

CHAPTER II

THEORY

2.1 Cellulose

2.1.1 The Structure of Cellulose

Cellulose is a carbohydrate polymer which has the empirical formula $C_6H_{10}O_5$. It is the chief structural element and major constituent of the cell walls of trees and of other higher plants. Cellulose is also found in lower forms of plant life such as mosses, ferns, algae, and fungi.

It is generally accepted that cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose unit joined together by β -1,4-glycosidic bond between C_1 and C_4 .

The formation of various derivatives of cellulose proves that three alcoholic hydroxyl groups are free. Further analysis of cellulose derivatives shows that two of the hydroxyl groups are secondary and one is primary (15). Figure 2.1 shows cellulose structure.

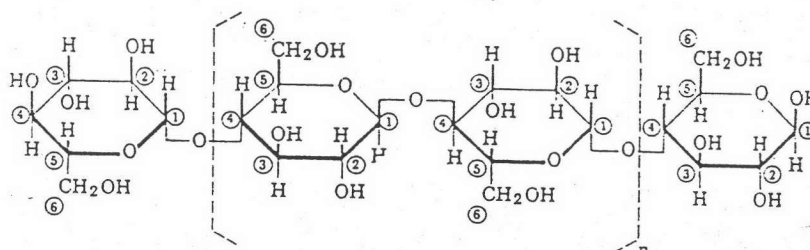


Figure 2.1 Cellulose Structure

On the basis of conformational analysis, a better structural presentation is probably given by a formula shown in Figure 2.2.

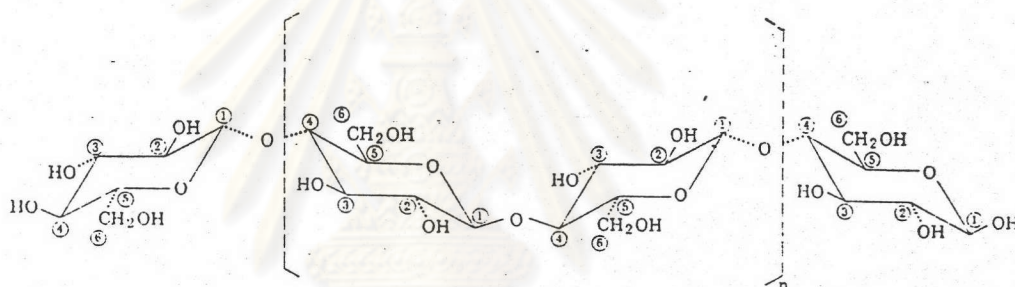


Figure 2.2 A Better Structural of Cellulose

The anhydroglucopyranose unit is in the chair form which, in conjunction with the β -glycosidic linkages, makes cellulose molecule stiff in comparison with molecule of amylose (a fraction of starch) which has α -glycosidic linkages between the 1,4-anhydroglucose units.

The number of repeating units of D-anhydroglucopyranose per molecule (degree of polymerization) is at least about 1,500 to more than 6,000 units. Molecular weight of cellulose may vary depending on plant sources(16).

Typical molecular weight values for cellulose and its derivatives from various sources are shown in Table 2.1

Table 2.1 Representative molecular weight values for cellulose and cellulose derivatives

Material tested	Molecular weight	Approximate degree of polymerization
native cellulose	600,000-1,500,000	3,500-10,000
chemical cotton	80,000-500,000	500-3,000
wood pulps	80,000-340,000	500-2,100
regenerated celluloses		
tire cord	65,000-89,000	400-550
staple fibre and- rayon filament	57,000-73,000	350-450
cellophane	45,000-57,000	280-350
commercial nitrocellulose	16,200-875,000	100-3,500
commercial cellulose- acetates	28,000-58,000	175-360

Each molecule in cellulose chain links together with hydrogen bonds. Two hydrogen bonds are intramolecular, with linkages between the hydrogen atom of the OH-group on C₃ and the oxygen atom in pyranose ring, the other one is the hydrogen atom of the OH-group on

C_2 and oxygen atom of OH-group on C_6 . Figure 2.3 shows intramolecular hydrogen bond of cellulose.

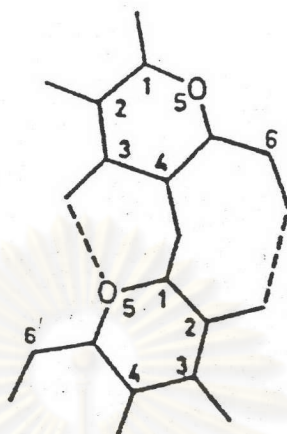


Figure 2.3 Intramolecular Hydrogen Bond of Cellulose

The molecular chains link together with inter-chain hydrogen bond between the hydrogen atom of the OH-group on C_6 and oxygen atom of OH-group on C_3 of the adjacent chain. Figure 2.4 shows intramolecular hydrogen bond and inter-chain hydrogen bond of cellulose.

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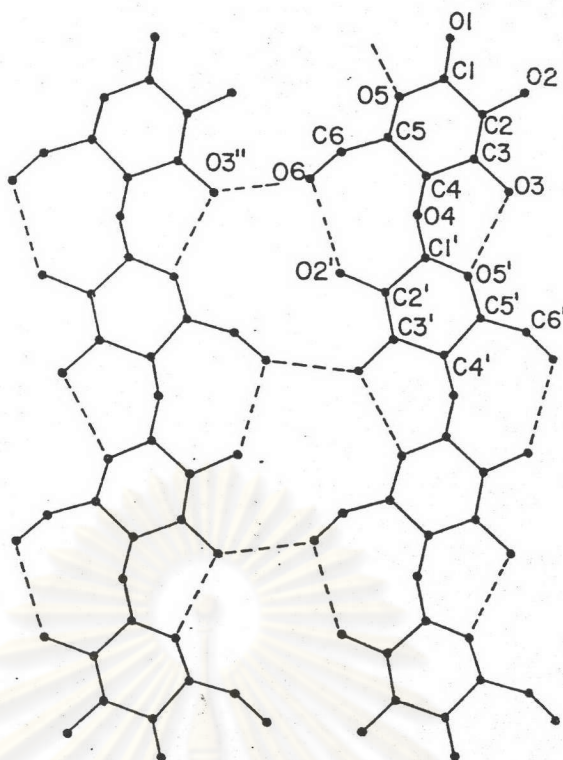


Figure 2.4 Intramolecular and Inter-Chain Hydrogen Bond of Cellulose

The intramolecular hydrogen bonds are the cause of complex structure that makes cellulose insoluble in water and difficult to be degraded by enzymes and chemicals.

The fact that cellulose never occurs in absolutely pure form in nature. Normally it is found closely associated with lignin and hemicelluloses in varying amounts, depending on the plant species. It thus makes the isolation and purification of cellulose difficult.

Lignins are complex hydrocarbon polymer with both aliphatic and aromatic constituents which are probably a highly cross-linked materials with a three-dimensional architecture. Their chief monomer units are various ring-substituted phenylpropanes.

The hemicelluloses are polysaccharides associated with cellulose. They are mainly heteropolymers, often branched, of various

sugars and some uronic acids.

Usually most of the lignin must be removed from wood fibres before the hemicelluloses can be extracted by alkaline (17). The hemicellulose and cellulose, which remain after lignin has been removed, are called halocellulose. The hemicelluloses are extractable from halocellulose by means of aqueous alkali. The cellulose composition and source of some woods are shown in Table 2.2.

Table 2.2 The source and composition of representative cellulosic fibres

Common name	Type or species	Composition, %dry weight		
		Cellulose	Hemicellulose	Lignin
softwoods	coniferous	42.2	ca 28	25-35
hardwoods	deciduous	42.2	ca 38	15-20
jute	Corchorus sp	71.6	13.3	13.1
hemp(marijuana)	Cannabis- sativa	74.4	17.9	3.7
sisal	Agave- sisalana	73.1	13.3	14.0
cotton, purified		99.9		

According to the study of cellulose fibre structure, it is found the largest in the part of secondary cell wall and decreases as getting into the middle lamella.

In the secondary cell wall, cellulose and other constituents arrange as a long line group, which is called microfibrils. Each microfibril which is parallel to each other is linked together with hydrogen bonding. The arrangement of the microfibrils in each cell wall layer is shown in Figure 2.5.

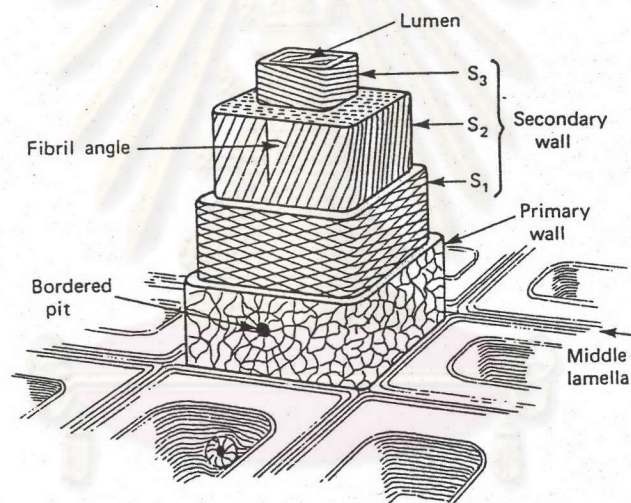


Figure 2.5 The Microfibrils in Each Cell-Wall Layer

Associated microfibril is called microcrystallites or micell as shown in Figure 2.6.

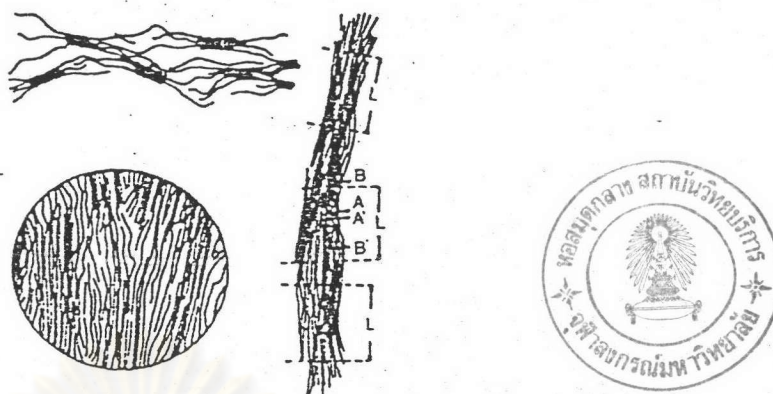


Figure 2.6 Microcrystallites or Micell

The distance between each micell is about 15-20 angstrom (A°) which liquid like water can move through the microfibrile so that it can effect the absorbent property of cellulose.

The region that cellulose molecules arrange with highly order is called crystalline region and the less order or disorder region are called amorphous or paracrystalline, as shown in Figure 2.7.

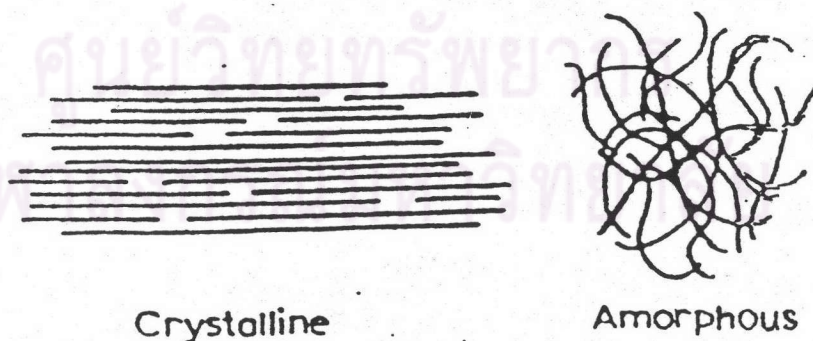


Figure 2.7 Crystalline and Amorphous Regions

The crystalline region is about 50-90 percentage and the remainder is amorphous. Each region has different properties in

reacting with vinyl monomer to form graft copolymer. The grafting reaction in the amorphous region occurs before and faster than in the crystalline region.

Since amorphous region of cellulose can absorb water and react with monomer better than crystalline region, increasing the amorphous region in cellulose is the key to achieve high absorbancy of modified cellulose.

There are many methods that use to increase amorphous region called prehydrolytic treatment. Each method such as mechanochemical process, freezing, acid hydrolysis, alkaline degradation, enzymatic hydrolysis and so on is used for the different objectives as:

- to decrease degree of polymerization.
- to decrease tensile strength.
- to damage the connection between crystallite in fibril.
- to decrease the length of crystallite.
- to decrease crystalline order.

2.2 Cyanoethylation

Cyanoethylation, is the reaction to incorporate the propanenitrile moiety into a molecule. The characteristic feature of compounds undergoing this reaction is their possession of a labile hydrogen atom that, once removed, produces a nucleophilic group which then attacks the most positive position in acrylonitrile. The reaction is most frequently performed with a basic catalyst, but acid and

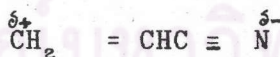
metallic compounds have also been used. Yields are usually high and the reaction is reversible with high temperature and strong base catalysts.

Examples of chemical types that undergo cyanoethylation include hydroxyl compounds (alcohols, phenols, and oximes), thiols (hydrogen sulfide, aliphatic mercaptans, and thiophenols), nitrogen compounds (ammonia, amide, and various heterocyclic compounds), some carbon compounds (benzyl cyanide, cyclopentadiene), and so on.

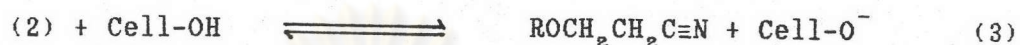
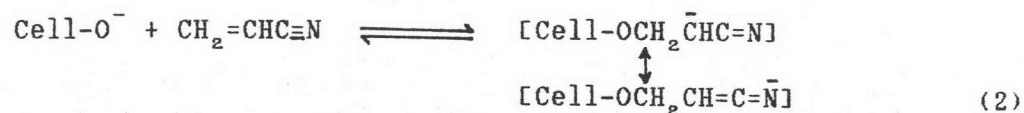
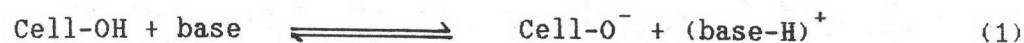
Thus cellulose which is the polyhydroxyl compound can undergo cyanoethylation like other alcohols.

2.3 Mechanism of Cyanoethylation

Because of the strong electron-withdrawing character of the nitrile group, the β -carbon atom of acrylonitrile is rendered relatively positive whereas the nitrile portion of the molecule is relatively negative. This effect is illustrated in structure below.



This molecule, therefore, is susceptible to attack at the β -position by a nucleophilic reagent. These nucleophiles may be anion, ie. alkoxide ions, or even neutral molecules possessing nucleophilic character such as amines. The generally accepted mechanism is summarized in equations 1-3 in which the cellulose is used as a reactant with acrylonitrile (18).



The catalyst is required only a small quantity to achieve a good yield of the cyanoethylated product.

2.4 Grafting Reaction

The grafting of vinyl monomers onto cellulose takes place in a heterogeneous reaction system. The celluloses are in a solid phase, whereas monomers are in vapor, liquid, or solid phases or in a solution phase as a solute or dispersed in an emulsion. To obtain cellulosic products with contents of grafted copolymers of several percent may take from minutes to hours.

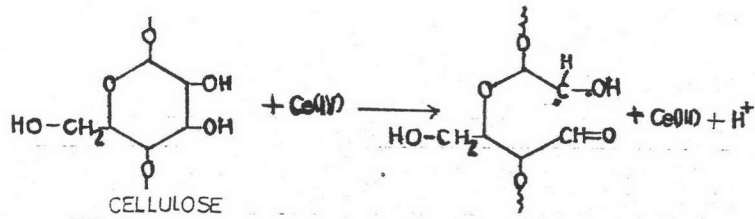
The most commonly used method for initiating monomer grafting onto cellulose is the application of monomer solution to cellulose before, during, or after the formation of macrocellulosic radicals. The selection of solvent is the most important factor. The monomer must be sufficiently soluble in the solvent to permit preparation of a solution with high enough concentration of monomer to maintain a chain reaction. In addition, the solution should interact with cellulose to swell or initiate changes in the morphological structure of cellulose and accelerate the diffusion rate of monomers to free-radical sites.

Graft copolymerization onto cellulose is effected through an initiation reaction involving attack by macrocellulosic radicals on the monomer to be grafted. The generation of the macrocellulosic radical is accomplished by a variety of methods such as (1) diazotization, (2) chain transfer reactions, (3) redox reactions, (4) photochemical initiation, and (5) radiation-induced synthesis.

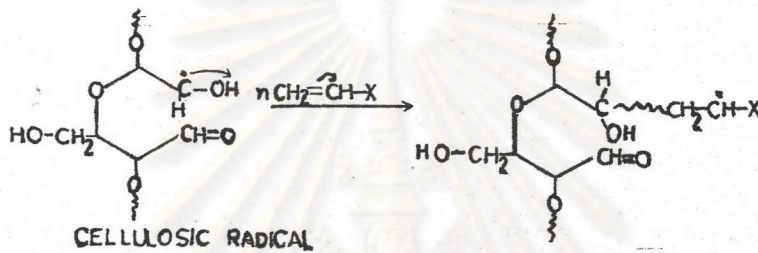
It has been mentioned earlier that redox reaction or redox method is successfully used for initiating graft copolymerization of vinyl monomer onto cellulose. Ceric ion system is one type of redox reaction which was used in this research.

Ceric ion initiation of graft copolymerization onto preformed polymers is the most promising and practical method. Schwab and co-workers(10) applied the ceric ion method of grafting onto cellulosic substrates. The reaction of ceric ion in aqueous solution with cellulose cleaves the anhydroglucose ring between carbon C_2 and C_3 with the formation of a short-lived radical on carbon C_2 and oxidation of carbon C_3 to a reducing group. Grafting occurs by reaction of the radical at carbon C_2 with monomer. Radical termination can occur by reaction of carbon C_2 with Ce^{4+} to yield Ce^{3+} and oxidation of carbon C_2 to a reducing group. Of course, it is equally likely that the roles of carbon C_2 and C_3 in the reactions could be reversed. In addition, oxidative depolymerization of macrocellulosic radical also occurs.

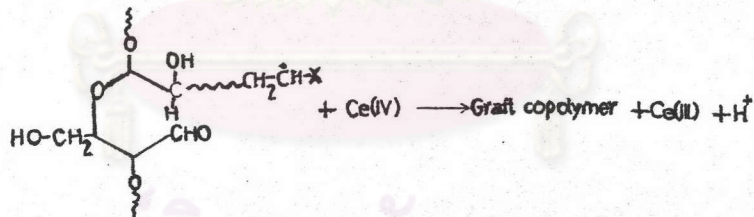
Radical Production:



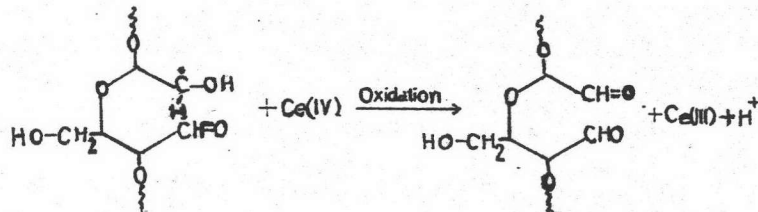
Grafting Initiation:



Grafting Termination: Termination is mostly by ceric ion.

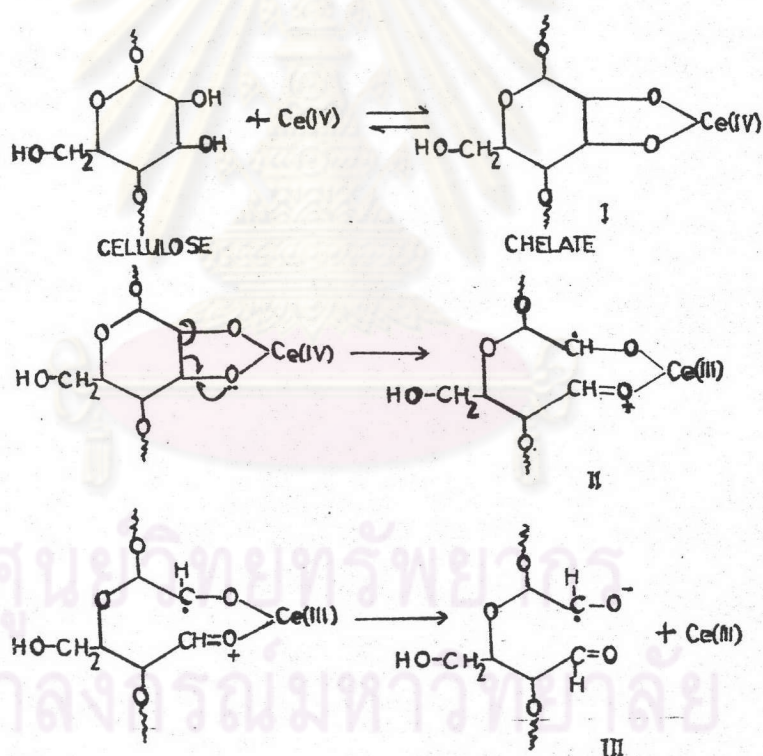


Oxidation: The macrocellulosic radical may suffer simultaneous oxidation.



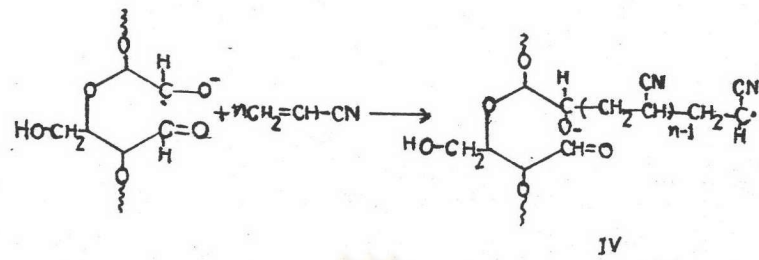
Arthur et al. suggested that ceric ion in acidic solution formed chelates with the hydroxyl groups on carbon C-2 and C-3 of the anhydroglucose unit of cellulose. Transfer of electrons from the cellulose to Ce^{4+} would follow, which would result in its reduction to Ce^{3+} and dissociate from the chelate. The anhydroglucose ring is scissioned between carbons C-2 and C-3 and forms a free radical site (19). Additional ceric ion could chelate with cellulose to form additional radical sites in the following manner:

Radical Formation:

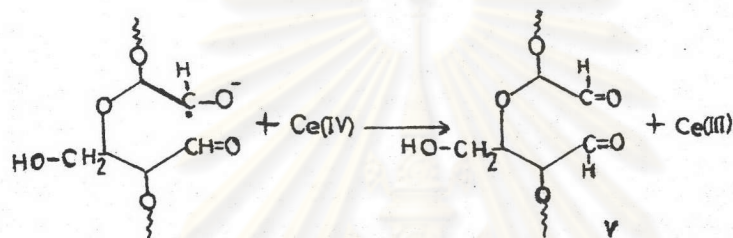


In the presence of monomer, grafting reactions are initiated.

Graft Copolymerization:



Radical Termination:



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