

**A!**

Aalto University  
School of Chemical  
Technology

# Fibres and nanofibers: structure-property relationships

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10<sup>th</sup> October 2023

CHEM-E2140

# Assignment

**Take a couple of minutes to answer the “Before the lecture” questions in front of you**

# Learning outcome

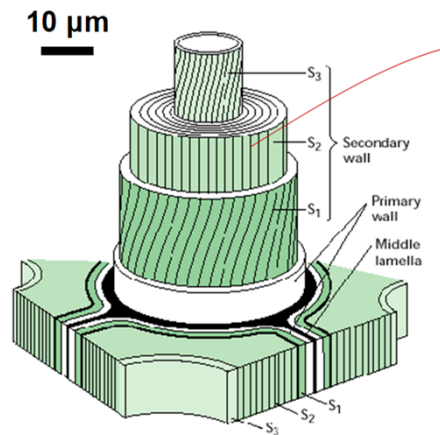
- Basic idea on what in the structure of fibres influences the properties of macroscopic objects made of fibres
- Awareness of quantitative theories on (nano) fibre networks
- Knowledge on how the presence and absence of water affects the properties of fibres and fibre products

# Contents

- (1) Plant fibres vs. others
- (2) Properties of single fibres and nanofibres
- (3) Fibre network: basic theories
  - Cox theory
  - Page equation
  - Gibson-Ashby theory
- (4) Case studies on structure-property relationship:
  - Effect of moisture on paper
  - Effect of removal of water on fibres and fibre networks
  - Effect of hemicellulose on the strength of nanopaper
  - Nanofibres and nanopaper

# Plant fibres vs. other fibres

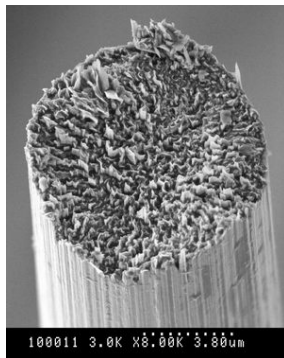
- All plant fibres are, by definition, composite structures:
  - Cellulose/hemicellulose/lignin



- Cellulose is the main structural (load-bearing) component
- Hemicellulose/lignin matrix gives flexibility and controls the moisture content
- Lignin protects against pathogen

# Plant fibres vs. other fibres

- Many synthetic fibres are monocomponent and homogeneous structures
- Most regenerated cellulose fibres are also monocomponent and homogeneous structures
- All fibres can be used as reinforcing phases in composites
- However, few fibres are composites by themselves



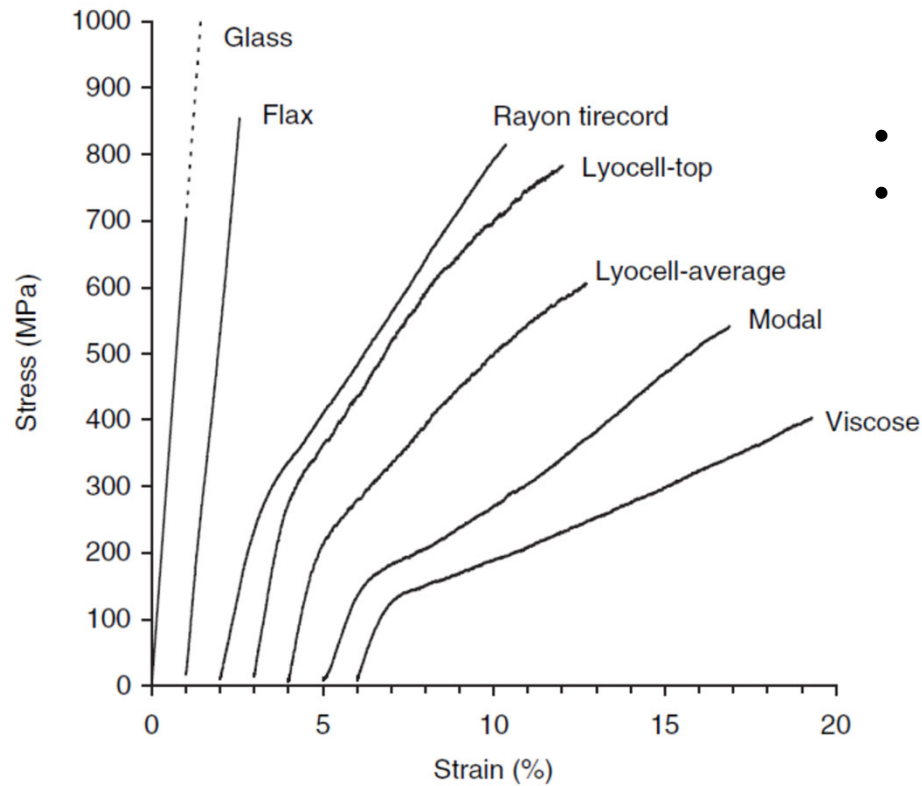
Carbon  
fibre

Viscose  
fibres



# Properties of single cellulose-based fibres

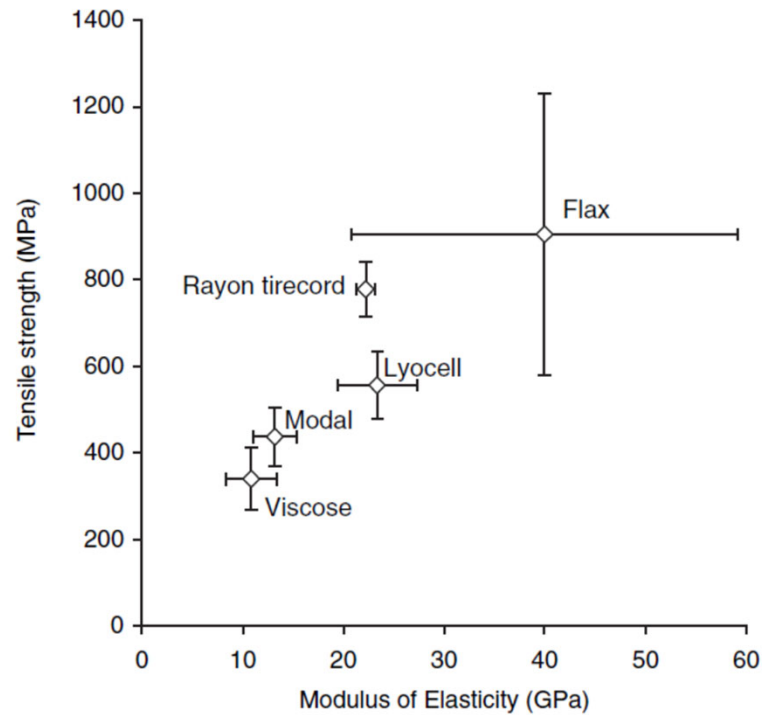
# Comparison of tensile properties



- Glass fibre goes up to 3000 MPa
- However, the density of glass fibres is ~2.5 whereas cellulose fibres possess typically a density of 1.5



# Tensile strength vs. modulus



- Natural cellulose fibres (like flax) are typically superior in tensile strength and modulus compared with regenerated cellulose fibres

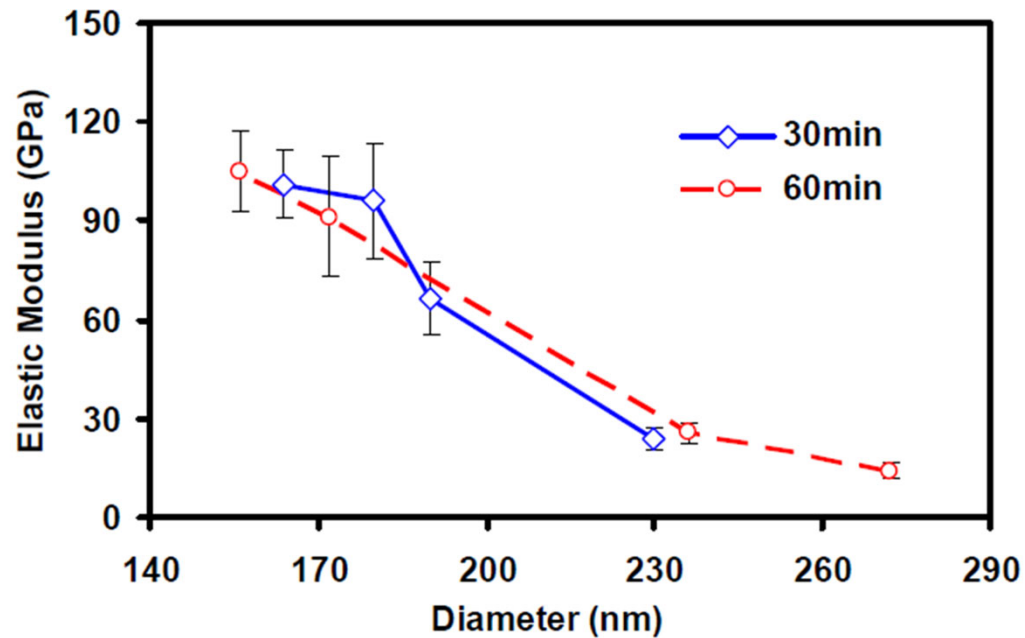
# Single fibre properties – comparison

**Table 1.**

Average tensile properties of regenerated cellulose and reference fibres (E – modulus of elasticity,  $\sigma_f$  – tensile strength,  $\varepsilon_f$  – elongation at break,  $W_{ef}$  – work to fracture, for lyocell top values are given in brackets).

Fibre	E (GPa)	$\sigma_f$ (MPa)	$\varepsilon_f$ (%)	$W_{ef}$ ( $J \cdot 10^{-3} \text{ mm}^{-3}$ )
Viscose	$10.8 \pm 2.5$	$340 \pm 73$	$15.4 \pm 2.2$	32.7
Modal	$13.2 \pm 2.2$	$437 \pm 69$	$10.4 \pm 1.8$	37.2
Lyocell	23.4 (30.5) $\pm 3.9$	556 (790) $\pm 78$	$8.7 \pm 1.6$	34.5 (47.1)
Rayon tirecord	$22.2 \pm 1.0$	$778 \pm 62$	$10.7 \pm 1.4$	40.8
Flax	$40.0 \pm 19.2$	$904 \pm 326$	$1.4 \pm 0.2$	6.7
Glass	$70.0 \pm 9.3$	$3000 \pm 356$	$4.3 \pm$	54.3

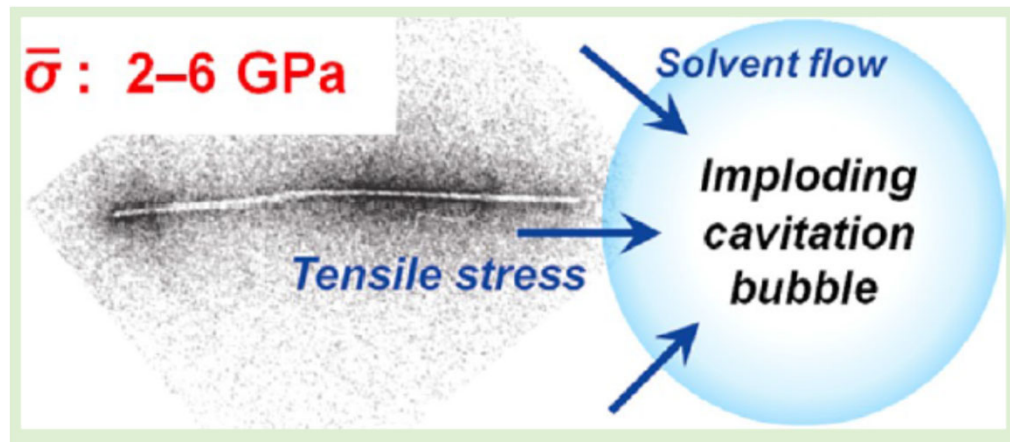
# Lyocell modulus – how fibre diameter affects the modulus



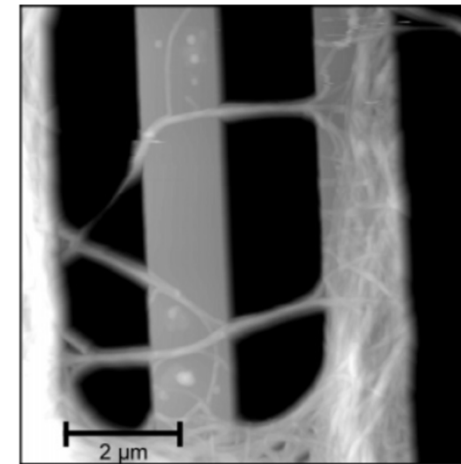
- Fibre diameter (increased surface area) has a drastic effect on the fibre modulus

# Cellulose nanofibres

- Strength and modulus depend on the method used for measuring and interpreting but in general they are considered very high for individual fibrils

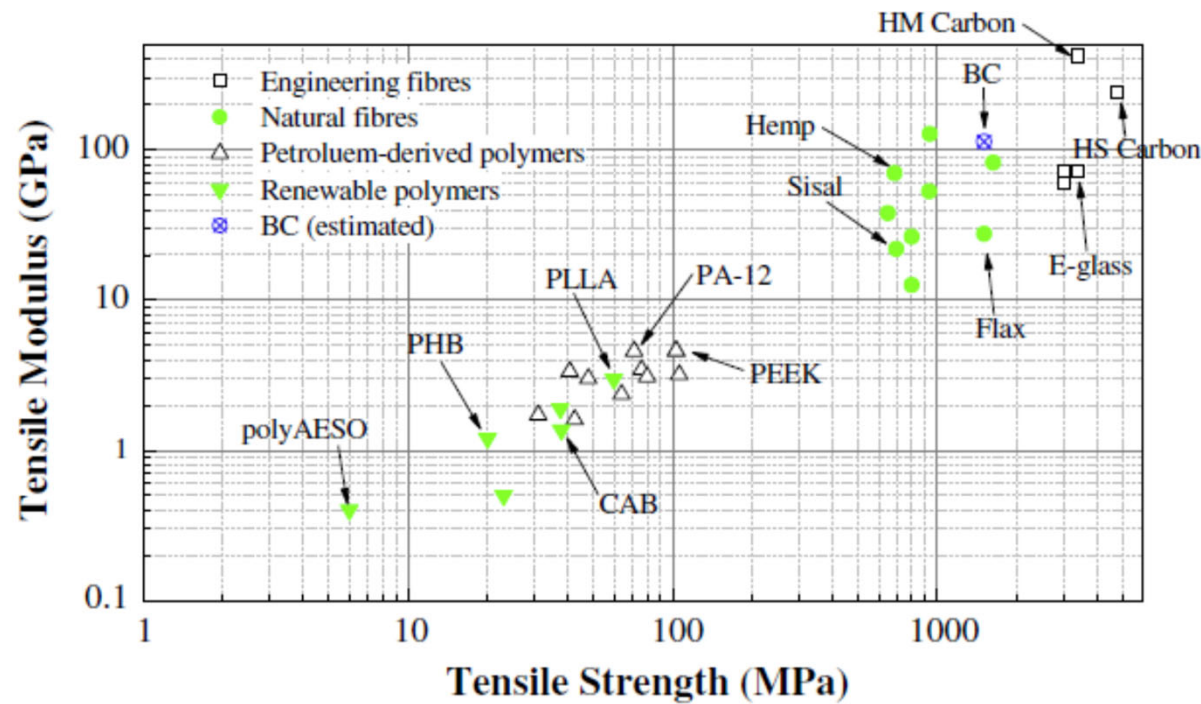


Tensile strength for TEMPO-oxidized nanofibres: 2-6 GPa



Elastic modulus for bacterial cellulose nanofibres: ~80 GPa

# Comparison of strength/modulus of various fibres



BC Bacterial cellulose  
 PLLA Polylactic acid  
 PEEK Polyether ether ketone  
 PHB Polyhydroxybutyrate  
 CAB Cellulose acetate butyrate  
 AESO Acrylated epoxidized soybean oil  
 HS High strength  
 HM High modulus

# Theoretical strength of crystalline cellulose

**Table 3**  
Theoretical tensile strength of cellulose crystals.

Calculation assumptions	$\sigma_{\text{theoretical}}$ (MPa)
Stress to cause cohesive fracture based on intra-chain link energy	7340
Stress to cause chain scission based on potential energy function	22600 <sup>1</sup> and 17150 <sup>2</sup>
Stress to cause separation of chains if ends are all in one transverse plane	280
Stress to cause sliding fracture	1260 <sup>1</sup> and 1190 <sup>2</sup>
Stress normal to chain axis to rupture hydrogen bonds	300
Ultimate shear strength	323

Strength of crystalline cellulose is theoretically extremely high.

# Nanopaper strength

- Nanopaper means a network (paper) made of cellulose nanofibres

Table 2. Physical and Average Mechanical Properties for MFC Films Prepared of MFC with Different DP<sup>a</sup>

material	porosity [%]	modulus, $E$ [GPa]	slope in the plastic region, $n$ [GPa]	yield stress, $\sigma_{0.2}$ [MPa]	tensile strength, $\sigma_c$ [MPa]	strain-to-failure, $\epsilon_c$ [%]	work to fracture, $W_A$ [MJ/m <sup>3</sup> ]
DP-410	20	13.7 (0.3)	- <sup>b</sup>	81.5 (4.7)	129 (8.7)	3.3 (0.4)	3.0 (0.5)
DP-580	24	10.7 (1.2)	1.27 (0.13)	83.6 (2.1)	159 (16.4)	6.4 (1.7)	7.1 (2.5)
DP-820		10.4 (0.5)	1.50 (0.07)	83.6 (2.8)	181 (12.7)	7.4 (1.5)	9.1 (2.3)
DP-1100	28	13.2 (0.6)	1.28 (0.16)	92.2 (5.2)	214 (6.8)	10.1 (1.4)	15.1 (1.9)

<sup>a</sup> The values in parentheses are the sample standard deviations. <sup>b</sup> Due to low  $\epsilon_c$ , the plastic region is limited and this value can not be calculated.

However, the strength of crystalline cellulose is not realized even in the highly dense nanopapers.

# Presemo

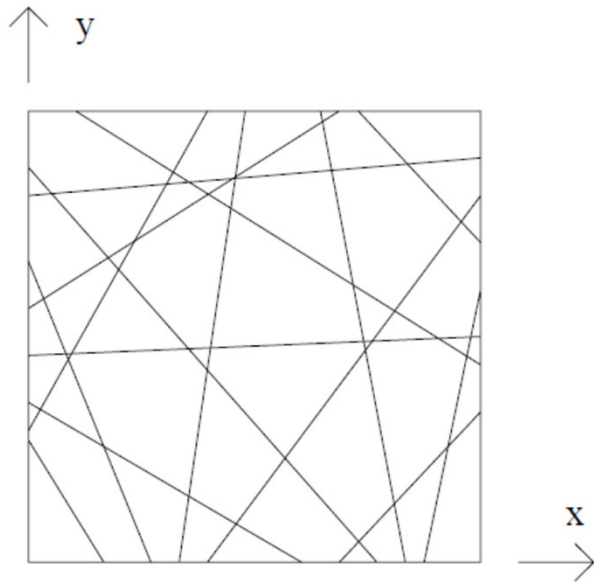
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# Fibre network

- Cox
- Page
- Gibson-Ashby

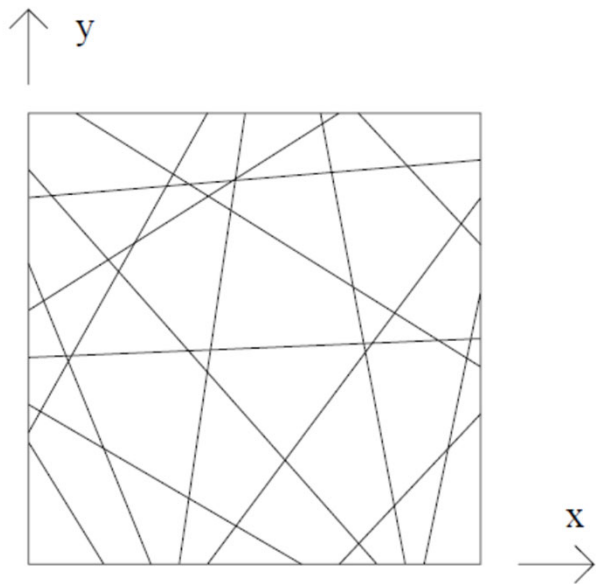
# Cox theory



Preconditions:

- Long, thin, straight fibres
- Uniform network
- Homogeneous strain field
- Fibres carry axial load only
- Fibres do not interact with each other

# Cox theory

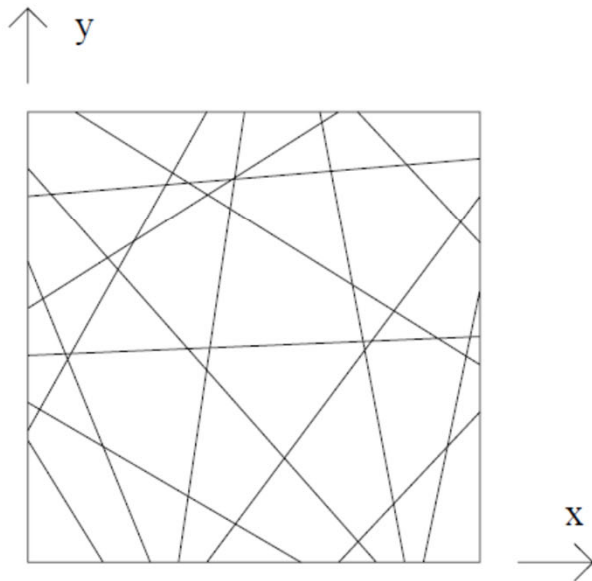


Strain ( $\epsilon$ ) is a vector and is related to strain in directions  $x$  and  $y$  as well as to angle of fibre around its own axis ( $\gamma$ )

$$\epsilon = (\epsilon_x, \epsilon_y, \gamma_{xy})$$

# Cox theory

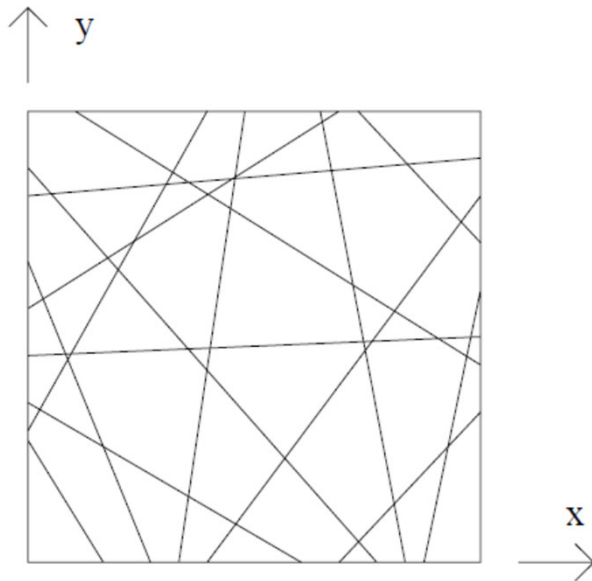
$$\epsilon = \epsilon_x \cos^2 \alpha + \epsilon_y \sin^2 \alpha + \gamma_{xy} \cos \alpha \sin \alpha$$



Axial strain ( $\epsilon$ ) in a fibre inclined at an angle  $\alpha$  to the x-axis

# Cox theory

$$F = E_f A_f (\epsilon_x \cos^2 \alpha + \epsilon_y \sin^2 \alpha + \gamma_{xy} \cos \alpha \sin \alpha)$$



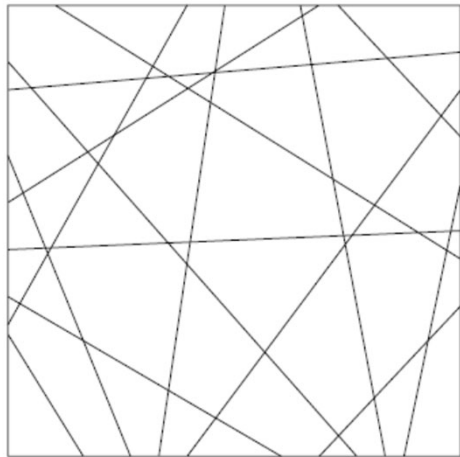
Force (F) on a fibre  
 $A_f$  is the cross-sectional area

The equation is derived from  
Hooke's law

# Cox theory

$$f(\alpha) = \frac{1}{\pi}(1 + a_1 \cos 2\alpha + a_2 \cos 4\alpha + \dots + b_1 \sin 2\alpha + b_2 \sin 4\alpha + \dots)$$

↑ y



Fibres can be presented as a matrix  
 $a_1, a_2 \dots$  are coefficients

$$\int_0^{\pi} f(\alpha) d\alpha = 1$$

For an isotropic network  $f(\alpha)=\pi$

# Cox theory

After matrix algebra, we derive the value K:

$$K = A_f E_f \rho = \frac{\rho_s}{\rho_f} E_f$$

where

$A_f$  is the cross-sectional area

$E_f$  is the elastic modulus

$\rho_s$  is the density of fibre network

$\rho_f$  is the density of a fibre

Network values:

$$E = \frac{K}{3} \quad \text{Elastic modulus}$$

$$G = \frac{K}{8} \quad \text{Shear modulus}$$

$$\nu = \frac{1}{3}, \quad \text{Poisson's ratio}$$

# Notes on Cox theory

- Seminal theory for fibre networks in general
- Works for well-bonded networks of long fibres
- Modulus values from Cox theory can be viewed as theoretical upper limits for cellulosic fibre networks
- In practice the modulus values predicted by the Cox theory are never reached for cellulosic fibres



# Page equation

$$\left[ \frac{1}{T} \right] = \left[ \frac{9}{8Z} \right] + \left[ \frac{(12g \cdot C)}{(P \cdot l \cdot b \cdot RBA)} \right]$$

Cannot be measured easily



- l = fiber length (length)
- b = fiber-fiber bond strength (N/m<sup>2</sup>)
- RBA = relative bonded area (unit less)
- g = gravitational constant -(length/second<sup>2</sup> = 9.8 m/s<sup>2</sup>)
- T = tensile breaking length (length)
- Z = zero span tensile (length)
- C = fiber coarseness (weight/length)
- P = fiber perimeter (length)

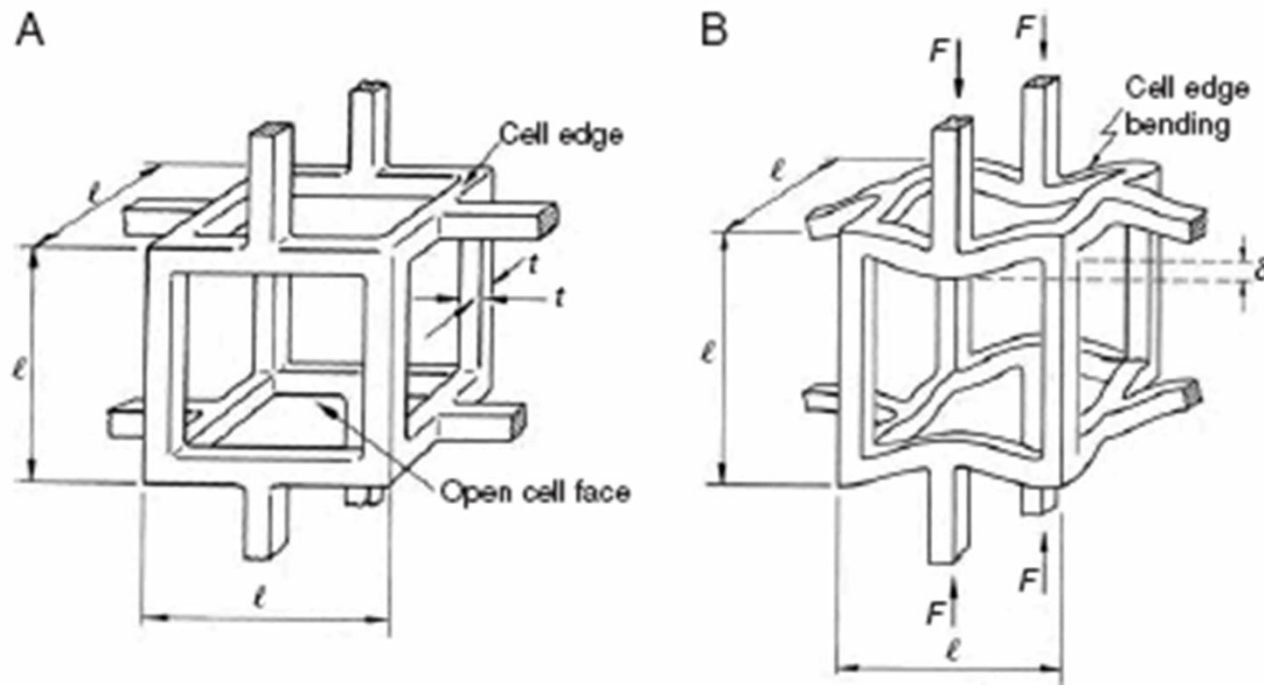
# Notes on Page equation

$$\left[ \frac{1}{T} \right] = \left[ \frac{9}{8Z} \right] + \left[ \frac{(12g \cdot C)}{(P \cdot l \cdot b \cdot RBA)} \right]$$

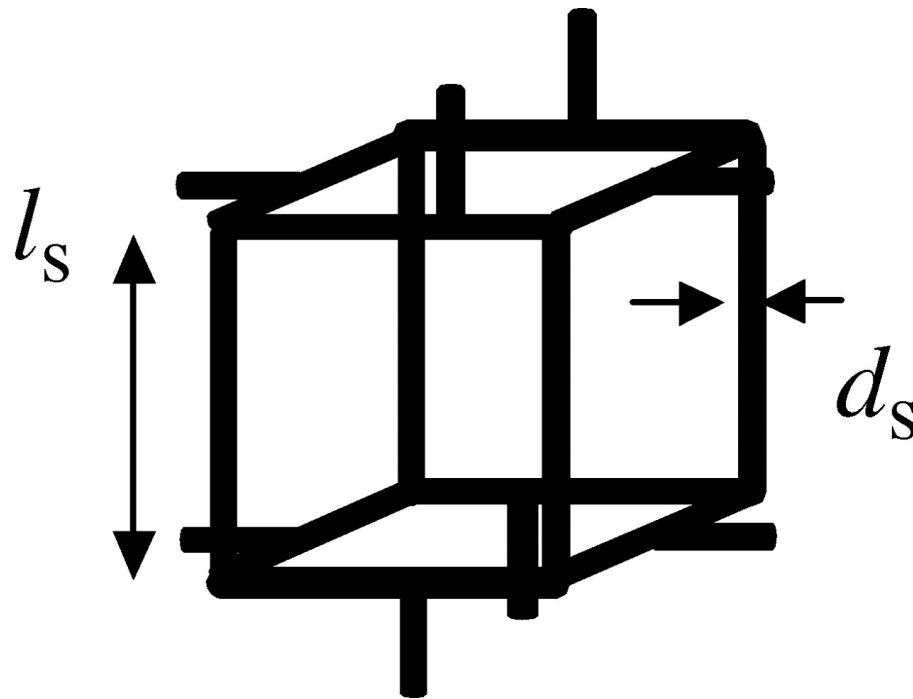
- Relative bonded area can be approximated from light scattering measurements because more inter-fibre bonds scatter less light
- Works well for papers from chemical pulp fibres, but also nanopapers have recently been well-described by the Page equation
- Although the Page equation was designed for paper (pulp fibres), it works mainly for relatively straight, unbroken fibres; they should be mostly free from kinks and curls

# Gibson-Ashby theory for cellular solids

Fibrillar networks can be approached as cellular solids



# Gibson-Ashby theory for cellular solids



$$\frac{E^*}{E_s} = \left\{ \frac{\rho^*}{\rho_s} \right\}^2$$

$E_s$  – Modulus of a fibril

$\rho_s$  – Density of a fibril

$E^*$  – Modulus of a film

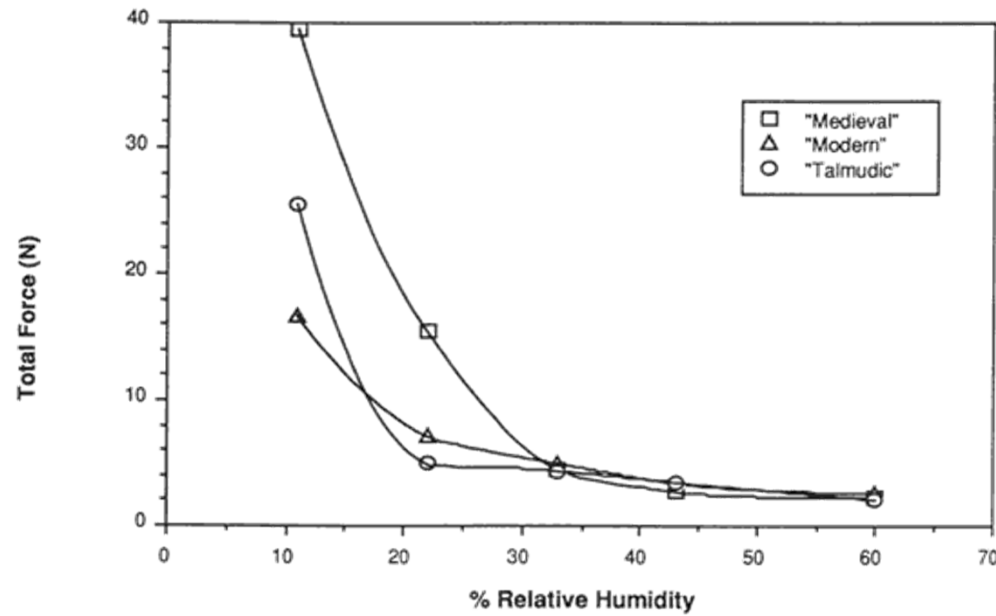
$\rho^*$  – Density of a film

# Presemo

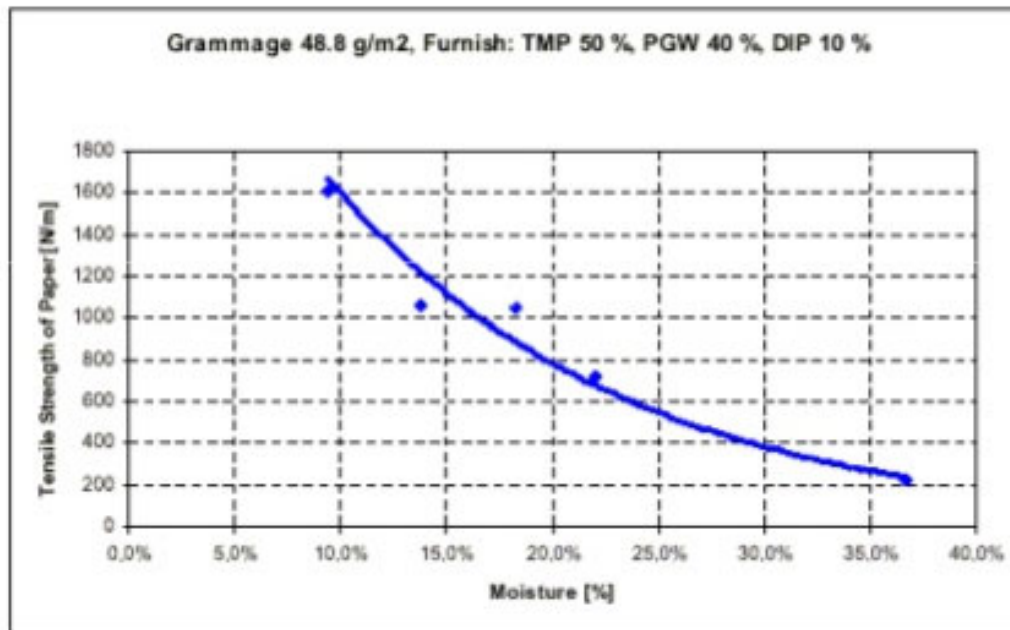
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# Simple case study: effect of moisture on paper strength

# Tensile strength goes down with increasing relative humidity



# Tensile strength decreases with increasing moisture content



- Notwithstanding the paper grade (historic, newsprint, art paper etc.), the detrimental effect of humidity on paper strength is clear

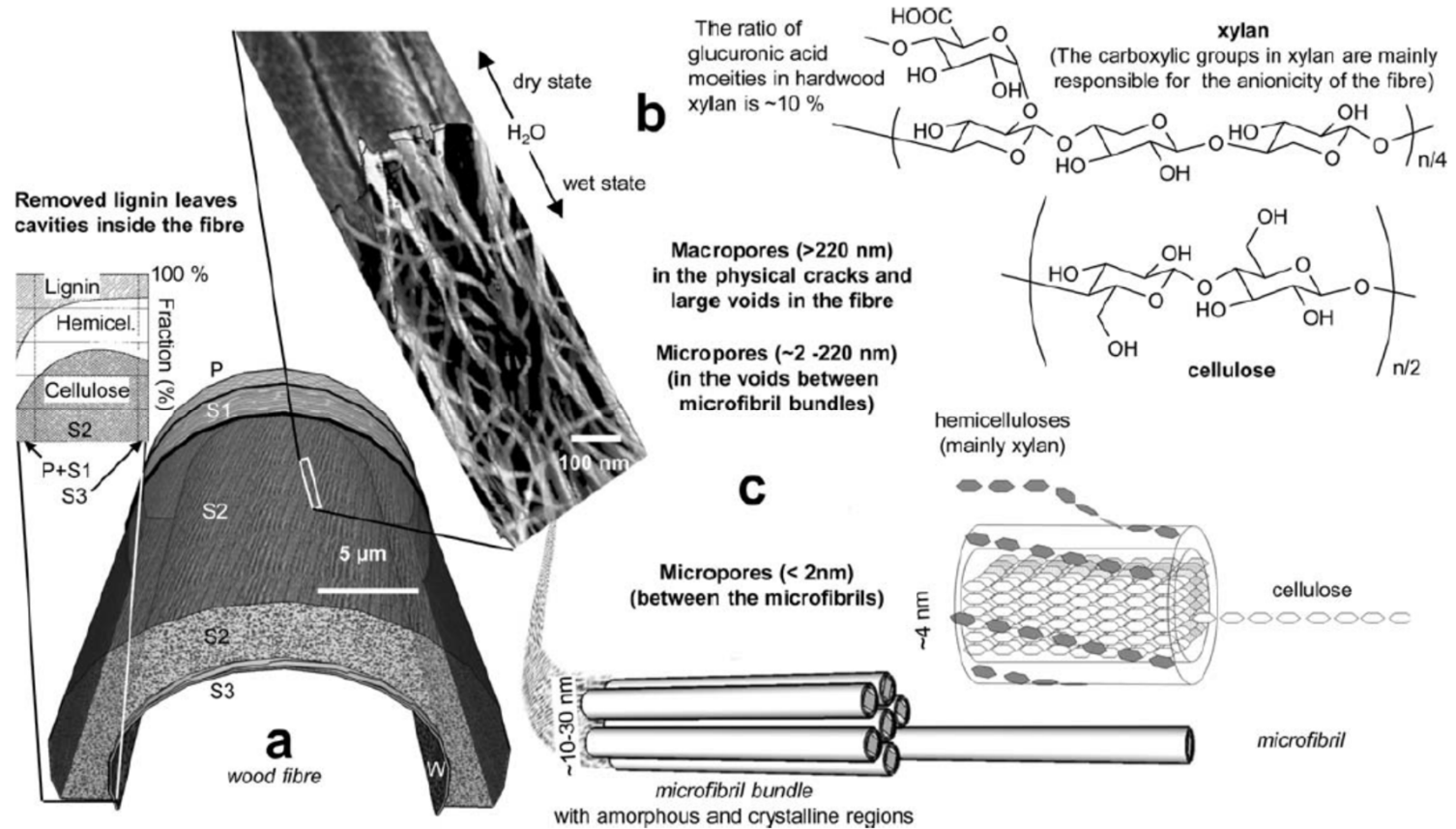


# Notes on humidity effect

- The effect of humidity, i.e., added moisture on a paper sheet is unambiguous: tensile strength goes down
- The reason for decreased tensile strength is the hydrophilic nature of cellulose: water penetrates between the fibre-fibre bonds and reduces their strength; moreover, water penetrates between the microfibrils and makes the fibres softer

# Case study on fibre networks: porosity of cellulose fibres

# Swelling of chemical pulp fibres



# Swelling of chemical pulp fibres

Verbal summary of the previous slide:

- Pulp fibres are full of pores because lignin has been removed from between cellulose microfibrils
- However, the pores exist only in presence of water; when dried, the microfibrils collapse together and the pores do not exist
- In other words, the presence of water-filled pores is equal to swelling of the fibre
- Water is attracted to cellulose because of its OH-groups but the presence of charged groups (like  $\text{COO}^-$  in xylan) strongly increases water sorption

# How to measure swelling/porosity?

The most straightforward measure is to determine the water retained in fibres, i.e., water retention value (WRV):

$$WRV = \frac{m_1}{m_2} - 1 \quad [1]$$

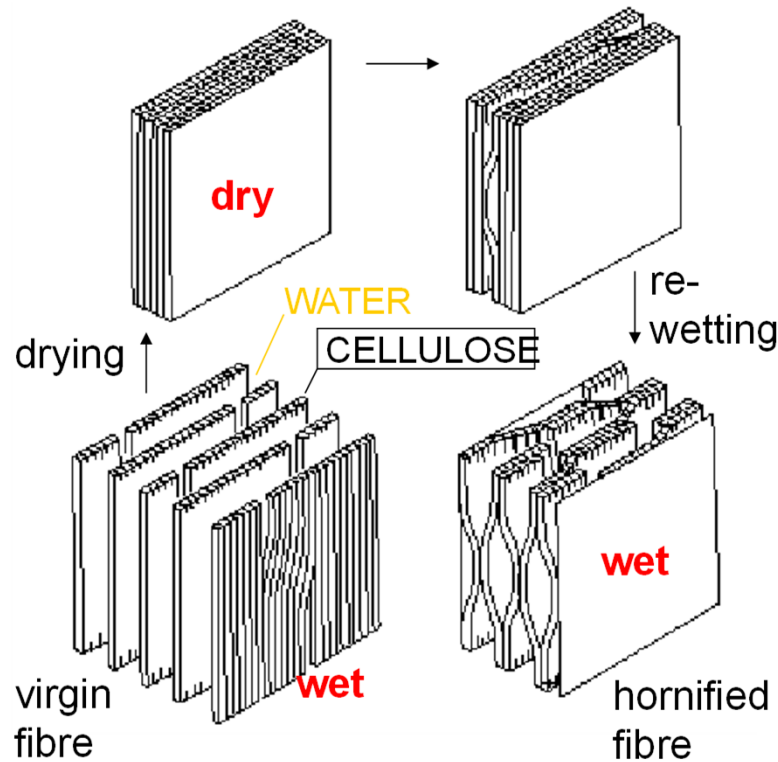
where

$m_1$  is the mass of the centrifuged wet test pad, in grams;

$m_2$  is the mass of the dry test pad, in grams.

Before the measurement, free water is removed by centrifugation, leaving behind the water bound (retained) in the cell wall of the fibre

# What happens when fibres are dried?



- When paper is recycled it needs to be slushed to pulp **in water**
- Rewetting of the fibre induces irreversible changes
  - Fibres do not swell to the same extent as they used to before drying (hornification)
  - Flexibility of the fibre is partially lost

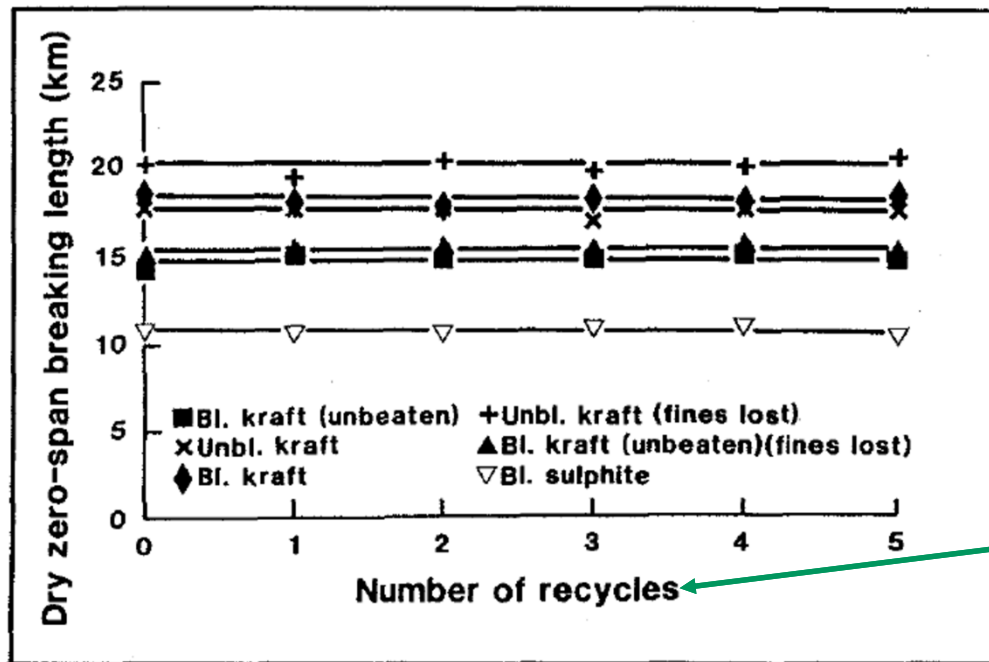
# Results of hornification: aggregation of cellulose microfibrils in fibre

**Table 1.** The Lateral Dimensions of Fibrils and Fibril Aggregates Before and After Drying \*

Sample	Average lateral fibril dimension (nm)		Average lateral fibril aggregate dimension (nm)		Hemicellulose (% on dry wood)
	Never-dried pulp	Dried handsheets	Never-dried pulp	Dried handsheets	
Kraft cook (H factor 2000)	4.8	4.8	18.1	23.1	10
Kraft cook (H factor 1600)	4.5	4.8	17.9	21.4	17
Kraft cook (H factor 1300)	3.9	4.5	15.4	17.6	22

\* Adapted from Hult *et al.* 2001; Copyright 2001 with permission from Elsevier

# Results of hornification: strength of single fibres

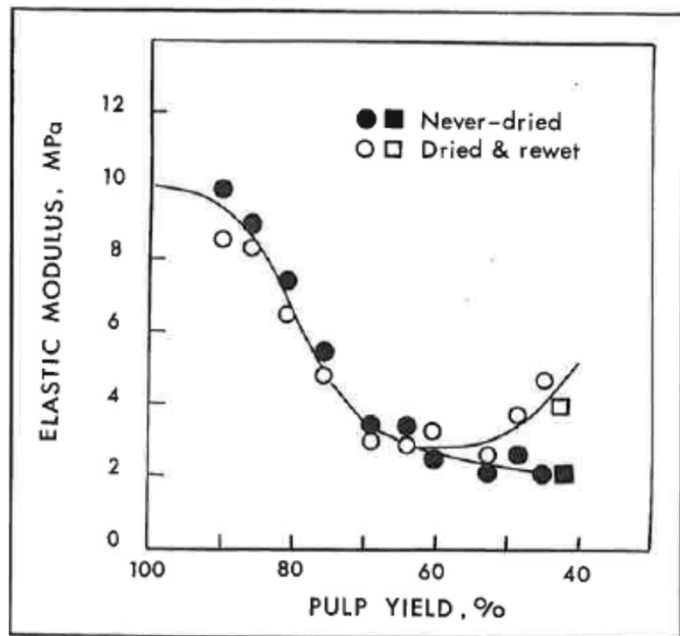


**Note:** Hornification does not affect the tensile strength of single fibres (as measured by zero-span measurement)

Number of drying steps

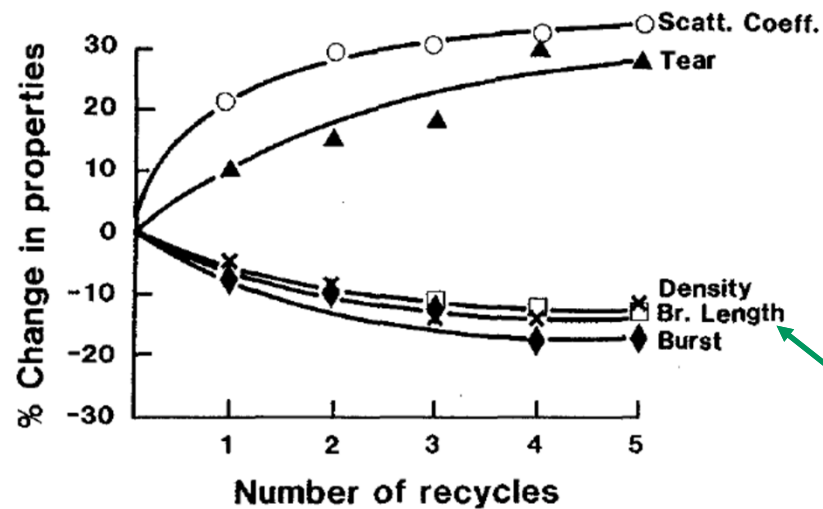


# Results of hornification: elasticity of single fibres



Hornification affects the elasticity (plasticity) of single fibres when the lignin content of the pulps is very low (i.e., pulp yield is low)  
→ Drying makes fibres stiffer when they consists of mainly cellulose and hemicellulose

# Results of hornification: loss of tensile strength in paper sheets (fibre network)



- Fibres become stiffer because of reduced swelling
  - Less conformation for favourable fibre-fibre bonds
  - Reduced tensile properties

Correlates with tensile strength

# Notes on hornification

- Many factors affect the changes in fibre morphology upon drying/rewetting; microfibril aggregation is just one of them
- For example, collapse of the hollow lumen plays a big role in the properties of the dried fibre and the subsequent fibre network
- Moreover, the effects of hornification are not straightforward: for example, reduced swelling is favourable for dewatering in the paper machine
- Many effects of hornification can be reversed by, e.g., beating fibres

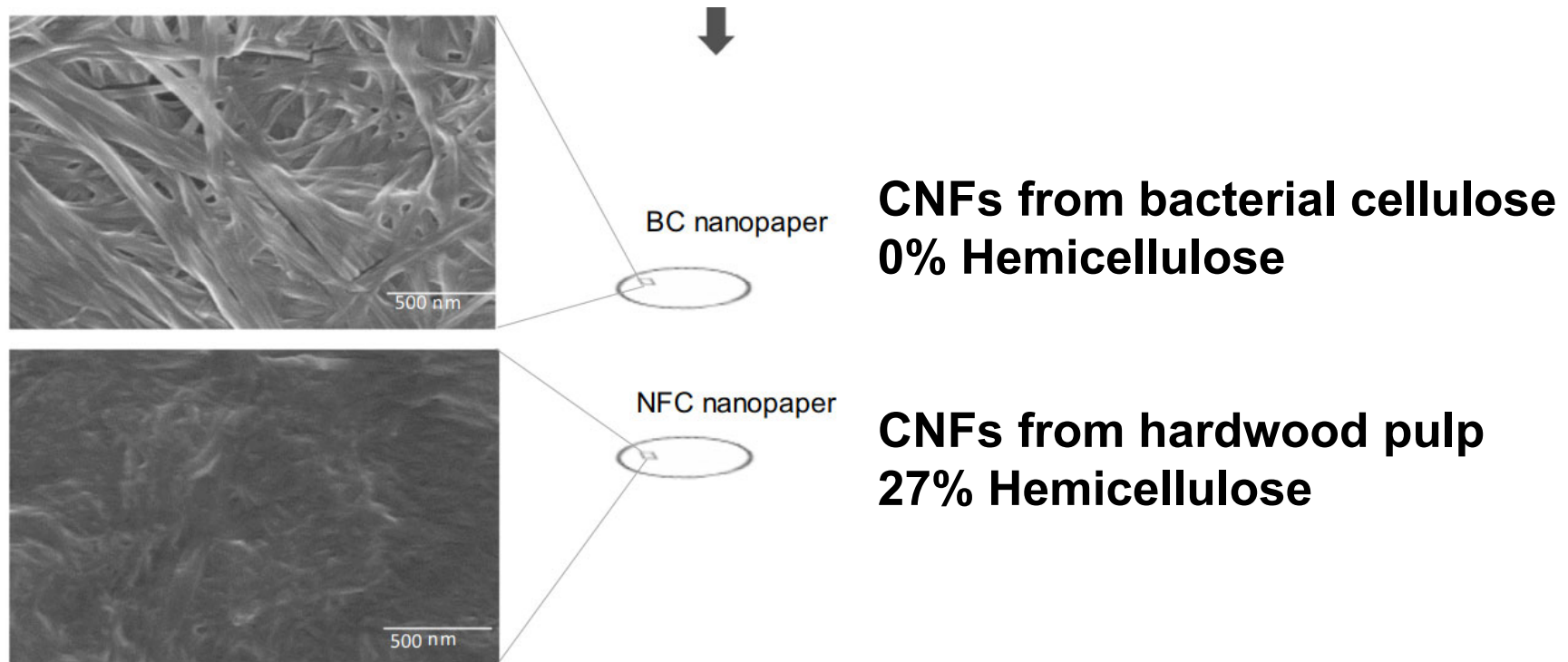
Lesson learned: structure-property relationship of native fibres is a very complex one – which structure affects which property

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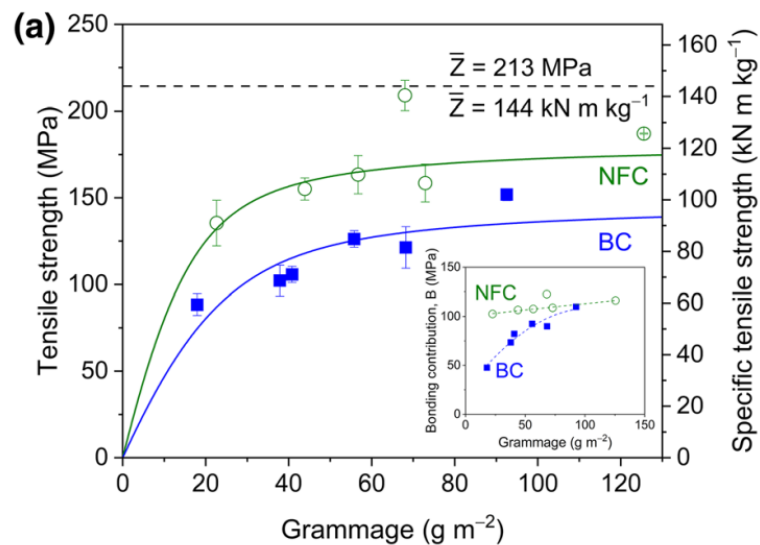
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# Case study on nanopaper strength: effect of hemicellulose

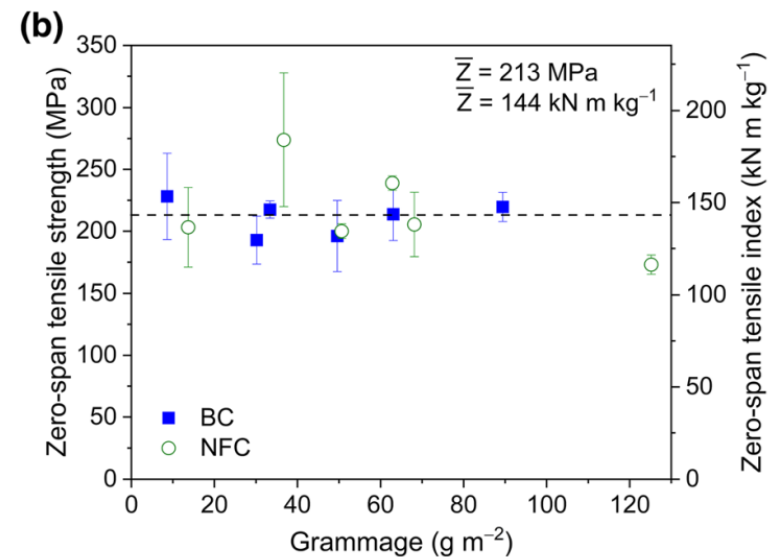
# Two types of nanopapers



# Tensile properties of two nanopapers

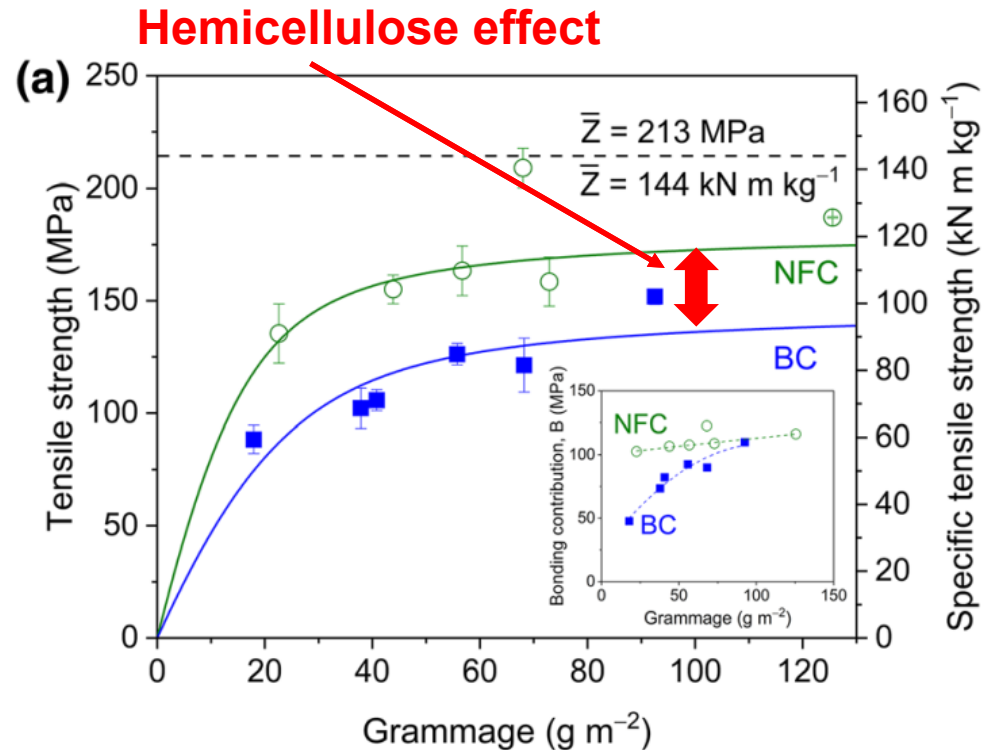


Wood-based CNFs (NFC) have a higher tensile strength



Zero-span strength (corresponds to individual fibre strength) is the same.

# Hemicellulose effect on strength



Page equation in *simple* form  
(without empirical constants):

$$\frac{1}{T} = \frac{1}{Z} + \frac{1}{B}$$

- Zero-span (Z) is the same for both nanopapers
- Bonding (B) is stronger for wood-based CNFs (NFC)
- The effect of hemicellulose on tensile strength (T) can be as high as 25%

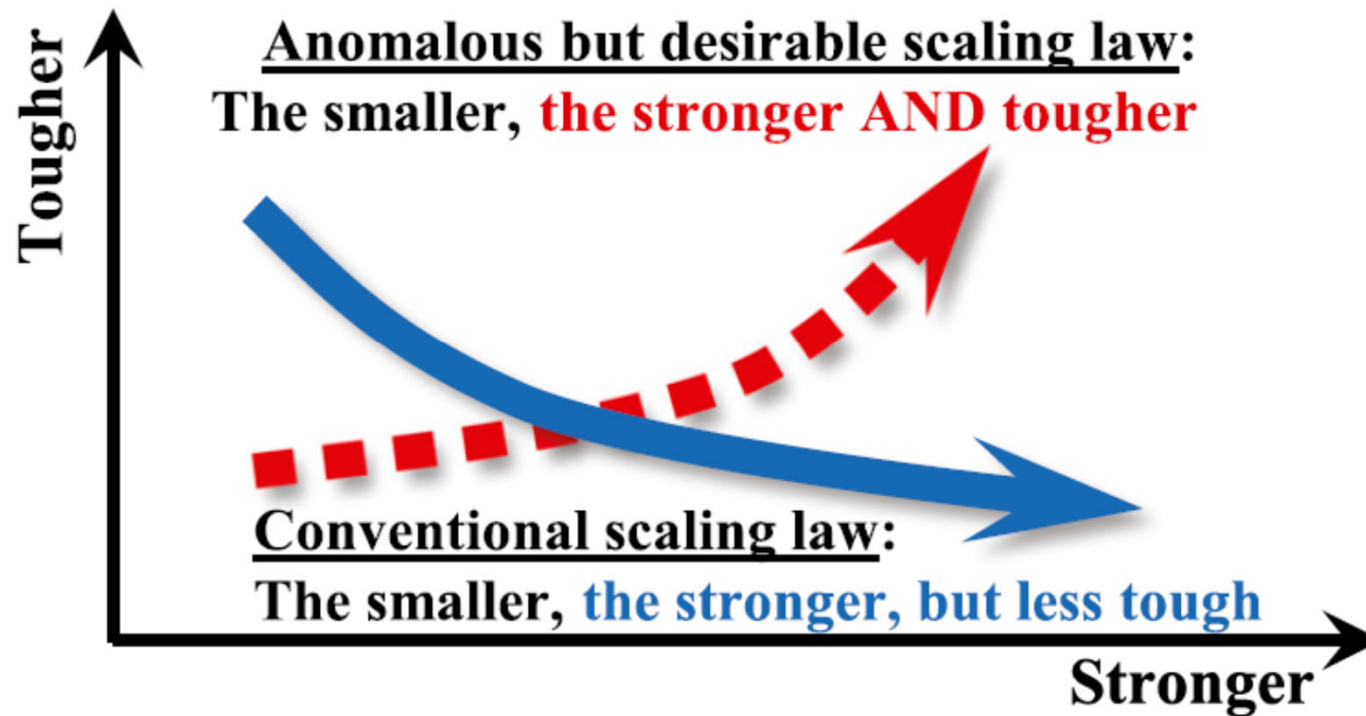


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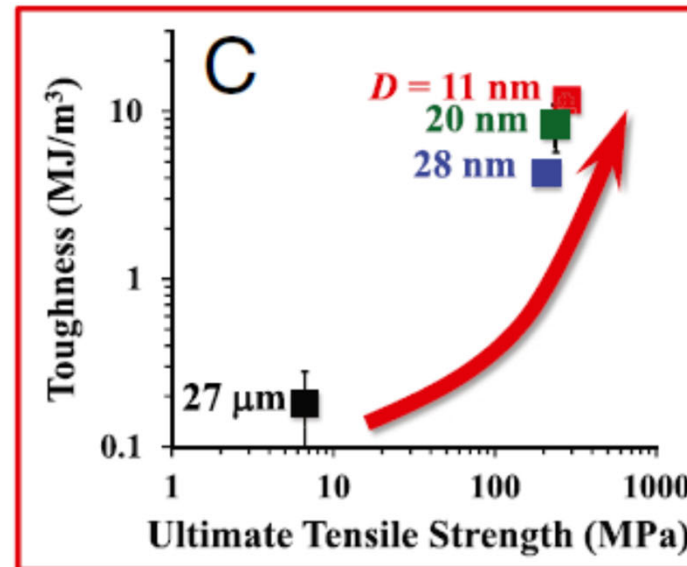
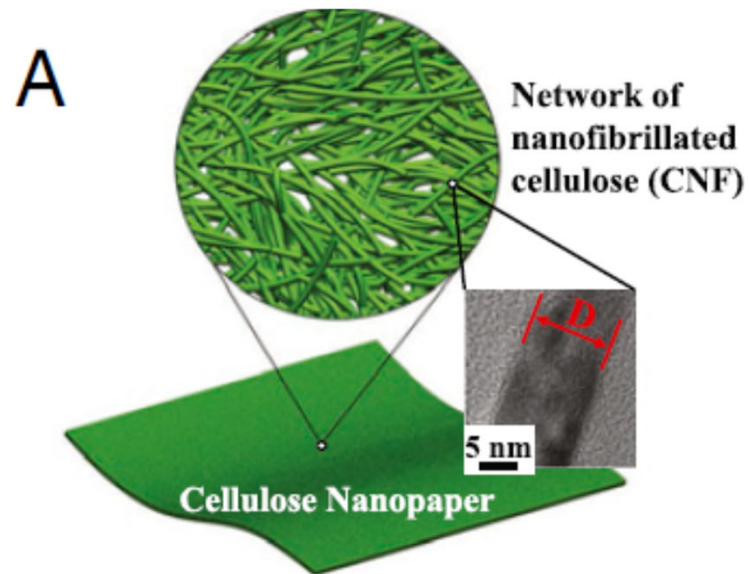
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# Case study with cellulose nanopapers - CNF size

# Scaling laws for strength and toughness

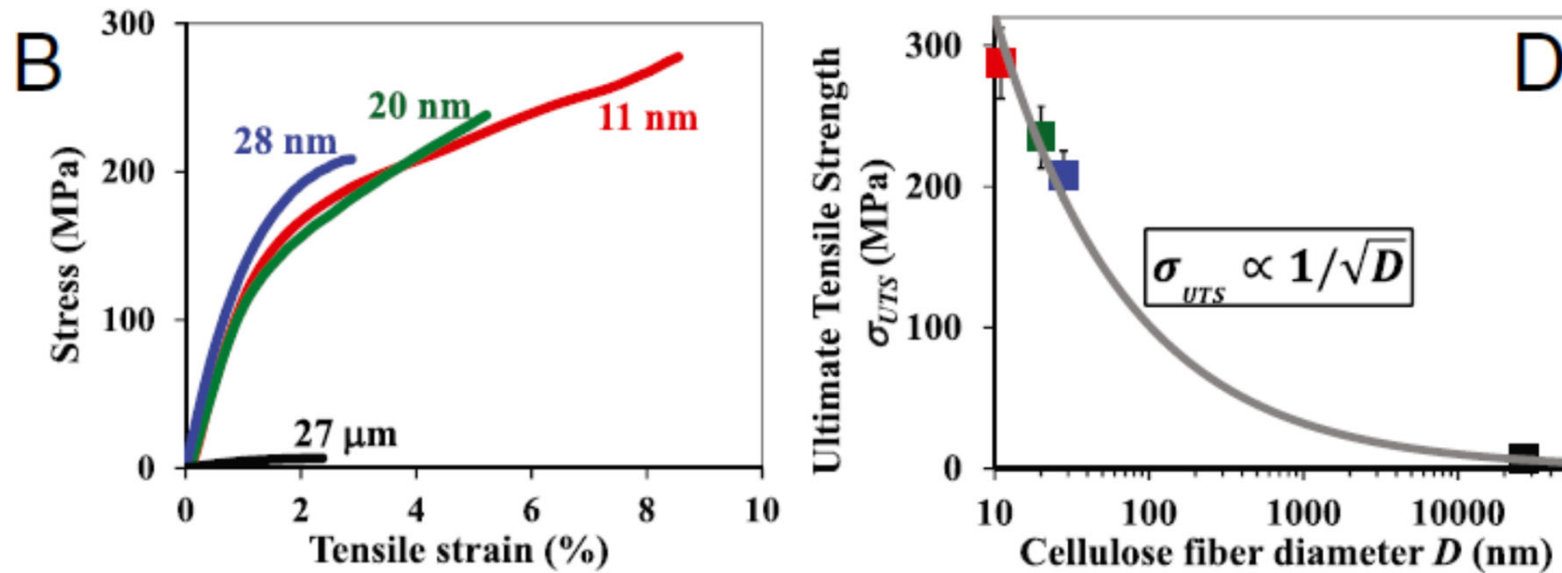


# Toughness development according to fibre diameter



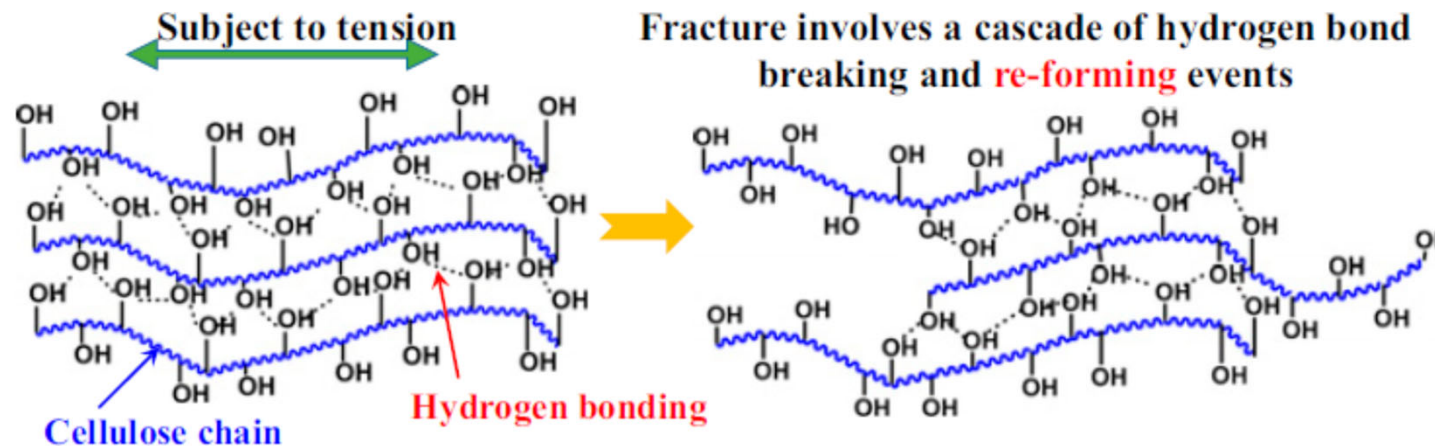
# Strength development according to fibre diameter

## Nanopaper strength vs. fibre diameter



# Anomalous scaling law – why?

- (1) Fewer defects in smaller fibres
- (2) Multiple hydrogen bonds between small CNFs can break and reform → dissipation of energy



# Presemo

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# Summary

- Particularly native cellulose fibres are very strong and stiff when compared with their density
- Strength of individual fibres or nanofibres is not manifested in the isotropic fibre networks to their full extent
- Cox theory is fundamental for fibre networks but does not work well for cellulose-based fibres
- Effect of moisture on paper is unambiguous: increased moisture decreases paper strength
- Anomalous scaling law for cellulose nanopaper: strength and toughness increase with decreasing CNF width
- Many structure-property relationships with cellulosic fibres and fibre networks are ambiguous



# Assignment

**Take a couple of minutes to answer the “After the lecture” questions in front of you**