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HYDROGEN BONDS AND MACROMOLECULES. THE INTERACTION BETWEEN WOOD CELLS AND WATER

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ABSTRACT

The work of Bengt Rånby in the 1950s on the electron microscopy of cellulose and pulp is discussed and related to later investigations of wetting wood and the hydrogen bonds involved in this process. The technical importance of the results are briefly examined.

INTRODUCTION

Chemical and mechanical pulping processes are complicated interactions among the composite wood structure, water, pulping chemicals, heat, and/or mechanical forces. The Swedish researchers and engineers over the last century have played a central role in the development of these concepts both theoretically and technically. Without referring to all the achievements in the field, it is evident that the doctoral thesis of Bengt Rånby [1] in 1952 on electron micrographs of celluloses of various origin and pulps must be counted as one of the important landmarks in the development of the characterization of celluloses and the products of the defibration processes.

As stated in the thesis: "Because of its resistance to chemical action it is easy to purify the cellulose in cotton, bacterial membranes and tunicate tissues. It is, however, more difficult to prepare a pure wood cellulose because wood contains resistant polyoses, as Hägglund concluded recently. It is evident that the yield of cellulose (from wood) depends very much upon the method of isolation." The central question discussed by Rånby was therefore the ultramicroscopic visualization of the fine structure and reactions of native cellulose from various sources and their reaction products. The ultramicroscopic method gave a completely new method to penetrate the reaction mechanism and to understand the fiber microstructure.

The general problem involved was naturally not completely new. In the group of The Svedberg at the University of Uppsala where Bengt Rånby worked, the nature of the natural polysaccharides had been studied by various other means [2], e.g., using sedimentation and ultracentrifuges. A real understanding of the mechanisms was still absent. Therefore, the observation by Rånby that disintegration of cellulose materials in water suspension with ultrasound revealed the existence of microfibrils (also called micelle strings) was especially important. Independent of the origin, the diameter of these strings was the same, 8–10 nm. When treated with other agents, e.g., sulfuric acid, the micelle strings were broken down to micelles which unexpectedly showed hydrophobic properties. It was also possible to calculate that the micelle strings contained approximately 240 cellulose chains.

The above-discussed work gave impetus to a rapid progress. Also, new instrumental methods such as scanning electron microscopy (SEM), scanning calorimetry (DSC), and vibrational spectral and magnetic resonance methods based on a Fourier Transform treatment of data added much to our understanding of the wood cell under dynamic change. The whole chain of progress will not be discussed here, but only one question which at present seems to be of central importance for understanding the various defibrations processes and the utilization of wood as, e.g., lumber or veneer. It is the role of hydrogen bonds in the stability of wood structure and their rearrangements under various chemical and mechanical conditions in the presence of water (cf. the review in Ref. 3).

LATER DEVELOPMENTS

At the time of the thesis of Bengt Rånby in 1952 it was not possible to visualize hydrogen bonds. It is still an intricate problem, especially in macromolecules. However, with the advent of supercomputers combined with theoretical calculations based on quantum mechanical *ab-initio* methods and dynamic modeling, a reasonably exact picture of the structural state may be obtained. The numerous papers in the present Symposium in honor of Bengt Rånby give good testimony to the present high state of this interesting art. We shall not add new aspects on this very interesting theme here, but study the influence of hydrogen bonds from the earlier presented points of view.

In his doctoral thesis in 1982 another Swedish scholar, Lennart Salmén [4] in Stockholm at the Royal Institute of Technology, threw light on the cellulose structures present in the micrographs by Rånby. Salmén analyzed the composite structural materials comprising paper and wood in terms of their thermal softening and hygroplasticization with regard to the constituent polymers. In particular, he tried to compare the softening occurring under dry conditions to that occurring under moist conditions.

In his still valid conclusions, Salmén proposed " . . . that the semi-crystalline cellulose exhibits a broad transition region and thus displays a gradual softening at increasing moisture contents. The crystallites restrict the motion of the molecules between crystallites in the microfibrils and thus shift the transition in these regions to higher temperatures or higher moisture contents." He also suggested a mechanical composite model where " . . . the softening effect due to water immersion results from a softening of the disordered zones between the cellulose crystallites in the microfibrils. Under these conditions the fiber is best represented by a discontinuous system in which only the cellulose crystals act as reinforcing elements."

In a later paper, together with Olsson, Salmén [5] studied another wood component, lignin in situ in wood, using mechanical spectroscopy. They concluded that under wet conditions the viscoelastic properties of the lignin, which to a somewhat lesser degree forms hydrogen bonds [6], govern the properties of the wood fiber. The differences noted between softwood and hardwood lignin could be explained by the smaller degree of crosslinking in hardwoods than in softwoods.

RECENT DEVELOPMENTS

In the process of wetting the wood and fiber structure, the point of humidity saturation of the cell wall, FSP, is important and for pine wood is about 30% humidity. At this point an abrupt change of physical properties is observed, e.g., the mean cell anisotropy (ratio of cell diameter in the 135 to 45° directions), which on drying causes a build up of strong stress forces. Our electron scanning micrographs combined with computer-aided image analysis [3] indicated that on drying, a rupture of the structure may occur at somewhat higher humidity values than the FSP. The rapid and chaotically unforeseeable rupture generally occurs along the middle lamella which is poor in reinforcing crystalline cellulose but rich in amorphous lignin.

A study of the dynamic cell wall properties of wood by Fourier Transform infrared spectra (FT-IR) combined with statistical covariance matrix analysis of the spectral bands [7] and dynamic proton magnetic nuclear resonance relaxation (PMR) [8] indicates that at lower humidity values than FSP, at about 13% humidity, and at room temperature the hydrogen bonds of water are completely associated with the wood cell structure. Using the data given by Back and Salmén [9], it is possible to estimate that cellulose is covered by a bimolecular layer of water corresponding to about 27% humidity of the amorphous part of cellulose at the dynamic saturation point.

CONCLUSIONS

Developments in the field of wood chemistry during this century have been continuous but, as a mature science, not so turbulent as in the art of macromolecules. In many respects, both branches of chemistry have been intimately associated. The present small historic presentation, which begins with the thesis of Bengt Rånby, indicates how a lot of the problems which have hampered the use of wood instead of synthetic polymers as a construction material for various technical purposes have been detected. Basic research has yielded much better and longer lasting paper qualities than those present forty years ago.

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