of algae *Valonia ventricosa* by X-ray intensity analysis and conformation energy analysis. They found that the chains of *Valonia* cellulose packed with parallel polarity maintained a twofold screw axis for a rigid components of the glucose ring. The most probable positions of the hydroxymethyl group rotations were near the trans-gauche position, which allowed extensive an hydrogen bonding.

Gardner and Blackwell(5) also studied the crystal structure of algae *Valonia ventricosa* using the rigid-body least-squares procedures. They found that the model for the cellulose chain was constructed as a twofold helix repeating and the reliability factors of the most probable chain conformation and the rotational position of hydroxymethyl oxygen were near the trans-gauche position.

Woodcock and Sarko(5) studied the crystal structure of ramie by X-ray diffraction analysis combined with the stereochemical refinement method and suggested that the structure of ramie cellulose was nearly identical to the *Valonia*. The chain arrangement was parallel and the hydroxymethyl oxygen was in the trans-gauche position.

Cellulose polymer chains contain three hydroxyl groups per anhydroglucose unit with the chair conformation of the glucose ring. It has the capability of forming numerous hydrogen bonds along the length of the polymer chains (intramolecular hydrogen bonds) and also between polymer chains into the same sheet (intermolecular hydrogen bonds) using the hydroxyl groups and the ring oxygens. In the conventional structural proposals, cellulose I has two intramolecular hydrogen bonds and one intermolecular hydrogen bond in each glucose residue of cellulose chain. O(3)-H--O'(5) and O(2)-H--O'(6) are intramolecular hydrogen bonds running along both sides of each cellulose chain. O(6)-H--O'(3) is an intermolecular hydrogen bond.(5,7) (Figure 2.6)

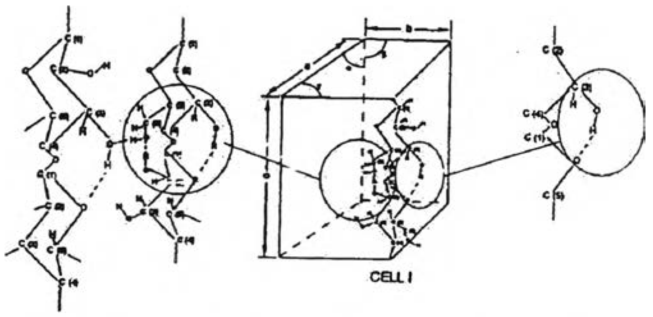

Figure 2.6 Hydrogen bonds in cellulose I.(11)

These hydrogen bonds and other secondary forces (mostly van der Waal forces) bind together the positions of the molecular chains into various degrees of lateral order, ranging from perfect geometrical packing of the crystal lattice to random arrangement.

2.1.3 Reactivity of Cellulose I

Reactivity and accessibility have been used to describe the ease with which cellulose can react. Reactivity is the ability of the chain molecule to react with other molecules. Accessibility is the ease by which the functional groups of chain molecule can be reached by the reactant molecules. Cellulose polymer chains contain three hydroxyl groups per anhydroglucose unit. One of these groups is a primary hydroxyl group ($C(6)H_2$-OH) and the other two groups are secondary hydroxyl group (C(2)H-OH) and (C(3)H-OH). Primary hydroxyl groups of cellulose chains are more reactive than secondary hydroxyl groups, but sometime secondary hydroxyl groups may be reacted before the primary groups if the primary groups are not accessible because of their steric relationships in the fine and gross structures of the cellulose material.(12) The hydroxyl groups in amorphous regions react readily in all chemical reactions due to their high accessibility. While in crystalline regions, close packing of the polymer chains and strong interchain bonding prevent the hydroxyl groups from reacting with the reactant molecules. Both primary and secondary hydroxyl groups of cellulose are slightly acidic in nature.

The absorption of water by cellulose is caused by the hydrogen bonding of water molecules to the accessible hydroxyl groups of cellulose. Generally, this event takes place in the amorphous region. X-ray diffraction shows that there is no change in the crystallized regions when cellulose is soaked in water because water penetrates only the amorphous portions.(13)

In industrial practice, it has been known that in order to keep the high reactivity of cellulose, swollen cellulose must not be allowed to dry. This is because in the amorphous regions, water molecules can form hydrogen bonds with cellulose and thus reduce the intermolecular hydrogen bonds of cellulose. When cellulose is dried, its reactivity is lost because the hydrogen bonding in cellulose is restored. Wetting cellulose with water breaks the hydrogen bonds in cellulose, seperates the cellulose chains by water molecules and increases the reactivity of cellulose. The changes in cellulose morphology brought about by water in the amorphous regions alone have marked influence on reactivity of cellulose.(12)

In general, There are two main reactions taking place in cellulose. The first involves the hydroxyl groups of cellulose and the second comprises a degradation of the chain molecules.

The former includes the following reactions

- Esterification : nitration, acetylation and xanthation.
- Etherification : alkylation and benzylation.
- Replacement of -OH by $-NH_2$ and halogen.
- Replacement of -H in -OH by Na
- Oxidation of $-CH_2OH$ to -COOH
- Oxidation of the secondary -OH groups to aldehyde and carboxyl
- Formation of addition compounds with acid, bases, and salts.

The degradative reactions of cellulose, for example, hydrolysis and oxidation reduce the degree of polymerization of cellulose and lead to the reduction in strength of the cellulosic fiber.

2.2 CELLULOSE II

2.2.1 Sources of Cellulose II

Cellulose II can be obtained by treating the cellulose I with a strong alkali solution such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and lithium hydroxide (LiOH). This process is called Mercerization. Other ways to obtain cellulose II are through the regeneration of cellulose in the viscose process and in the solution of cellulose/ MMNO (N-methyl morpholine N-oxide) / water.

2.2.2 Molecular Structure of cellulose II

The crystal structure of cellulose II was studied by Sarko et al. on Fortisan, and Blackwell et al. on rayon and mercerized cotton.(5) The cellulose unit cell parameters for these fibers are listed in Table 2.1. They found that these celluloses were monoclinic unit cell containing two chains. The backbone of cellulose chains was kept rigid, with a twofold screw axis.

Table 2.1 Unit cell parameter for various cellulose II.(5)

Source	Crystal system	Unit cell parameter				Space group
		a/nm	b/nm	c/nm	γ (deg)	
Fortisan	monoclinic	0.909	0.796	1.031	117.3	$P2_1$
Rayon	monoclinic	0.918	0.793	1.031	117.3	$P2_1$
Mercerized cotton	monoclinic	0.899	0.802	1.036	116.6	$P2_1$

Stipanovic and Sarko.(5) solved the crystal structure of regenerated cellulose II (Fortisan) by combined stereochemical packing refinement and X-ray diffraction analysis. They found that cellulose II crystallizes to an antiparallel packing model with an extensive hydrogen bonding network. The intersheet hydrogen bonding between the corner and the center chains, which is absent in the cellulose I structure, stabilizes the structure. The positions of the hydroxymethyl oxygen are trans-gauche at the corner chain and gauche-gauche at the center chain. (Figure 2.7)

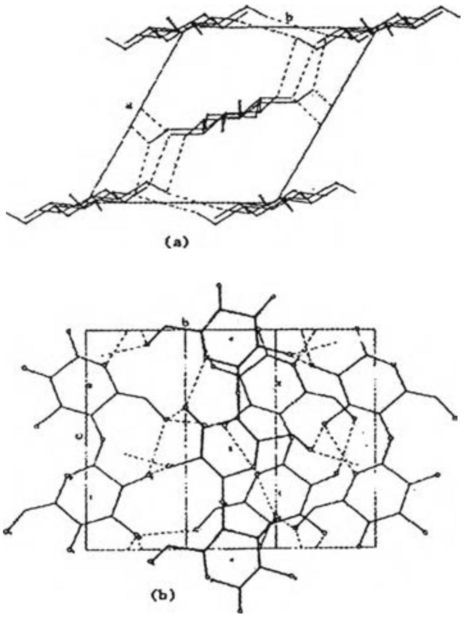

Figure 2.7 Projections of cellulose II (Fortisan) unit cell : (a) ab plane ; (b) bc plane. Hydrogen bonds are indicated by dashed lines, residues are number.(5)

Antiparallel cellulose II is the lowest energy form because of an extensive hydrogen bonding network.(14) It has been suggested that upon regeneration of cellulose, the polarity of the chain packing in the crystal structure must at some point change from parallel of cellulose I to antiparallel of cellulose II.(15)

Jones(16) observed and calculated the X-ray intensities for models of the cellulose II. The most favorable structure based on infrared spectra has the chains in an antiparallel arrangement.

Sarko and Muggli(17) were unable to use a potential energy packing analysis to choose between a number of parallel and antiparallel chain models, although they considered the antiparallel model to be the most favorable form because of the extensive hydrogen bonding possibilities. Electron microscopy experiments on the conversion of cellulose I to cellulose II appear that chain folding may occur during this process. Nevertheless, in the mercerization process, swelling in alkali solution changes cellulose I to cellulose II. This change is accompanied by only a small decrease in length, which has been used as an argument against chain folding.

The concept of antiparallel packing of chains in cellulose II was originated by Mayer and Misch. Their calculations indicated that antiparallel chains pack more comfortably than parallel chain into the cellulose II unit cell dimension. Turbak and Sokthivel(18) studied the structure of cellulose II and found that the interatomic contact and interaction in both the parallel-up and antiparallel models are equally acceptable. Parallel and antiparallel models have nearly equal van der Waals energies of -45.7 and -43.8 kcal/mol respectively. The lattice parameters for parallel-up and antiparallel models are different by less than 0.904°A and it is impossible to distinguish these two models on the basis of the lattice parameter differences. This dose not require an antiparallel structure but allows either parallel structure to form, whichever is the most probable for the adjacent chains at the time.

However, a major task in the study of cellulose II has been the determination of whether adjacent chains are packed parallel or antiparallel to each other. Traditionally, the chain polarity has been assumed to be antiparallel, to account for crystallization from solutions of randomly organized cellulose chains. However, a difficulty arises because the dominant result from the study of the polymer chains of cellulose I are parallel. Since the mercerization process converts cellulose I to cellulose II without dissolving the material, the mechanism of conversion from parallel to antiparallel would have to be subtle.

2.2.3 Mercerization

In 1850, Mercer (19) discovered that cotton yarn or fabric immersed tensionless in caustic soda (NaOH) solution exhibited swelling and shrinking in width and length. It became denser and stronger and the dyeability improved. Then, Lowe found that the fabric shrinkage could be prevented by stretching the fabric during the caustic soda treatment and during washing. The process was later called "mercerization". Changes in the fine structure, morphology and conformation of the cellulose chains occur with this mercerization. More specifically, the treatment of the cellulosic fibers with sodium hydroxide solution produces a polymorphic change of cellulose I to cellulose II (see X-ray diffractograms in Figure 2.8). A concurrent increase also occurs in fiber accessibility to chemical reagents and dyes due to a decrystallization or lower degree of order by rearrangement of cellulose chains and hydrogen bonds between the chains.

This morphological change in the cellulose probably affects the conformation of the O-H groups on the cellulose chains and the hydrogen bonding pattern along and between the chains. The extend of conversion of cellulose I to cellulose II, the degree of polymerization and the degree of morphological change depend on fiber type, tension, time, temperature and concentration of alkali solution.

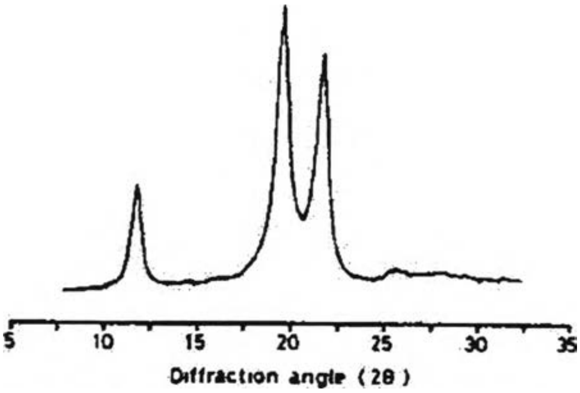

Figure 2.8 X-ray diffractograms of cellulose II.(2)

Sodium hydroxide is called " caustic soda", soda lye, and sodium hydrate. In water solution, depending on concentration, caustic soda can form five hydrates containing 1,2,3,5 and 7 molecules of water respectively. Hydrate formation is an exothermic reaction.(20) Sodium hydroxide has a fairly large dipole hydrate in mercerization. It can induce intracrystalline swelling of cellulose by molecules penetrating between the 110 planes of the crystallites. Intrafibrillar swelling in sodium hydroxide is higher than in liquid ammonia.(21) Sodium hydroxide uptake is an adsorption process, not a chemical reaction. One mole of sodium hydroxide and five or six moles of water are absorbed per anhydroglucose unit, in the form of a hydrated ion and free water molecules, in solution of 14-23% sodium hydroxide. Sodium cation (Na^+) carries its associated hydration water molecules penetrating into the fiber. Fiber must swell sufficiently to accommodate the diffusion of Na^+ with its water molecules. Hydrogen bonds within the sheets of chains are broken and the sheets are pushed farther apart by the entrance of Na^+ and its cluster of water molecules.(22)

2.2.4 Effects of Mercerization on Cellulose Properties(23)

A. Swelling and Shrinkage

When cellulose is immersed in sodium hydroxide solution, water and alkali diffuse in and the material swells. The fiber quickly commences to untwist from its twisted ribbon like form and tends to become cylindrical rod like surface due to deconvolution. The lumen of the fiber diminishes and the diameter of the fiber becomes more round. The surface of the nearly cylindrical cotton fiber after mercerizing reflects light more evenly to all sides than the kidney-shaped cotton fiber and the fiber surface becomes more lustrous. As the fiber swells along the transverse direction, the fiber shrinks in length. To obtain maximum fiber swelling and fiber penetration, it is necessary to mercerize cotton at 15 - 23% sodium hydroxide at 0-25°C.(19)

B. Structural Modification

Due to swelling of cellulose in sodium hydroxide solution, many hydrogen bonds are broken, the planes of molecular chains move apart, molecular structure tends to become decrystallised, the chains or spaces within the cellulose structure become more uniform and the chains of glucose residues show a slight twist. Because of the distortion of polymer network and changes in crystalline structure, the process of mercerization is irreversible. Mercerization also affects the crystallites and the orientation of the crystalline region.

C. Luster

Unmercerized cotton has a general appearance of a flat ribbon with spiral twists. Its surface is rough and its cross-section is a bean-shaped. Lumen, the central canal, is broad, irregular and resembles a collapsed tube. All these factors result in less luster. When cotton is brought into an aqueous solution of sodium hydroxide, cotton fiber begins to swell immediately, and on further swelling it becomes a circular shape and the lumen is practically eliminated.

The changes taking place in the cross-sectional shape of cotton fiber during mercerization are shown in Figure 2.9.

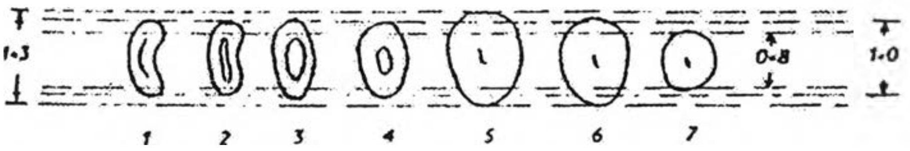

Figure 2.9 Seven successive stages of changes in the cross-sectional shape of cotton fiber as produced during mercerization.(23)

Stages 1 to 5 show changes from a twisted ribbon like fiber at stage 1 to a uniformly cylindrical fiber with maximum swelling at stage 5. Stages 6 and 7 show some contraction without loosing its cylindrical form when the fiber is washed with water and then dried. Fiber shows an increase in luster. During the last three stages, fiber maintains its shape, but shrinkage proceeds uniformly towards the center. Lumen does not recover to its original size.

D. Strength

Mercerization increases fiber strength uniformly along the length by increasing the cohesion between individual cotton fiber. The physical properties of mercerized fibers are related to the orientation factor; Young's modulus increases with increase in the molecular orientation. The elongation acts in reverse, decreasing as the molecular orientation increases. An increase in the orientation of the crystallites with respect to fiber axis can be attributed to such factors as fiber deconvolution, a reduction in crystallinity of the fiber and a decrease in lengths of crystallites. In case of a slack mercerized cotton, an increase in fiber strength is accompanied by an increase in extensibility, thus deconvolution is not the only factor influencing the changes in mechanical properties on mercerization apart from decrystallization and length of crystallites.

E. Moisture Absorption

Mercerized fibers absorb more water, obtain higher regains and are easier wet than unmercerized fibers. When caustic soda solution penetrates into fibers, many hydrogen bonds along the polymer chains are broken and it is estimated that the number of available hydroxyl groups are increased by about 25%.(23) Mercerization decreases the amount of crystalline part or increases the amorphous content of the fiber. An increase in the proportion of an amorphous part is directly related to the moisture sorption. Moisture is assumed to be absorbed by suitable groups in the amorphous region and on the surface of the crystallites. When mercerization is carried out under tension, the changes in crystalline portion is comparatively lower than that without tension and hence also the moisture. Standard cotton has moisture content of about 7%, mercerized cotton with tension has about 9% and that of without tension about 11%.(23)

F. Dye Adsorption

Mercerization improves the dyeability of cotton fibers. Mercerized cotton can be dyed to deeper shade and with faster rate of dyeing than unmercerized cotton. An increase in depth of shade of mercerized cotton has been attributed to an optical effect arising from the modifications of fiber size and shape, as well as to an actual increase in dye uptake due to an increase of amorphous parts in fibers.

G. Reactivity

Mercerization not only increases dye uptake and moisture absorption of cotton fibers, it also increases the reactivity of fibers. Mercerized fibers are sensitive to degradation and provide faster reactions with acids and oxidizing agents.

H. Immature Cotton

Mercerization has been recognized as a method for removing immature and dead fibers to obtain a level dyeing effect on cotton fabrics. Dead fibers are underdeveloped and appear as flat or slightly twisted tapes. They are non-crystalline fibers. Convolutions are sometimes absent. Their cell walls are extremely thin, lumens are collapsed and hence they do not absorb dye to the same extent as matured fibers.

I. Physical compactness

Mercerization improves the dimensional stability of cotton woven fabrics and also gives a moderate improvement in the crease recovery of cotton fabrics as well as some protection against the decrease of tensile strength caused by easy-care finishing.

2.3 CELLULOSE III

2.3.1 Sources of Cellulose III

Beside sodium hydroxide treatment (mercerization), another swelling treatment commercially available is the treatment of cotton and other cellulosic fibers with liquid ammonia.

Research studies on liquid ammonia treatment were initially conducted in the mid 1930's when Barry et al.(19) observed that cotton fibers swelled and plasticized in liquid ammonia, and changed in polymorphism to cellulose III. Cellulose III can be obtained by treating cellulose I or cellulose II with liquid ammonia followed by an air evaporation of the ammonia.(3,4,24,25) Cellulose III obtained from an ammonia treatment of cellulose I is called cellulose III_I and that obtained from an ammonia treatment of cellulose II is called cellulose III_{II}. The completion of the cellulose transformation depends on the treatment conditions and the ammonia removal method. Cellulose III is obtained only when ammonia is removed from the sample by an air evaporation. If the ammonia is removed by immersing sample in water, cellulose I is obtained.(19,26)

2.3.2 Molecular Structure of Cellulose III

Cellulose III can be prepared from cellulose I or cellulose II. X-ray diffraction diagrams indicate that the unit cell for cellulose III is the same whether the sample is derived from cellulose I or cellulose II. But Marrinan and Mann(27) discovered that the infrared spectra of cellulose III$_{I}$ were quite different from cellulose III$_{II}$. CP/MAS ^{13}C-NMR spectra also show different resonance shapes and chemical shifts of carbon-13 in cellulose III$_{I}$ and cellulose III$_{II}$. (Figure 2.10) Both celluloses have almost identical carbon 13 signals at C(4) and C(6) but the signals at C(1), C(2), C(3) and C(5) are different.(3)

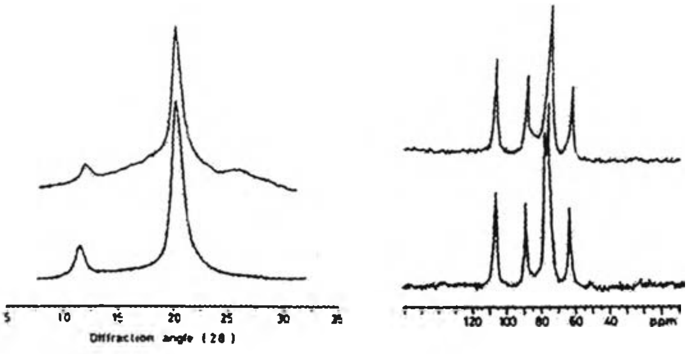

Figure 2.10 X- ray diffractograms (left) and CP/MAS^{13}C-NMR spectra (right) of cellulose III$_{I}$ (down) and III$_{II}$ (up).(3)

Sarko et al.(5) studied the crystal structure of cellulose III$_{I}$ obtained from the treatment of native ramie cellulose with liquid ammonia. He determined through the combined stereochemical structure refinement and X-ray diffraction analysis and found that the structure of cellulose III$_{I}$ was very similar to that of cellulose I. Both cellulose polymorphs contained parallel polymer chains and same hydrogen bonding pattern. The only different was the relative stagger between adjacent sheets. Sarko et al. also predicted that cellulose III$_{II}$ would possess a structure similar to cellulose II.

Sarko and coworker(28) believed that when cellulose was treated with liquid ammonia, the ammonia probably broke all hydrogen bonds in cellulose and the structure rearranged into another least energy form that might be an ammonia-cellulose complex. Because the cellulose chain is stiff and the ammonia treatment is not sufficiently drastic to solubilize the structure, chain folding does not occur in this complex. Upon evaporation of the ammonia, the cellulose structure reforms its intrasheet hydrogen bonds but settles into the nearest minimum energy which is cellulose III_I in parallel structure. On the other hand, when cellulose I is solubilized and subsequently regenerated or just mercerized, the chain may fold and seek out the true global minimum for cellulose crystal structure, the antiparallel cellulose II. Then when ammonia is added to this cellulose II and followed by an evaporation, an antiparallel cellulose III_{II} is formed.

2.3.3 Liquid Ammonia Treatment

In the middle of 1960' s, two patents(29,30) indicated that liquid ammonia could be used to treat cotton yarns and sewing threads for some properties improvement. At around 1967, liquid ammonia treatment was available for industrial applications. It was first applied to cotton yarns and then to woven and knitted goods.(31)

Ammonia is a natural substance with the chemical formula of NH_3. It has a boiling point of -33.35°C and a freezing point of -77.7°C. It is colorless. Preparation of ammonia solution is an exothermic reaction. Ammonia molecules exist in water in the forms of either $NH_3.H_2O$ or $2NH_3.H_2O$, not NH_4OH.(20) Each ammonia molecule has a pyramidal structure. It is a strong Lewis base and an excellent hydrogen bond acceptor even with the weakest donors. Ammonia molecules use their unshared pairs of electrons of the nitrogens to form hydrogen bonds with other compounds. It can be prepared in three forms; gas, liquid and solution. To swell cotton with ammonia, only anhydrous liquid ammonia is appropriate. Liquid ammonia can swell both inter and intracrytalline regions of cellulosic fibers while ammonia gas and ammonia solution can not swell the intracrystalline region.

When cellulose is immersed in anhydrous liquid ammonia, the small dimension of the ammonia molecule and the weak surface tension of liquid ammonia favour the penetration into the fiber core, without destroying the microfibrils. Then liquid ammonia complexes with hydroxyl groups of cellulose after breaking hydrogen bonds in crystalline region and increases distance between cellulose chains in crystallites.(23) Furthermore, ammonia produces changes in the structure of cellulose such as reorganization of the crystalline network with cellulose chains rotating or translating around their axes and giving a better accessible network to reagents. Swelling in ammonia is very rapid and uniform. Ammonia swells not only along the longitudinal direction of the celluloses but also along the cross-sectional direction.(32) Sorption and desorption of ammonia are accompanied by an intermolecular swelling.

The nitrogen atom in ammonia, with its unshered pair of electrons can interact with the hydroxyl groups in cellulose, replacing the OH--O' (hydrogen-bond between and within the cellulose chains) with the OH-NH_3 and forming a swelling ammonia-cellulose complex. Although the OH--N bond of cellulose-ammonia is a strong bond, it is easily broken when the ammonia is removed, either by an evaporation or by an interaction with water.(33) When ammonia is removed by an evaporation, the process takes place rapidly and produces short crystallites in the crystalline region.(34)

2.3.4 Cellulose Properties after Liquid Ammonia Treatment

Treatment with liquid ammonia to form cellulose III modifies the cellulose morphology and changes considerably the properties of the cotton fiber such as decrease in crystallinity of the original cellulose, increase in reactivity of cellulose(19) (toward dye sorption and sensitivity to chemicals), increase luster, increase moisture regain, improve tenacity; elongation; toughness; abrasion resistance; tensile and tearing strength and provide soft and pliable handle and touch even after many washes. The mechanism of such changes in the mechanical properties, however has not been well understood at the molecular and fine structure levels.(26) The ammonia treatment barely decreases the degree of polymerization of cellulose thus does not produce any appreciable degradation.(35) Liquid ammonia is also found to reduce fibrillation in the laundering of resin-finished fabrics.[23]

Ammonia is used to treat cotton fabric prior to certain finishing process in order to improve the wrinkle recovery, mechanical properties, softness, flexibility, and resiliency, with only a small amount of cross-linking agent needed.(23)

Liquid ammonia treatment is found to have less pollution problem but comparatively an expensive process. The most important cost element is the recovery of ammonia which involves refrigeration.(23)

2.3.5 Advantages of Ammonia Treatment (31)

- There is no ammonia residue left in treated sample after the ammonia treatment.
- The penetration of the reagent into the fiber core and the elimination of the function characteristics result in a constant and reproducible effect.
- Ammonia treatment does not produce polluting waste neither in a gas nor in a liquid form, the ammonia used is entirely recovered, purified by distillation and recycled in the installation with a yield of nearly 100%.
- There is no danger to the machine operators since the machines are hermetically sealed and the process is carried out in closed system which is under slight vacuum.

2.4 CELLULOSE IV

2.4.1 Sources of Cellulose IV

Cellulose IV was formerly called cellulose T (high temperature polymorph). It has subclasses of celluloses IV_I and IV_{II} depending on their sources. It may be prepared from cellulose I, either directly or via cellulose III, by high temperature glycerol treatment at 260° C (4,36) or prepared from cellulose II, by heating in water at 190°C for 2 hours.(3,38)

2.4.2 Molecular Structure of Cellulose IV

The cellulose IV prepared from cellulose III_I (cellulose I family) is called cellulose IV_I and that prepared from either cellulose II or cellulose III_{II} (cellulose II family) is called cellulose IV_{II}.

Gardiner and Sarko(5) analyzed celluloses IV_I and IV_{II} and found that both have almost the same orthogonal unit cell but the structures differ in chain polarity. The orientation of the polymer chains in cellulose IV_I is parallel, whereas in cellulose IV_{II} is antiparallel. The structures of both polymorphs are shown in Figure 2.11. In addition to the usual two intramolecular hydrogen bonds presented in all crystalline celluloses, both polymorphs seem to be well-stabilized by the intramolecular hydrogen bonding along the (200) plane.

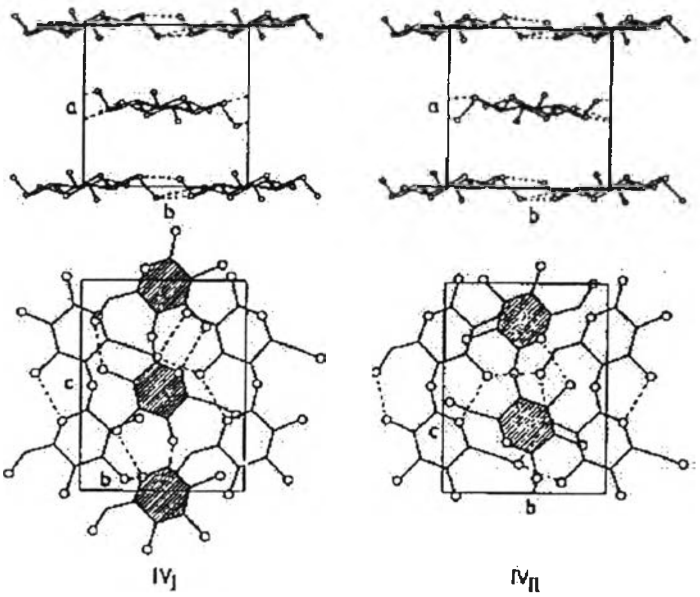

Figure 2.11 Projections of cellulose IV$_I$ and cellulose IV$_{II}$ unit cells. Hydrogen bonds are shown by dashed lines.(5)

Marrinan and Mann(27) found that the dimensions of the unit cells of celluloses IV$_I$ and IV$_{II}$ are similar and close to those of cellulose I. X- ray data indicate that the unit cells of cellulose IV$_I$ and cellulose IV$_{II}$ are very similar, the relative arrangements of the chains in the unit cells of both celluloses could be very similar.

Gardiner and Sarko(39) reported that both celluloses have identical unit cell size but may have different polarities of cellulose chains; parallel for cellulose IV$_I$ and antiparallel for cellulose IV$_{II}$.

Isogai and coworker(3) prepared cellulose IV$_I$ from cellulose III$_I$ and prepared cellulose IV$_{II}$ from cellulose II and obtained a yield of 80-85% cellulose IV$_I$ and 55% cellulose IV$_{II}$. They then analyzed the celluloses with CP/MAS^{13}C-NMR and X-ray diffraction and obtained some distinguishable X-ray diffractograms and NMR spectra of cellulose IV$_{I}$ and cellulose IV$_{II}$ even though both celluloses were not pure cellulose IV$_{I}$ and cellulose IV$_{II}$ (Figure 2.12).

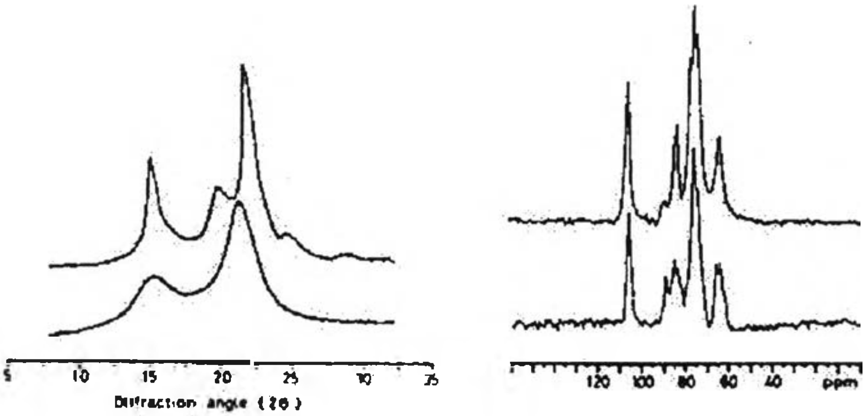

Figure 2.12 X-ray diffractograms (left) and CP/MAS^{13}C-NMR spectra (right) of celluloses IV$_{I}$ (down) and IV$_{II}$ (up).(3)

The crystal lattice of cellulose IV differs slightly from cellulose I. The hydrogen bonding and chain packing in cellulose IV$_{I}$ have been proposed to be the same as in parallel models of cellulose I. For cellulose IV$_{II}$, a structure similar to antiparallel model of cellulose II has been proposed. There is no complete structural determination of cellulose IV.(7)

2.5 Previous Research Work on Cellulose Polymorphs

Several research teams have conducted many studies on cellulose polymorphs. The following works are some examples.

Atsuka Ishikawa, Takeshi Okano and Junji Sugiyama(4) studied for the changes in fine structures and tensile properties of ramie fiber during the transformations of cellulose polymorph I to II, III_I and IV_I. They found that the integral crystallinity index and the crystalline size decreased, the internal surface area increased, Young's modulus of the fiber decreased, and the ultimate strain increased.

Takashi Nishino, Kiyofumi Takano and Katsuhiko Nakamae(37) studied for the elastic modulus of the crystalline regions of cellulose polymorphs in the direction parallel to the chain axis using an X-ray diffraction technique. They found that the crystal transition of cellulose brings about the skeletal contraction accompanied with the change in intramolecular hydrogen bonds. These will cause a drastic change in the crystal modulus for cellulose polymorphs.

Akira Isogai and coworker(3) used solid-state ^{13}C-NMR and X-ray diffraction studied the cellulose polymorphs which prepared from a highly crystalline and purity cellulose sample. They found that celluloses I, II and III were different in the ^{13}C-NMR spectra.

Wakida T. and coworker (6) studied for the dyeability of cotton fiber treated with liquid ammonia. Raw materials used consisted of scoured and mercerized cotton fibers. They found that liquid ammonia treatment increased the rate of dyeing, equilibrium dye adsorption, standard affinity, heat of dyeing and change of entropy of scoured cotton fibers. While the dyeing properties of mercerized cotton fibers were adversely affected by subsequent liquid ammonia treatment.

Menachem Lewin and Luis G. Roldan(25) studied the effect of liquid ammonia treatment on cotton fabric using an X-ray diffraction (XRD) and electron microscopy. They found that the transition from cellulose I to III proceeded through the liquid ammonia treatment. Cellulose III was obtained upon drying the ammonia-cellulose complex without the presence of water. Treatment of the ammonia-cellulose complex with water brought about the formation of cellulose I. The crystallites of cellulose III were much smaller than those of cellulose I. The interaction of ammonia with cotton cellulose was faster than with other swelling agents. The penetration of ammonia into the secondary wall of cotton fiber was along the concentrical ring and radially across the ring.