

Advanced study of the natural cellulose. Surface nanostructure

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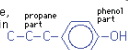
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Glossary

Cellulose (C₆H₁₀O₅)_n - the carbohydrate that is the principal chemical constituent of wood. It forms the framework of wood

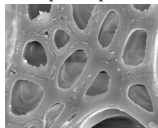
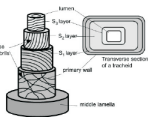
Wood chemistry

Component	Approximate composition by weight	Structure
Cellulose	50%	linear chains of glucose (beta-bond)
Hemicellulose	25%	branched chains of various sugars
Lignin	25%	phenylpropane, a unit of lignin



Wood cell

SEM image of the cross-section of European aspen cells



Cell Types in Wood

Cell Type	Softwood	Hardwood	Both
Cell Type	Tracheid	Vessel Elements Fiber	Parenchyma
Function	conduction+support	conduction support	storage, defense
Shape	long, narrow	short, narrow	various
Arrangement	connected with pits	Wide connected end to end into long Vessels	Oriented radiate in rays and, in hardwoods, longitudinally near vessels

Microfibrils (MF)- bundles of cellulose polymer chains and associated polysaccharides of other types that are united at some regions in highly ordered crystalline lattices known as crystallites and less highly ordered zones between the crystallites (amorphous regions)

Primary cell wall- initial layer of the cell wall; formed during following cell division and later modified during postcambial differentiation of cell. Thickness of the primary wall is 0.1 μm, and it consists 70% of lignin and 10% of cellulose, MFs lie as criss-cross network around the cell

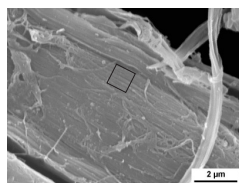
Secondary cell wall is composed of three distinct layers. S1-the first few (4-6) microfibrils spiraled around the cell interior with the long axes of MFs nearly perpendicular to or 50-60 degrees from the long of the cell. S2-the next layer with spiraling angle changing to 10-30 degrees. It is much thicker, 30-40 cells in earlywood to 150 or more in latewood. This layer has the greatest effect on how the cell behaves. S3- last several layers are arranged similar to S1, with 60-90 degree angle to the long axes

Tracheids are long, narrow cells with closed end and bordered pits. The average length of tracheids varies from 2-6 mm

Parenchyma cells are divided into longitudinal parenchyma and ray parenchyma cells and their task is storage. Longitudinal or wood parenchyma occur in strands, which in some wood consist in part of strand tracheids. They have a simple pits, and are often conspicuous because of the presence of dark-colored inclusions. Longitudinal parenchyma is never abundant in softwoods. Ray parenchyma cells are rather bricklike, thin-walled living cells. They have also simple pits, which provide liquid transport to the other ray cells and longitudinal tracheids.

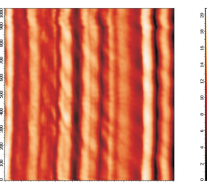
Experimental observations

SEM images are obtained with JEOL JSM- 840A
AFM images are obtained with Stand-alone SMENA scanning head from NT-MDT in the air, using the tapping mode

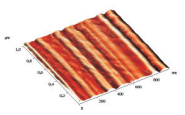


Laboratorially not treated pulp of European aspen. On the SEM image are visible residues of middle lamellae and P and S1, also parallel fibres of S2.

The AFM image show more fine structure.



On the 3D image one can see the winding structure



Abstract

Cellulose is the most abundant polymer in nature, made up of repeating units of glucose, the simple sugar. Cellulose occurs in almost pure form in cotton fibre (98%) and in combination with other materials, such as lignin and hemicelluloses, in wood, plant leaves and stalks, etc. The special properties of cellulose result from the association of the long chains to form fibres called microfibrils. These are 2-20 nm diameter and 100-40 000 nm long and form the structurally strong framework in the cell walls. Cellulose has many uses as an anticake, emulsifier, stabilizer, dispersing agent, thickener and gelling agent. Recently one-dimensional nanostructures prepared through chemical precipitation, thermal evaporation under various cooling down procedures, sol-gel or other procedures have been run up. The results are nanoparticles, nanorods or nanolinters what are intriguing targets for different applications like semiconductors, photocatalysts etc. Essential factor for the controllable growth is the physical template environment around growing structures. There are numerous techniques to produce such fine structures. Using lignocellulosic network as an intermediate framework to orientate producible nanostructures it is possible to create highly porous linter-like nanostructures. During the growth of wood cell wall structure has been self-assembled in complex way forming tight fibrillar network. This network is used to orientate the growth of nanostructures.

Introduction

Cellulose is a major component of wood. All wood cells have specific functions to perform. There are different types of cells in softwood and hardwood.

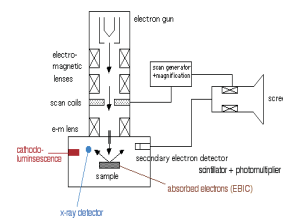
On the bases of functions, the cells can be divided into three groups: conducting cells, supporting cells, and storage cells. Hardwoods (HW) are more advanced and more complex in their structure than softwoods (SW). In SW the functions of conduction and support are performed by one type cell. Conducting and supporting cells are elongated, axial cells. In HW, the conductive cells consist of vessel elements and the supporting cells consist of fibres. HW cell consist of primary wall, 3 secondary walls (S1, S2 and S3) and a lumen, cells are separated by middle lamellae. In the S1 the microfibrils are laid down on a criss-cross pattern, the S2 is the thickest and microfibrils are relatively parallel. The secondary walls are the most important of these parts, it is the section of fibre which predominates after chemical pulping of wood.

However, although the thickness of primary wall is only 0.1 μm, it consists up to 70% from lignin and about 10 % from cellulose and is with S1 especially strong. To get the pure cellulose microfibrils (S2) it is necessary to remove primary wall and S1 completely. The impact of removing technology is different by the species of wood.

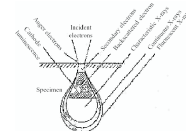
Methodology

Scanning Electron Microscope (SEM) is usual tool for material scientists. SEM is based on a simple principle of bombarding a sample with an electron gun which induces scattering of electrons that are detected. The collision of the primary electrons with the sample results elastic and inelastic scattering electrons. Backscattered electrons are primary electrons that re-emerge from the sample after collision with the nuclei in the bombarded sample- this is elastic scattering. Secondary electrons emerge when the primary electrons transfer energy to the sample. The SEM image is produced by detecting either backscattered or secondary electrons. Anyway, electrons with some kinetic energy penetrate the sample. Electron beam penetration and diffusion area depend on acceleration voltage: clear surface structure images can be obtained with lower accelerating voltage but it causes low resolution. High acceleration voltage achieves high resolution but can damage the surface and structures are unclear.

Principle of SEM



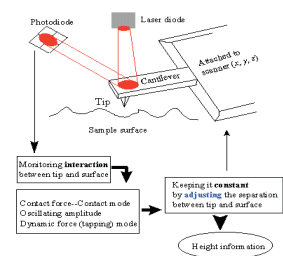
SEM interaction



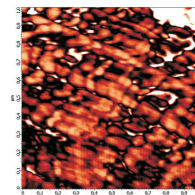
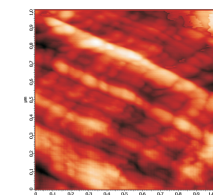
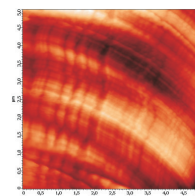
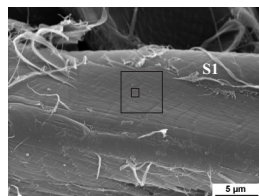
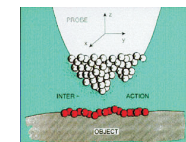
Atomic Force Microscope (AFM) is a little newer tool (from year 1986) for scientists. In AFM the main tool for giving the image is a sharp tip attached on the loose end of cantilever, the tip scans in the near-field of the surface (usually 10 nm), and the deflections in the cantilever due to the surface forces between the tip and sample are recorded. There are no problems if the tip is point-like and tip-sample interactions are negligible. In practice, these conditions are hardly realized. The tip-shape anisotropy can induce various artifacts in large and atomic-scale images. Even the use of tips with perfect shape might lead to a nontrivial image perturbation because of the inevitable tip-sample interactions. The scanning tip can exert strong vertical and lateral forces on the sample, thereby causing surface deformation and removal of weakly bound and defective layers.

There are three types of forces available: attractive/repulsive forces, forces due the sample deformation and deflection of cantilever. Consideration of tip-sample interactions is critical in the imaging of soft organic materials as cellulose fibres. Moreover, always there is a contamination layer of water on the surface of the sample during a scanning in the air. So, the image interpretation is the key problem in AFM applications.

Principle of AFM

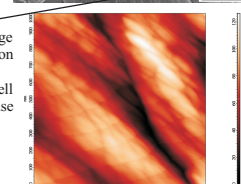
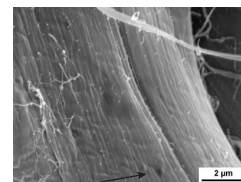


AFM interaction



Laboratorially treated and 20 minutes milled aspen pulp. On this image one can see the pure S2.

The dark spot on the lower part of SEM image is damage by the electron beam. The squamiform structure is specially well shown on the AFM phase image (down). It waits the explanation.



Laboratorially treated and 10 minutes milled aspen pulp. On the upper part of SEM image the pure S1 can be seen, in the centre one can see the trenced S2, this structure has no good explanation yet. Right below is the phase image. Phase shift between cantilever oscillation and driving ac voltage is defined not only by topography, but also shows strong dependence of sample properties as adhesion, elasticity and viscoelasticity. Dark areas correspond to softer and brighter areas to harder surface. Their origin needs explanation yet.