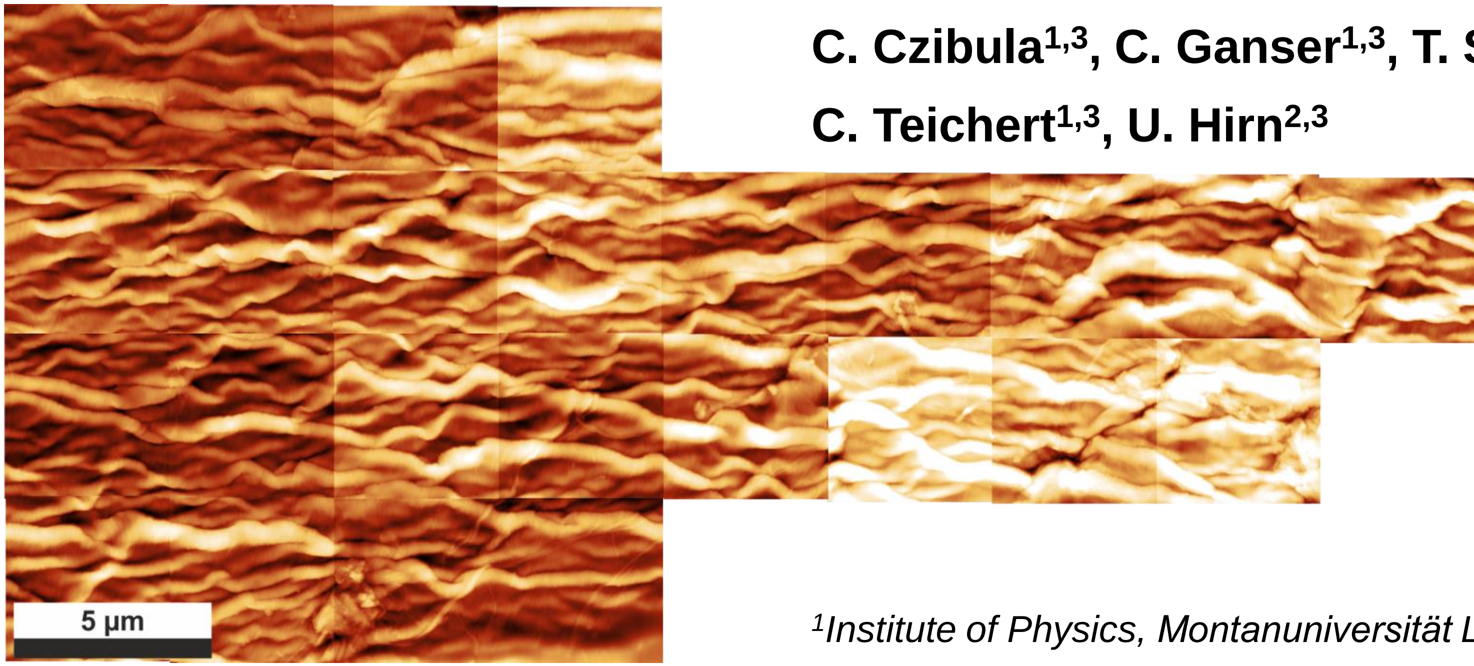
TRANSVERSE VISCOELASTIC PROPERTIES OF PULP FIBERS INVESTIGATED WITH ATOMIC FORCE MICROSCOPY

C. Czibula[1,3], C. Ganser[1,3], T. Seidlhofer[2,3], C. Teichert[1,3], U. Hirn[2,3]



[1]Institute of Physics, Montanuniversität Leoben, Austria

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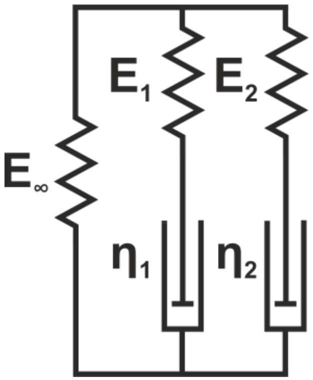
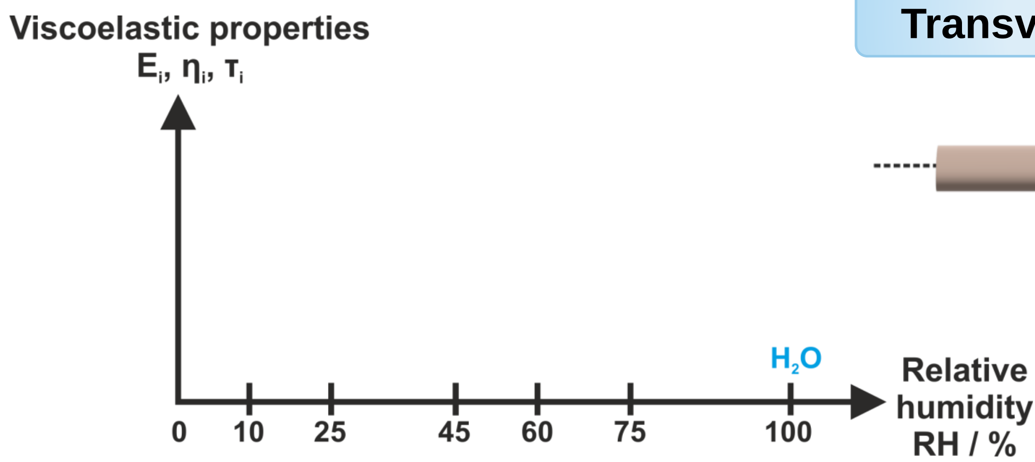
ПРОБЛЕМЫ МЕХАНИКИ ЦЕЛЛЮЛОЗНО-БУМАЖНЫХ МАТЕРИАЛОВ
Архангельск, 11.09.2019

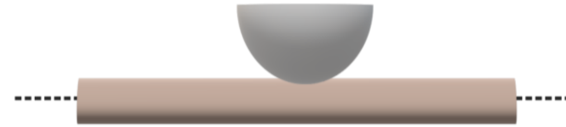
Motivation



Viscoelasticity

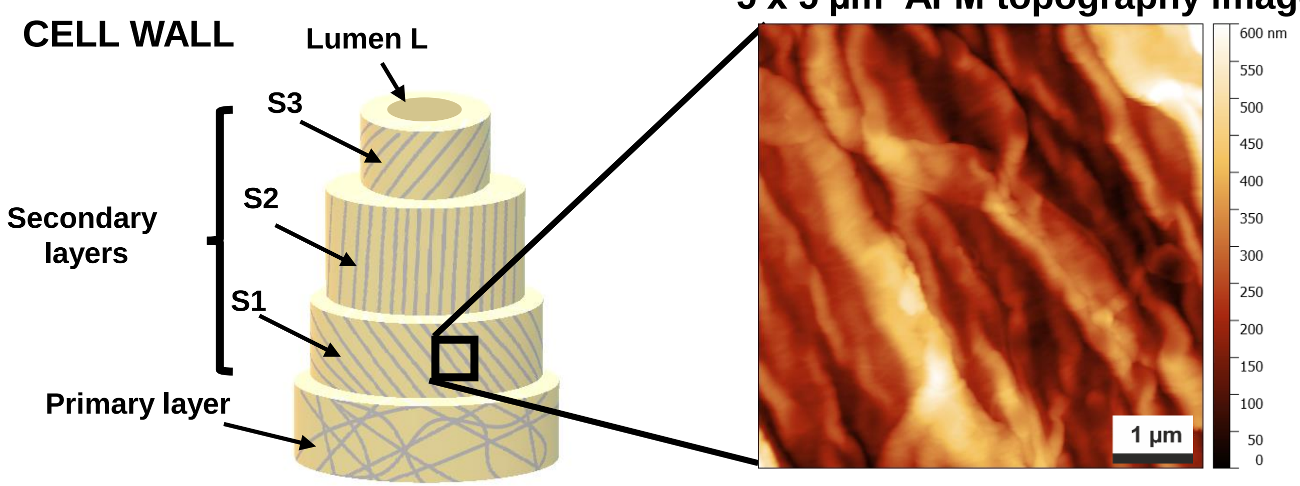


Transverse fiber direction



Hierarchical structure of pulp fibers

5 x 5 µm² AFM topography image

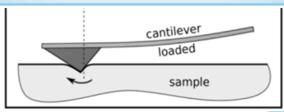


Challenging: rough surface & anisotropic properties

Background

Influence of relative humidity

AFM Nanoindentation

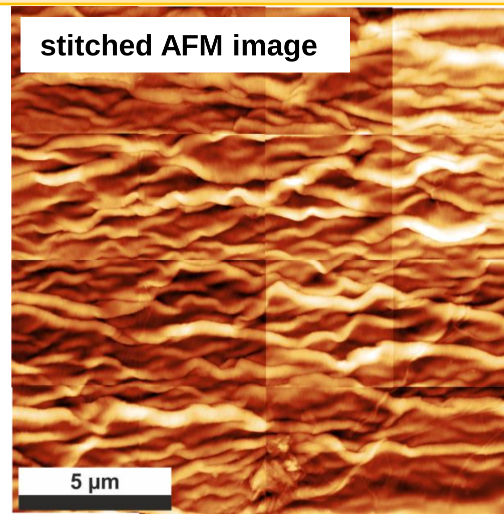


C. Ganser et al., *Holzforschung* **68** (2014) 53-60.

C. Ganser, C. Teichert, in "Applied Nanoindentation of Advanced Materials", Ed. A. Tiwari, pp 247-267, Wiley, 2017.

Reduced modulus E_r & Hardness H

Transversal viscoelastic properties of single cellulose fibers with AFM methods



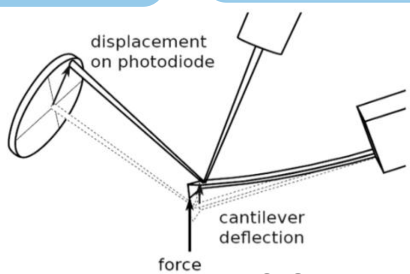
Validation of the method with Polycarbonate (PC) & Polymethylmethacrylate (PMMA) and comparison with tensile testing and nanoindentation

C. Ganser et al., *Soft Matter* **14** (2018) 140-150.

Past experience

Adhesion force F_{ad}

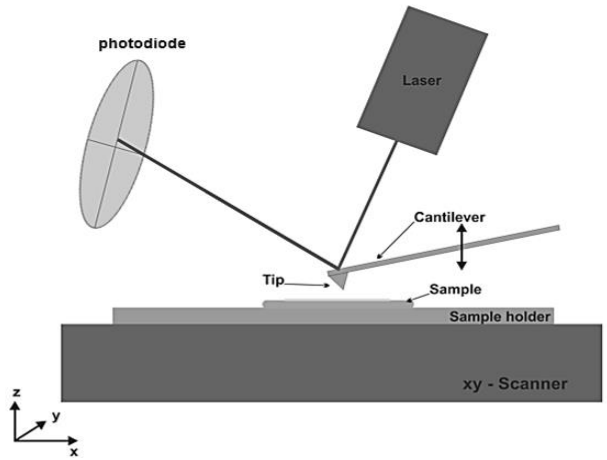
AFM force measurements



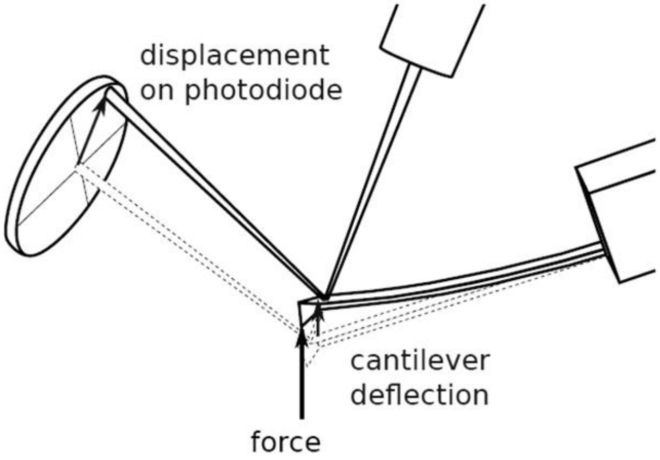
Chemical contrast with functionalized probes

C. Ganser et al., *Holzforschung* **70** (2016) 1115-1123.

Atomic force microscopy (AFM)

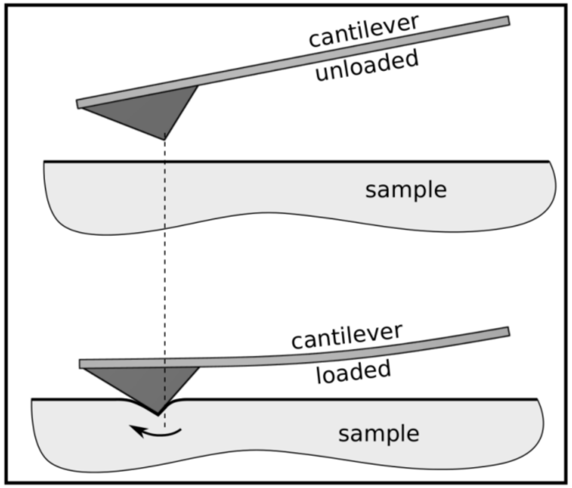


Force measurements



- Cantilever deflection ↔ Force
- Adhesion, mechanical properties

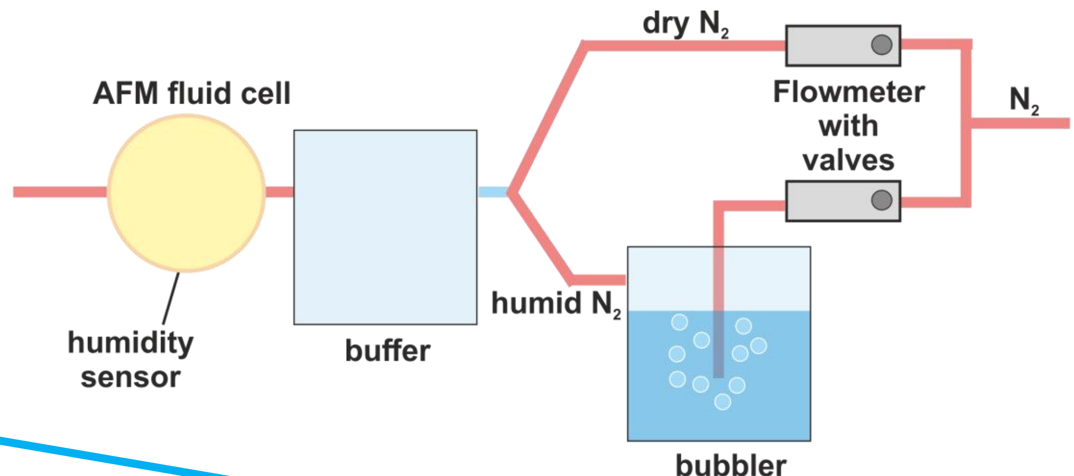
AFM nanoindentation (AFM-NI)

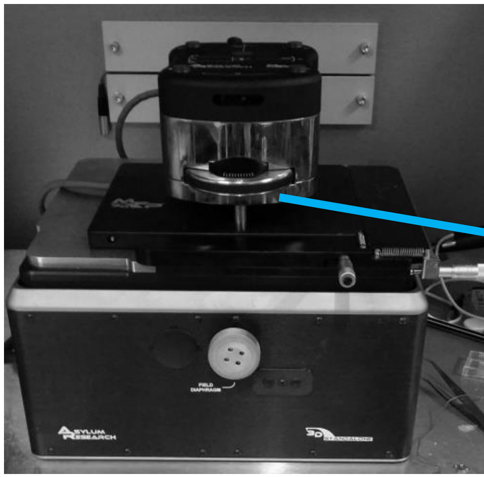


- Lateral movement of the tip
- Force application not purely vertical

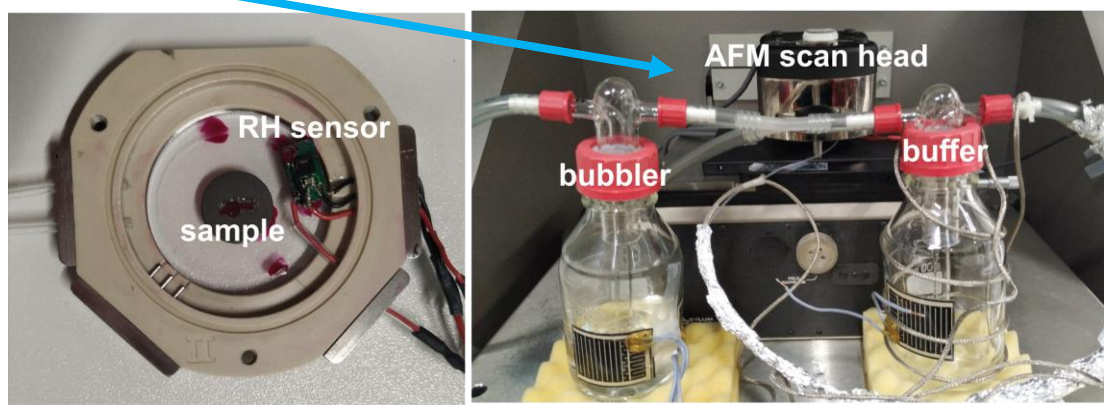
Experimental setup

Relative humidity (RH) setup





AFM: Asylum Research MFP 3D



With the setup it is possible to measure between ~10 and ~80 % RH for the viscoelastic experiments.

C. Ganser et al., *Holzforschung* **70** (2016) 1115-1123.
C. Ganser, C. Teichert, in "Applied Nanoindentation of Advanced Materials", Ed. A. Tiwari, pp 247-267, Wiley, 2017.

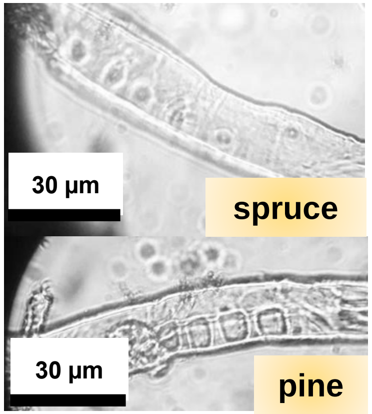
Experimental

Samples

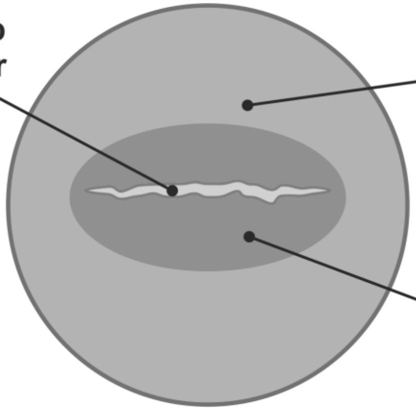
Pulp fibers

Unbleached, unrefined kraft pulp fibers; mixture of spruce and pine (4 spruce & 2 pine fibers)

d ~ 20 – 30 µm, l ~ 3 – 5 mm



Sample preparation



W. J. Fischer et al. *Cellulose* **21** (2014) 237-249.

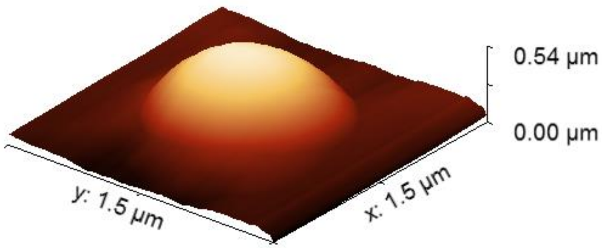
AFM probe

Large radius hemispherical probe

tip radius ~ 300 nm

spring constant of the cantilever ~ 250 N/m

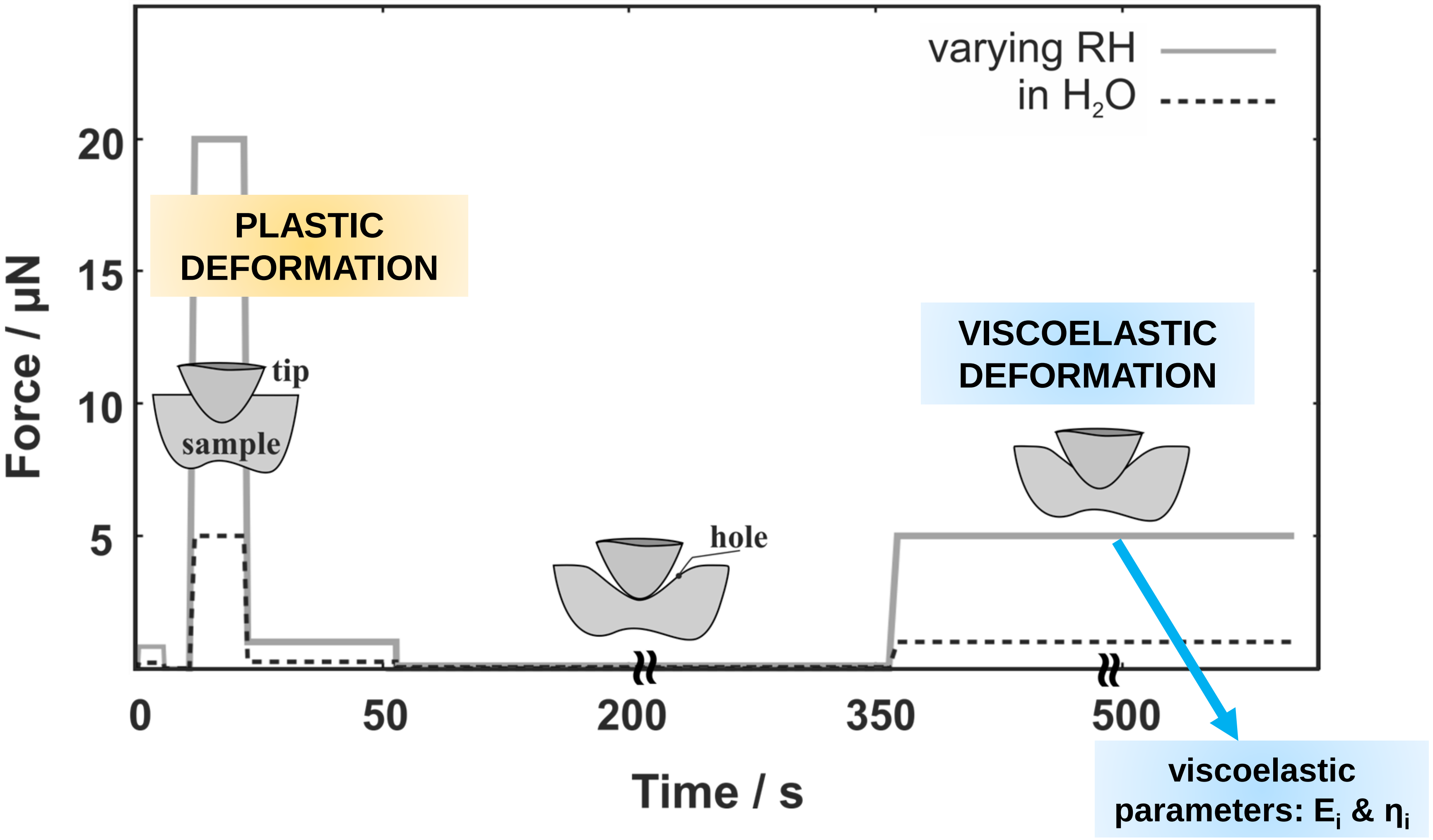
(Team Nanotec)



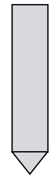
- **Tip geometry** is well known
- **Larger radius → higher forces** possible

Drawback: reduced lateral resolution

Load schedule

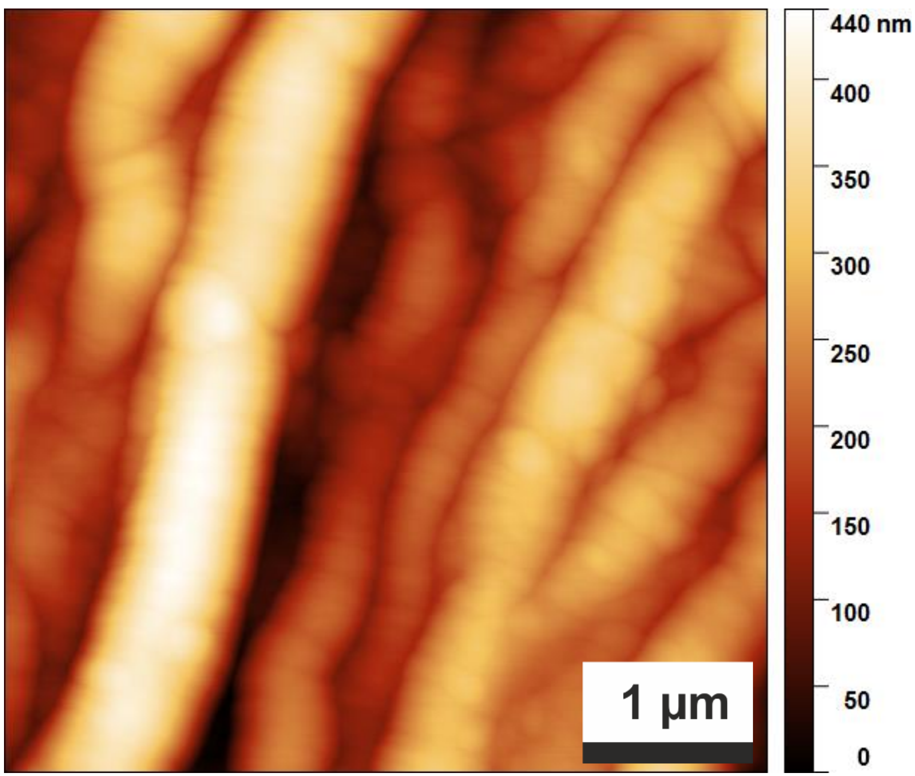


Measurements – 5 x 5 μm^2 topography images

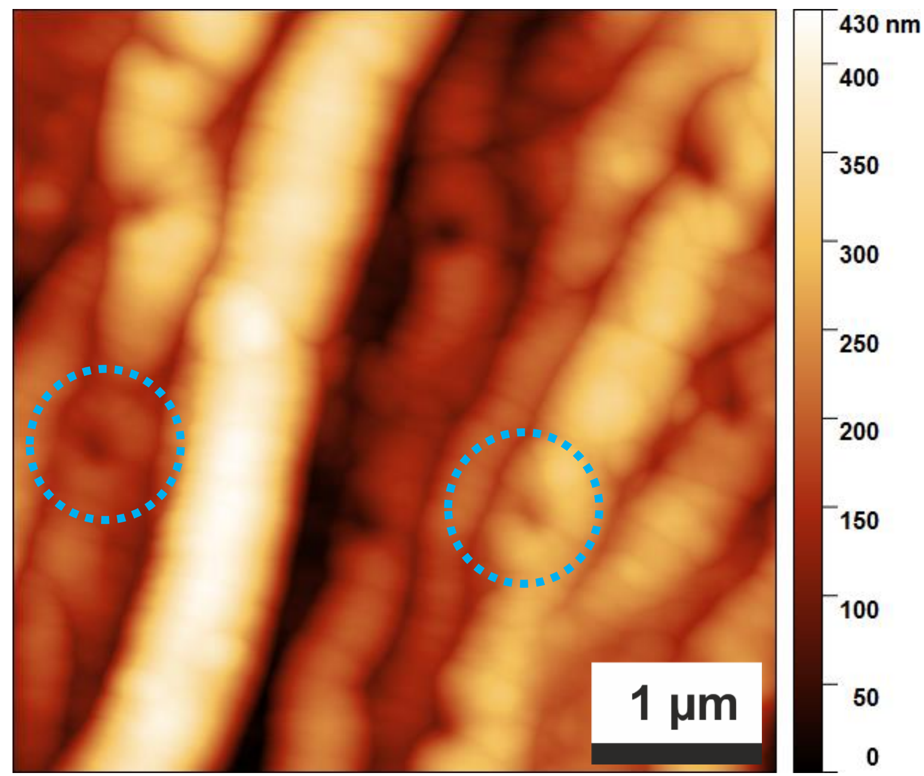


Cantilever orientation along the long fiber axis

Before AFM-NI

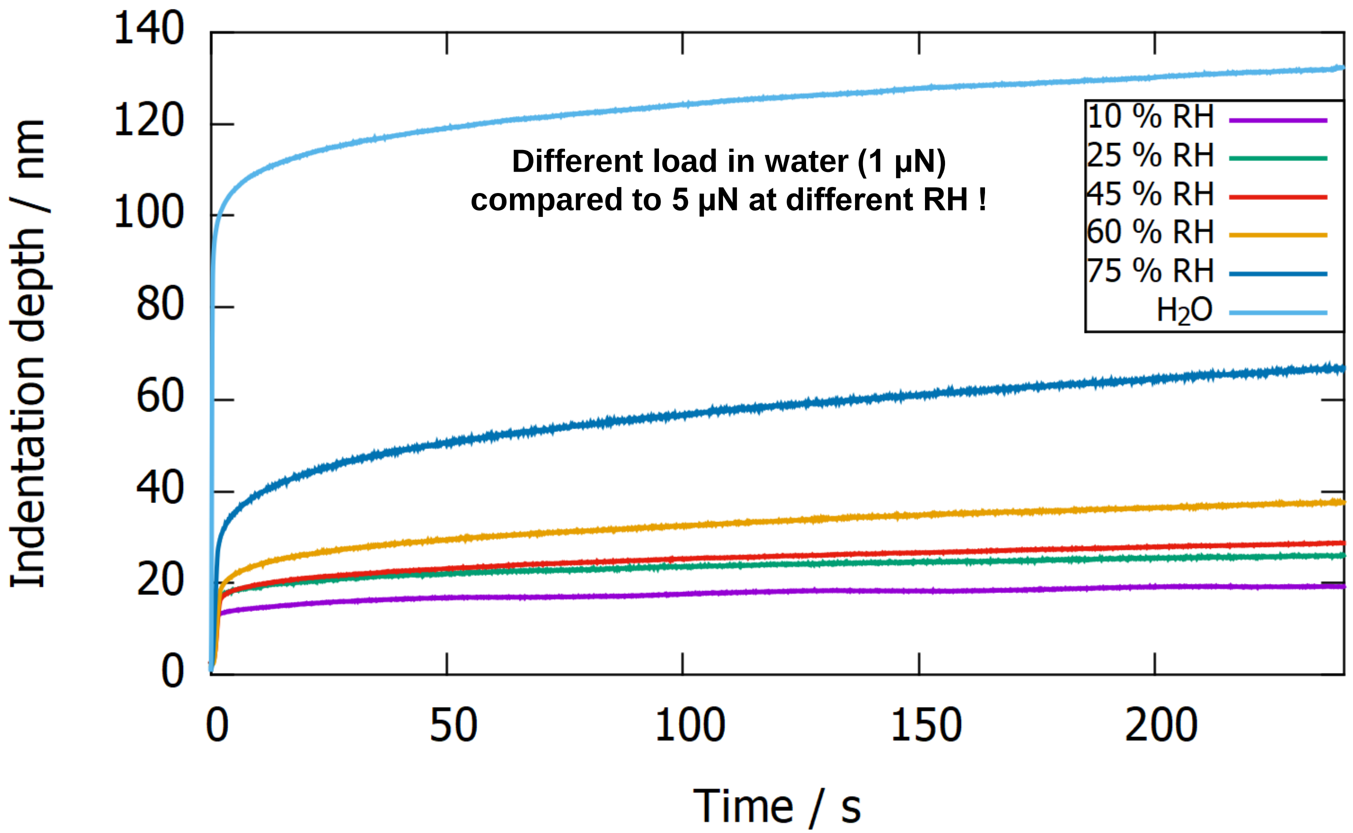


After AFM-NI



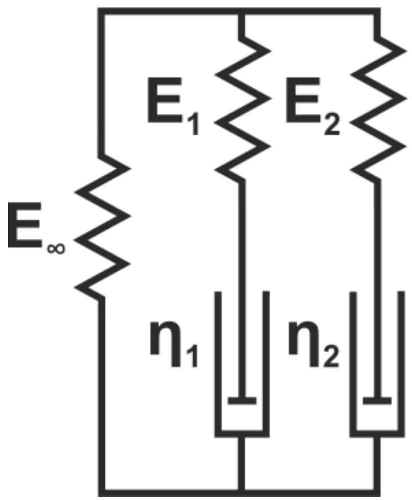
Experimental creep curves

Averaged curves from 6 different unbleached pulp fibers



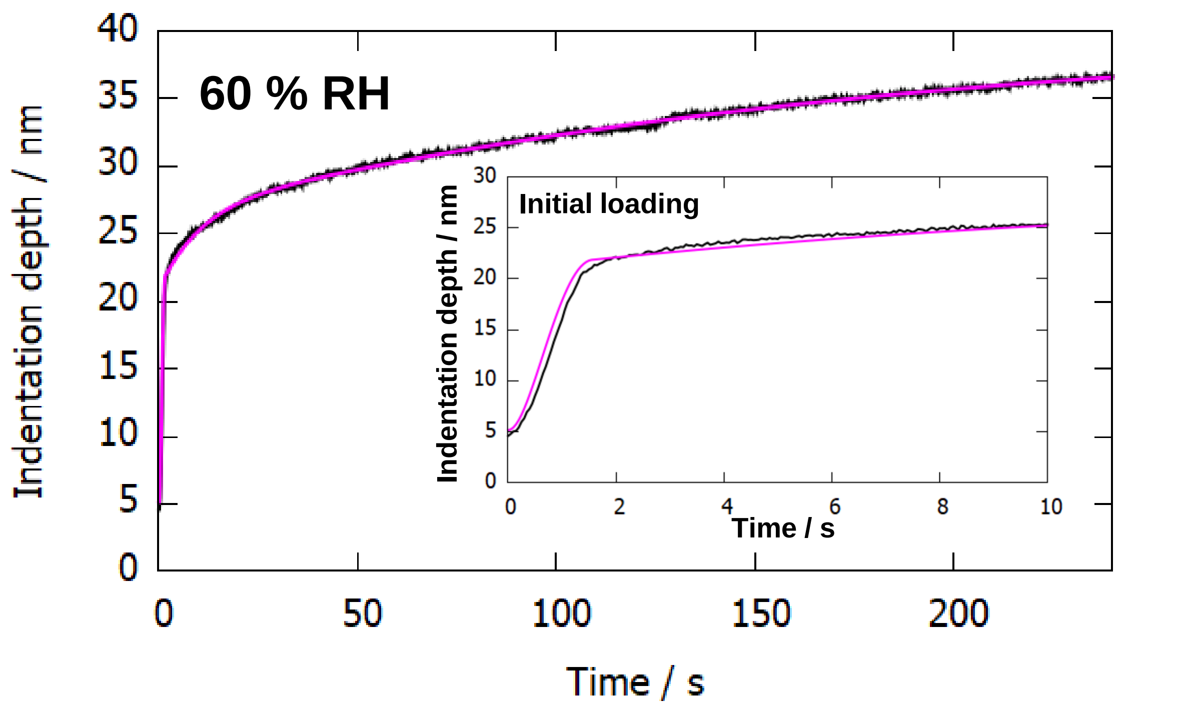
Indentation depth and **slope increase with increasing RH** as expected.

Generalized Maxwell model of order 2 (GM2)



$$\sigma = A\varepsilon + B\dot{\varepsilon} + C\ddot{\varepsilon} - D\dot{\sigma} - E\ddot{\sigma}$$

Experimental (black line) & fit (pink line) curve for a pulp fiber



H.T. Banks, S. Hu, Z.R. Kenz. *A Brief Review of Elasticity and Viscoelasticity*. N. C. S. University. Rayleigh, 2010.

D. Roylance. *Engineering Viscoelasticity*. Massachusetts Institute of Technology. Cambridge, 2001.

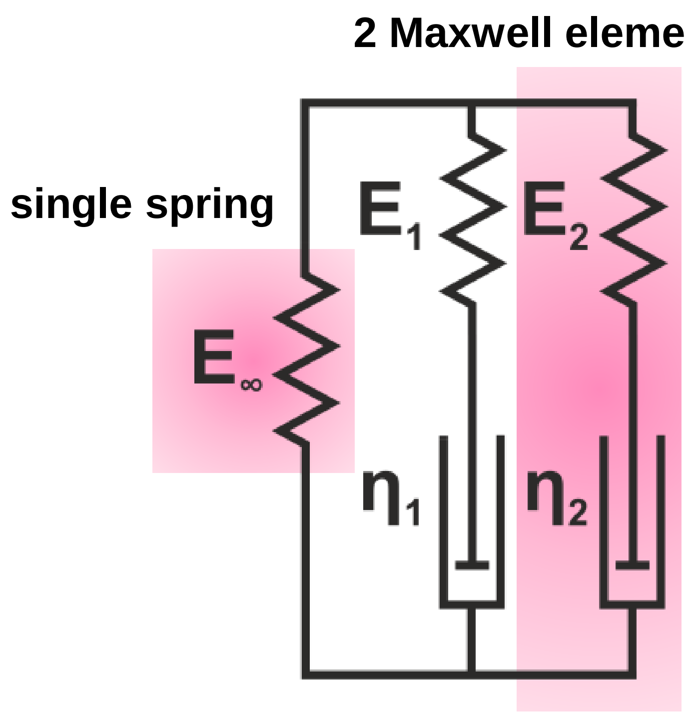
Dissecting the GM2 model

infinitely slow loading:

$\mathbf{E}_\infty$

infinitely fast loading:

$\mathbf{E}_0 = \mathbf{E}_\infty + \mathbf{E}_1 + \mathbf{E}_2$



Relaxation time

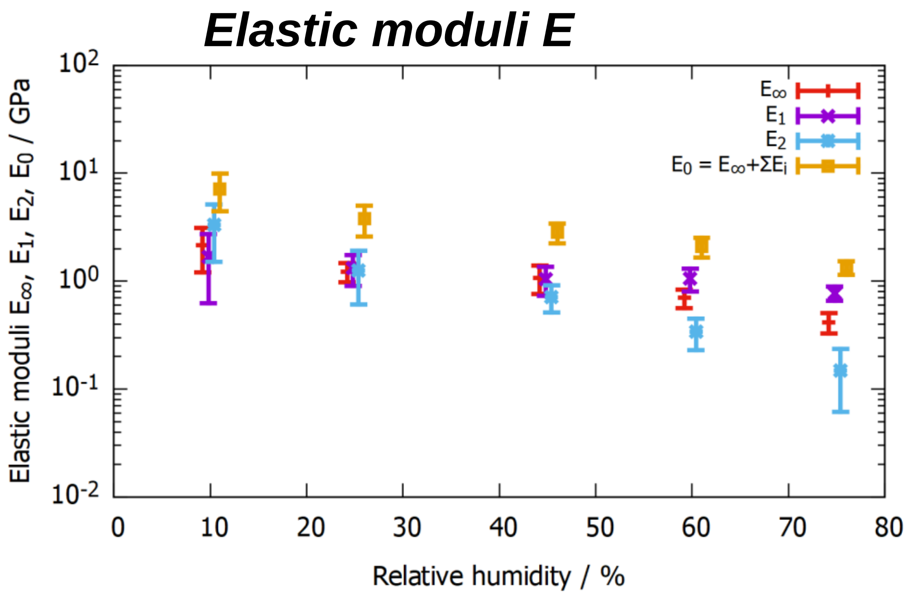
$$\tau_i = \frac{\eta_i}{E_i}$$

ratio between viscosity and stiffness

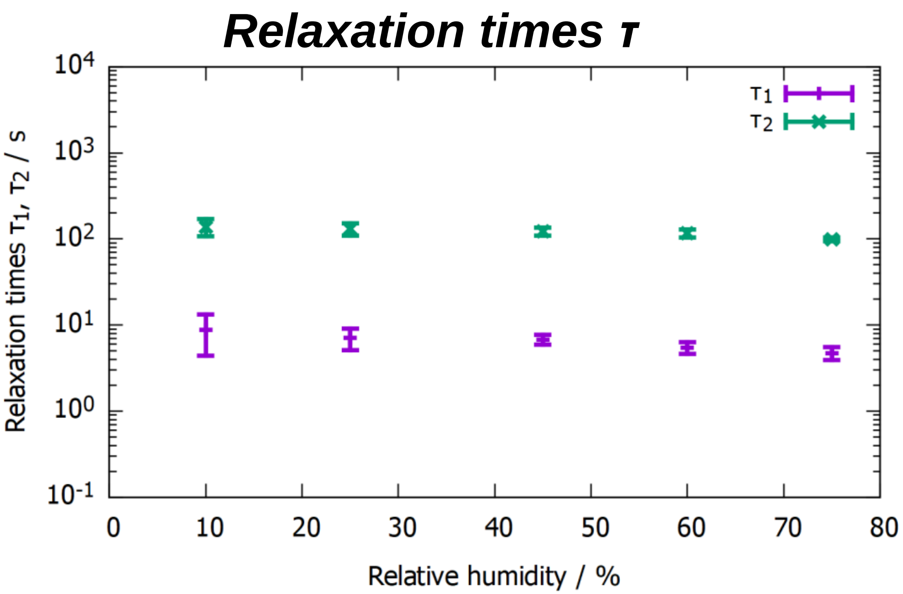
Viscoelastic characterization:

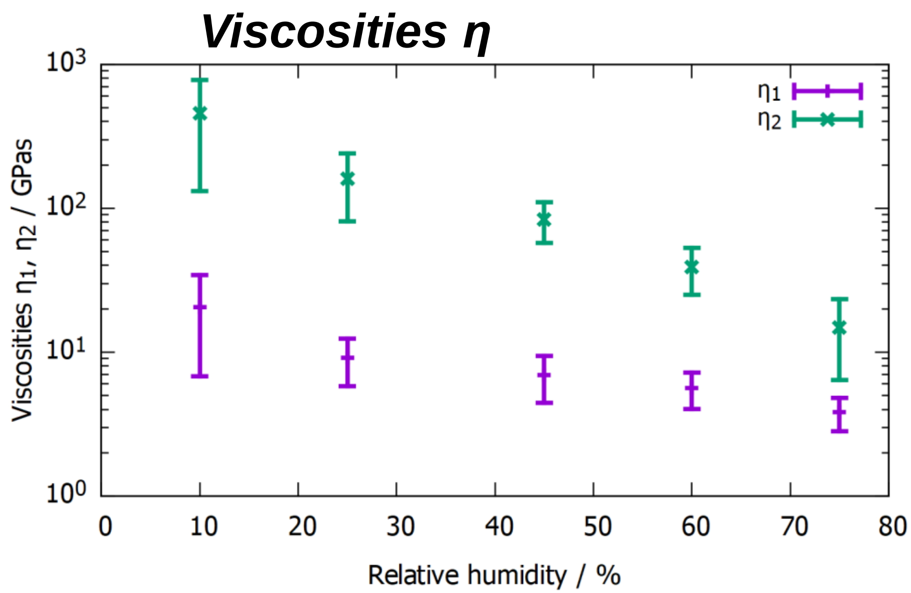
- ***Elastic parameters:*** E_∞, E_1, E_2, E_0
- ***Viscous parameters:*** η_1, η_2
- ***Relaxation behavior:*** τ_1, τ_2

Results for unbleached pulp fibers at different RH



6 unbleached fibers (4 spruce and 2 pine fibers)



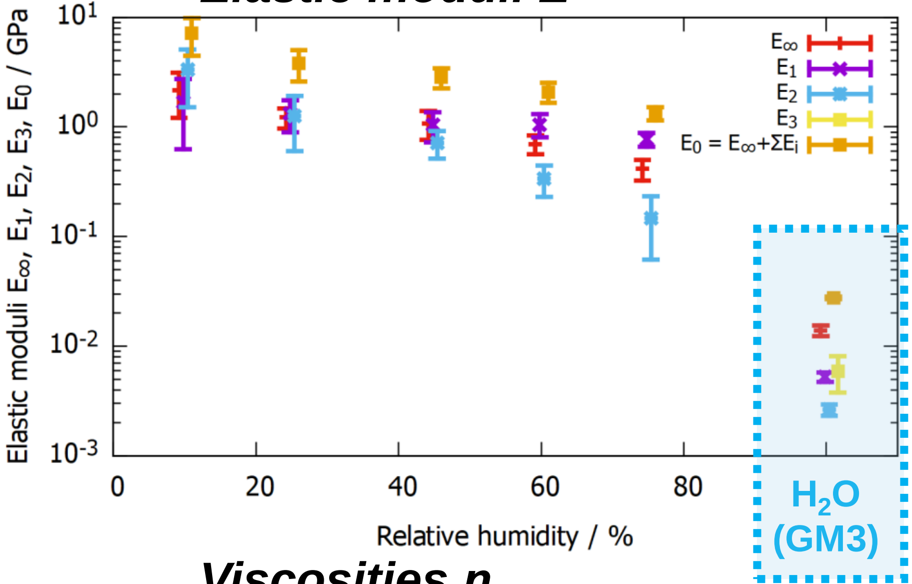


Both, elastic moduli and viscosities show a gradual decrease with increasing RH.
The relaxation times show little change.

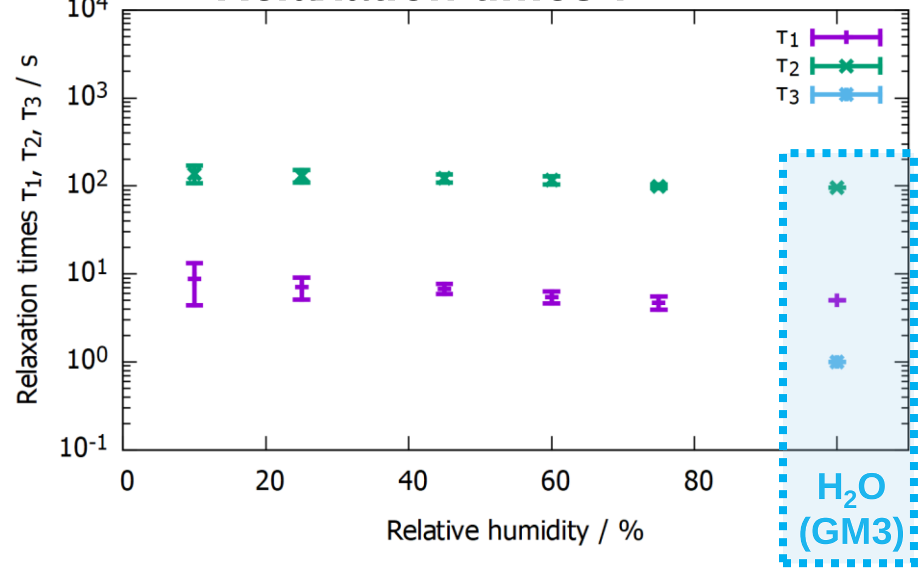
Results for unbleached pulp fibers

6 unbleached fibers (4 spruce and 2 pine fibers)

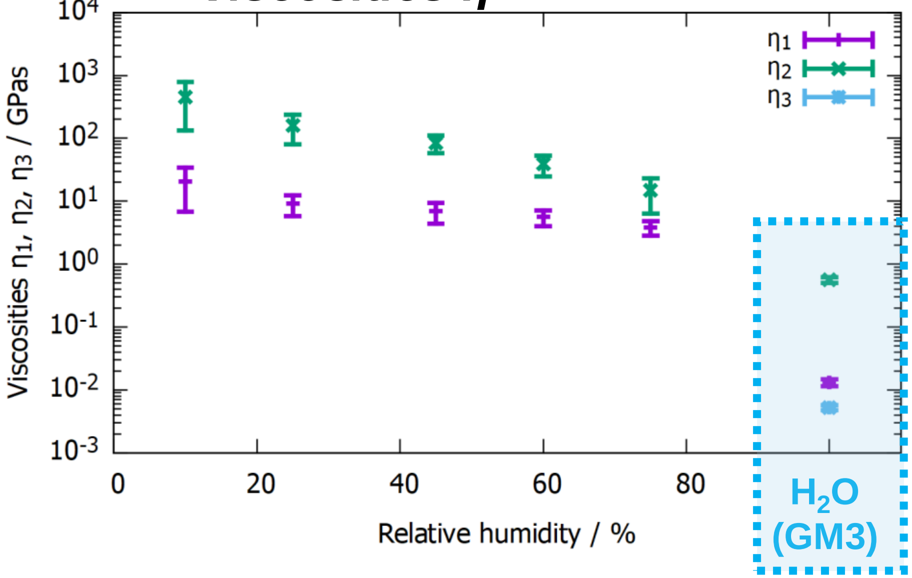
Elastic moduli E



Relaxation times τ



Viscosities η



Both, elastic moduli and viscosities show a decrease with increasing RH. In water the decrease is highest.
The elastic moduli and viscosities decrease by a factor of 2 and 4, respectively.
The relaxation times show little change, only at higher RH and in water a third one was added.

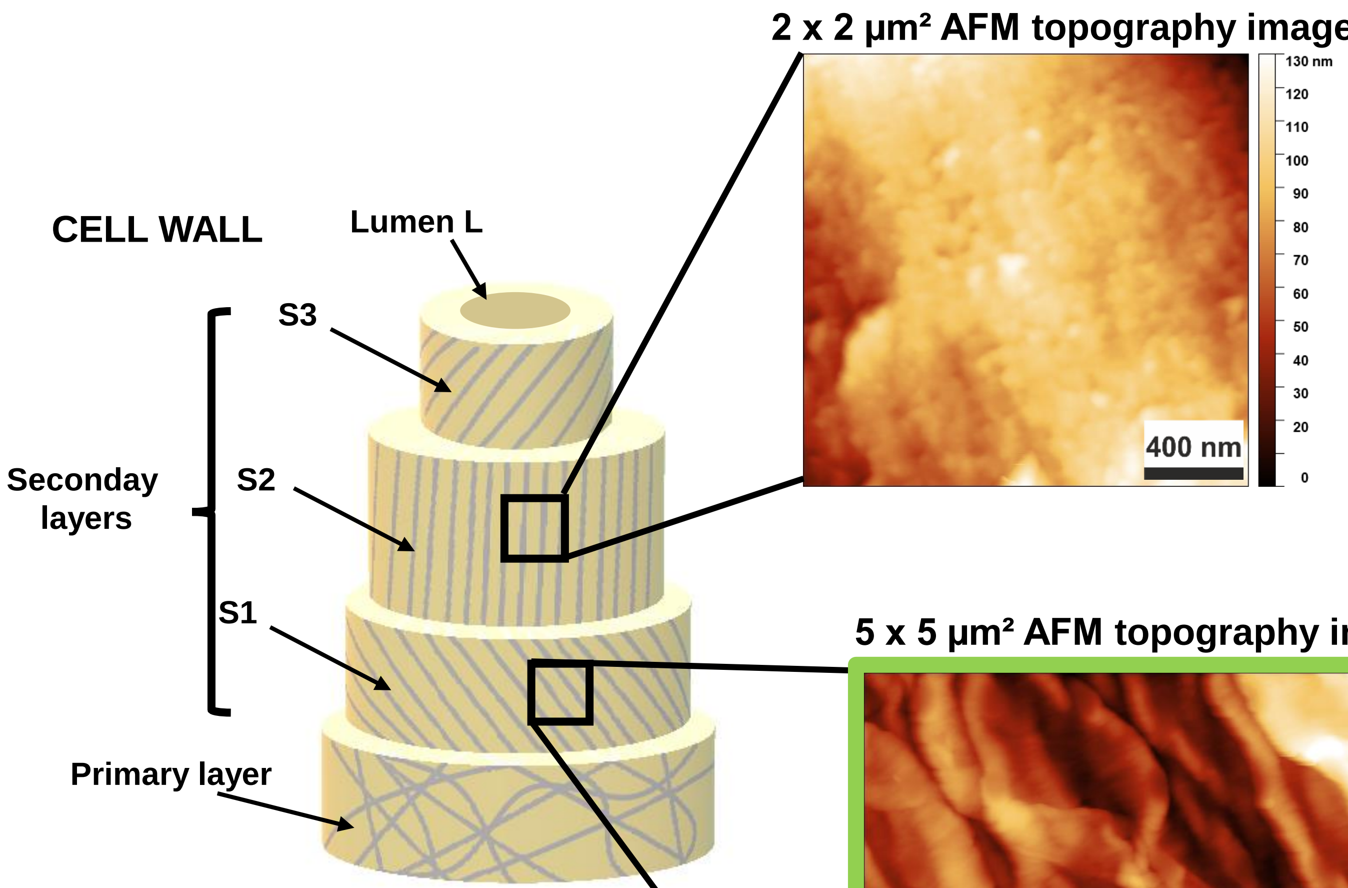
Conclusions

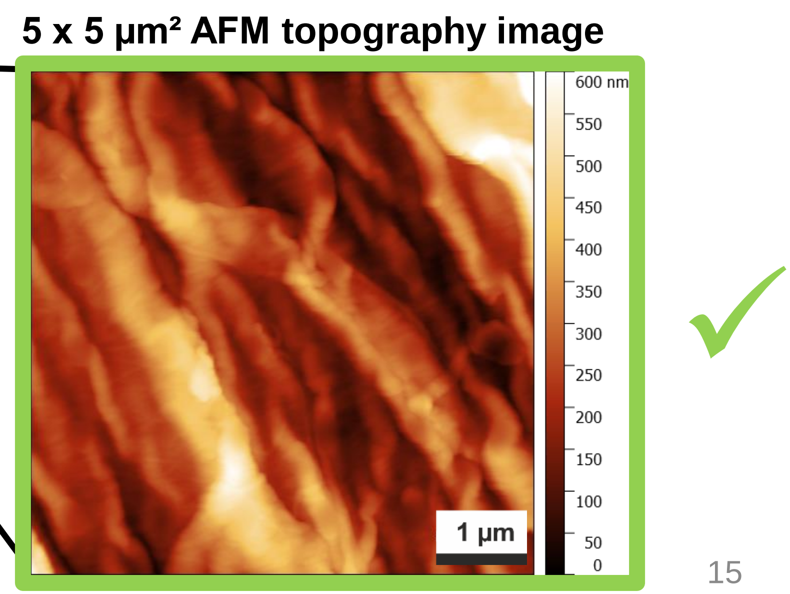
- An AFM based method to investigate the **viscoelastic properties of pulp fibers** was presented.

- Both, **elastic moduli** and **viscosities** show a **decrease with increasing RH**. The **relaxation behavior** stays **constant**.

- **In water**, a **GM3 model** is needed to fit the data properly (hydrogel-like behavior, poroelastic approach).

Outlook:
microtome cuts to access the S2 layer





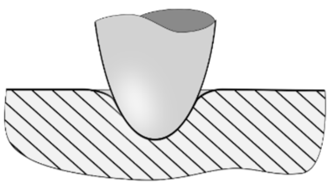
C. Czibula, C. Ganser, T. Seidlhofer, C. Teichert, U. Hirn,
J. Mater. Sci. **54** (2019) 11448-61.

T. Seidlhofer, C. Czibula, C. Payerl, C. Teichert, U. Hirn, M. Ulz,
J. Mech. Mat. **135** (2019) 149-161.

THANKS FOR YOUR ATTENTION !!

Theory behind data analysis

Contact mechanics model



Johnson-Kendall-Roberts (JKR)

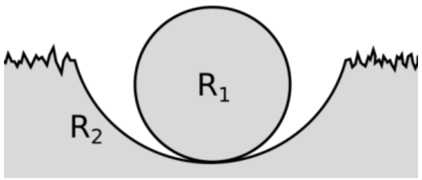
Assumptions:

- Tip is a sphere
- Sample: plane, sphere, **hole**
- Topography: smooth
- Regime: elastic
- Adhesion: **YES**

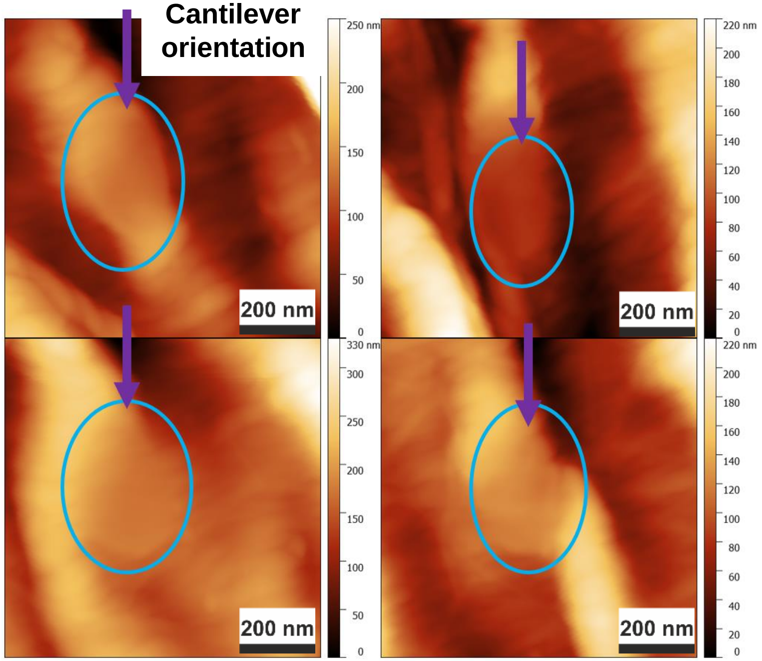
K.L. Johnson, K. Kendall and A.D. Roberts, *Proc. R. Soc. Lond. A*, **324** (1971), 301-313.

+

How to define the tip-surface contact ?



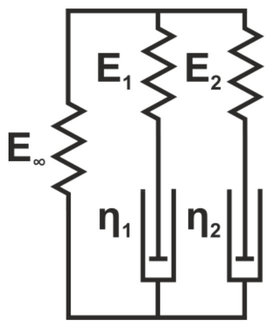
Contact in a hole

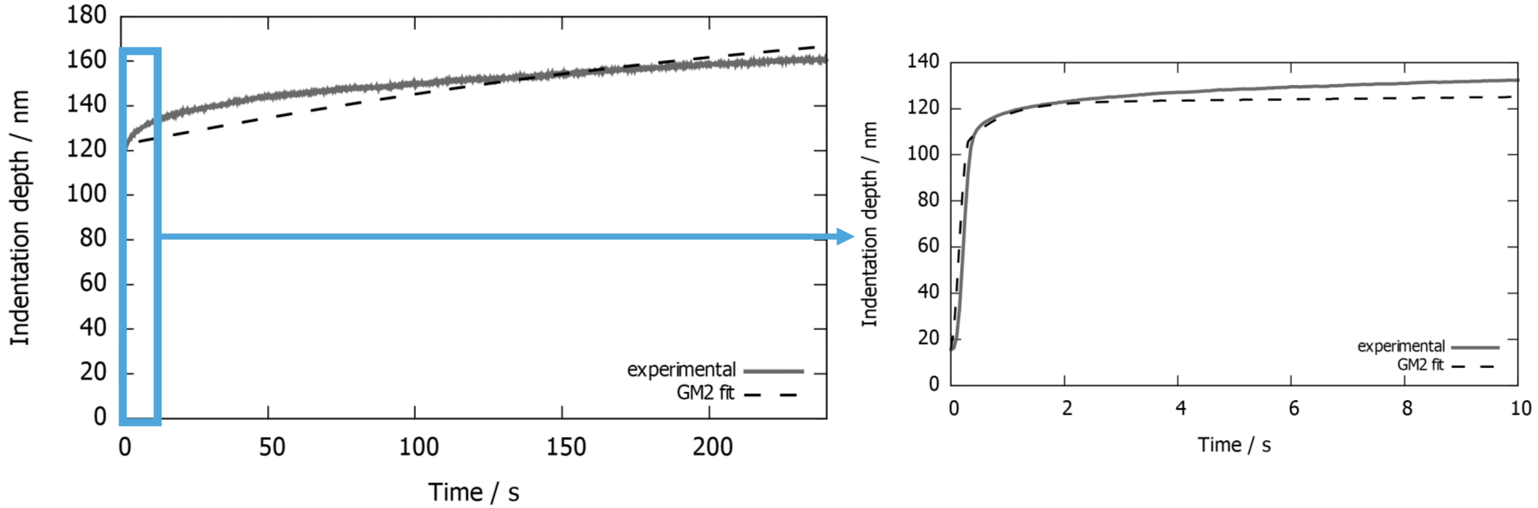


+ Viscoelastic model

Comparison of GM2 and GM3 fits for H_2O measurements

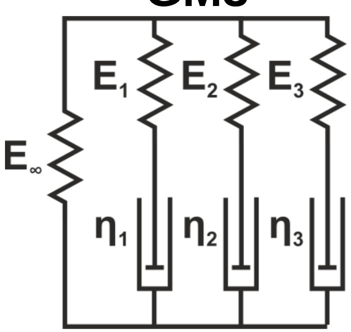
GM2

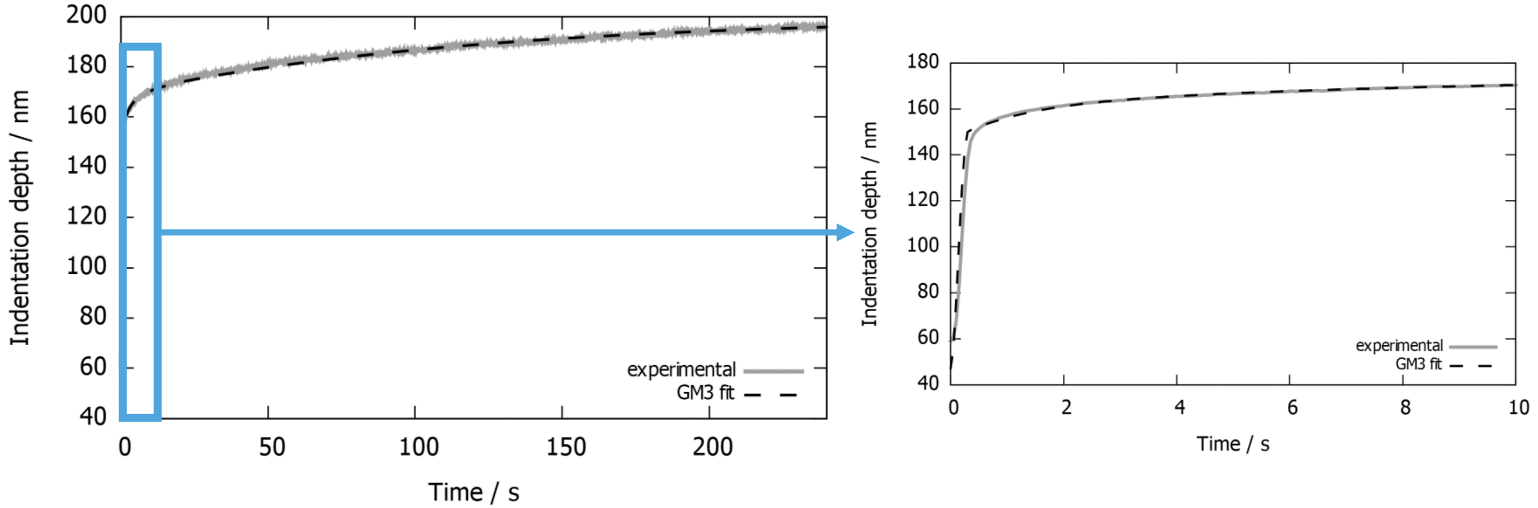




Introduction of a third Maxwell element with fixed relaxation times: τ_1 = 1 s, τ_2 = 5 s, τ_3 = 100 s

GM3





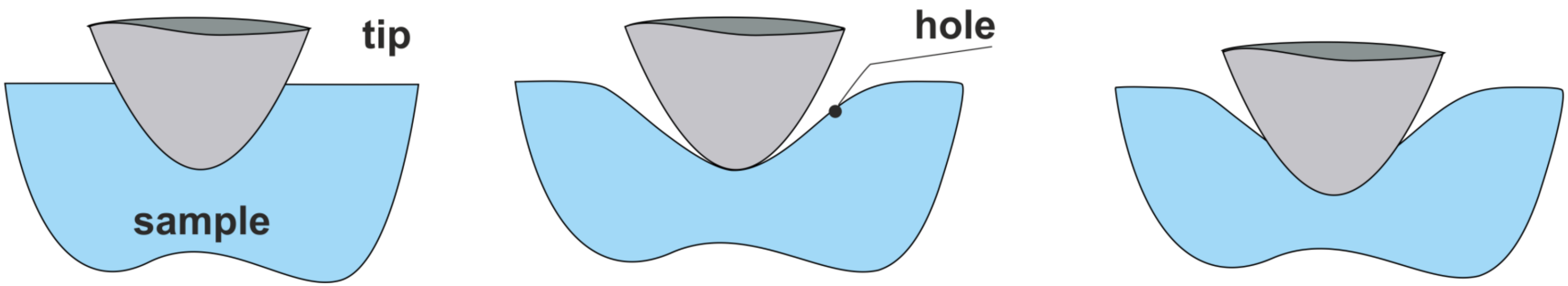
The GM3 model fits the experimental curves from the water measurements much better.

Overcoming surface roughness

(I) Plastic deformation

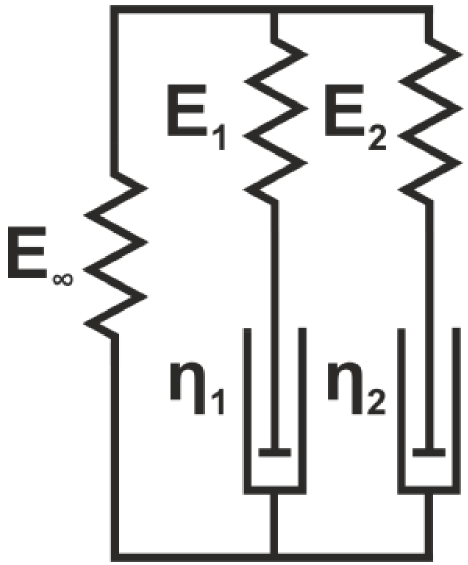
(II) After plastic deformation

(III) Viscoelastic deformation

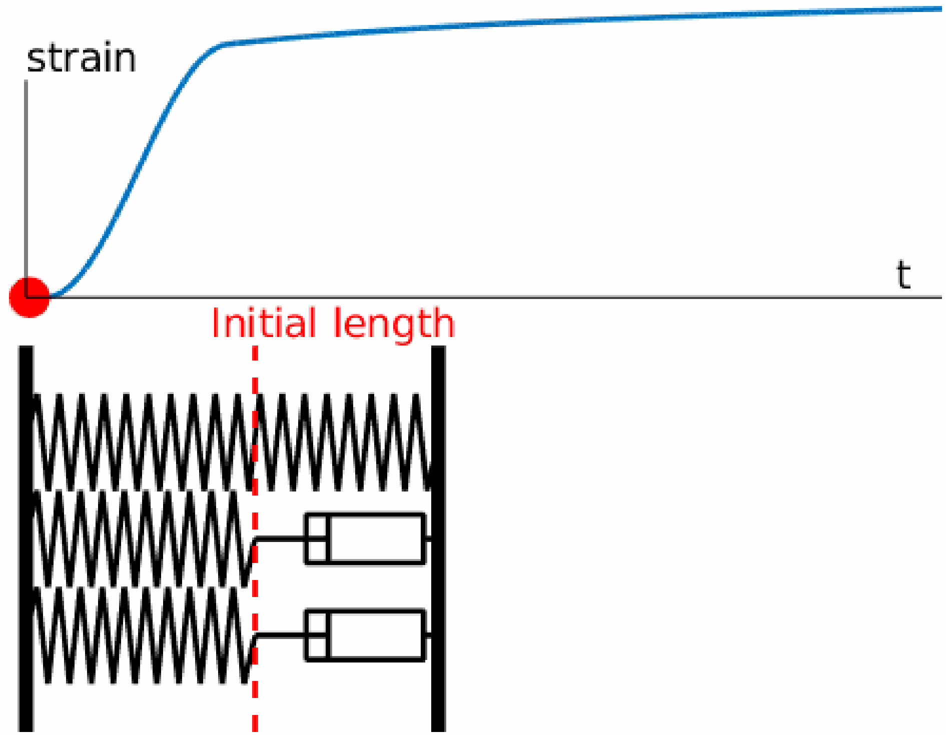


- surface roughness reduced
- defined contact area
  → contact in a hole

Generalized Maxwell order 2 (GM2) model



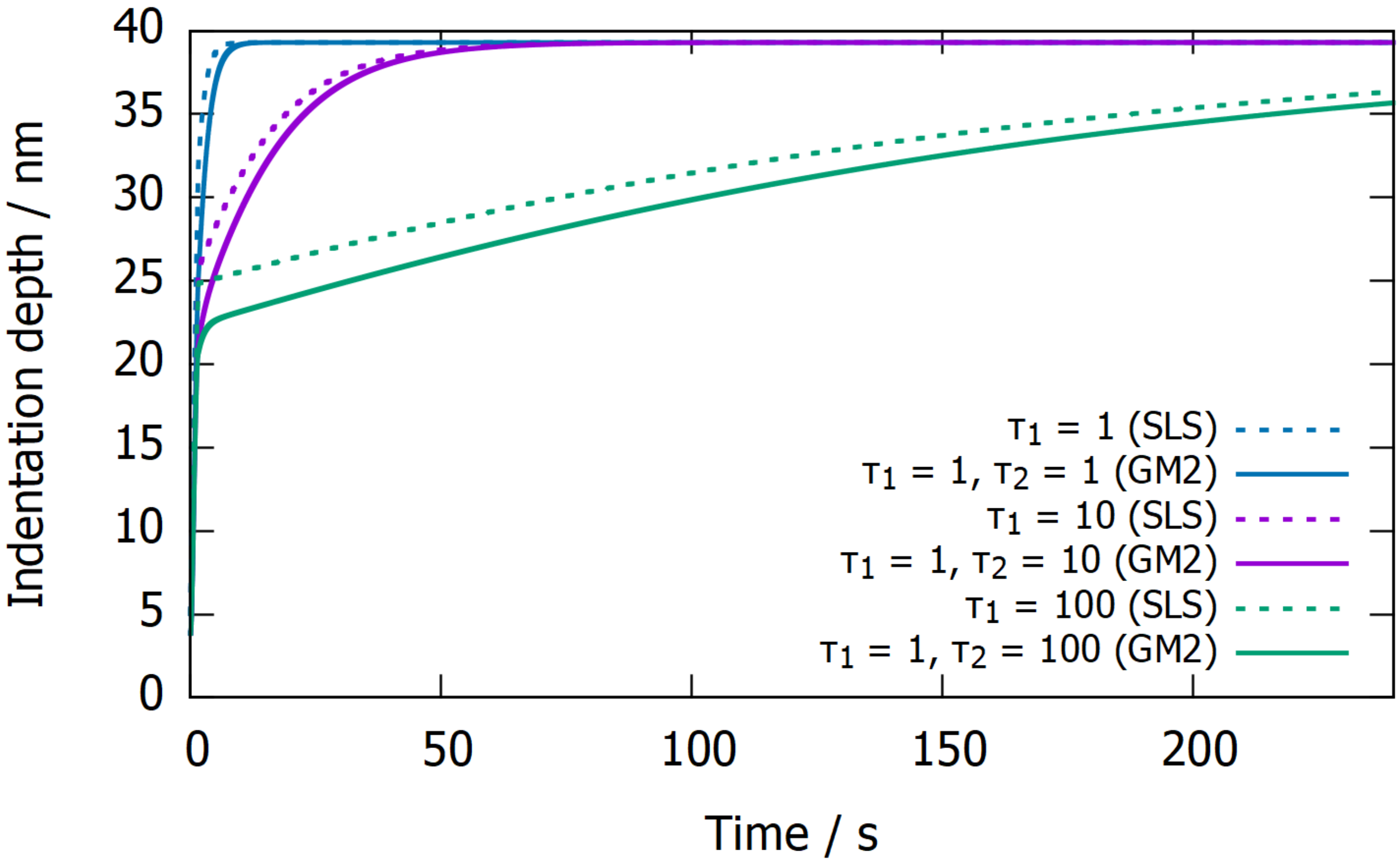
$$\sigma = A\varepsilon + B\dot{\varepsilon} + C\ddot{\varepsilon} - D\dot{\sigma} - E\ddot{\sigma}$$



Courtesy by T. Seidlhofer

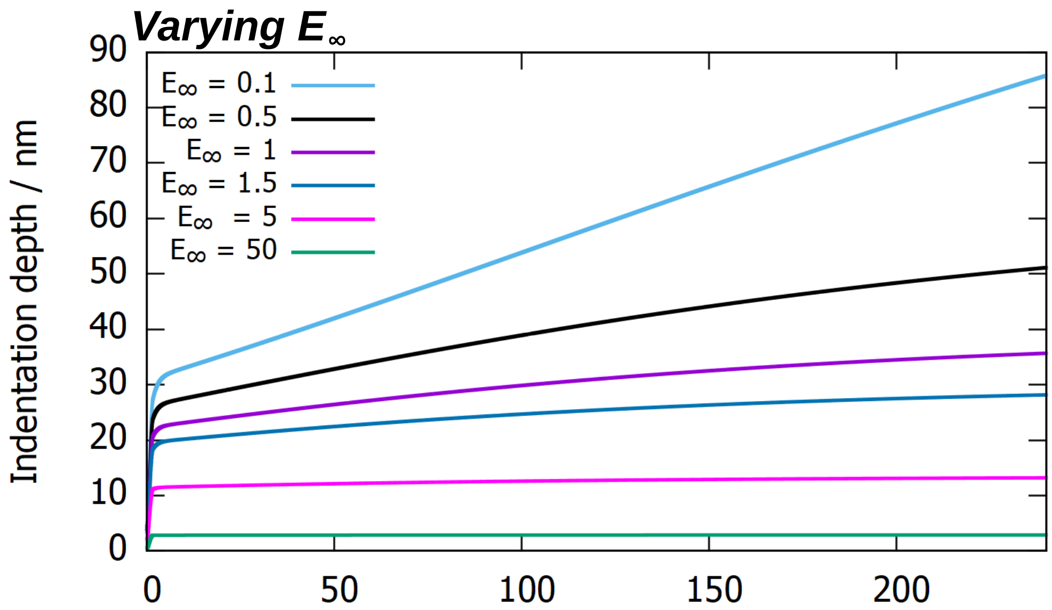
H.T. Banks, S. Hu, Z.R. Kenz. *A Brief Review of Elasticity and Viscoelasticity*. N. C. S. University. Rayleigh, 2010.
D. Roylance. *Engineering Viscoelasticity*. Massachusetts Institute of Technology. Cambridge, 2001.

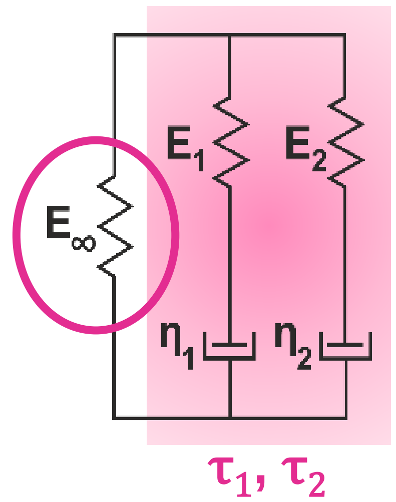
Comparison SLS & GM2

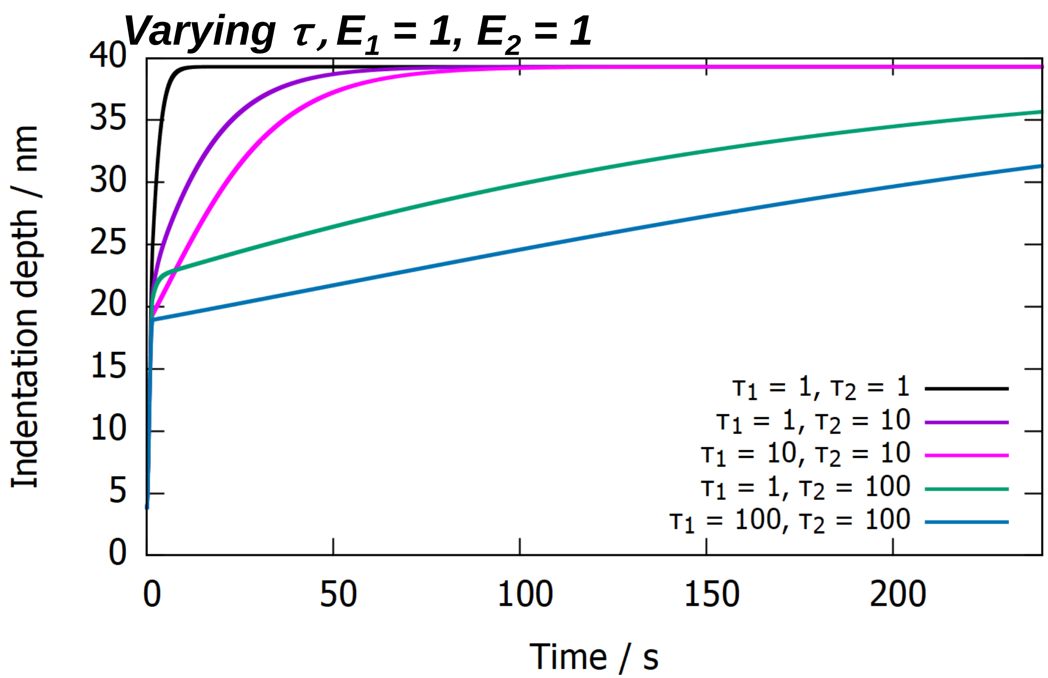


Comparison between the SLS and GM2 model show that the additional Maxwell element influences the slope/form of the curves.

GM2 model







The form and depth of the indentation curve is mainly influenced by E_∞.

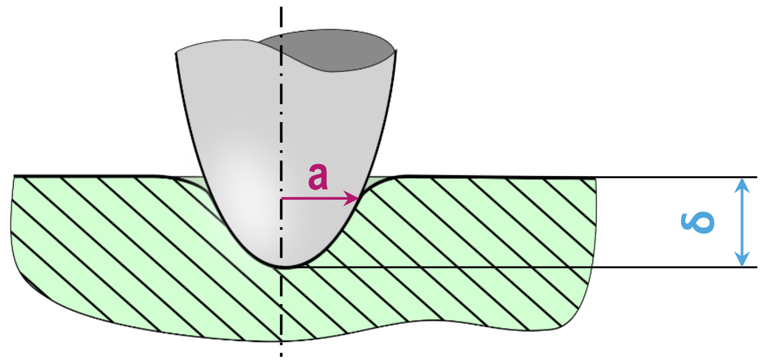
The Maxwell elements are influencing mostly the initial slope and form of the indentation curve.

Contact mechanics model

Johnson-Kendall-Roberts (JKR)

A contact mechanics model is applied to convert force and indentation depth into stress and strain.

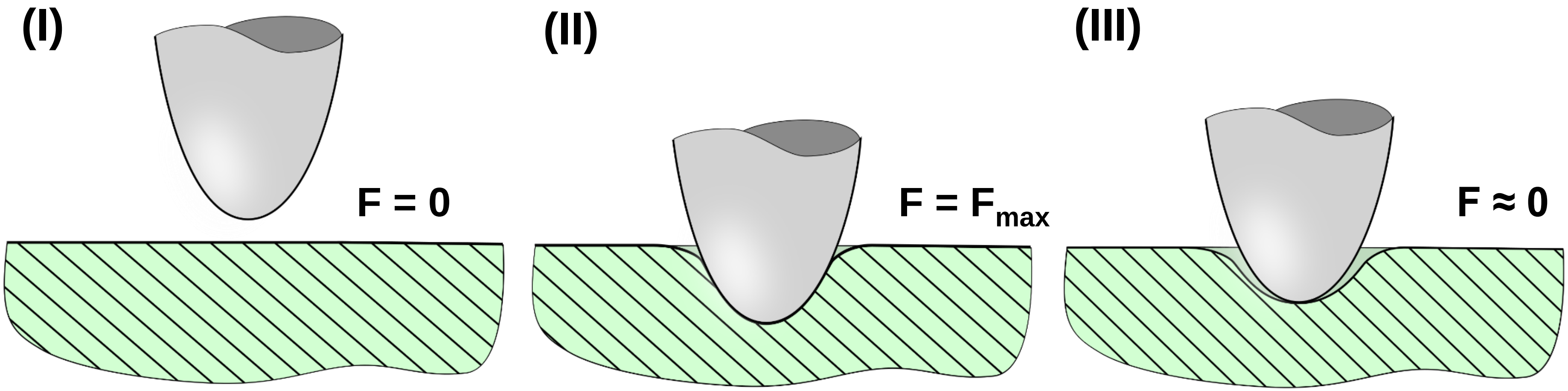
<u>JKR - Assumptions:</u>
- **Tip:** sphere
- **Sample:** plane, sphere, hole
- **Topography:** smooth
- **Regime:** elastic
- **Adhesion: YES**



	contact radius a	indentation depth δ	stress σ	strain ε
JKR	$a^3 = \frac{3R}{4E}\tilde{F}$	$\delta = \frac{a^2}{R} - \left(\frac{4a}{3R}\frac{F_a}{E}\right)^{\frac{1}{2}}$	$\sigma = \frac{\Delta(\tilde{F})}{R\delta}\left[\frac{3}{8}\tilde{F} - \frac{1}{2}\left(\tilde{F}F_a\right)^{\frac{1}{2}}\right]$	$\varepsilon = \left(\frac{\delta}{R}\right)^{\frac{1}{2}} \frac{1}{\Delta(\tilde{F})^{\frac{1}{2}}}\left[\frac{1}{2} - \left(\frac{F_a}{\tilde{F}}\right)^{\frac{1}{2}}\right]$

K.L. Johnson, K. Kendall and A.D. Roberts, *Proc. R. Soc. Lond. A*, **324** (1971), 301-313.

Contact mechanics in a hole

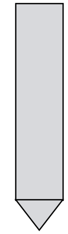


I. undeformed, virgin surface

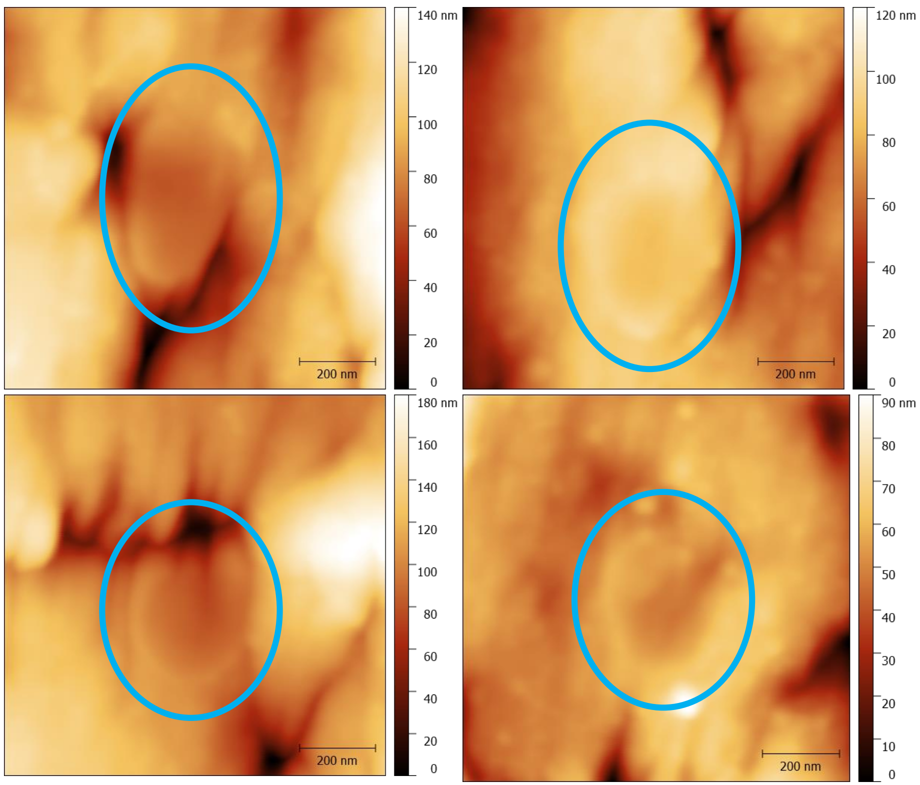
II. plastic deformation under maximum load

III. after unloading, the surface is different from (I) due to plastic deformation

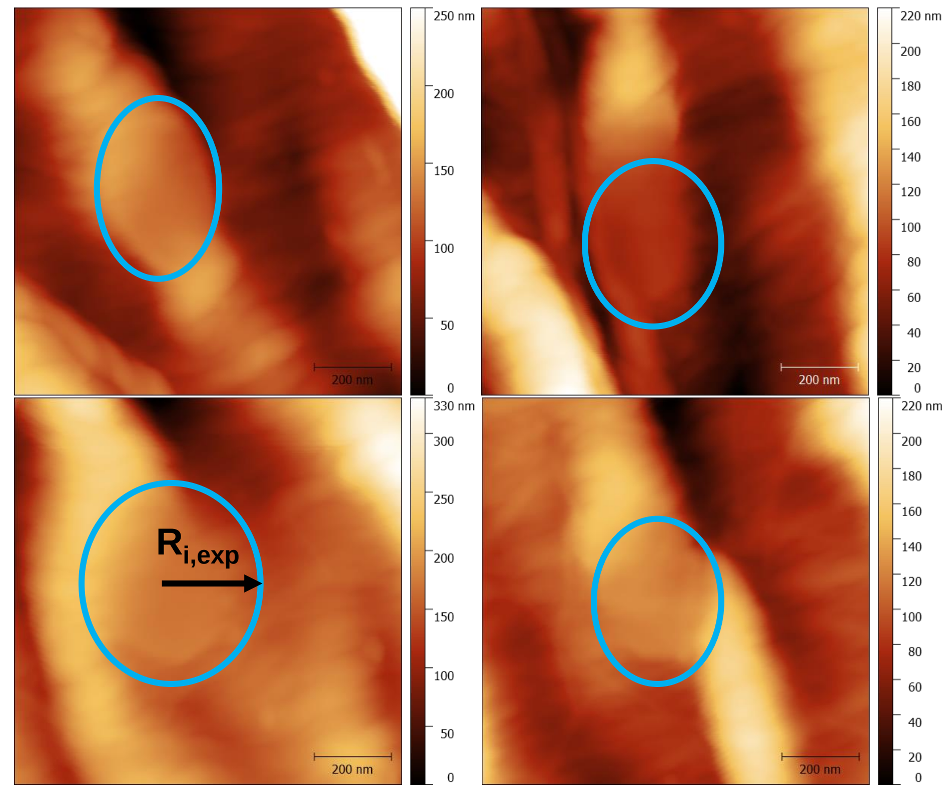
After AFM-NI



Viscose fiber



Paper fiber



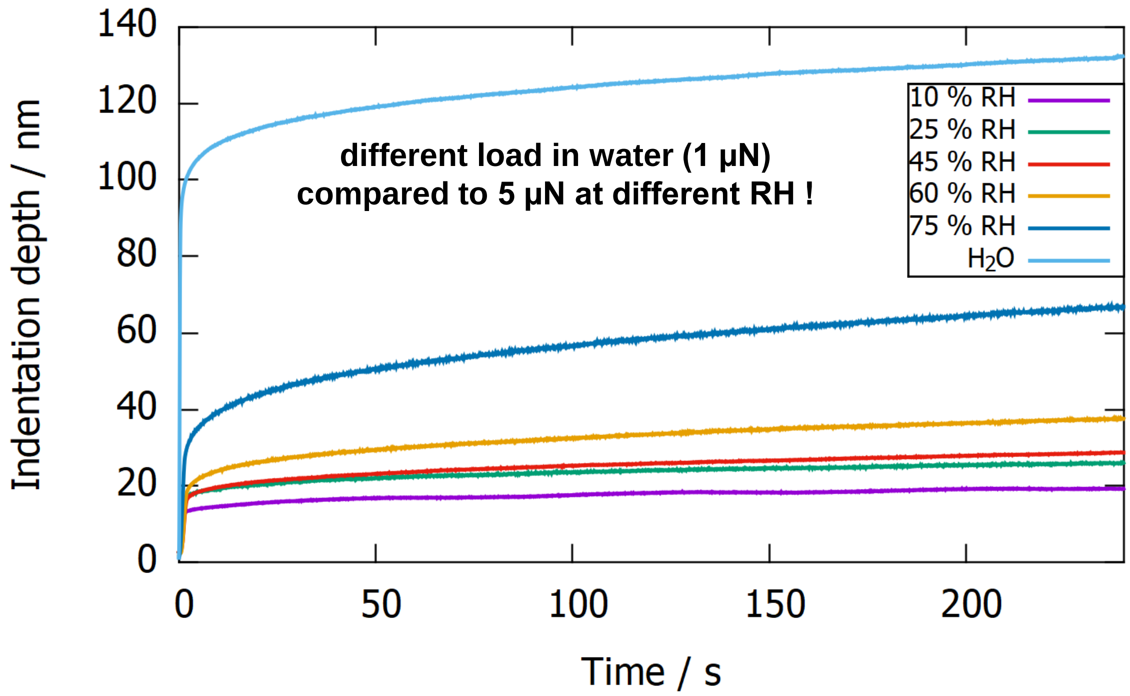
$R_{i,exp}$ .. Experimentally measured hole radius

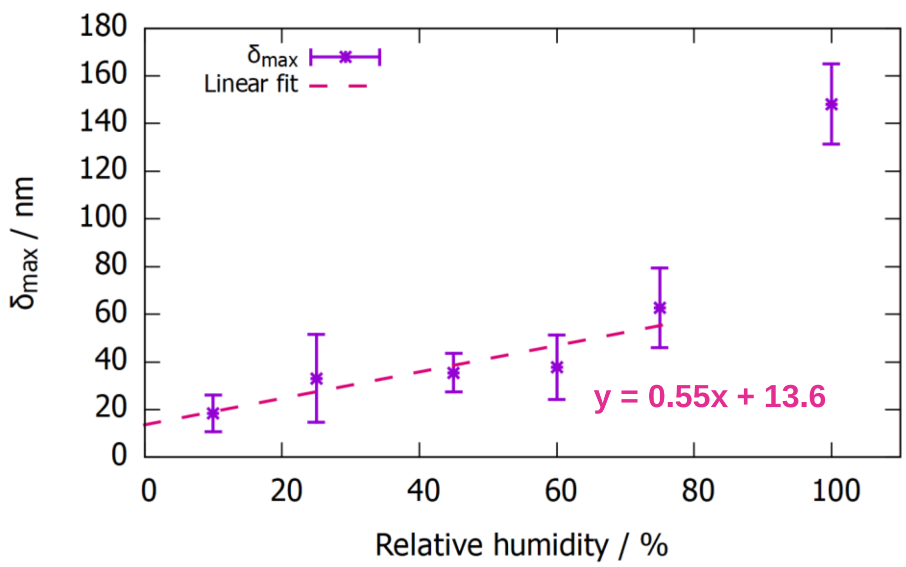
Sample	$R_{i,exp}/R_{tip}$
Viscose fiber	8.55 ± 5.15
Paper fiber	4.15 ± 2.30

The hole radius is larger than the tip radius.

Experimental curves

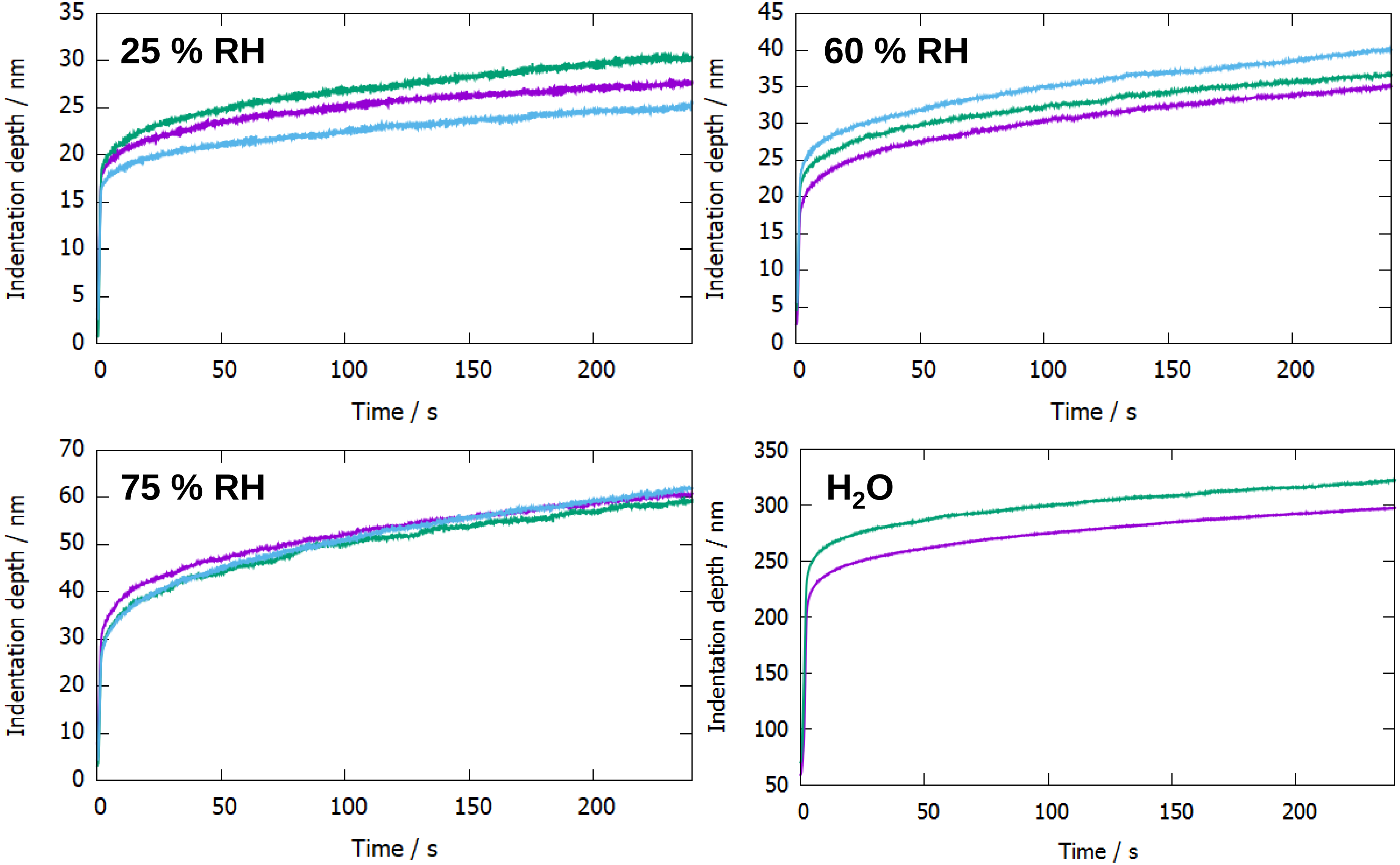
Averaged curves from 6 different Monopol X pulp fibers





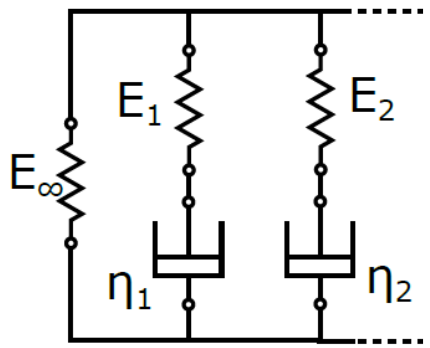
Indentation depth and slope increases with increasing RH as expected.

Indentation depth at different RH



Indentation depth and slope increases with increasing RH.

Generalized Maxwell order 2 (GM2) model



$$\boldsymbol{\sigma = A\varepsilon + B\dot{\varepsilon} + C\ddot{\varepsilon} - D\dot{\sigma} - E\ddot{\sigma}}$$

Parameters: elastic moduli & viscosities

$$A = E_\infty \qquad B = \left(\frac{\eta_1 + \eta_2}{E_\infty} + \frac{\eta_2}{E_3} + \frac{\eta_1}{E_2}\right)E_\infty$$

$$C = \eta_1\eta_2\frac{E_\infty + E_1 + E_2}{E_1E_2} \qquad D = \frac{\eta_2}{E_3} + \frac{\eta_1}{E_2}$$

$$E = \frac{\eta_1\eta_2}{E_2E_3}$$

Parameters: elastic moduli & relaxation times

$$A = E_\infty \qquad B = \left(\frac{E_1\tau_1 + E_2\tau_2}{E_\infty} + \tau_1 + \tau_2\right)E_\infty$$

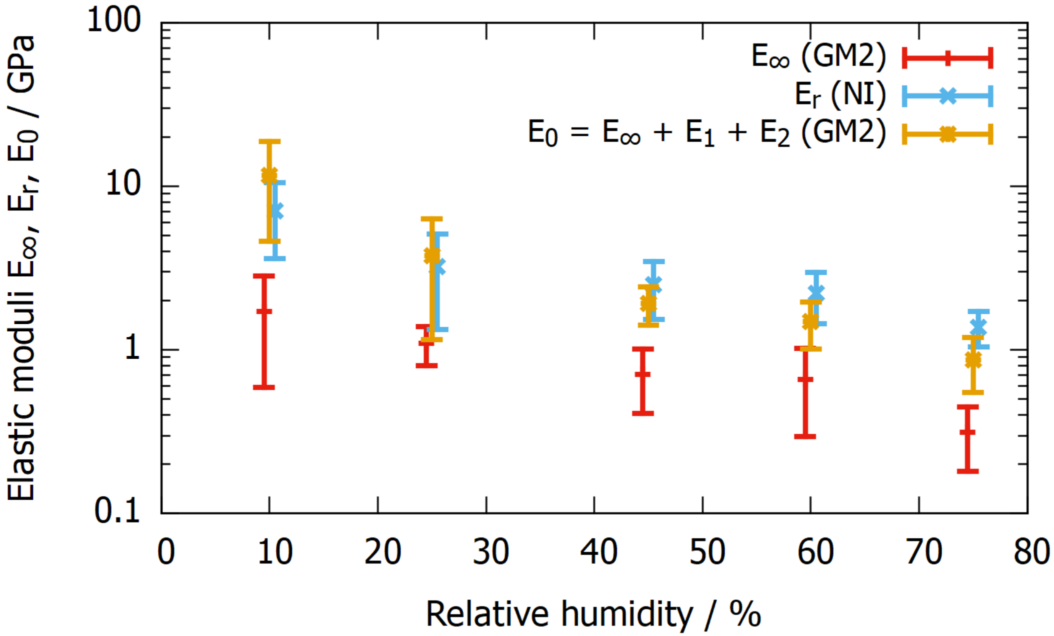
$$C = \tau_1\tau_2\ (E_\infty + E_1 + E_2) \qquad D = \tau_1 + \tau_2$$

$$E = \tau_1\tau_2$$

$$\boldsymbol{\tau_i = \frac{\eta_i}{E_i}}$$

H.T. Banks, S. Hu, Z.R. Kenz. *A Brief Review of Elasticity and Viscoelasticity*. N. C. S. University. Rayleigh, 2010.
D. Roylance. *Engineering Viscoelasticity*. Massachusetts Institute of Technology. Cambridge, 2001.

Comparison of AFM-NI and GM2 E-moduli results



infinitely fast loading; upper limit:

$$\mathbf{E_0 = E_\infty + E_1 + E_2}$$

infinitely slow loading; lower limit:

$$\mathbf{E_\infty}$$

$E_r > E_\infty$

$E_r \sim E_0$

The comparison shows that E_0 of the GM2 model are very close to E_r of AFM-NI whereas the E_∞ values are much lower.