CHEM-E2105

Wood and Wood Products

Cell wall and mass-volume relationships

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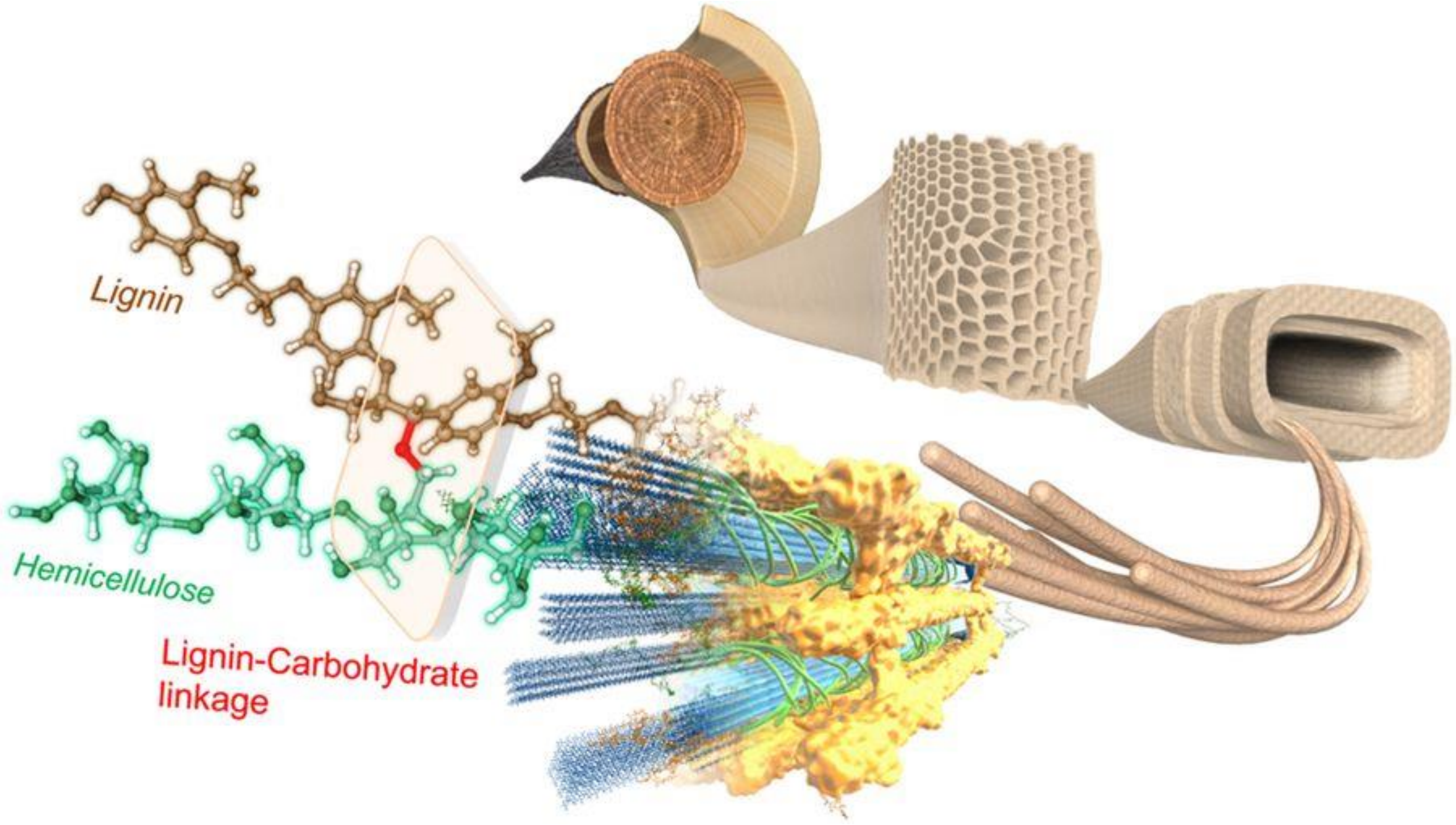
18th January 2019

Today

- **The wood cell wall**
- Mass-volume relationships

Hierarchy of wood



(Source: Nishimura et al. (2018) Scientific Reports, volume, 8, Article number: 6538)

Composition of the cell wall

Chemical composition

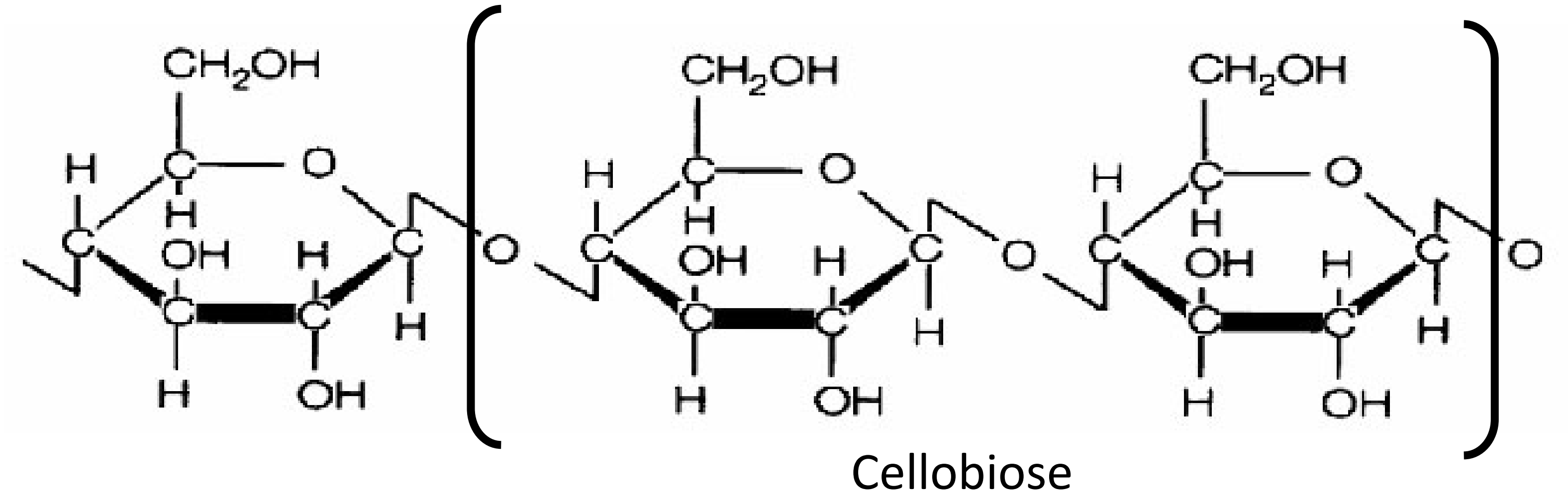
- Three main structural polymers
  - Cellulose
  - Hemicelluloses
  - Lignin
- Analogous to fibre-reinforced-plastics
- Additional polymeric compounds known as “extractives” (because they can be extracted from the wood, i.e. they are not “bound” to the cell wall, by various organic solvents)
  - Generally these have a range of properties, e.g. some are more hydrophobic than others and so tend to be soluble in different solvents: hot water, methanol, acetone, toluene, or a mixture of these
- Inorganic material – ash, large amount of silica

Chemical composition

Component	Mass		Polymeric state	Molecular derivatives	Function
	Softwood (%)	Hardwood (%)			
Cellulose	42±2	45±2	Crystalline, highly oriented, large linear molecule	Glucose	Fibre Reinforce-ment
Hemicellulose	27±2	30±5	Semicrystalline, slightly branched, smaller molecule	Galactose Mannose Xylose	Matrix
Lignin	28±3	20±5	Amorphous, large 3-D molecule, not fully elucidated	Phenylpropane	
Extractives	3±2	5±4	Principally compounds soluble in organic solvents (e.g. water, toluene, ethanol)	Terpenes, polyphenols, stillbenoids	Extraneous

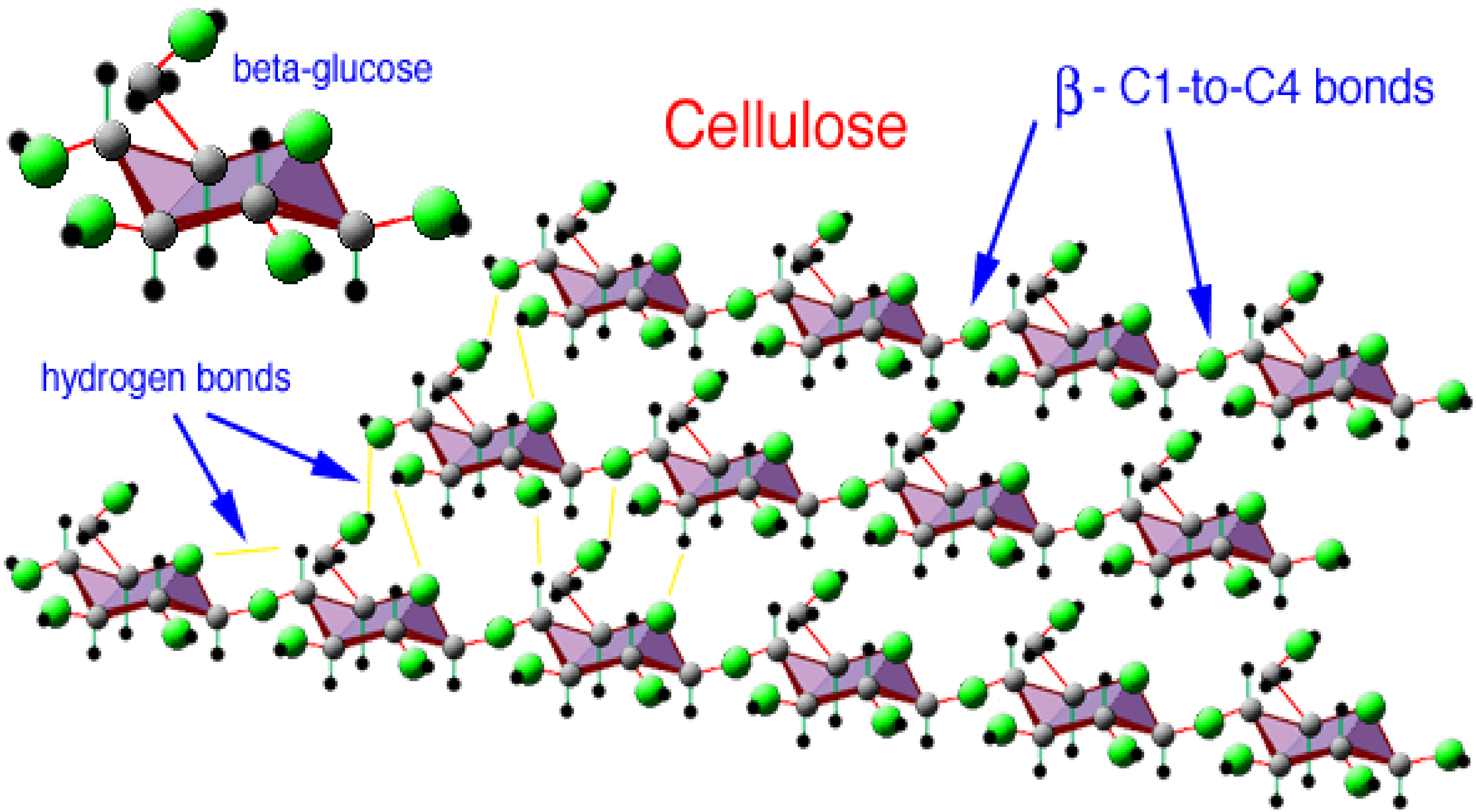
(Adapted from Dinwoodie, 2000)

Cellulose

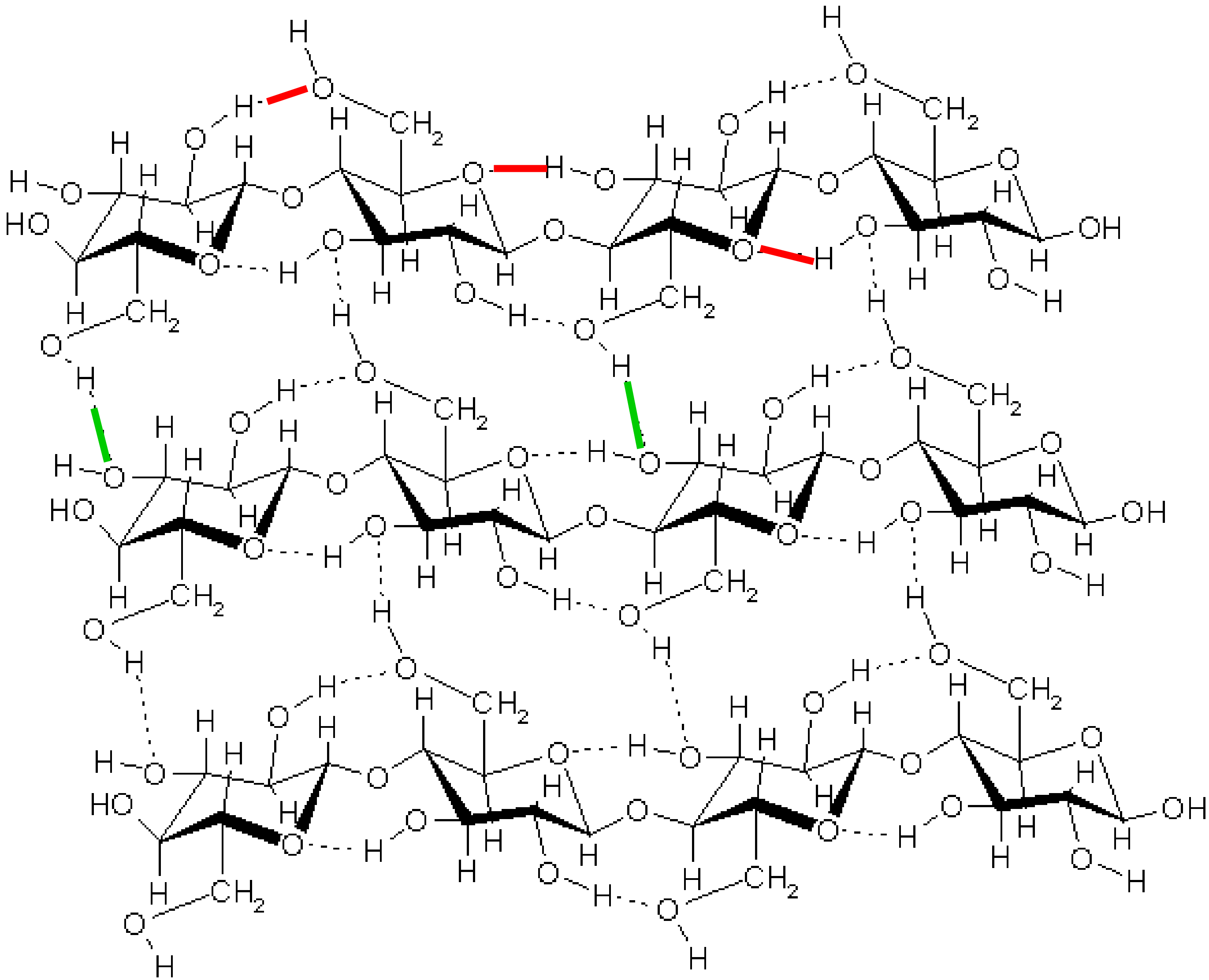


- General structure $(C_6H_{10}O_5)_n$
- Based on glucose molecule $(C_6H_{12}O_6)$
- Smallest repeating unit is cellobiose (two anhydroglucopyranose units)
- Long thin chain molecule, containing 8000-10000 units per cellulose chain in secondary wall, 2000-4000 in primary cell wall
- Cellulose form the basic structural component of the cell all. The molecules aggregate to form highly crystalline structures through intermolecular bonding, forming the basis for the ***microfibril***, the basic building block of the cell wall

Intermolecular bonding



Inter- and intra- molecular hydrogen bonding



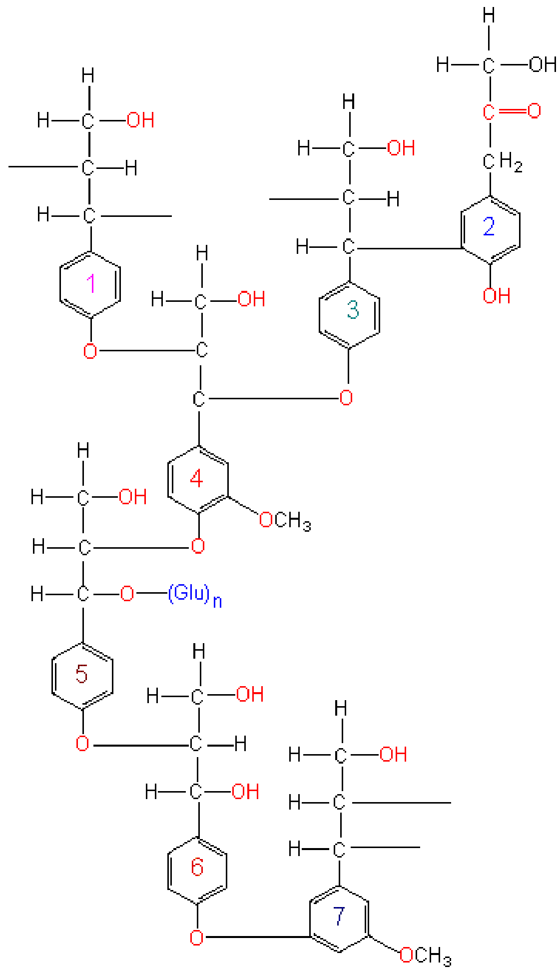
Properties of cellulose

- The Young's modulus of cellulose has been estimated to be in the region of **135 GPa** (similar to Aramid fibre and almost twice that of glass fibre!)
- Very high tensile properties are seen in fibres like flax, hemp and ramie which have a high proportion of cellulose (>80%), oriented nearly parallel with the fibre axis
- Cellulose therefore provides the structural strength of wood and can be thought of as the ultimate "fibre reinforcement" (using the analogy with fibre-reinforced composites) of the wood cell wall

Lignin

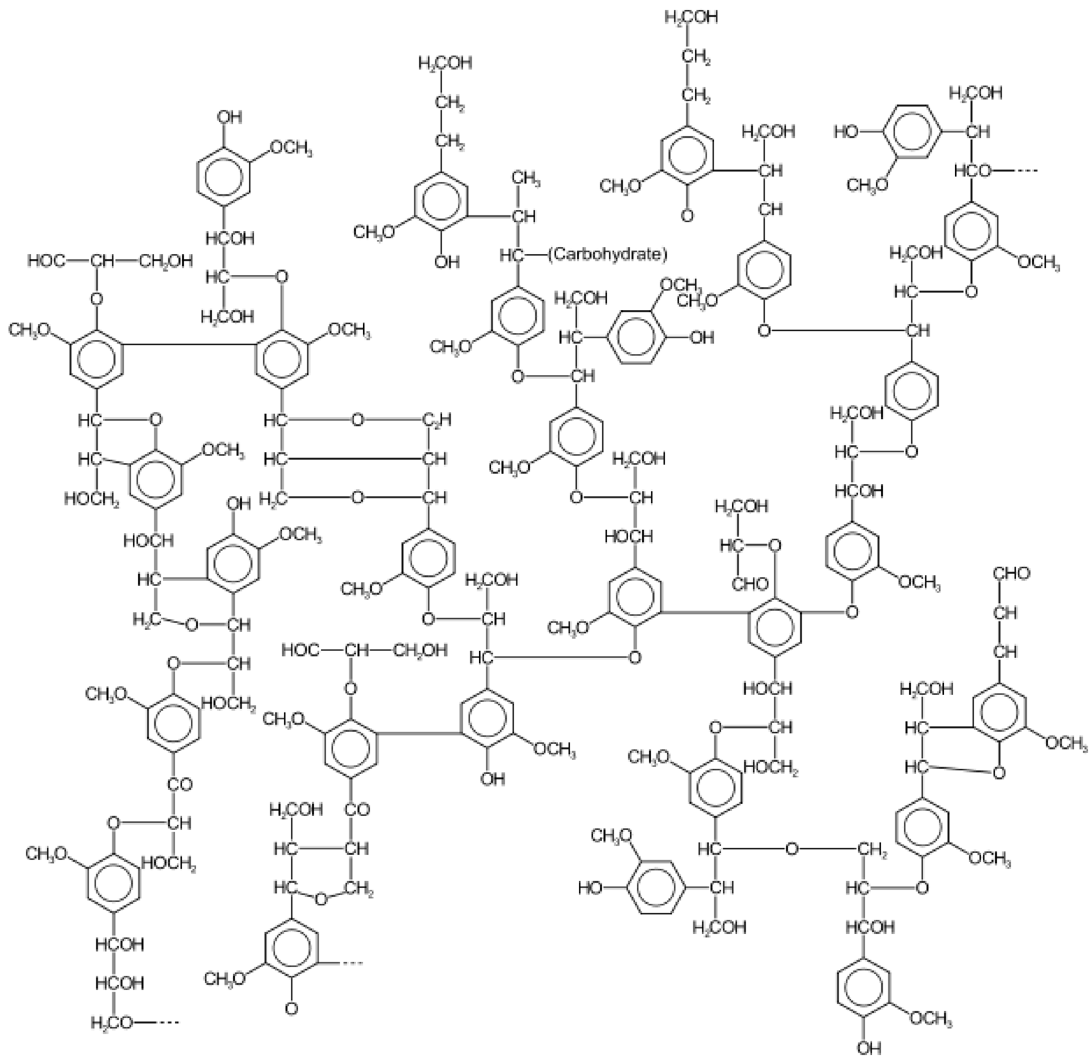
- Complex 3-D molecule composed of short, branched molecules
- Structure of lignin not fully understood, as removal from wood affects its structure
- Lignin more hydrophobic than hemicellulose and mediates moisture
- Young's modulus of lignin **~4 GPa** (similar to unreinforced polymers like epoxy, unsaturated polyester)
- Lignin forms the "matrix" to cellulose's "reinforcement"

Structure of lignin



Possible lignin structure

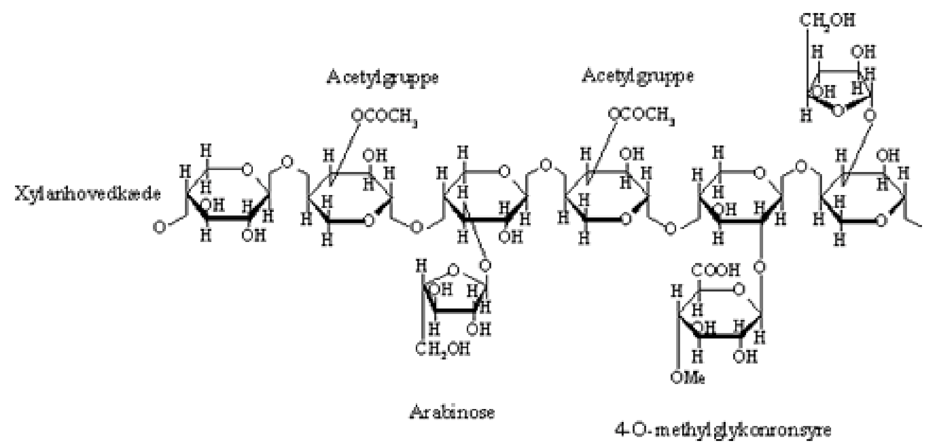
Structure of lignin



Another possible lignin structure!

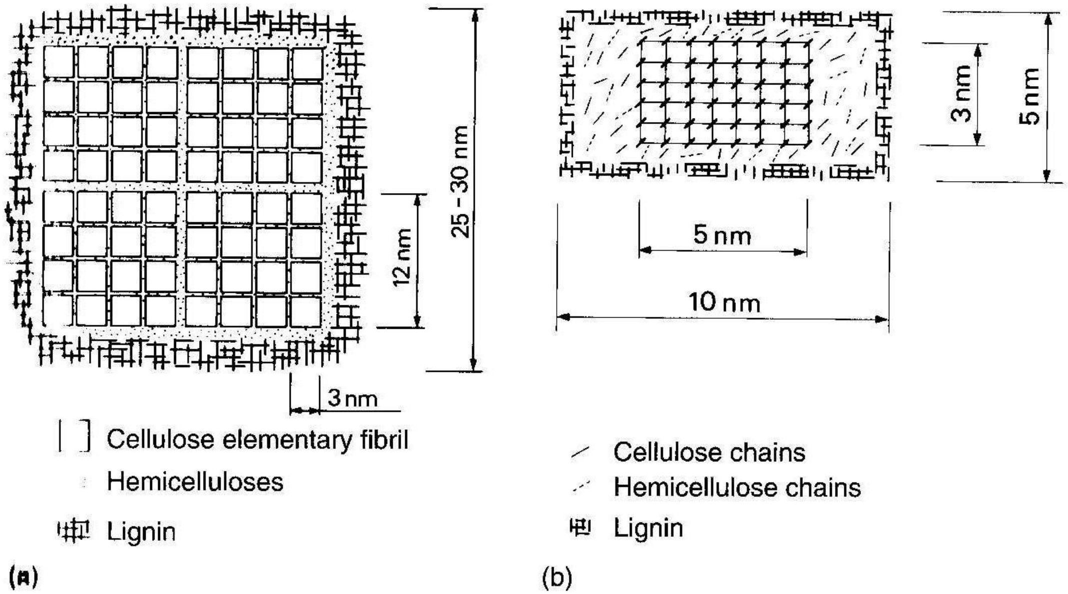
Hemicelluloses

- Range of sugar molecules (e.g. Galactose, glucose, mannose, arabinose
- Degree of polymerisation (number of units) lower than cellulose (~200)
- Mainly linear but sometimes branched
- Lower degree of crystallisation
- Young's modulus of hemicellulose **~8 GPa** (<< cellulose)
- Functions as an "interfacial coupling agent" between the cellulose "reinforcement" and lignin "matrix"[1]



[1]Hughes et al (2015)

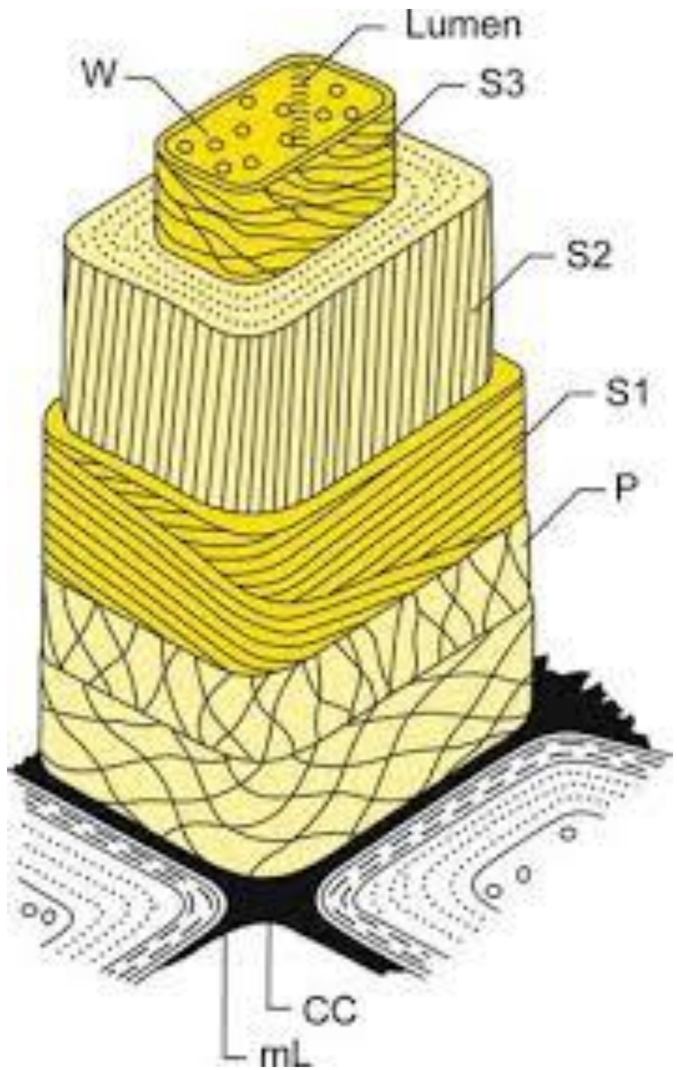
The microfibril



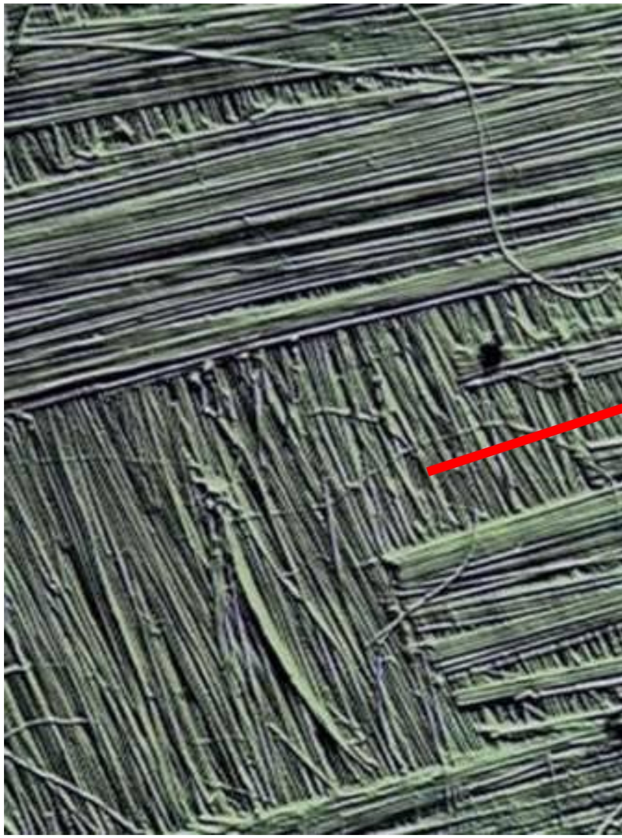
Models for the structure of microfibrils (Dinwoodie, 2000)

- The basic fibrous building block of the cell wall
- Composed of a backbone of cellulose, surrounded by a sheath of hemicellulose and lignin

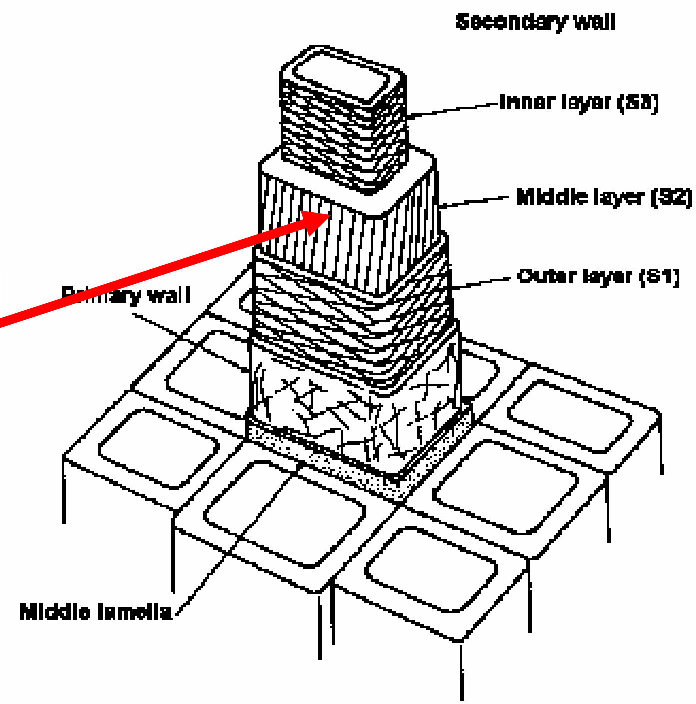
Cell wall structure



Ultrastructural wood



Microfibrils



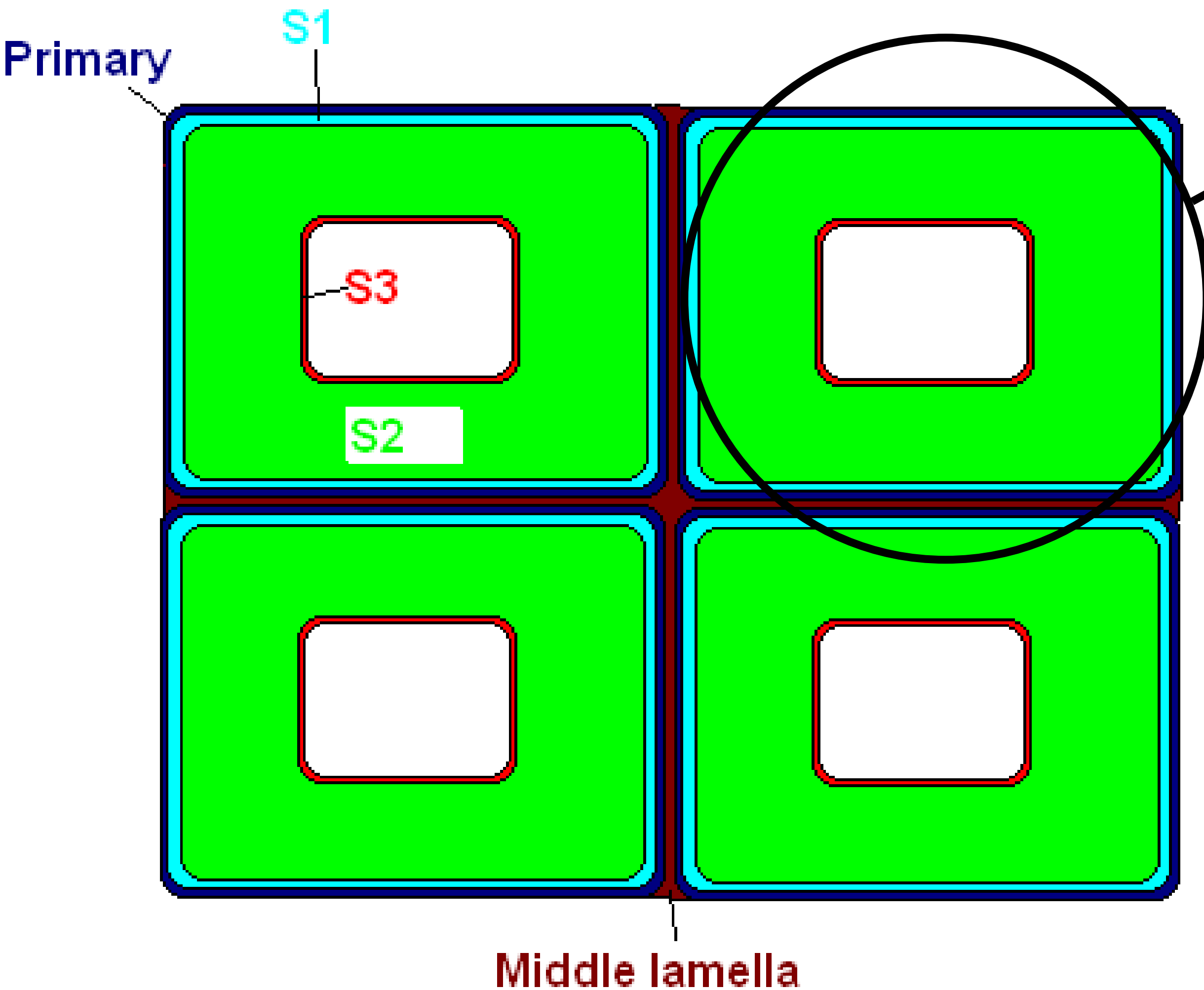
Cell wall structure

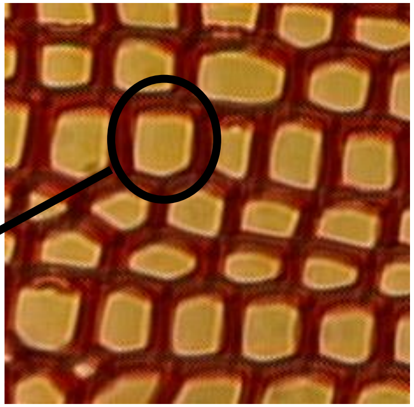
(Adapted from: Dinwoodie, 2000)

Cell wall structure

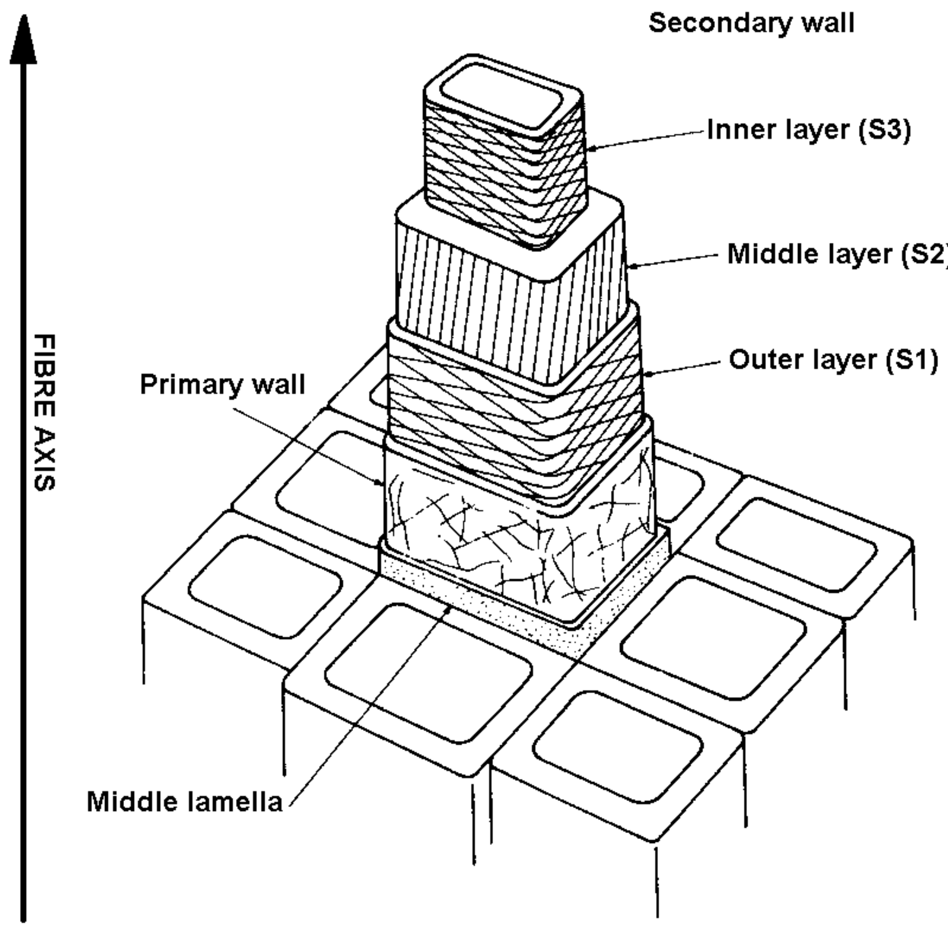
- Cell wall composed of the **primary** and **secondary** walls
- Secondary wall composed of three layers, known as $\mathbf{S_1}$, $\mathbf{S_2}$ and $\mathbf{S_3}$ layers
- Region between cells known as the **middle lamella**, composed of a lignin-pectin complex. It does not have any microfibrils

Cell wall cross-section





Cell wall structure



(Adapted from: Dinwoodie, 2000)

Lamellar structure

Wall layer	Approx. thickness (%)	Angle to fibre axis (degrees)
P	3	random
S1	10	50-70
S2	85	10-30
S3	2	60-90

(Source: Dinwoodie, 2000)

- Microfibrils in primary wall loosely packed random arrangement
- S1 layer: 4-6 concentric lamellae in left and right hand spirals (S and Z helix)
- S2 layer: 30-150 lamellae, all in Z helix
- S3 layer: few lamellae
- Warty layer inside

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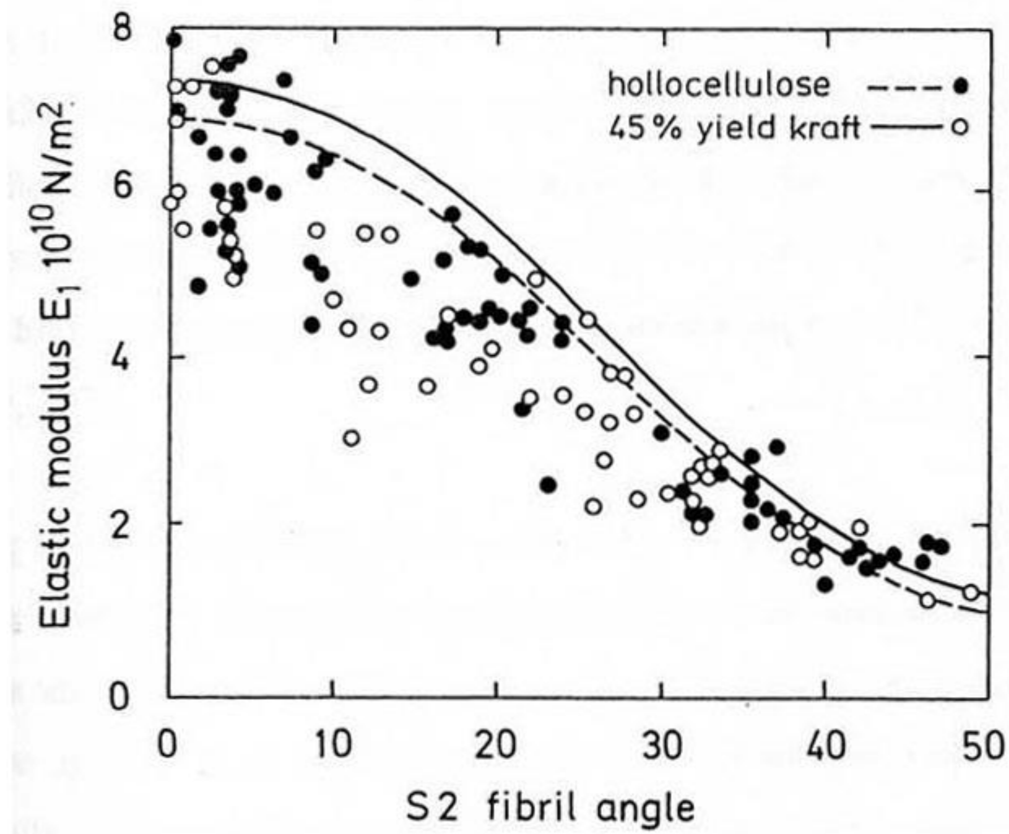
S_2 layer and wood properties

- Since ~85% of secondary wall is consists of the S_2 later, mechanical and other properties are dominated by the winding angle of this layer



Summary

- Wood is structured at many levels - chemical, ultra-structural, micro-structural and macro-structural
- Features at all level affect the properties and behaviour of wood

Mass-volume relationships

Density

- Density is mass per unit volume:

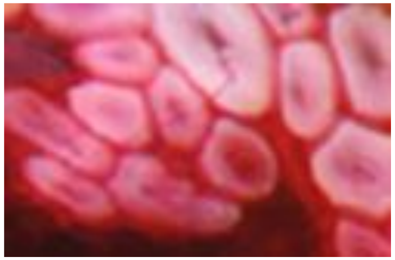
$$\rho = {}^{m}\!/_{v}$$

- Density is an important material parameter since it affects other properties such as thermal conductivity and mechanical properties
- Consider wood : what will affect it's density?
- Moisture content:
  - Will affect both **mass** and **volume**!
- Composition - presence of extractives:
  - Will affect mass (can be a few percent up to 10% of the mass)

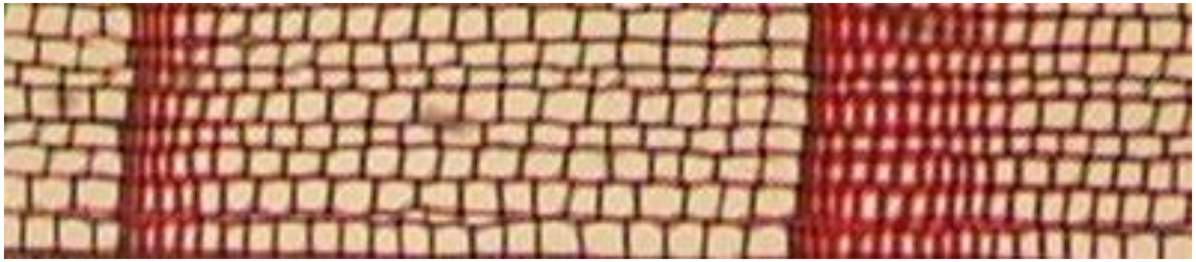
Wood density

- The density of wood at 12% moisture content ranges from balsa (176 kg/m^3) to lignum vitae (~1250 kg/m^3)
- Since the density of the cell wall is, more or less constant, the difference must be due to the voids, i.e. the cellular structure of the fibre and wood

Timber	Density (kg/m^3)
Balsa	176
Norway spruce	417
European redwood	481
Beech	673
Greenheart	977



Flax



Softwood

Density and specific gravity

- Since moisture affects both the mass and volume of wood, it is important to measure both at the same moisture content, and this is usually at 12% (approximately equivalent to equilibrium at 65% RH; 20 ^{o}C – “standard conditions” for wood)
- Specific gravity (SG) is traditionally the ratio of density to that of water at 4 ^{o}C (1000 kg/m^3):

$$G = \frac{\rho_t}{\rho_w}$$

Where:

ρ_t is the density of timber
ρ_w is the density of water at 4 ^{o}C

- But since the mass and volume of wood vary with moisture content, so too will SG. It is therefore usual to quote SG based on the oven dry mass of wood to that of the oven dry volume of wood, or, the volume at some specific moisture content, so:

$$G = \frac{m_o}{V_\mu \rho_w}$$

Where:

m_0 is the oven dry mass of timber
V_μ is the volume of timber at moisture content μ

Density of the cell wall

- The density of the cell wall is sensibly independent of species and in wood is around 1500 kg/m^3
- The density of dry cell wall material varies from 1451 kg/m^3 to 1525 kg/m^3. What is the reason for the discrepancy?
- Depends on the measurement method used:
  - Measurement of volume by displacement in a liquid
  - Optical measurement of the cross-sectional area of microtome slices of wood

Measuring the density of dry cell wall material

- The oven dry mass can be measured accurately. However, the presence of extractives will affect the mass. It may be necessary to remove them prior to measurement, if the species/sample contains a high percentage of extractives
- The volume can be measured by displacement in a liquid
- However, the properties of the liquid will affect the measurement of volume
- A polar liquid like water will be able to penetrate the void (pore) space in the cell wall (estimated to occupy in the region of 5% of the cell wall volume), whereas a non-polar liquid such a toluene, will not be able to do so and therefore the volume displaced by any given sample will be different if it is measured by displacement in either a polar or a non-polar liquid

Measuring the density of dry cell wall material

- Another way of measuring the volume is to directly measure the cross-sectional area of thin microtomed specimens
- This generally leads to a lower measure of cell wall density because of damage caused to the cell wall and optical effects

Porosity

- Using the composite analogy, the porosity, *p*, - the void space in wood and fibres - can be determined using the RoM:

$$p = 1 - V_f$$

- Where in this case V_f is the volume fraction of the cell wall substance
  - This will be affected by the moisture content……
  - But as a good approximation can be given by:

    Bulk density / cell wall density

Density and other properties

- Density is well known to be correlated with certain wood properties like strength and stiffness

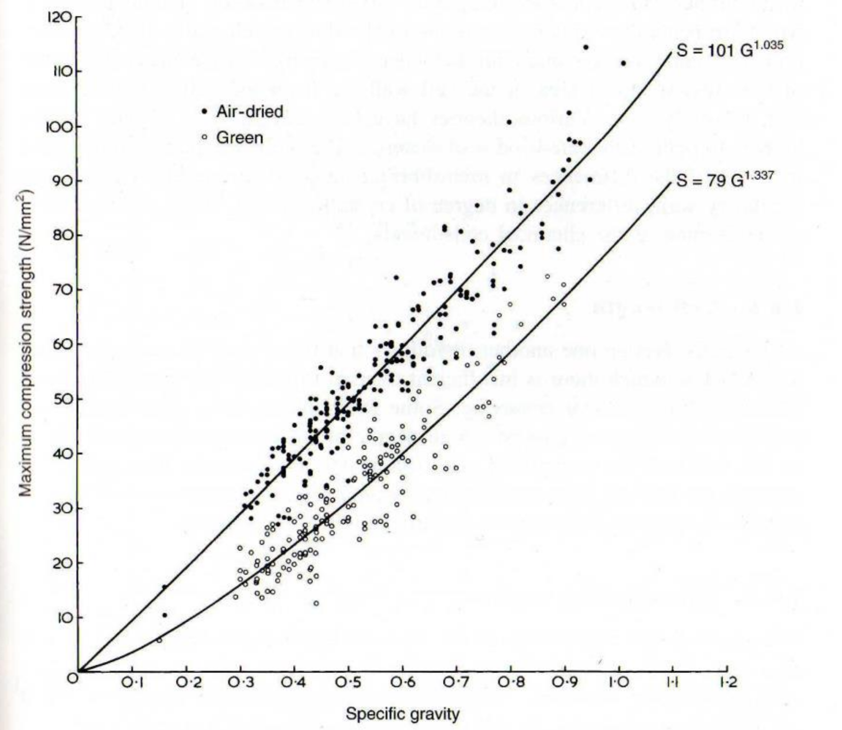
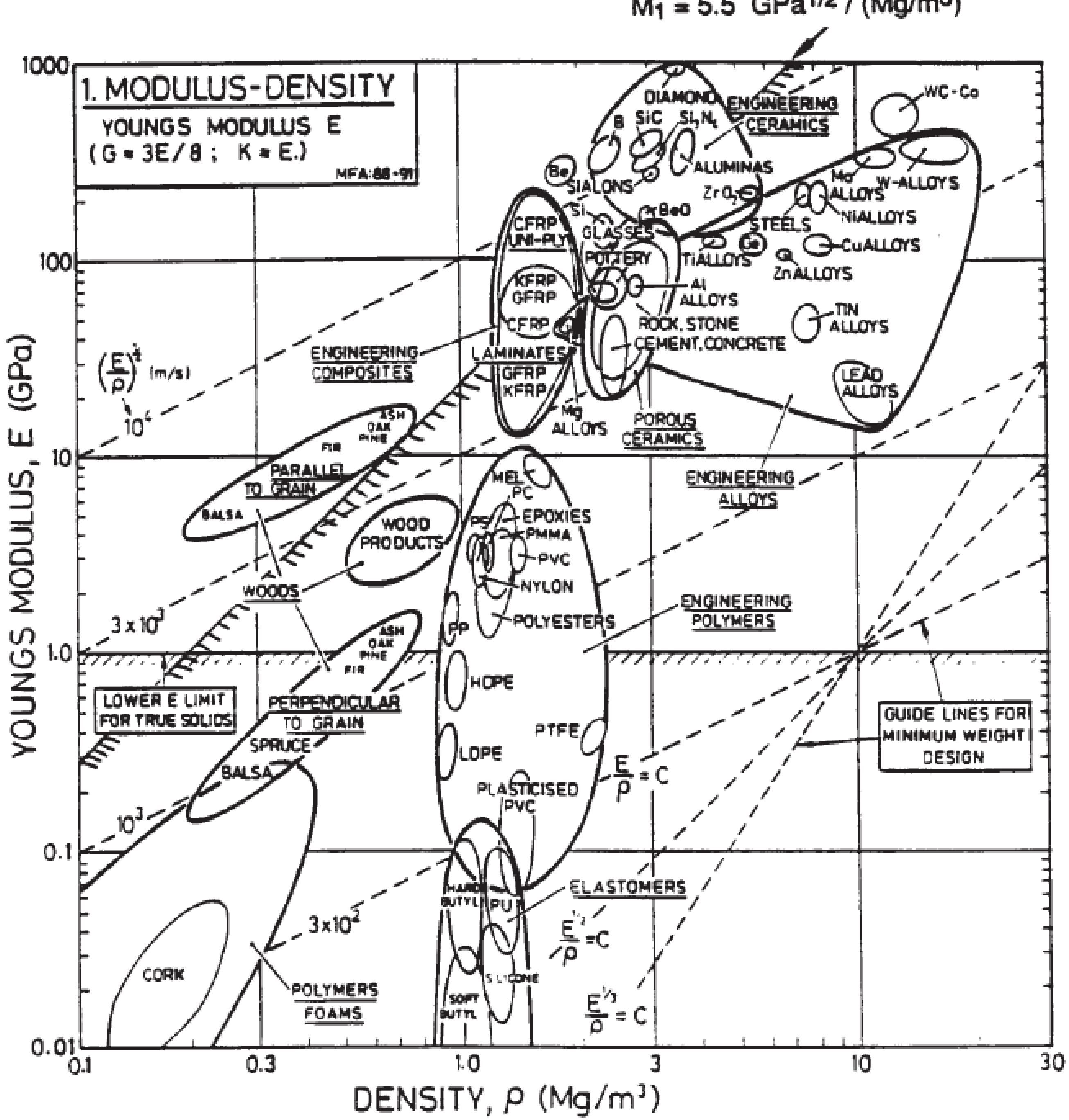


Figure 7.8 The relationship of maximum compression strength to specific gravity for 200 species tested in the green and dry states. (© BRE.)

(Source: Dinwoodie, 2000)

Specific properties

- Materials can be given a “merit index” or “performance index”, based on a property “normalised” by its density
- Material property charts can be created enabling materials selection to be made.
- Also useful in designing new materials, such as composites
- This is useful in materials design and selection…..



(Ashby and Cebon, 1993)

Comparison of mechanical properties

Material	Specific gravity	Young's modulus (GPa)	Tensile strength (MPa)	Fracture toughness (MPa $m^{0.5}$)
Rubber	1.2	0.01	20	0.1
Concrete	2.4	40	20	0.2
Nylon	1.1	2.5	80	4
Spruce wood (parallel to grain)	0.6	16 **(27)**	80 **(133)**	6 **(10)**
Mild steel	7.8	208 **(27)**	400 **(51)**	140 **(18)**
Flax	1.4	50 **(36)**	500 **(360)**	-
Glass fibre	2.6	76 **(29)**	2000 **(770)**	-
Fibre reinforced composite	1.8	20 **(11)**	300 **(166)**	40 **(22)**

(Figures in parentheses are specific values, i.e. value divided by specific gravity)

References and further reading

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