Wood Chemistry

Wood Chemistry

PSE 406 / Chem E 470

Cellulose

Lecture 6

Wood Chemistry

Agenda

- Amorphous versus crystalline cellulose
- Cellulose structural considerations
- Cellulose I
  - » Orientation
  - » Bonding
- Cellulose II
- Cellulose physical properties

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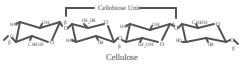
Is Cellulose Like Spaghetti?

- In the woody cell wall, exactly what is the cellulose doing?
  - » Is cellulose like uncooked spaghetti? i.e. random orientation of rigid cellulose chains.
  - » Is cellulose like cooked spaghetti? i.e random orientation of flexible cellulose chains
  - » Or is cellulose like those clumps of spaghetti you get when you don't stir the spaghetti when cooking?



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Amorphous Cellulose

- A portion of the cellulose in the cell wall can be thought of as flexible spaghetti. This is amorphous cellulose.
- Every different cellulose preparation has different percentages of amorphous and crystalline cellulose (see next slide).
- These 2 forms of cellulose have different properties and reactivities.

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Cellulose
Crystalline versus Amorphous*

Cellulose	Crystallinity (%)
Cotton Linters	71.3
Bleached Kraft (spruce)	68
Bleached Sulfite (spruce)	67.8
Bleached Kraft (birch)	65.1
Bleached Kraft (bamboo)	59.9
Rayon	45

* See Sjostrom pg 13 for a drawing

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Cellulose
Structural Considerations

- If you look at a picture of a cell wall →→→→→→→→ you can see what looks like threads. These are crystalline bundles of up to 2000 cellulose molecules known as microfibrils . These can range in diameter from 10-30 nm.
- There are theories that the microfibrils are made up of smaller units known as elementary fibrils with diameters of 2-4 nm.

- This is an electron microscopic image of a shadowed preparation of cellulose microfibrils from green algae (D. G. ROBINSON, 1986).

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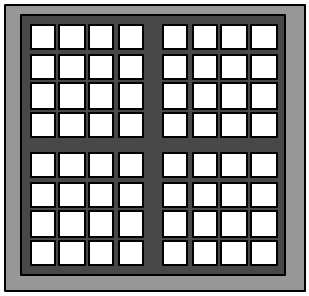
Representation of Cell Wall Components



Cellulose

Hemicelluloses

Lignin

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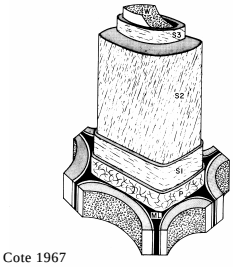
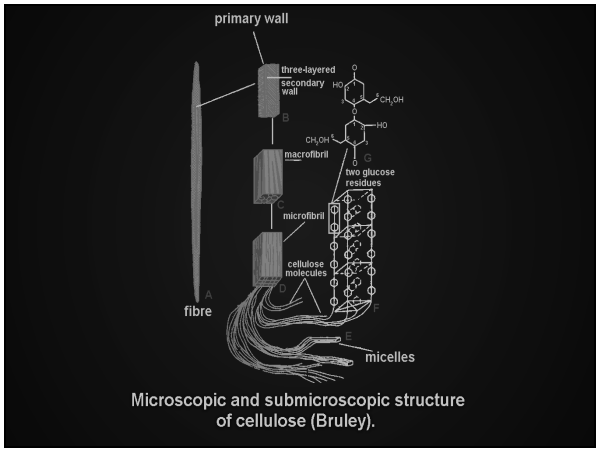
Cellular Microscopic Structure



Cote 1967

- Woody cells consist of several different layers
- The area between cells is known as the middle lamella
  - » Very high lignin content
- The lignin content lowers through the cell
- The idea in chemical pulping is to :
  - » Release the fibers by removing the lignin in the ML
  - » Remove color by removing lignin in the rest of the cell



Microscopic and submicroscopic structure of cellulose (Bruley).

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Types of Cellulose

- Cellulose I: Native cellulose (cellulose as found in nature.
- Cellulose II: Native cellulose which has been soaked in alkali or regenerated cellulose. Large structural changes have occurred in the molecule
- Cellulose III or IV: Forms of cellulose which have been treated with various reagents

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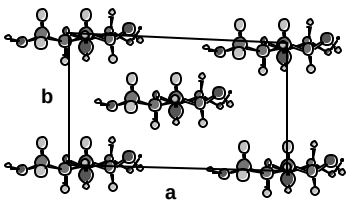
Cellulose I Unit Cells



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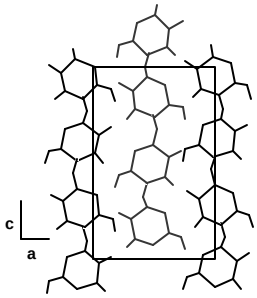
Cellulose I Orientation

- By looking at the a-c plane, you can see that the cellulose chains are parallel and oriented (direction of reducing end) in the same direction. The center chain of the 5 chains (in red) is off set slightly from the other chains.



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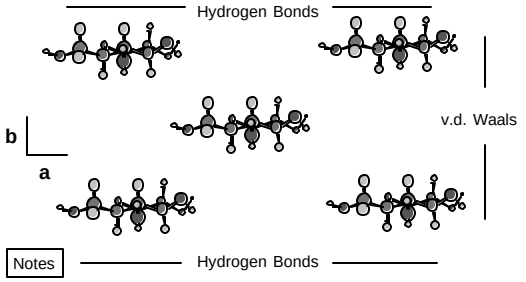
Cellulose I Bonding



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Bond Strength Comparison

Linkage	Compound	Energy kJ/mol
v.d. Waals	H_2O	0.155
O-H····O	H_2O	15
O-H····O	Cell-OH	28
O-H		460
C-C		347

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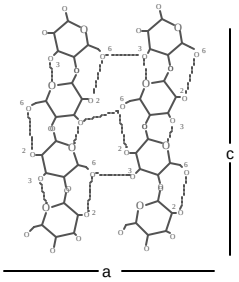
Hydrogen Bonds in Cellulose I

- Intramolecular Bonds
  - » O(6) to O(2)H
  - » O(3)H to ring oxygen
- Intermolecular Bonds
  - » O(3) to O(6)H
- These Bonds in the AC Plane. Bonding in the b plane through van der Waals forces*



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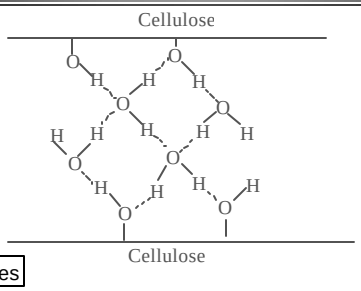
Cellulose & Water



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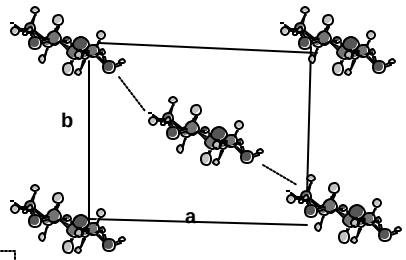
Cellulose II Structure



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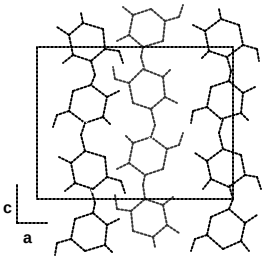
Cellulose II Structure

- From the a-c plane it is possible to see that although the cellulose molecules are parallel in Cellulose II, the orientation of the center cellulose molecule (in red) is opposite to the corner cellulose molecules. The reducing ends are opposite.



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Cellulose Physical Properties

- Sorptive Properties
  - » Crystalline cellulose does not dissolve in most solvents
    - – Molecular length
    - – Inter molecular bonding
  - » Amorphous regions have large number of hydrogen bonding sites available
    - – Cellulose can absorb large amounts of water
    - – Fully hydrated cellulose very flexible
    - – Dry cellulose inflexible and brittle
  - » Swelling of cellulose
    - – 8.5 -12% NaOH
    - – Others

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Other Cellulose Information

- a-Cellulose
  - » “Cellulose” that is insoluble in 18% NaOH
  - » DP>200
- b-Cellulose
  - » Material that precipitates after 18% NaoH neutralized
  - » DP 10-200
- g-Cellulose
  - » Remaining material, DP<10