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Measuring elasticity of wet cellulose fibres with AFM using indentation and a linearized Hertz model

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The mechanical properties of different pulp fibres in liquid were measured using an atomic force microscope. Specifically a custom-made sample holder was used to indent the fibre surface, without causing any motion, and the Young's modulus was calculated from the indentation using a linearized Hertz model.

In recent years, cellulose has become a widely investigated material in many research studies around the world. As a naturally occurring material cellulose provides excellent biodegradability at a very low cost. In many fields cellulose is now being used to replace oil-based materials, which show poor or no natural degradability at all.¹ Dry cellulose has inherently good mechanical properties such as strength and toughness, making it ideal for reinforcement applications.² Naturally occurring cellulose forms a hierarchical structure where cellulose chains are arranged into fibrils that are aligned and embedded in a lignin/hemicellulose matrix forming larger fibres that have excellent mechanical properties.³ For more than a century cellulose fibres have been used for a wide range of applications⁴ such as paper, packaging,⁵ hygiene products⁶ and in composites.⁷ However, during the last decade, the properties of cellulose on different length scales have been investigated.^{2,8–11}

Cellulose is normally used in end products in dry conditions because the mechanical properties of cellulose change drastically when the fibres are wet. Additionally, moulding and degradation (hydrolysis, enzymatic, *etc.*) of the cellulose can result in a failure of the dry material unless it is not protected. Nevertheless many new applications are taking advantage of the change in mechanical properties in the wet state and wet cellulose materials have become more in focus.^{12–14}

For all cellulose fibre applications it is important to have a fundamental understanding of the mechanical properties of

the fibres and their interaction with water (swelling and enthalpy gain¹⁵). Unfortunately, the determination of the mechanical properties of the wet fibres is challenging and literature data relating to the elasticity in the wet state for different fibres is limited.

One instrument used to measure the mechanical properties of a wide range of nano- and microscale materials is the atomic force microscope (AFM). AFM has become widely used to investigate a variety of material properties including the moduli of polymer films and composites^{16,17} and additionally, the elasticity of benign and cancerous cells.^{18–20}

Various methods have been used to evaluate and measure the mechanical properties of fibres by AFM, for example tensile and three-point bending tests. Fibre tensile properties are evaluated by spanning the fibre between an AFM tip and a hard surface and performing uniaxial stretching along the fibre axis. While individual mineralized collagen fibrils,²¹ individual collagen fibres²² polyethylene oxide nanofibers²³ and poly (*L*-lactic-*co*-glycolic acid) fibres²⁴ have been measured, attachment of the fibres to the AFM tip makes tensile measurements technically challenging. In a three-point bending test, fibres are deposited on a substrate with holes or grooves. Fibres lying over such a hole or groove are then bent using an AFM tip in the centre of the fibre bending it in one direction. Such measurements have been made on earlywood and latewood kraft pine fibres²⁵ and Lyocell fibrils.²⁶ Unfortunately, both tensile and three-point bending tests become challenging and time-consuming in a liquid (due to surface adhesion and fibre flexibility), making them not suitable when studying the wet mechanical properties of fibres.

In the present study, the mechanical properties of wet cellulose fibres in liquid have been investigated using a simple indentation measurement in the fibre walls using AFM. Fibres are clamped in the liquid onto a surface by a custom-made sample holder which prevents motion or bending of the fibres. The measured force vs. indentation profile can then be used to fit one of the existing contact mechanics models to extract the Young's modulus for the fibres. The most frequently

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The TEMPO-mediated oxidation (4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-AcNHTEMPO)) of K48-60 was performed on never-dried pulp following the procedure describe by Tanaka *et al.* 2012.³¹ In brief, the fibres were dispersed in 0.1 M acetate buffer at pH 4.8, after which 4-AcNH-TEMPO and sodium chlorite were added to the dispersion followed by the addition of NaClO. The reaction was allowed to

The linearized Hertz model is given by:

$$E = \frac{\pi}{2} \left(\frac{\Delta(F_{\text{cone}})^{1/2}}{\Delta\delta} \right)^2 \frac{1 - \nu^2}{\tan \alpha}, \quad (2)$$

^a Data obtained from ref. 30.

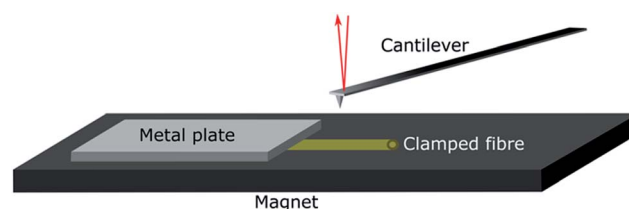




Fig. 2 The force vs. separation curve from a single fibre raw data (BSW) converted with the algorithm explained by Senden *et al.*³⁵ The zero point is arbitrary set at maximum load. The grey line is the approach of the tip to the fibre surface and the black line is the retraction from the surface, force range used for the fitting was 20 to 70 mN m^{-1} (top). Elasticity map of a measurement with 5×5 measurement points over $5 \times 5 \mu\text{m}$ on the fibre surface close to the clamp shown as the Young's modulus calculated for each data point (bottom).

where F_{cone} is the force applied to the sample surface, E is the Young's modulus, α is the half cone opening angle, ν is the Poisson ratio and δ is the indentation depth.

The Young's moduli of the different fibre samples are shown in Table 1. Measurement in bending mode for TMP and BSW samples from a previous paper³⁰ have been included in the table, to make it possible to compare the properties obtained by using two different AFM methods.

The measured and calculated Young's moduli for the TMP fibres are 49 ± 40 kPa and 53 ± 23 kPa for the indentation method and bending method, respectively, and the Young's moduli for the BSW fibres are 7 ± 4 kPa and 5 ± 3 kPa. The values obtained by the two AFM methods show good agreement and are thus not significantly different, confirming that the local indentation of the fibre surface gives the same mechanical properties as the bending of the whole fibre. This agreement indicates that the quicker and simpler local indentation method can be used to determine the Young's modulus in place of whole fibre bending.

The Young's modulus of the TMP fibres is approximately ten times greater than that of the BSW fibres. The BSW fibres have been treated chemically at a high temperature, in contrast to the TMP fibres, and it can be assumed that this makes the BSW

fibres softer, more flexible and elastic due to the removal of lignin.³⁴

In all the measurements, the standard deviations are relatively large. These large deviations are expected for natural fibres, as cellulose fibres have structural differences and regions of varying crystallinity along the fibre length.

The Young's modulus of unmodified K48 with a charge density of $60 \mu\text{eq. g}^{-1}$ (K48-60) had a significantly higher Young's modulus 14 ± 6 kPa compared to the K48 fibres with higher charge density. After TEMPO oxidation, the Young's modulus decreased with increasing charge of the fibres. At a charge density of $300 \mu\text{eq. g}^{-1}$ (K48-300) the Young's modulus was 12 ± 4 kPa, at $600 \mu\text{eq. g}^{-1}$ (K48-600) 7 ± 4 kPa and at $900 \mu\text{eq. g}^{-1}$ (K48-900) 3 ± 1 kPa.

This decrease in Young's modulus can be explained by two different mechanisms: (1) The introduction of carboxylic groups into the fibre increases the pore size and thus increases the swelling in liquid.³⁵ (2) Any lignin residues in the fibre cell walls are significantly degraded by the TEMPO oxidation, leading to a more flexible fibre.³⁶

The addition of salt significantly lowered the Young's modulus of the fibre samples K48-60 ($60 \mu\text{eq. g}^{-1}$) and did not change for K48-900 ($900 \mu\text{eq. g}^{-1}$), and the two fibre samples had the same Young's modulus when immersed in 100 mM sodium chloride solution.

When a system such as a pulp fibre swells, three components to the Gibbs free energy of the swelling system balance the swelling; an ionic contribution, a mixing contribution and a network contribution.³⁷ When the fibres were chemically modified to increase the charge of the fibres, it was observed that at low ionic strength the ionic contribution dominates and controls the elasticity of the fibres. The highest charged fibres are thus the most elastic with the lowest Young's modulus. When 100 mM sodium chloride was added to the dispersion, the increase in ionic strength screens the charges in the fibre and the highest charged and lowest charged fibres then had the same Young's modulus. This is likely due to the screened electrostatic contribution as the fibres should have the same network and mixing contribution. Since they have the same origin from the same pulping process. This is an interesting behaviour and needs a more thorough evaluation in a future study.

Conclusions

The mechanical properties of different cellulose pulp fibres were measured using a simple indentation method with an AFM. The measurements were carried out in a liquid environment using a custom-made sample holder that prevents motion and bending of the individual fibre. The method gives the same results as an earlier study where the fibres were bent over an edge to evaluate the fibre flexibility.³⁰ The new indentation method makes it possible to determine a fibres' elasticity more quickly than three-point bending and tensile measurements using the AFM. The method can be used for all types of fibres, including never-dried fibres provided that the fibre mounting is done under liquid.



A bleached softwood kraft pulp and an unbleached TMP pulp were used to validate the method and the calculated mechanical properties were the same as previously reported values for the same fibres. The Young's modulus of the bleached unbeaten softwood kraft pulp decreased with increasing charge density. The presence of salt screens the charged groups in the fibre, and the fibres coming from the same original pulp behaved similarly regardless of charge density.

Conflicts of interest

There are no conflicts to declare.

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