NATURAL CELLULOSE-BASED HIERARCHIES:

CONCEPTS FOR NOVEL MATERIALS AND ADDED FUNCTIONALITY

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- Cellulose fibres from plants
- Advantages and limitations of cellulose fibres/nanofibres
- Cellulose fibres/nanofibres as reinforcement in composites
- Benefits of hierarchical structures
- Conclusions







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Sources of cellulose fibres and nanofibres



+ Bacterial Cellulose

Typical properties of cellulose nanofibres







Young's modulus (fibre direction) Tensile strength Density

Nanofibre diameter Nanofibre aspect ratio (L/d) 134 GPa 7.5 GPa 1500 kg/m³

50 ~ 200 nm 10 ~ 30 [Frone et al., 2011] [Eichorn et al., 2010]









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HOW CAN THESE PROPERTIES BE EXPLOITED EFFECTIVELY ????



Advantages of cellulose nanofibres (CNF)

High modulus and high specific modulus [compares well with glass, aramid an carbon]

High tensile strength

[theoretical strength of solids is of the order of E/10, CNF has a value of E/18]

Limitations of cellulose nanofibres

length diameter aspect ratio (L/d)

surface chemistry (compatibility with polymer matrix systems for composites)

loss of hierarchical organisation and limited control of fibre orientation (benefits of cell wall structure/density)

limited compressive strength because of fibre buckling

Length-diameter aspect ratio



Composite modulus for a unidirectional fibre composite as a function of cellulose nanofibre aspect ratio at a volume fraction of fibres of 50% (PP matrix)

$$L_{i} = \left(\frac{d}{\tau_{y}}\right) \left(\frac{E_{f}\sigma_{c}}{E_{c}^{continuous}}\right)$$

d = diameter τ_y = matrix shear strength E_f = fibre modulus E_c = composite modulus σ_c = composite tensile strength

Fibre orientation

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Cox Model (2D), 1952:
$$\overline{E} = \frac{E_f v_f}{3} \qquad \overline{G} = \frac{E_f v_f}{8} \qquad v = \frac{1}{3}$$
Cox Model (3D), 1952:
$$\overline{E} = \frac{E_f v_f}{6} \qquad \overline{G} = \frac{E_f v_f}{8} \qquad v = \frac{1}{4}$$
Tsai - Pgano Model (2D), 1968:
$$\overline{E} = \frac{3}{8}E_1 + \frac{5}{8}E_2 \qquad \overline{G} = \frac{1}{8}E_1 + \frac{1}{4}E_2$$

$E_f = Fibre modulus$

 E_1 , E_2 , G_{12} = Elastic and shear moduli of unidirectional discontinuous fibre composite

Fibre orientation, volume fraction and fibre/matrix modulus ratio



Dependence of Normalised Composite Modulus (random fibres) on fibre/matrix modulus ratio and fibre volume fraction.

 ${\sf E}_1$ is the Young's modulus of a continuous unidirectional fibre composite in the fibre direction

Fibre buckling in plant cell walls

















Benefits from hierarchical structures

- Compensation for limitations of unidirectional composite
- Cellular structures possible (low density)
- Beneficial fibre pre-stressing in tension (buckling)
- Control of swelling
- Multiple energy absorption mechanisms against fracture
- Modulation of multiple interfaces

Layered composite structures





Hygro- or thermal expansion of angleply composite structures Individual plies with non-zero coefficients of thermal expansion can create a laminate structure with zero thermal expansion coefficient

Similar effects are possible with hygro-expansivity





Energy absorption $\propto E\varepsilon_{failure}^2$

Dependence of Young's modulus and failure strain in wood as a function of microfibrillar angle in S2





Fig. 4. Tensile failure in Sitka spruce (*Picea sitchensis*). Folding inward of the S2 wall as a result of cracks parallel to the microfibrillar direction.





Glass sponge Euplectella – hierarchical architecture

Layered structure as a defense against brittle fracture

Aizenberg et al., 2005; Weaver et al., 2007; Fratzl,2010





Semi-ductile fracture of nacre in tension (95% brittle ceramic) resulting from hierarchical organisation and control of interfaces



Hierarchy of nacre











POLYMER MATERIAL IN TENSION

Transition from semi-brittle to ductile fracture induced by layered hierarchies





Jeronimidis, 1978

Bolton & J.A. Petty, 1975

Preventing fracture from bordred pits via modulation of fibre orientation

GROWTH AND HIERARCHICAL STRUCTURES







(b)



(C)













The role of microtubules for cellulose fibre organisation in cell walls



CONCLUSIONS

- We cannot replicate growth and all its associated control, sensing and modulation mechanisms which lead to successful biological hierarchical structures
- However, we can extract principles of good composite design from biological systems which are continuously adapting and compromising
- Introducing levels of hierarchy can provide better utilisation of fibres and achieve higher levels of functionality

"MATERIAL" LEVEL

Fibres, Matrices, Anisotropy, Heterogeneity



"STRUCTURE" LEVEL

Hierarchies, Dimensions, Geometry, Shape

FUNCTIONAL INTEGRATION AT THE "SYSTEM" LEVEL



