CELLULOSE AND PULP

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Summary

Cellulose is abundantly found in wood and other lignocellulosic plants. It has been mainly derived from wood since Burgess and Watt in England employed caustic soda to pulp wood chips in 1851. Cellulose is a long chain polymer built up of a great many anhydroglucose units containing both crystalline and amorphous structures. The very easily formed intra-and intermolecular hydrogen bonds allow cellulose to function as a structural polymer. The degree of polymerization (DP) of cellulose varies according to its sources, acquiring processes and further treatments. Cellulose also undergoes changes in crystalline structure while treated with chemicals or solvents. Due to the high DP and partial crystalline structure, cellulose can only be dissolved in certain specific complexes and concentrated acids and bases.

Cellulose esters and ethers are the two most important value-added cellulose derivatives with a wide range of applications. Cellulose nitrate and acetate are the predominant cellulose esters that find a market in plastics, lacquers, adhesives, films, fibers and explosives. The degree of substitution in these derivatives determines the properties and uses of the products. Viscose rayon and cellophane are obtained from cellulose xanthate as an intermediate. Alkyl cellulose and carboxyalkylcellulose and hydroxyalkylcellulose are the major cellulose ethers derived through reactions on alkali cellulose. Most cellulose ethers are water soluble, exhibiting very different properties from the original cellulose. It is not surprising that the application of the ether derivatives are extremely versatile. Improved strengths and chemical resistance can be achieved by graft copolymerization on cellulosic materials.

Chemical synthesis of cellulose is feasible through a stepwise synthetic method or a ring opening polymerization. The success of this process enables the preparation of tailored cellulose derivatives with specific properties.

Pulp wasn't made from the most dominant and renewable lignocellulosic material-wood until about 150 years ago. Besides wood, nonwood fibers and secondary fibers from recycling paper products are increasingly adopted as the raw materials for pulp manufacturing. Chemical, semi-chemical and mechanical pulps are the three major categories of pulp distinguished by the manufacturing processes. Low yield dissolving pulp, very high in cellulose content, occupies only a small fraction of the world pulp production. It is suitable for use in the transformation to cellulose derivatives. CTMP (chemithermomechanical pulp) and NSSC (neutral sulfite semi-chemical) pulps have gained more and more market and environment interest due to their higher yield and satisfactory properties. Morphological, physical, chemical, strength and optical properties such as fiber length distribution, viscosity, residual lignin, burst strength and brightness, etc. are usually determined after pulp is made to evaluate the suitability of the process and decide the route of its end products. Paper and board are the two main fields for pulp uses. There are hundreds of different end products from each category, such as newspaper, magazine, xerox paper, box board, food carton, etc.

With the estimated 2.8% annual growth rate for world consumption of paper and board over the next decade, the global pulp requirement in 2010 will reach 250 million tons, of which nearly 75% will still be produced in the industrialized, developed countries. Asian and South American countries are catching up to gain a bigger share of world production.

1. What is Cellulose?

Cellulose, the most abundant organic compound on Earth, manifests itself in various forms: as hair in cotton, as bast in flax, and as fiber in wood. As a natural product of biological origin, cellulose gives a feeling of "warmth" and "softness" to the touch. Cellulose in wood, both hardwood and softwood, makes up between 40% to 47% of the wood, with the content in hardwood a little higher than that in softwood. Eighteen to thirty eight percent of the wood components is lignin and the rest hemicellulose, except some 3 to 5% which are extracts which could be dissolved or extracted by common neutral solvents. Lignin acts as cement in a concrete structure, of which the wood cell

wall could be depicted. There is evidence that hemicelluloses are chemically linked to lignin, which then makes up the matrix of the wood cell wall. Cellulose makes up 95% of cotton, 70-75% of bast fibers, but only 30% of wheat straw. Mankind has, for millennia, used sources of cellulose for economic utilization. Textiles, ropes or even parachute were, besides paper and board, recorded as products of cellulose.

Starting from the mid-eighteenth century, commercial cellulose came mainly from wood. Basically there are three means -mechanical, semi-chemical and chemical - to acquire cellulose from wood or other lignocellulosic plants. The main purpose is to make it into pulp and paper. Because of the great abundance of these materials and the increasingly various adaptable techniques for their utilization, cellulose and its derivatives find their place in every area of human activities.

2. Fundamentals of Cellulose

2.3. Structure at Molecular Level

The cellulose molecule is an aggregate of a great number of individual glucose anhydride (anhydroglucose) chains, arranged more or less parallel to each other and stabilized in the lateral direction by hydrogen bonds between opposite hydroxyl groups. Cellulose is found in lattices with ordered as well as slightly disturbed regions. It is better not to divide the state of order into two absolute parts as crystalline and amorphous; there are intermediate degrees of crystalline order. Through X-ray analysis, cellulose definitely shows a crystalline nature with submicroscopic units, called crystallites or micelles, of varying length but of fixed breadth and thickness. The smallest morphological units of ordered native cellulose, with a diameter of about 3.5 nm are found on the surface of elementary fibrils. The different elementary fibrils aggregate to form larger microfibrils. Other investigations found that microfibril size can range from 1.5 nm as in quince slime, to more than 30 nm in diameter as in the giant microfibrils of *Boergesenia*. The cellulose from vascular plants, particularly those of woody plants and cotton, is quite similar. Being a high polymer, cellulose also has a fibrous structure and colloidal nature , which explain the enormous utility of cellulose for a great variety of purposes.

Naturally packaged in the form of the cell wall, which is generally not a pure substance, the cellulose component must be extracted and purified to varying degrees depending upon the ultimate marketable product. The isolated cellulose molecule is a linear condensation polymer consisting of D-anhydroglucopyranose as its basic building unit linked by β-1,4 glycosidic bonds (see Figure 1). With β-D-glucopyranose as its unit monomer, cellulose is a straight, unbranched, hydrophilic polysaccharide. At the ends of each cellulose molecule, the one with a free OH at C_1 is called the reducing end group of cellulose, while the other one with a free OH at C_4 is called the non-reducing end. The building monomer, the glucose unit, rotating by approximately 180 degrees relative to its neighbor makes the D-anhydroglucopyranose chain a highly extended conformation. Cellulose has a strong tendency to form intra- and intermolecular hydrogen bonds, which stiffen the straight chain and promote aggregation into a crystalline structure. Two chain-stabilizing intramolecular hydrogen bonds between $O(_{3'})$-H and $O(_5)$ and also between $O(_{2'})$-H and $O(_6)$ help maintain the highly extended

conformation which allows cellulose to function as a structural polymer. Due to the very easily formed intramolecular hydrogen bond, the linearity of the cellulose chain may appear not only in the solid state but also in some solutions. The presence of intra- and inter-molecular hydrogen bonds in solid cellulose leads in some cases to a heterogeneous distribution of constituents when derivates are to be produced. When fully extended, the linear polymer, also known as the glucan chain, of the cellulose molecule is in the form of a flat ribbon with hydroxyl groups protruding laterally. Each anhydroglucopyranose unit maintains three free hydroxyl groups, at the 2,3 and 6 positions, besides the two end positions' hydroxyl groups at the C_1 and C_4 positions of the chair-form hexagonal glucose ring (see Figure 2).
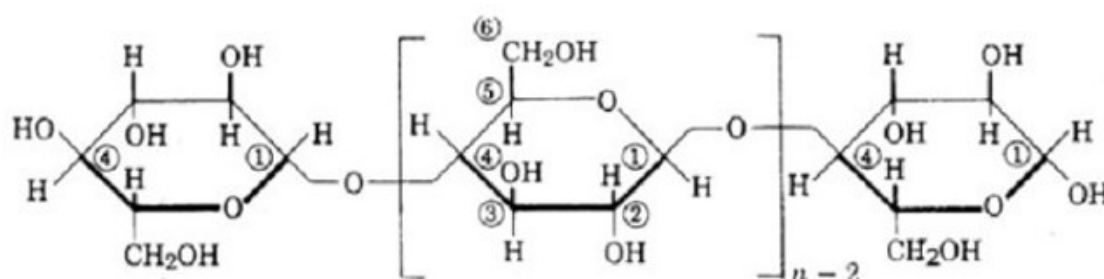

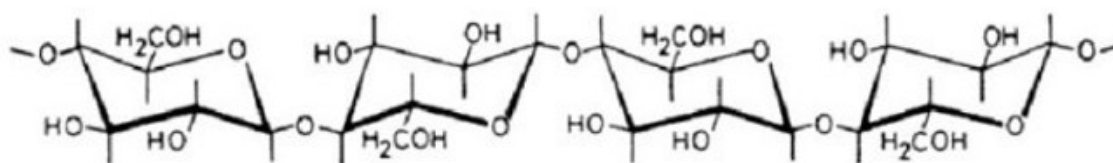Figure 1. The schematic linear structure of cellulose
(Browning 1963).

Figure 2. The chair form cellulose chain
(Fengel and Wegener 1984).

2.4. The Degree of Polymerization, DP and Crystallinity of Cellulose

The average degree of polymerization (DP) of cellulose is in the range of 3 000 to 15 000 depending upon the source, and is about 10 000 in wood. How the cellulose chains are arranged in the elementary fibrils and microfibrils is not known in detail. The glucan chain polymers are assembled, after the formation of the terminal complex, into organized macromolecular complexes - microfibrils - which can now be visualized by the freeze fracturing technique. During the formation of the primary wall, the terminal complex of few subunits is relatively short, and small microfibrils are synthesized. Studies based on X-ray diffraction, Raman? spectra and solid state ^{13}C-NMR (nuclear magnetic resonance) have led to the identification of the model structures of the individual chain and the aggregation of the chains.

Being a partially crystal structure, cellulose is not penetrable by water inside of its crystalline domain at room temperature. Crystalline microfibrils (bundles) of the native cellulose chain are 2-5 nm in width for higher plants and 10-15 nm for algal celluloses.

The supramolecular state of the cellulose, its crystalline as well as its fibrillar structure, are of importance for the mechanical properties of both wood fibers and pulps. The presence of crystalline cellulose, with regions of less order (the amorphous portion), and the size of the elementary fibrils work together to produce an interesting combination of contrary properties such as stiffness and rigidity on the one hand and flexibility and toughness on the other.

Many of the physical and chemical properties of the cellulose are determined by its DP and the degree of crystallinity. The higher the DP of cellulose, the greater is its resistance to tensile and other forces. The crystallinity percentage (degree of crystallinity, or crystallinity index [CI]) of cellulose ranges from 50 to 90% depending on the source and the method of measurement. Higher crystallinity of certain cellulose implies much well organized arrangement of their microfibrils that have a direct bearing on the industrial utilization of the product.

Cellulose undergoes changes in crystalline structure with relative ease. Swelling treatments of native cellulose with some solvents bring about conversion to other crystal structures and/or partial de-crystallization. By dissolution and regeneration, or simply by treating cellulose I (native cellulose) with sodium hydroxide, cellulose II is formed upon washing of the thus-formed alkali cellulose. Cellulose III derives from the treatment of native cellulose with liquid ammonia or an organic amine followed by washing with alcohol. Both cellulose II and III differ from cellulose I in the molecular packing.

3. Cellulose and Liquids

Solid cellulose in any form is typically a gel. It has colloidally dispersed structures consisting of a solid and a liquid phase or perhaps also of two liquid phases, and having shape and cohesion (elastic properties). Being a gel, cellulose can pick up or lose water with corresponding swelling or shrinkage. Other liquids such as ether and benzene do not cause swelling of dry cellulose while methyl and ethyl alcohol produce very little swelling. Cellulose will swell in water, in dilute caustic soda solution, or in zinc chloride solution without any change in the dimensions of the crystal lattice.

The properties of cellulose from different sources, as well as the patterns of their response to process conditions come from the nature of the cellulose in its native state. Cellulose in alkaline media is able to undergo a peeling reaction, which is mainly attributed to the reducing end group located at the hemiacetal end of the long chain molecule. The peeling reaction, also called endwise de-polymerization is significantly influenced by the nature and concentration of the alkali. On average, 68 glucose units are eliminated before a stable end group is formed.

Due to the well arranged partial crystalline structure, along with the very easily formed intra- and intermolecular hydrogen bonds, cellulose is almost not soluble in common solvent. Complexes such as cuprammonium hydroxide and copper ethylenediamine hydroxide are the two main solvents, besides concentrated acids and alkalis, used for complete solution of cellulose.

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