THE STRUCTURE OF CELLULOSES

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Cellulose is the major component of the cell walls of higher plants and is also produced by some bacteria, algae, fungi, amoebae and sea-animals. Not only does cellulose form the basis of the textile and wood fiber industries, but it also plays central roles in food quality, biobased products and agriculture. Recently, cellulose has become central to the President's Advanced Energy Initiative, because of the potential advantages of cellulosic biofuels over other alternatives to conventional energy sources.

Cellulose occurs predominantly in the form of high tensile strength microfibrils, nanometers thick and up to millimeters in length. These microfibrils are biosynthesized by membrane bound synthase complexes that act as biological spinnerets, polymerizing glucose residues into chains and then assembling hydrogen-bonded parallel chains into non-soluble, crystalline microfibrils. In plant cell walls the microfibrils are encrusted in lignin and hemicellulose. This complex architecture, together with the crystallinity of cellulose makes untreated cellulosic biomass recalcitrant to conversion to fermentable sugars in the bioethanol industry.

Two distinct crystal phases, namely Iα and Iβ, have been found not only within the same cellulose sample but also in different domains along a given microfibril. Whereas Iα rich specimens are found in the cell wall of some algae and in bacterial cellulose, Iβ rich specimens have been found in tunicin and also in wood. A number of industrial applications involve pretreating raw cellulosic biomass so that its cell wall architecture is changed and so that the cellulose crystal structure is transformed. In particular, the processes of regeneration and mercerization yield cellulose II. Pretreatment of cellulose I and II with liquid amonia yields cellulose III_I and cellulose III_{II}. This talk will discuss how neutron and X-ray diffraction studies of cellulose fibers are providing detailed crystal structures and hydrogen bonding arrangements for cellulose polymorphs and structural pathways involved in pretreatments. The results of this work provide a scientific basis for understanding the principles governing the biological, physical and chemical reactions, of cellulose microfibrils and their structural and physical properties.