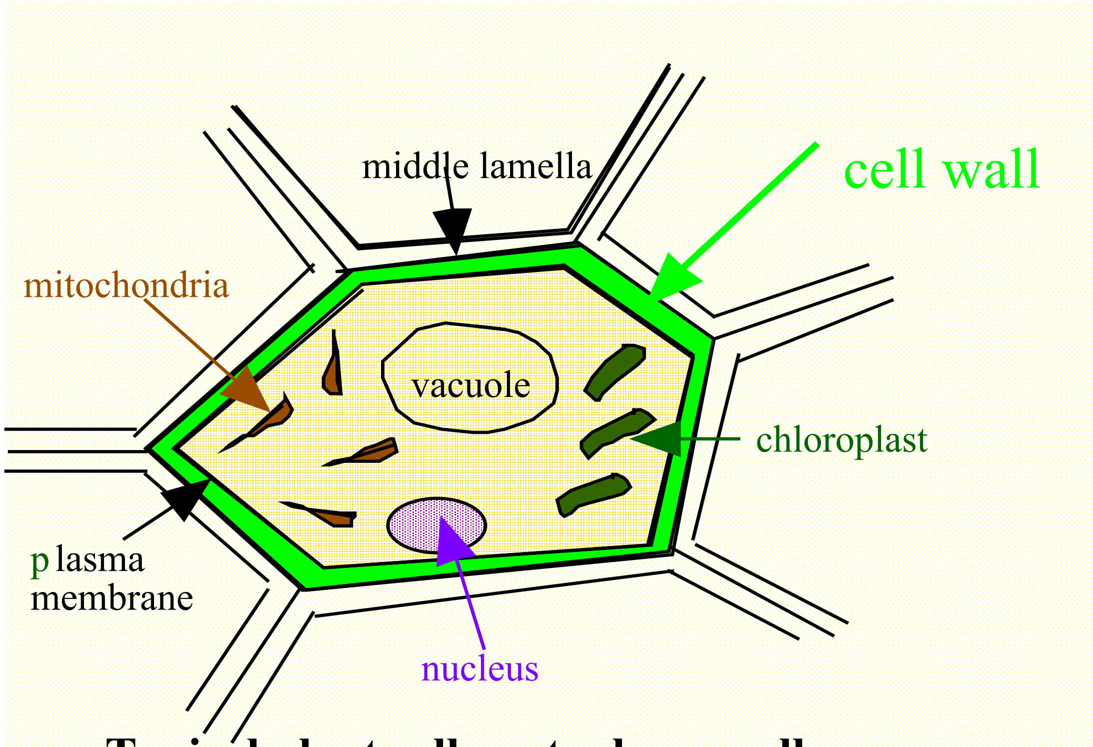
# Self Assembly of Cellulose in Plant Cell Walls

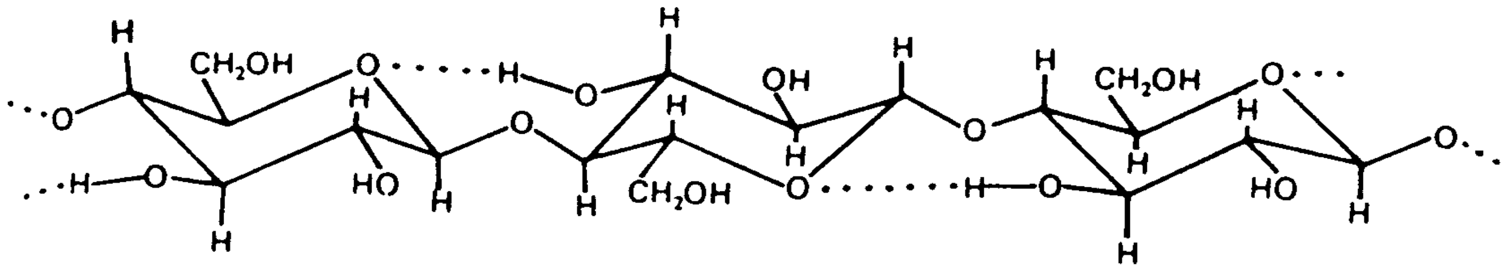
- **The main constituent is cellulose - a useful material for mankind.**
- **There is an awful lot of the material - ~$10^{11}$ tonnes of cellulose produced each year.**
- **Its role is vital in both supporting the cell and providing stiffness to the plant and protecting the plant from the external environment.**




**Typical plant cell - actual organelles Present depends on type of cell**

**Each cell wall is separated from the cell contents by the plasma membrane, and from neighbouring cells via the middle lamella.**

# Cellulose




- **Cellulose is a strongly hydrogen bonded polysaccharide.**

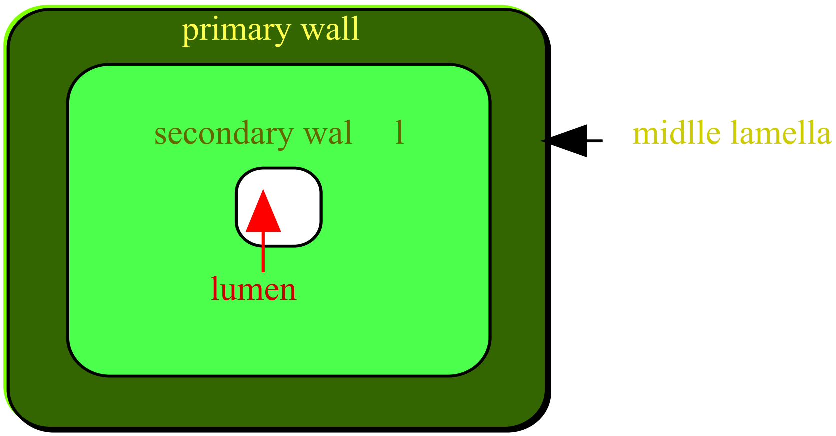
- **This is why it is difficult to dissolve, and unpleasant solvents are needed in the paper and textile industries.**

- **The hydrogen bonding also leads to a very stiff and straight chain.**

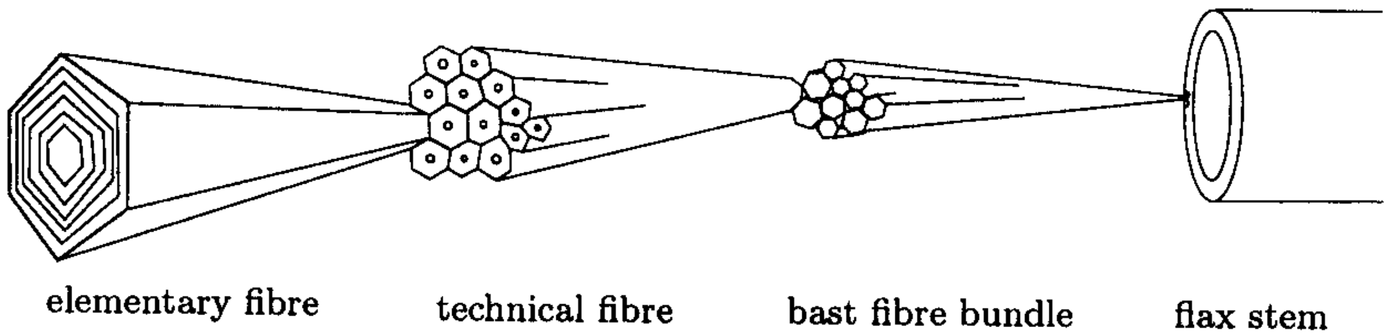
# Cell Wall Structure

- The middle lamella, primarily pectin, 'glues' neighbouring cells together.
- **Primary cell wall**,
- The first wall laid down during growth.
- This is soft and flexible so that the cell can expand during growth.
- It contains a mixture of biopolymers, with typically ~20-30% cellulose
- Once growth has stopped, the secondary cell wall is laid down, which provides structural support for the cells.
- **Secondary Cell Wall Structure**
- Some cells have very thick secondary cell walls, to provide maximum support.
- In the case of flax it can be µm in thickness (compared with ~100nm for the primary wall), and this was why flax was used for this study.
- Typical cellulose content is ~50%, though can reach ~100% for e.g. cotton.
- Structure is complex, and thought to consist of aligned layers of cellulose microfibrils in a general biopolymer matrix, with systematic misorientations between the layers.
- This structure is known as 'helicoidal'.

# Flax as  Model for the Secondary Cell Wall




- **Very thick secondary wall, comprising structures at different lengthscales.**




**Cell walls are made up of cellulose microfibrils (~70%) in a matrix of hemicelluloses (15%), pectins (10-15%), and lignins (2-5%), with a hierarchical structure.**

**The microfibrils inside the elementary fibres are µms long and ~3nm thick.**

# Helicoidal Structure

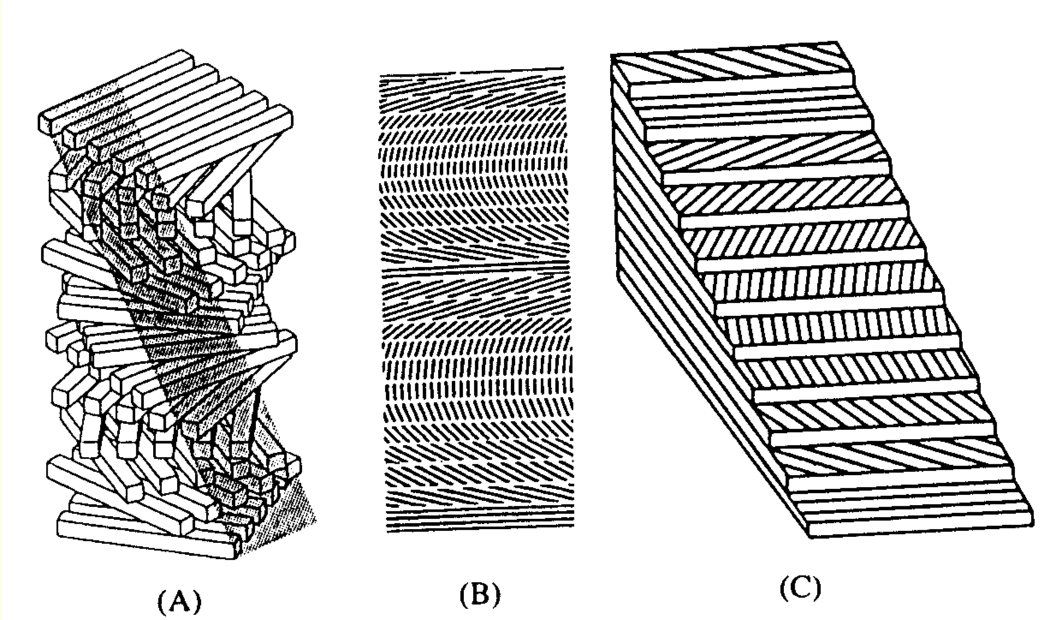
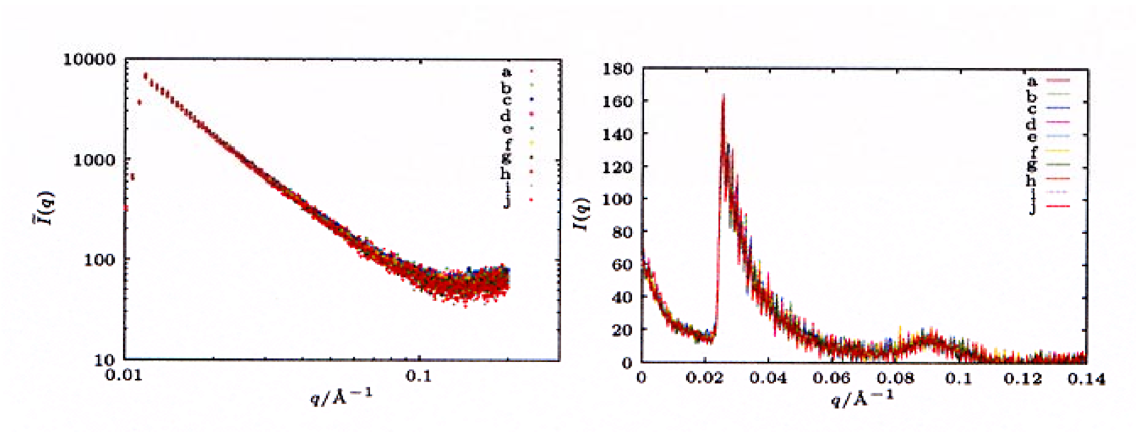



*Figure 4.16.* As for Figure 4.15, showing the ranks of arced patterns typical of helicoidal structure. The cellulose microfibrils are heavily stained. The system is cholesteric liquid crystalline and is an excellent example of gradation of pitch, of angular rotation, and of number of planes of microfibrils making up an arc. From Abeysekera and Willison (1990), by permission of Editions Scientifiques Elsevier, Paris, and of the authors.


- Like plywood - and for the same reason.
- Not having all layers with same orientation strengthens the material overall.
- Is often observed in oblique section as a series of arcs

# Uniaxial Tension Experiments on Flax

- **The flax can be stretched *in situ* and both the SAXS and WAXS patterns looked at.**
- **For the SAXS curves, no changes are seen on stretching dry fibres.**

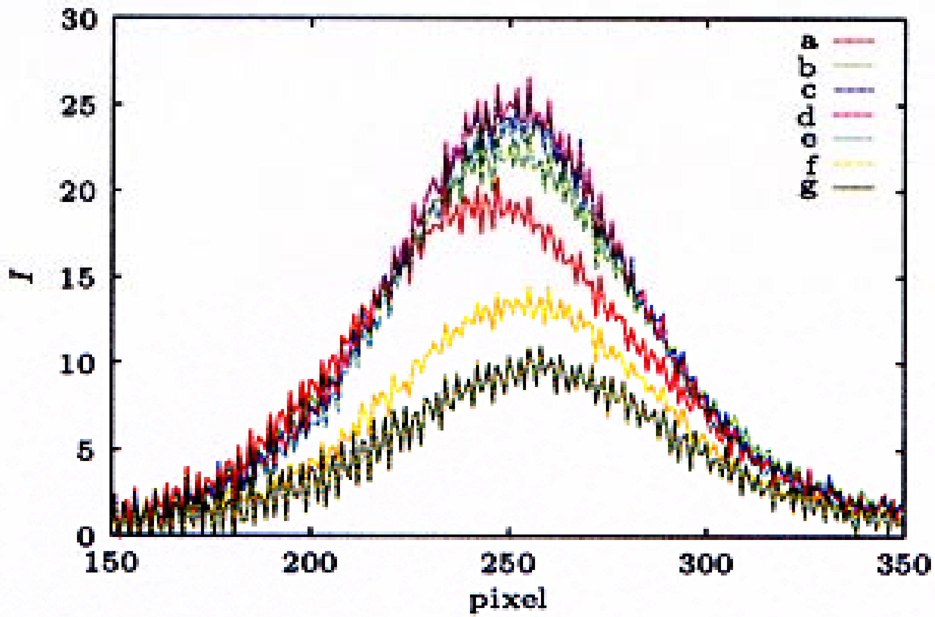


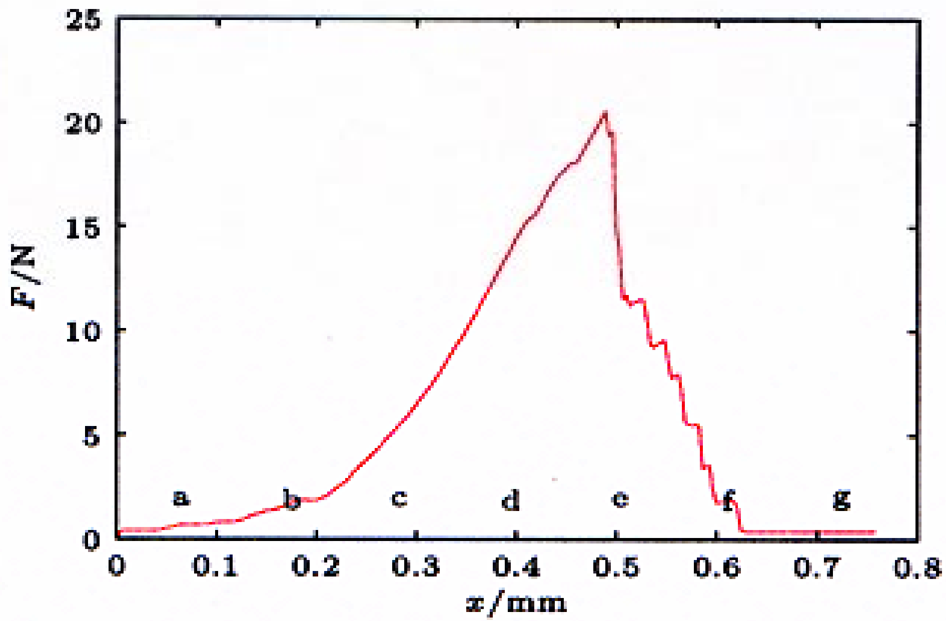

(a) Equatorial (b) Meridional

- **Even looking in detail, peak shape does not change - Reorientation of the microfibrils is not occurring.**

# WAXS Patterns during Stretching

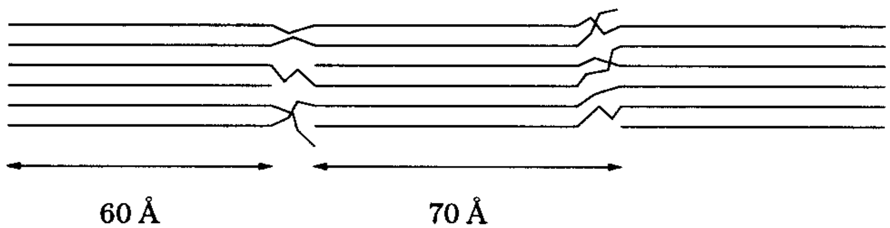
- In contrast to SAXS significant changes occur.
- The patterns below are for the 002 peak.
- Initially the peak intensity grows and shifts to slightly higher angles.
- After failure, the intensity falls again.



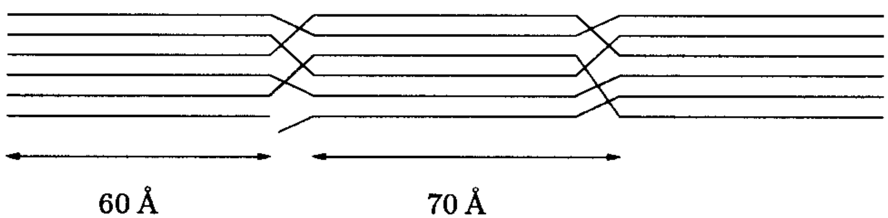



# Strain Induced Crystallisation

- **The most likely explanation for the increase in WAXS intensity is due to strain induced crystallisation, as discussed for rubbers during straining.**



(a)

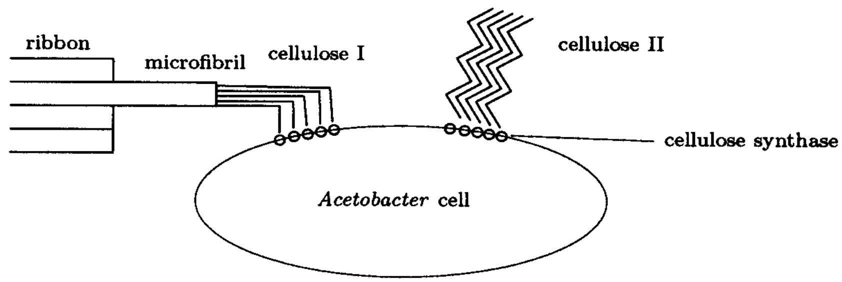


(b)

**It does not seem likely that stretching of the whole repeat is occurring, or changes would be seen in the SAXS.**
**So the nearly parallel chains in the amorphous regions must be being drawn into the crystals to increase the overall crystallinity.**

# Acetobacter

- **The bacterium *Acetobacter xylinium* produces cellulose.**
- **This is usually in the form of ribbons in the cellulose I modification, at a rate of ~2μm min$^{-1}$.**
- **Different conditions of temperature can promote tapes of cellulose II instead.**

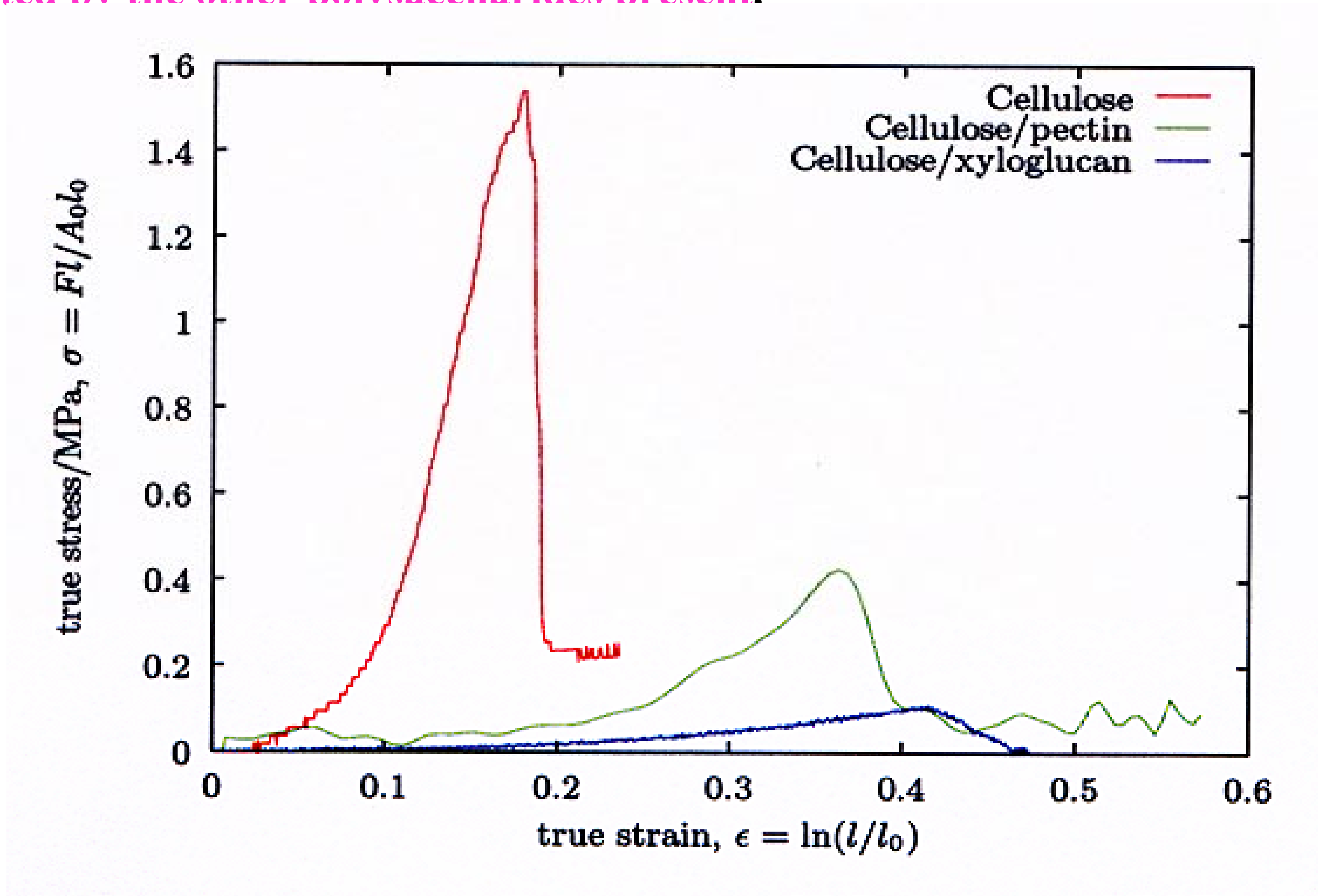



**By incubating the bacteria in a medium with other polysaccharides present, it is possible for the cellulose to incorporate these to produce a material more akin to an average cell wall.**

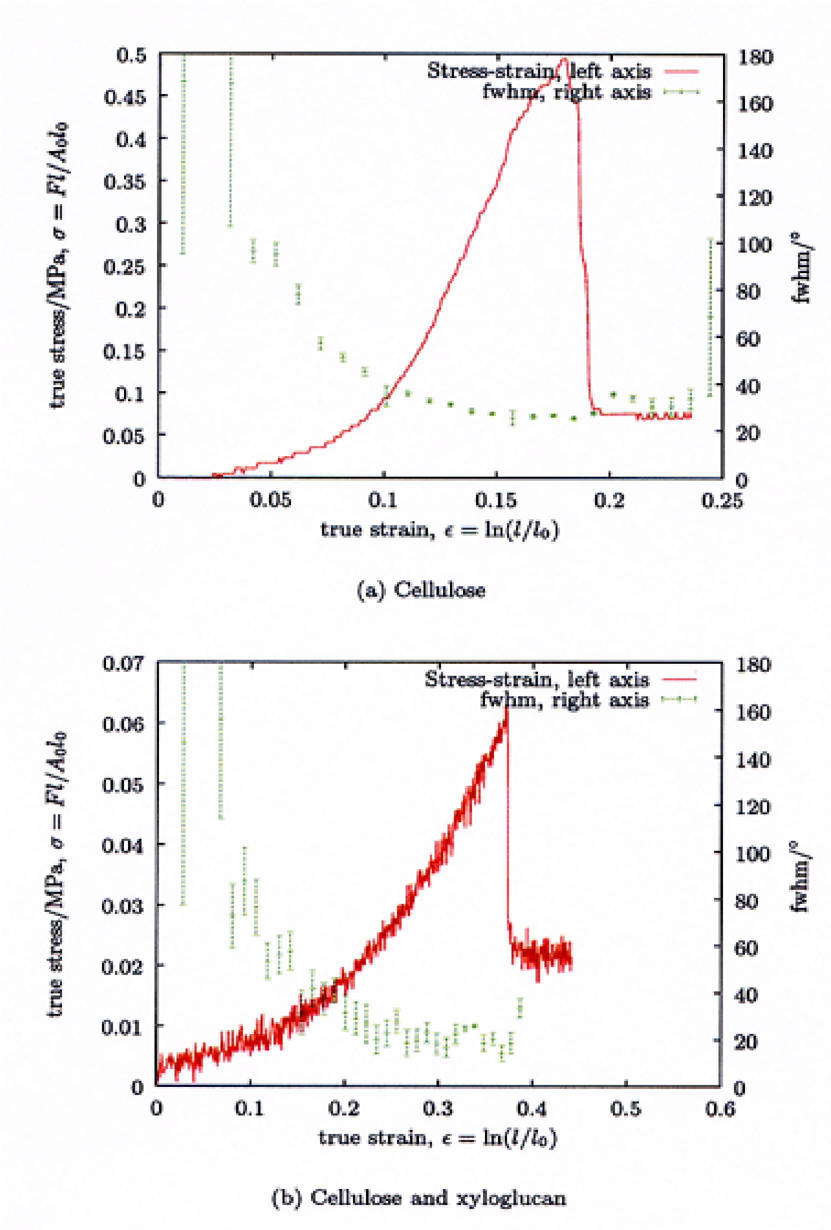
**Work has examined the effect of**
**Tamarind seed xyloglucan**
**Pectin**
**Pectin, subsequently removed with EDTA.**

# Mechanical Properties

- It has been shown that the mechanical properties of these cellulose composites is affected by the other polysaccharides present.



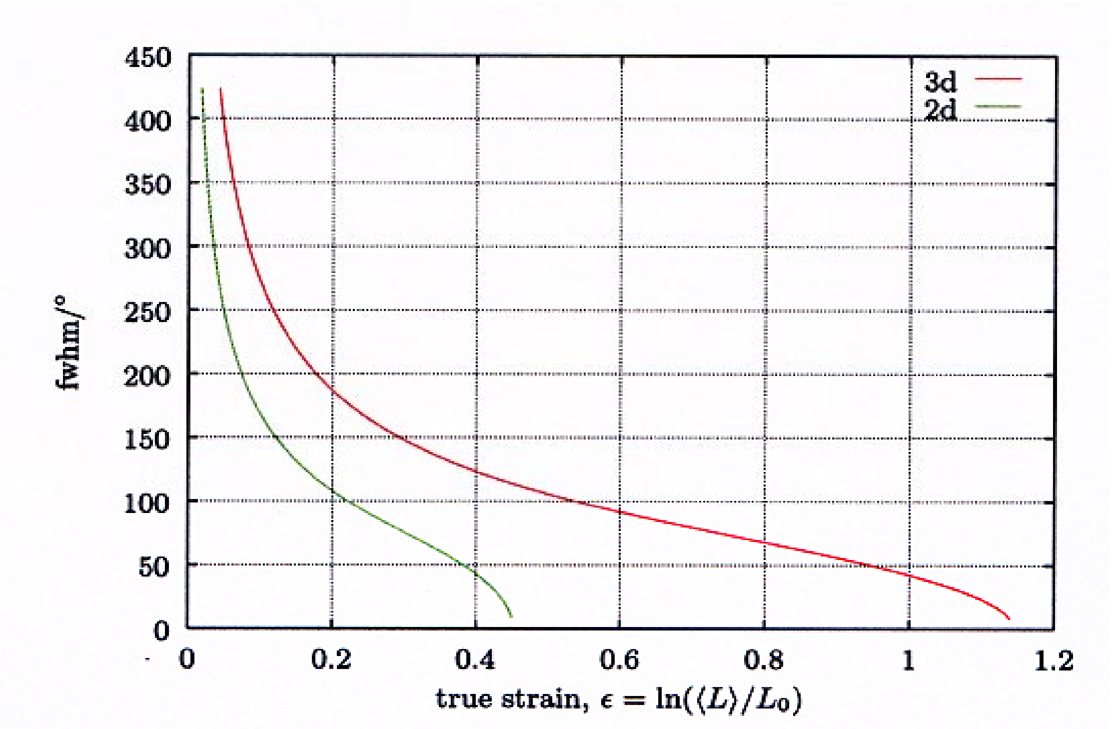
# Comparison of Reorientation of the Composites




- **Although the degree of extensibility varies, all composites show broadly the same reorientation behaviour.**
- **The width of the SAXS curves rapidly decreases, flattening off well before the maximum stress and failure.**
- **Differences in the mechanical properties cannot be attributed to differences in reorientation behaviour.**

# Possible Reasons for the Differences Between the Composites.

- Initially the scattering is isotropic, but reorientation does not proceed to complete alignment.
- Either entanglements or specific interactions between the cellulose microfibrils must be limiting the reorientation.




- This view is supported by modelling the reorientation as a function of strain for non-interacting rods.
- The curve shape is not at all the same as that observed experimentally.

# Conclusions on the Effect of Other Polysaccharides

- **The ability to reorient is essentially the same for all samples.**
- **But stress/strain curves are very different (although removing the pectin by CDTA treatment appears to have little effect).**
- **It is possible that the presence of the minor polysaccharides may de due to some sort of biological control during biosynthesis to affect mechanical properties.**
- **Xyloglucan has been shown to cause cross-linking, and this may affect the ability to form entanglements between neighbouring ribbons.**
- **The ribbons do not appear to behave as independent entities, and the number of crosslinks and entanglements appear to supply the crucial difference between the composites.**