

THE MICROSTRUCTURE OF CELLULOSE FIBERS

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By

G. J. RITTER, Senior Chemist

This report is a brief review of the literature on the microstructure of cellulose fibers during the last three years.

The first portion gives the generally accepted concepts regarding the fiber structure and also the controversial concepts which were of significance at the beginning of 1938. New ideas and modifications of old ideas about the fiber structure are then discussed in connection with the various papers that have appeared during 1938-1940, inclusive.

In a review of the literature some articles are generally missed. Accordingly, this reviewer wishes, at the outset, to acknowledge the likelihood of his missing articles that should be included, and to beg the pardon of any author who has been overlooked.

Generally Accepted Fiber Structures Previous to 1938

A reading of the articles on the microstructure of cellulose fibers, which appeared during the five years previous to 1938, seems to give general agreement on the following points.

Main Divisions of Cell Wall

The cell wall is divided into a primary and secondary layer and sometimes a tertiary layer. The primary layer is adjacent the middle lamella. The secondary layer is adjacent the inner face of the primary; it is considerably thicker than the primary layer even in thin-walled fibers and much thicker than the primary layer in thick-walled fibers. The tertiary layer is adjacent the inner face of the secondary layer, difficult to distinguish in normal fibers but easily distinguished in some types of abnormal fibers; its presence in normal fibers is sometimes questioned on account of the difficulty of recognizing it.

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Sleeves

The secondary layer is divided into layers or sleeves. The number of sleeves which have been reported vary from approximately 8 to 12 in wood and as high as 30 in cotton.

Fibrils

The primary layer of the wall and ^{/the} sleeves of the secondary layer appear to have been dissected into long slender fibrils. The presence of fibrils, to this reviewer's knowledge, has not been definitely demonstrated in the tertiary layer. In some abnormal fibers a coil springlike structure loosely associated with the secondary layer is discernible; some research workers may consider that the coil-like structure demonstrates the presence of fibrils in the tertiary wall.

Substructure of Fibrils

Microscopically visible substructures of the fibrils have been reported. They comprise dermatosomes, ellipsoids, fusiforms, and spherical units. These are considered substructures of the fibrils because they are each isolated by a treatment of the fibrils under rather carefully controlled conditions. The treatment selected produces substructures of approximately the same magnitude and shape. They can be produced from the fibers directly if the treatment is less severe than that employed for dispersing the cellulose. In dispersing the cellulose rather concentrated solvents are employed, which quickly swell the fiber and disperse the cellulose without visibly separating the cell wall into the fibrils and their visible substructures.

Submicroscopic Structures

The largest submicroscopic structural unit of cellulose at the end of 1937 was believed to be the micelle; since then the name "crystallite" has been generally applied to the micelle on account of its crystal properties. The crystallite is assumed to be composed of long cellulose chains which, in turn, are composed of anhydroglucose residues.

A preponderance of evidence favored orientation of the crystallites in the primary wall to be approximately parallel with the perimeter of a cross section of the fiber; also it favored orientation of the crystallites in the secondary layer of the cell wall to be from 0 to 15 degrees to the long axis of normal fibers.

Controversial Aspects of the Fiber Structure Previous to 1938

Previous to 1938 heated arguments had developed for and against the presence of "cross walls" in cellulose fibers. The proponents of the cross

walls contended that ringlike structures divided the cellulose fiber wall into segments approximately 40 microns in length. The structural units in the cross walls were supposed to be oriented with their long axis parallel with the crosswise perimeter of the fiber. This type of arrangement would restrain the fiber from shrinking and swelling transversely. If the fiber were treated with a swelling agent more drastic than water, the cross walls were supposed to be responsible for the ballooning phenomenon which developed. The presence of cross walls also limited the length of fibrils to the length of the fiber segments between two such cross walls. No information as regards the chemical composition of the cross walls was given. The idea of cross walls was opposed by a large majority of research workers who contended that the constrictions disclosed in the ballooning phenomenon were caused by the primary wall fibrils.

Vigorous controversies were carried on regarding the chemical nature of the cementing material between the various microstructural units described above. For example, advocates of the cross-wall concept admitted that nothing was known about the composition of the cross walls. They further advocated the presence of a mysterious material surrounding each of the layers, sleeves, fibrils, dermatosomes, and micelles. Thus the largest cellulose particle existing by itself was the micelle which was separated from its adjacent micelles by the mysterious cementing substance.

Other research workers advocated the presence of a pectin-like material surrounding the ellipsoidal particles.

Hemicelluloses were also advocated as being present in the cell wall but no definite stand was taken regarding its distribution among the various microstructural units of the cell wall.

Articles Published During 1938-1940 Inclusive

Bailey, I. W. Cell Wall Structure of Higher Plants. Ind. Eng. Chem. 30:40 (1938). The cell wall is divided into a primary and a secondary layer. Each layer is composed of a coherent matrix of porous anisotropic cellulose whose microstructural units gradually diminish to the resolving power of the microscope (0.1 microns or less). Lignin and non-cellulosic materials may be deposited in the interstices of the cellulose so as to form two continuous interpenetrating phases. One phase may be removed without severing the continuity of the other. The structure of the secondary wall varies (1) in porosity in successively formed parts, (2) in the arrangement of the aggregates of the chain molecules, (3) in the distribution of noncellulosic materials, and (4) in the presence of noncellulosic layers. The secondary portion of the wall can be dissected into layers, fibrils, fusiform bodies, dermatosomes, and other substructures of varying shapes and sizes.

Frey-Wyssling, A. Submicroscopic structure and maceration pictures of native cellulose fibers. Papier-Fabr. 36:212 (1938). The author advances

the micellar theory of Nägeli with the modification that the micelles are held together by chain molecules which are a part of the two joined micelles.

Clark, S. H. Fine structure of the plant cell wall. *Nature* 142:899 (1938). The principal idea of fiber structure conveyed by the article relates to the crystallite structure. It is suggested that the cellulose chains are arranged parallel in zones and nonparallel at intervals between the zones. In this manner the crystallites or micelles are a more or less continuous mass consisting of regularly and semiregularly arranged cellulose. Lignin is believed to exist in the intermicellar spaces. The author divides the cell wall into middle lamella, primary layer, and secondary layer.

Frey-Wyssling, A. The micellar theory explained by the example of the fine structure of fibers. *Kolloid-Z.* 85:148 (1938). This article also advocates the idea of the cellulose micelles and the intermediate substances being attached to one another so as to form a continuous phase. The author suggests that the term "micelle" be retained in the literature. Micelles are about 60 Å. wide, whereas the spaces between them are 100 Å. wide.

Hess, Kurt. Recent results of the investigation of the structure of the vegetable cell wall. *Papier-Fabr.* 37:28 (1939). The article reports findings obtained by means of photomicrographs in which ultraviolet light was employed as the light medium. The article indicates that the results obtained suggest a theory on fiber structure differing from that put forth by Frey-Wyssling.

Bailey, I. W. The microfibrillar structure of the cell wall. *Bul. Torrey Bot. Club* 66:201 (1939). This article conveys the idea of two structural phases in the cell wall, one composed of cellulose and the other composed of noncellulosic materials, each phase being continuous. The author contends that the cellulose is regularly arranged in the microfibrils, but that the microfibril arrangement fluctuates from layer to layer in the secondary portion of the cell wall, thereby causing a phenomenon interpreted as random crystallite arrangement. The remainder of the article is similar to that published in *Ind. Eng. Chem.* 30:40 (1938).

Bailey, A. J., and Brown, R. M. Diameter variations in cellulose fibrils. *Ind. Eng. Chem.* 32:57 (1940). The diameters of fibrils isolated from various types of cellulose fibers were measured microscopically and found to range from 0.923 to 0.956 micron. Fibers can be divided into fibrils and hydrogel by mechanically agitating the fibers in water.

Hock, Chas. W., and Seifriz, W. Microdissection of paper pulp fibers. *Paper Trade J.* 110, no. 5:31 (1940). Fibers from paper pulp were treated with boiling water and phosphoric acid and examined microscopically. The examination revealed that fibers are made up of many fibrils arranged parallel to the long axis of the fiber. These fibrils are wrapped in an outer layer of transversely arranged fibrils and are bordered by an inner winding which subtends the lumen. Balloon formation is due to uneven weakening of the interfibrillar forces of the outer wrapping.

Lewis, H. F., and Brauns, F. E. Existence and nature of fiber membranes. Paper Trade J. 110 no. 5:36 (1940); Tech. Assoc. Papers 22:475 (1939). Cellulose pulp fibers containing different percentages of lignin were dispersed in cuprammonium solution. Presumably, the insoluble residue so obtained was considered to be a fiber membrane similar to that advocated by Lüdtke. The residue recovered from dispersing unbleached pulps consisted of more than half lignosulphonic acid and small amounts of carbohydrates; the residues from bleached pulps consisted of compounds of copper and carbohydrates.

Kühnel, Ernst. Making the inner structure of cellulose fibers visible by embedding foreign substances. Kunstseide 22:3, 35 (1940). The article describes preliminary trials on impregnating and depositing metals in the microstructure of fibers. The treatment consists of two stages, one to swell the fiber wall and the other a diffusion of a salt solution into the fiber wall and deposition of the metal which is microscopically visible. This technique affords a means of measuring the magnitude of the fine capillary structure of fibers.

Kratky, O., Kainz, K., and Treer, R. Micellar structure of native cellulose. Holz Roh u. Werkstoff 2:409 (1939). The cell wall is impregnated with a solution of a noble metal salt and the metal salt subsequently reduced to finely divided metal which is deposited in the interstices between the cellulose micelles. An approximation of the size of the interstices is made.

Preston, R. D. Wall of the conifer tracheid as a single spiral complex. Proc. Leeds Phil. Soc. 3, part 9:546 (1939). The micellar arrangement of the primary layer is in general lengthwise in the fiber. The arrangement in the secondary layer shows angular dispersion.

Kundu, B. C., and Preston, R. D. Submicroscopic structure of cell walls. Proc. Royal Soc. (London) B128:214 (1940). The article conveys the idea that the cellulose chains are arranged lengthwise in the primary layer of the cell wall in contradistinction to the circular transverse arrangement around the fiber as advocated by other research workers.

Farr, Wanda K. Structure and composition of plant cell membranes. Nature 146:153 (1940). The article is a brief review of the author's concepts given in previous articles. Cellulose ellipsoids about 1.1 by 1.5 microns are the microstructural units of the cellulose membranes. They are covered and cemented together by means of a pectin-like material.