Pulp and Paper Testing Methods at TU Graz

U. Hirn, TU Graz

ITN Network 'FibreNet' – Training Event 2019-02

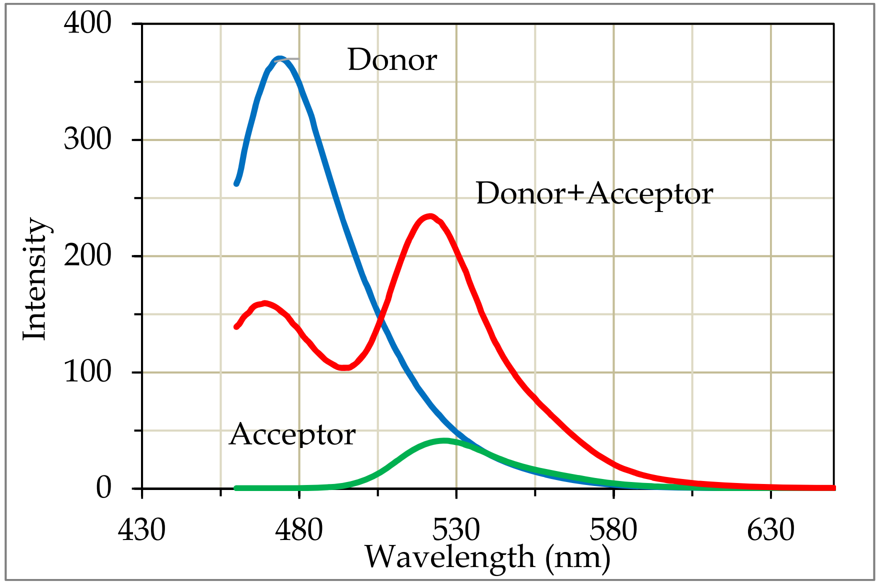
Overview

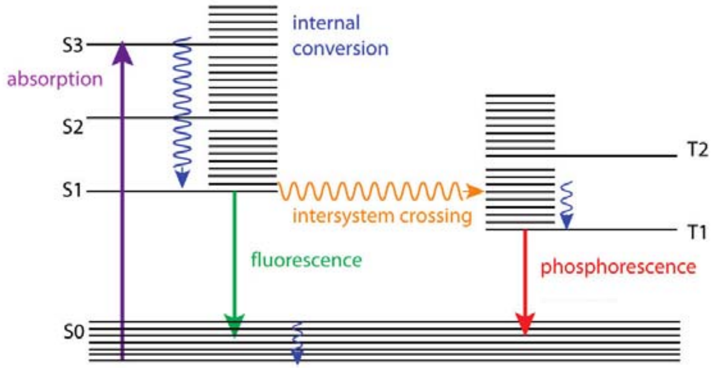
- Fluorimetry / FRET microscopy
- Microtomy cross sections of paper and fibers
- Single fiber mechanical testing
- Pulp fines and cellulose thin films
- Paper handsheet making and coating
- Paper hygro- and hydroexpansivity
- Paper liquid penetration and wetting
- Paper structure
- Paper mechanical testing
- High resolution paper surface properties

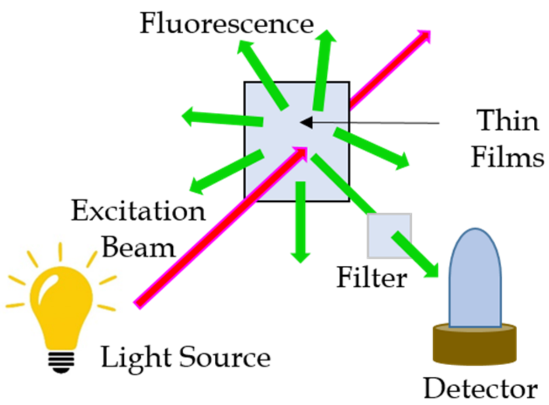
Spectrofluorimeter

- A Fluorescence Spectrometer is an equipment used to measure **fluorescence spectra**, taking advantage of **fluorescent properties** of some compounds.
- A certain excitation wavelength is selected, and the emission is observed either at a single wavelength, or a scan is performed to record the intensity versus wavelength, also called an emission spectra.
- The fluorescence spectra provide information about the **concentration and chemical environment** in a sample.

Example:

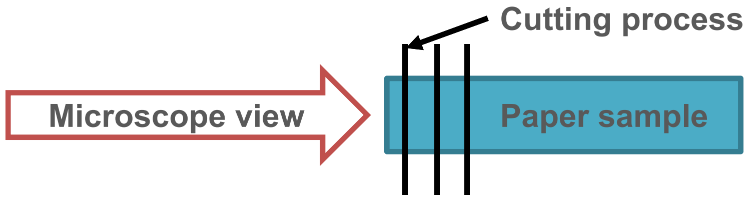


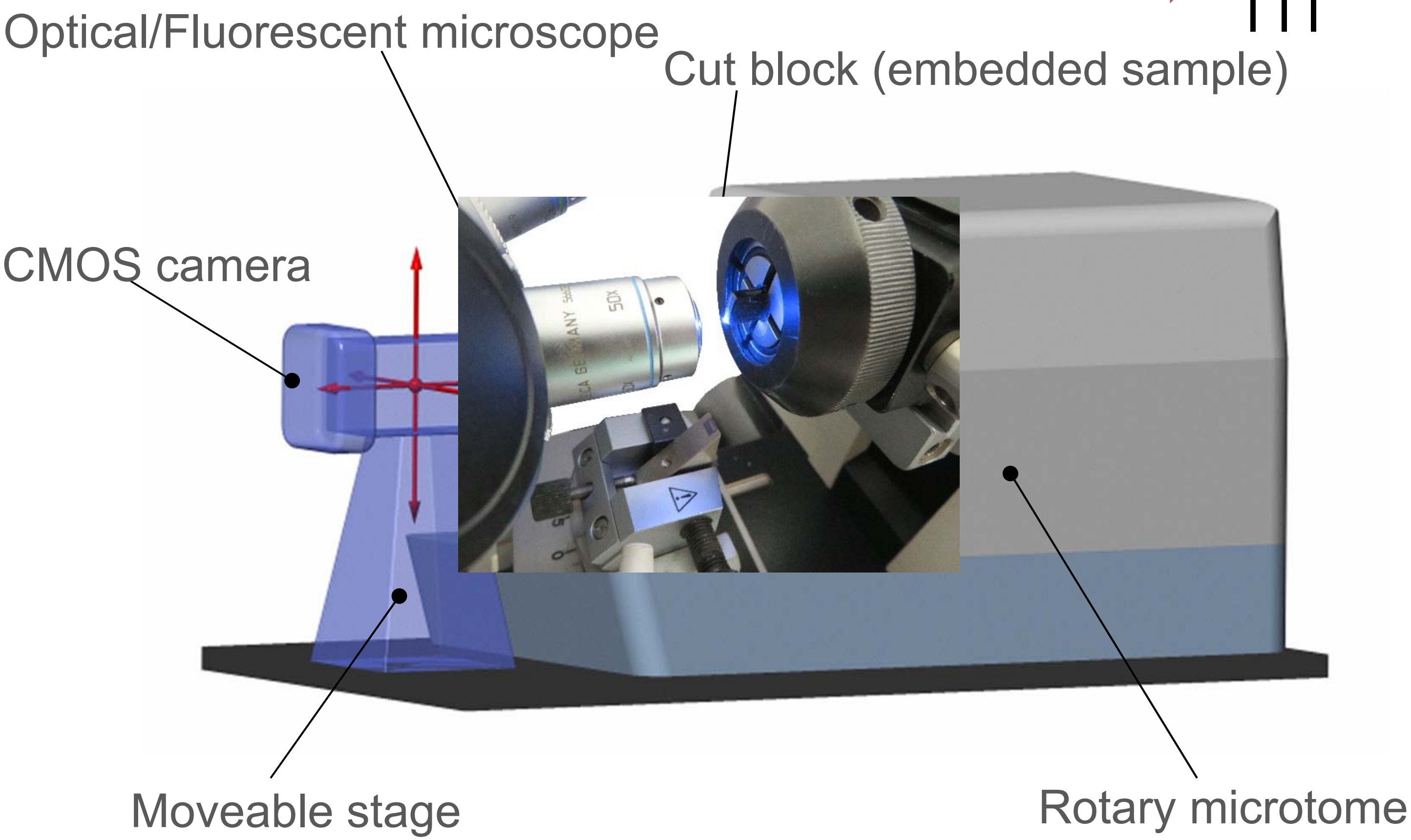




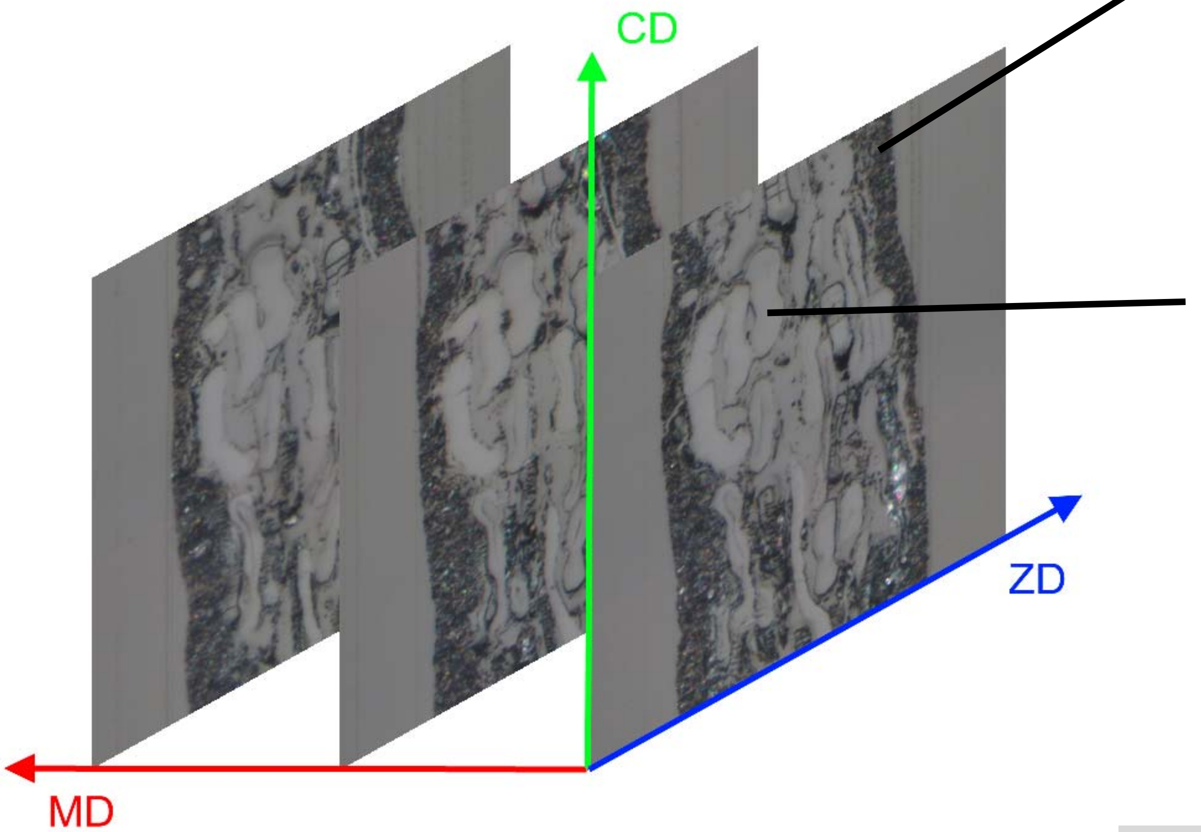
Microtome
- Paper cross sections

Automated Serial Sectioning





Automated Serial Sectioning



Coating Layer:
- Uniformity
- Coating coverage
- Coating holdout

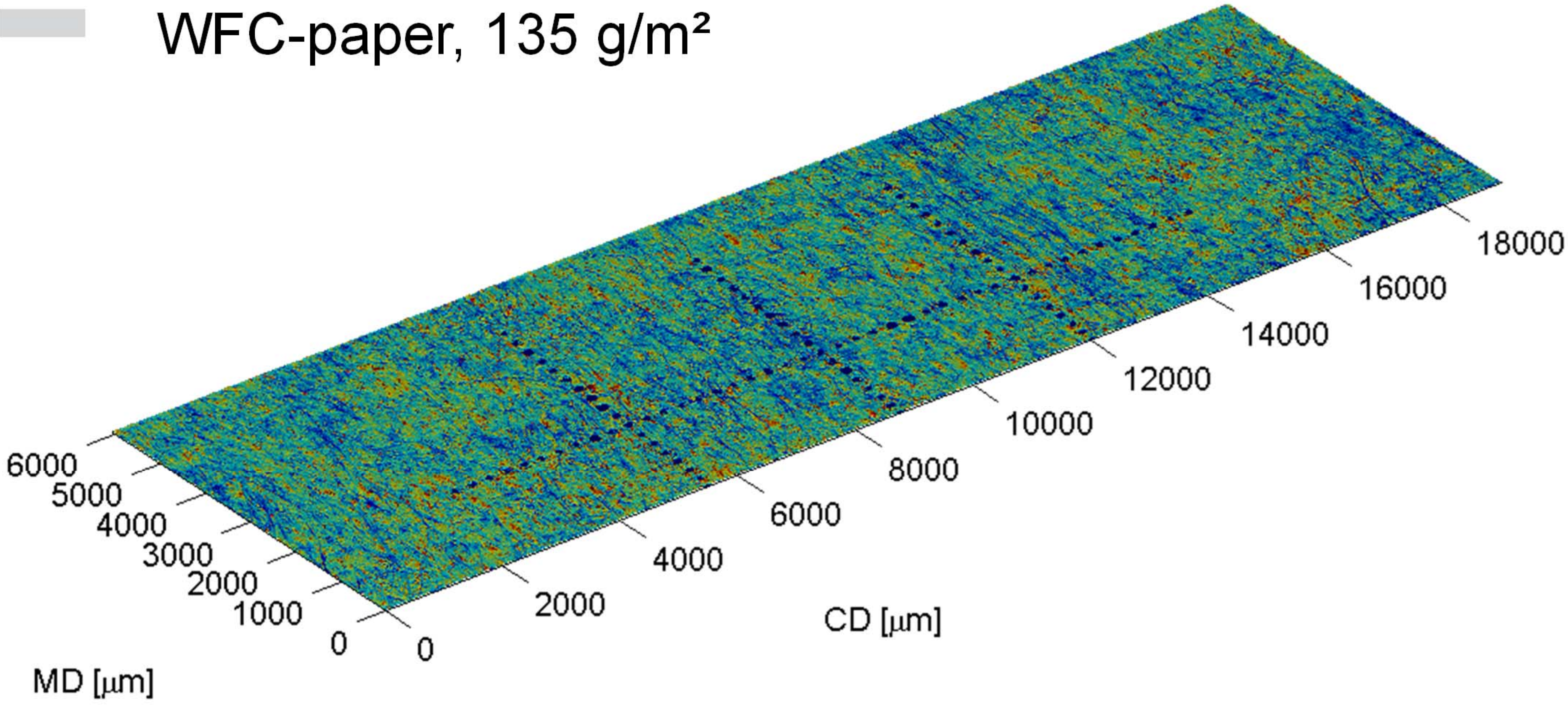
Fiber Cross Sections:
- Fiber Wall Thickness
- Coarseness

Other properties:
- Printing ink penetration….

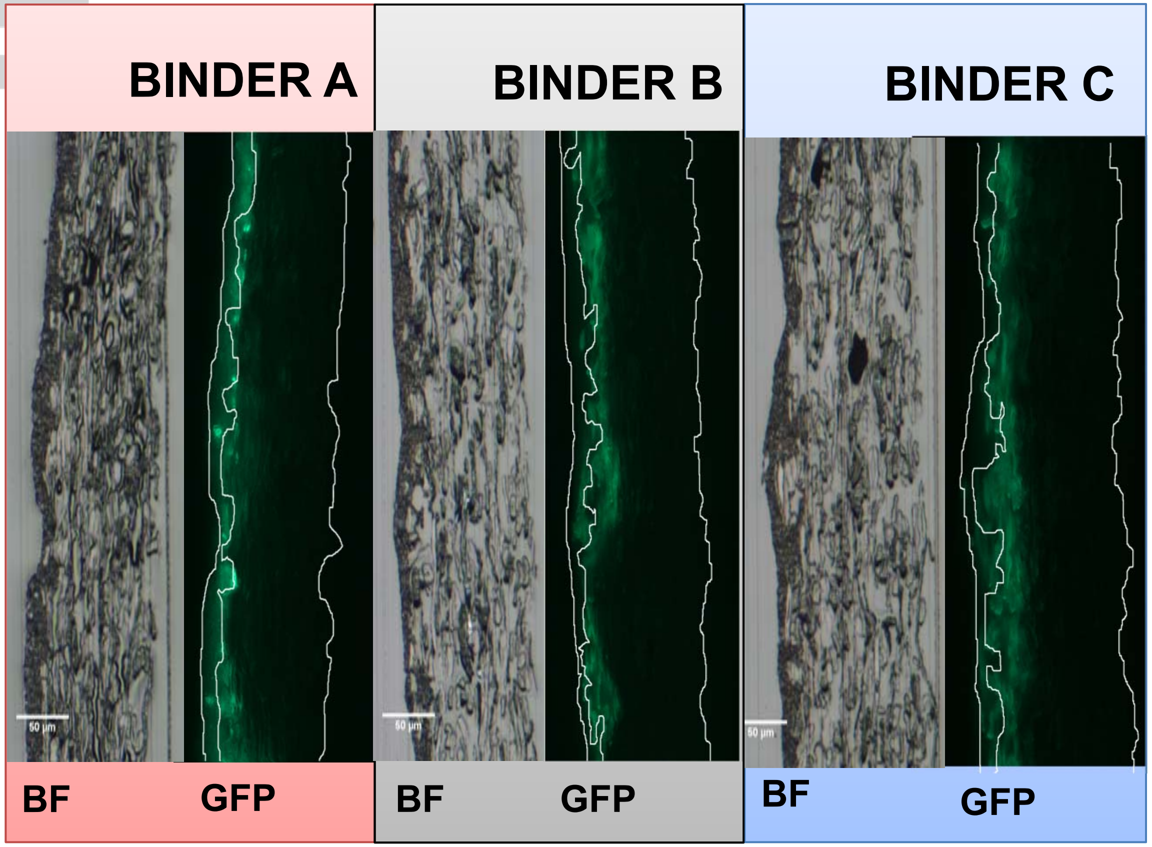
Coating Layer Analysis

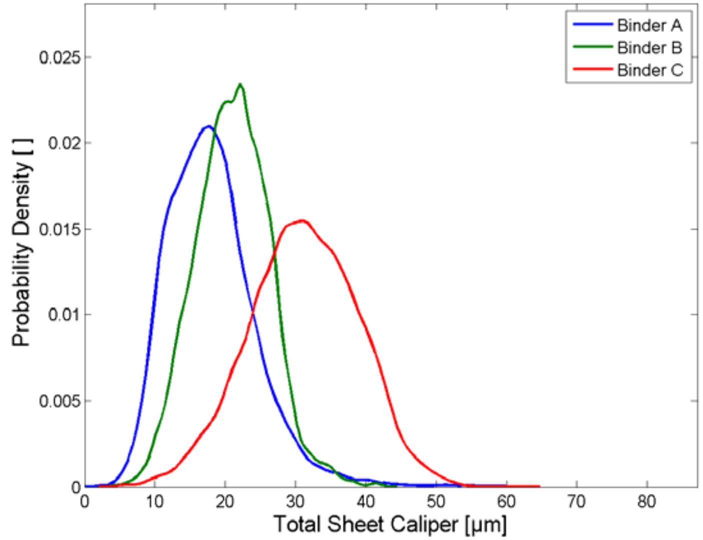
Coating thickness map

WFC-paper, 135 g/m²



Coating Binder Penetration

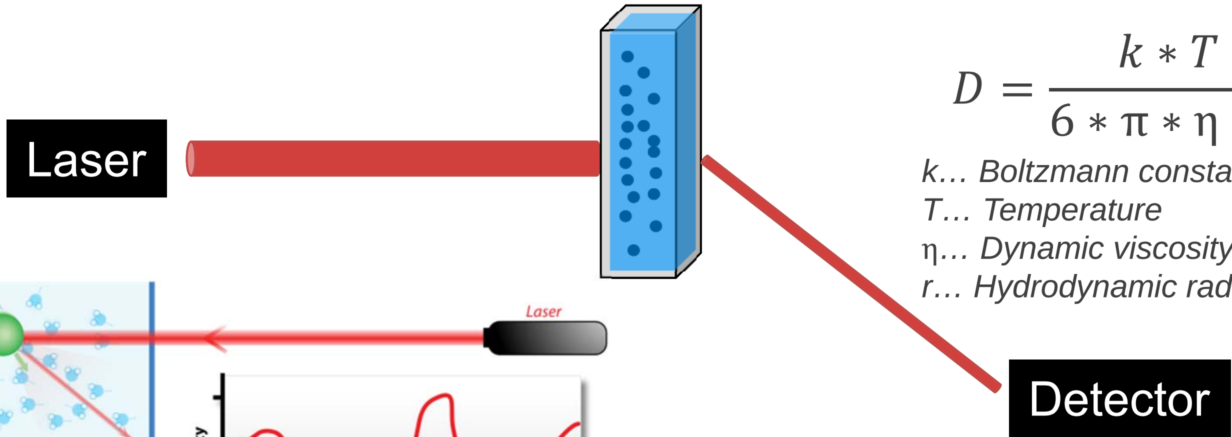




Particle analysis
Fiber morpology
Fiber mechanics

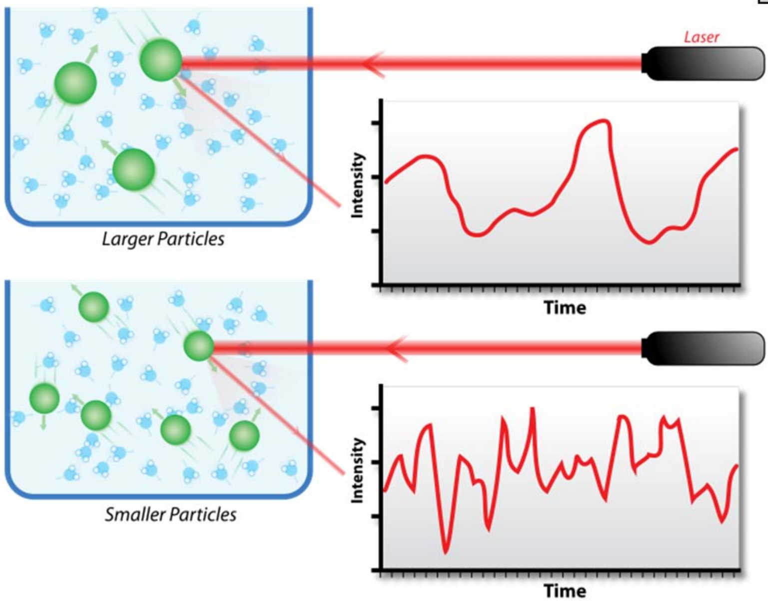
Dynamic Light Scattering (DLS)

Determination of the hydrodynamic radius of particles or polymeris in dispersion or solution with a size of approx. 1 nm – 1 µm at 0.1-1 mg/ml content.



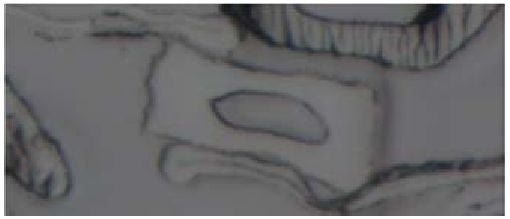
$$D = \frac{k * T}{6 * \pi * \eta * r}$$

k… Boltzmann constant
T… Temperature
η… Dynamic viscosity solvent
r… Hydrodynamic radius



Cross Sectional Fiber Morphology

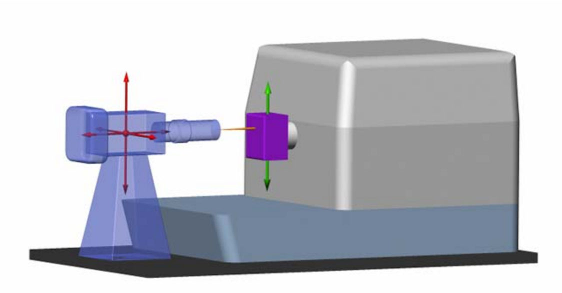
Sample Preparation



Fiber Digitization

Fiber Binarization

Fiber Correction

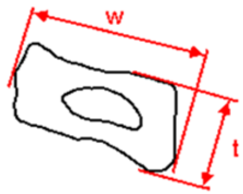


Fiber Properties

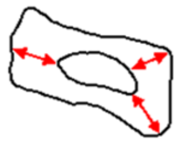
Fiber Wall Area

Fiber Lumen Area

Fiber Perimeter



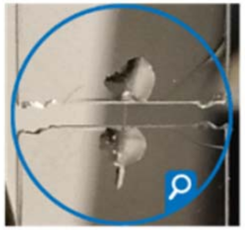
Fiber Width and Fiber Thickness

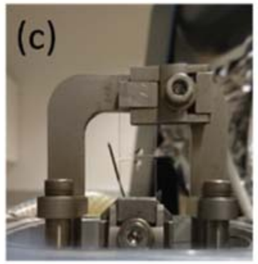


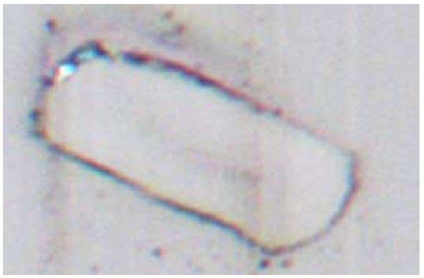
Fiber Wall Thickness

Fiber longitudinal mechanics, Fiber bending

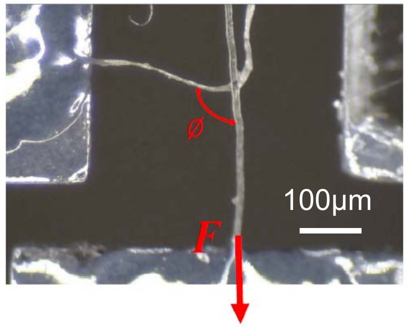
- Fiber properties
  - E-Modulus
  - Yield point
  - Bending stiffness
  - Viscous properties





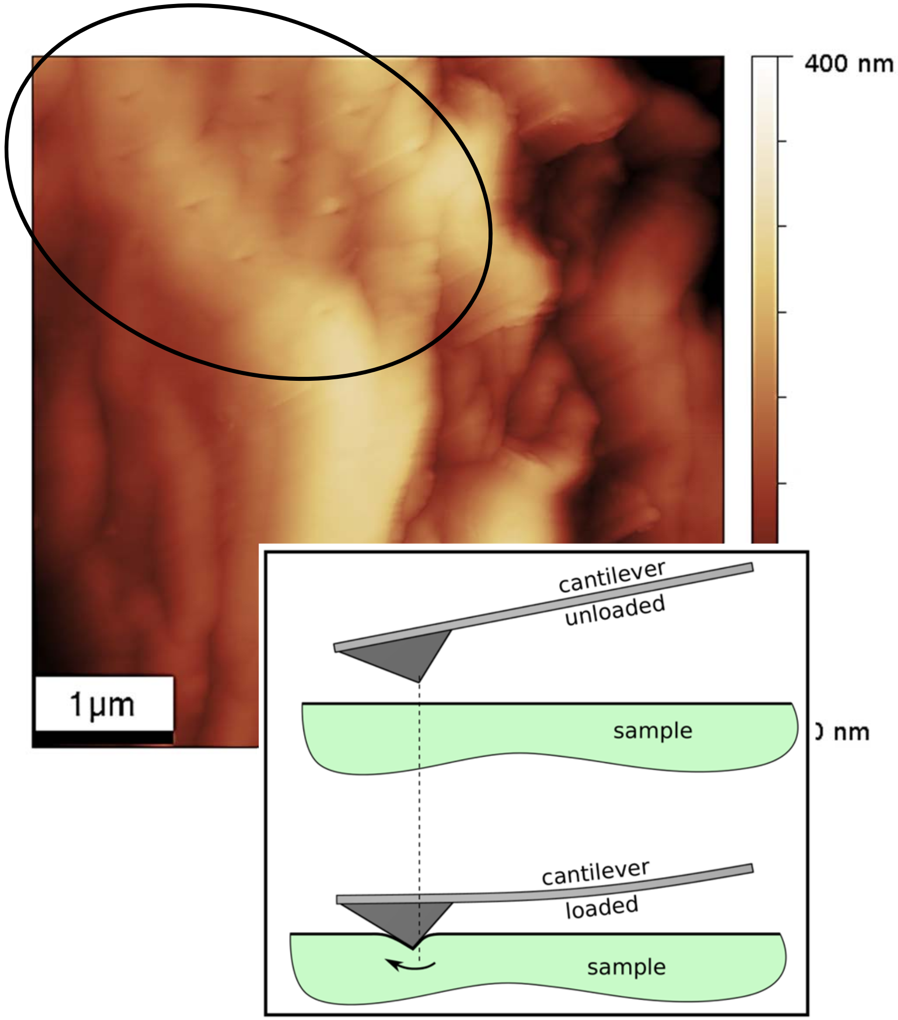


Fiber cross sectional shape
→ microtomy



Fiber transversal mechanics – AFM

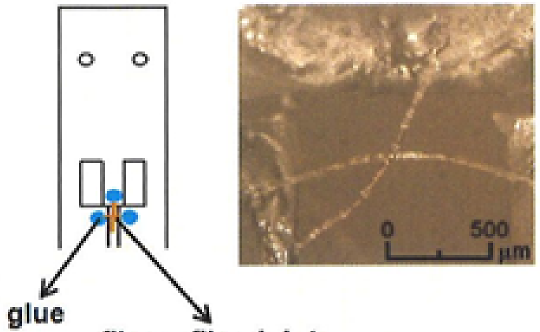
- Fiber properties
  - E-Modulus
  - Yield point
  - Bending stiffness
  - Viscous properties



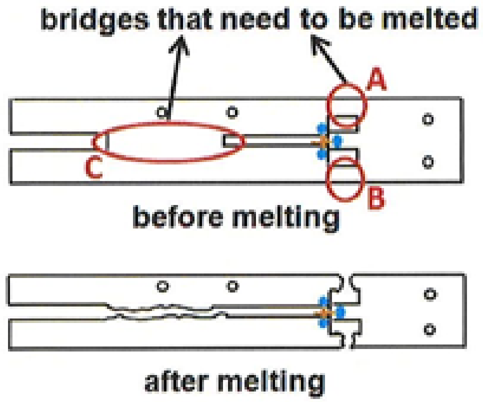
Fiber-Fiber Bond Testing

Bond strength
Bonding energy

- **Opening (mode I)**
- **Shear (mode II + III)**



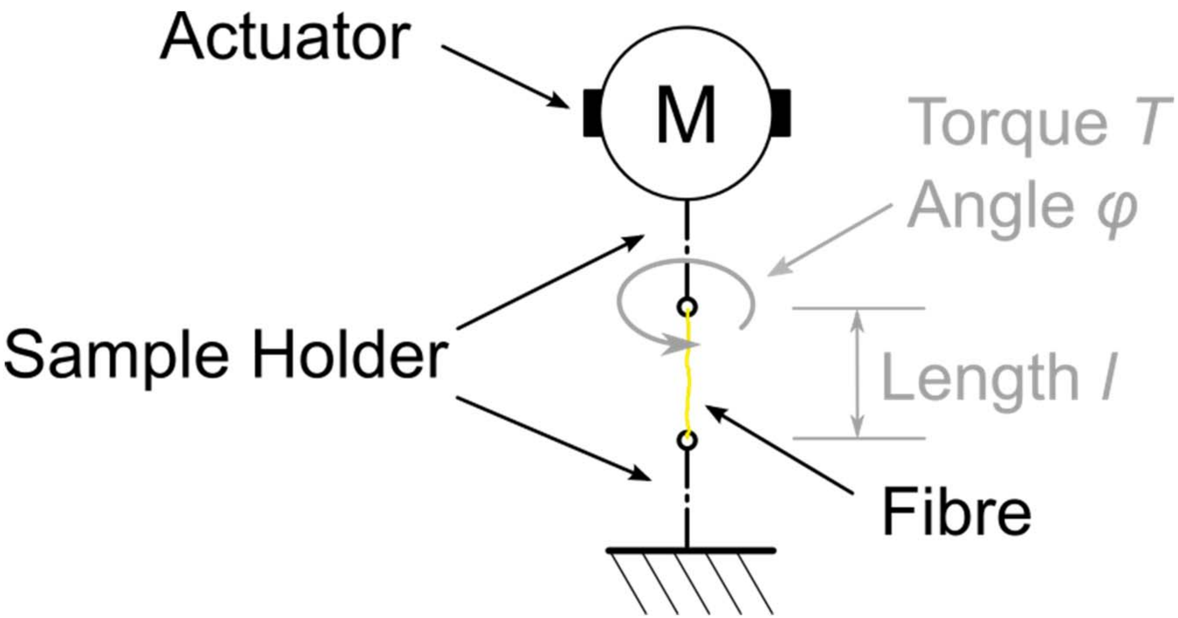
(a) Fixation of joint



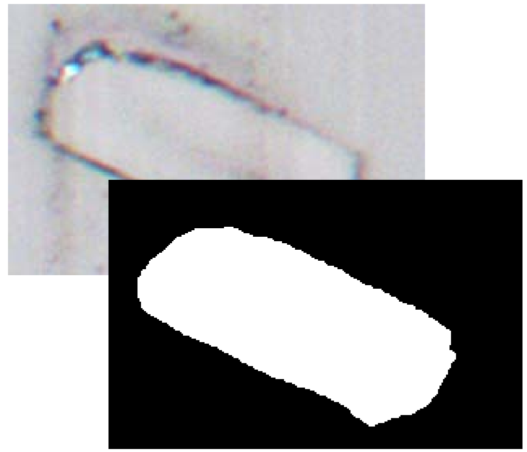
(b) Melting of bridges

Fiber torsional shear testing

Torsion Experiment



Microtomy

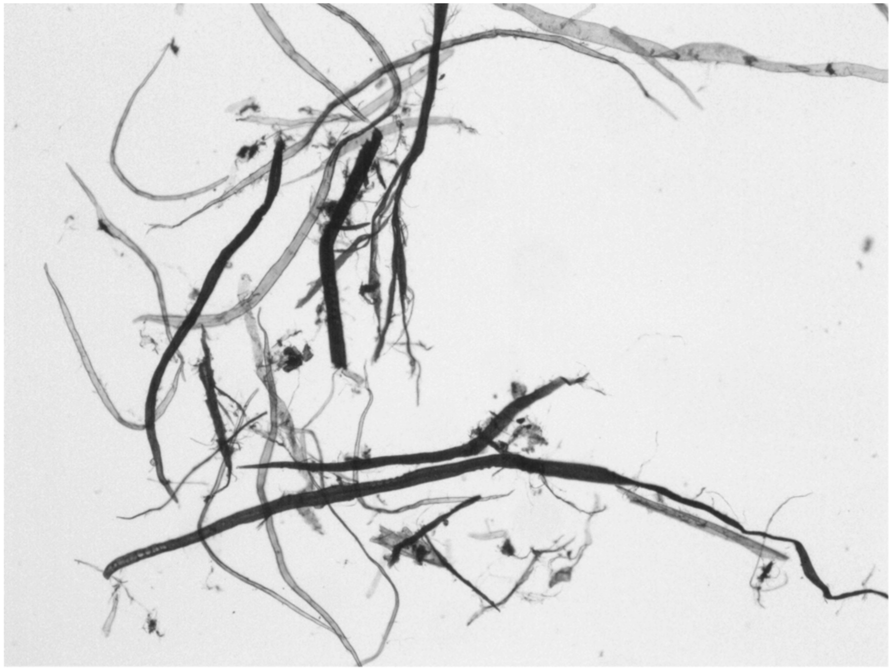


Polar area moment of inertia I_P,

From T, φ, l and I_P we calculate the shear modulus $$G = \frac{T \times l}{I_P \times \varphi}$$

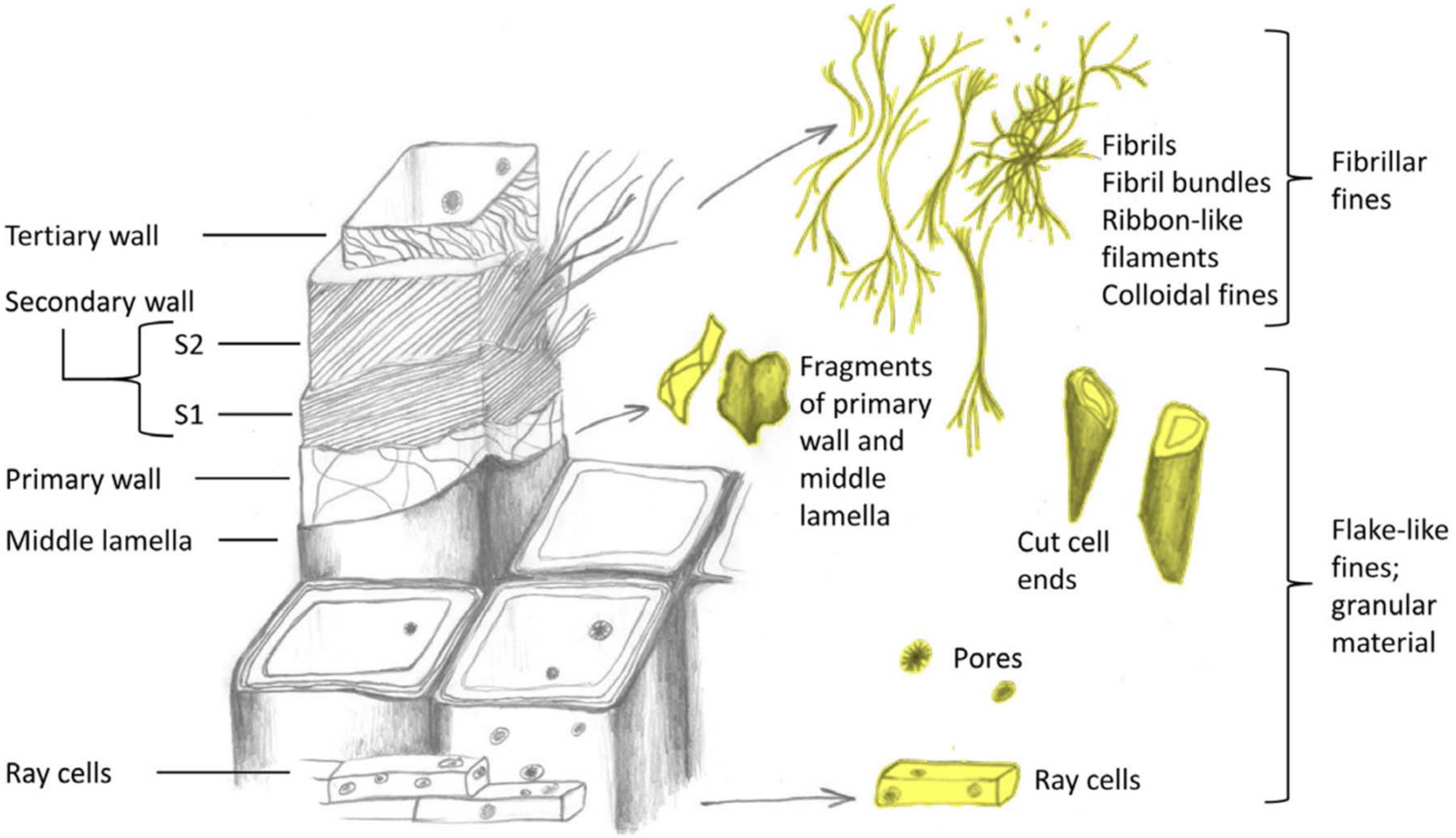
Fiber morphology

- Fiber length
- Kink / Curl
- Fiber width
- Fines analysis



Cellulose thin films
Pulp fine material

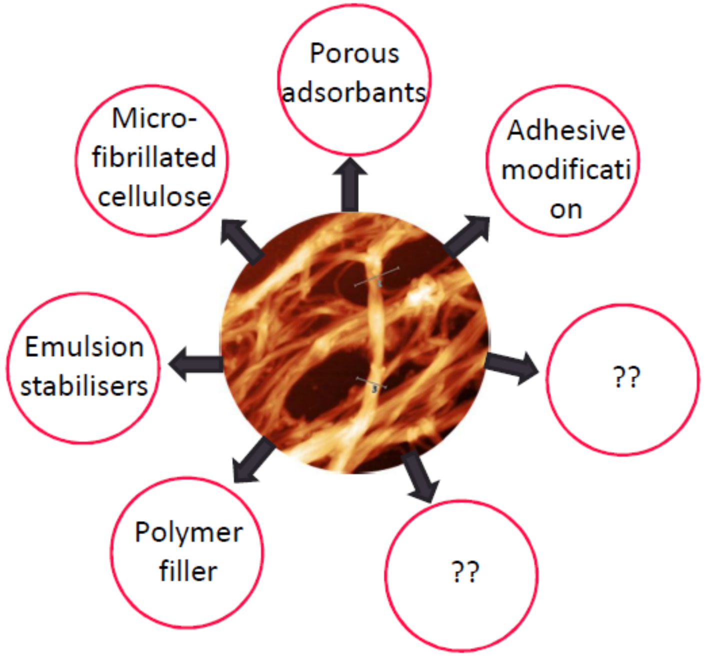
Pulp fine material



Source: Chemische Modifizierung und Nutzung von Zellstoff in Papierqualität und Fraktionen daraus | Odabas (2016)

Non-paper applications of fines

- Valorisation of fines as a sidestream
  - Pulp production
  - Papermaking



Fines separation

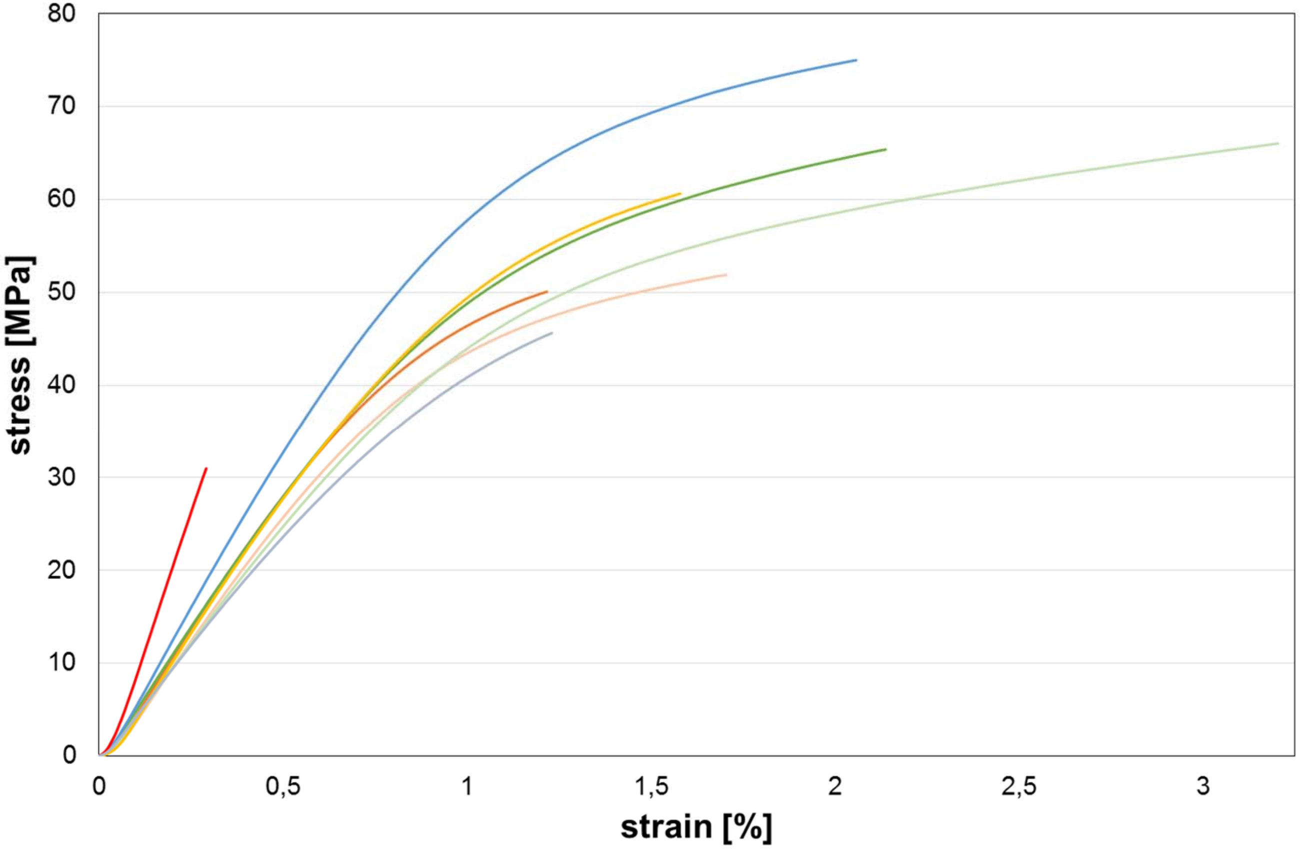
Pressure Screen

Column Flotation

Stress-strain curves of sheets from cellulosic fine materials

- PF sulfite pulp
- SF sulfite pulp
- PF kraft pulp
- SF kraft pulp
- NFC Masuko
- NFC Microfluidizer
- Fines Whitewater A
- Fines Whitewater B

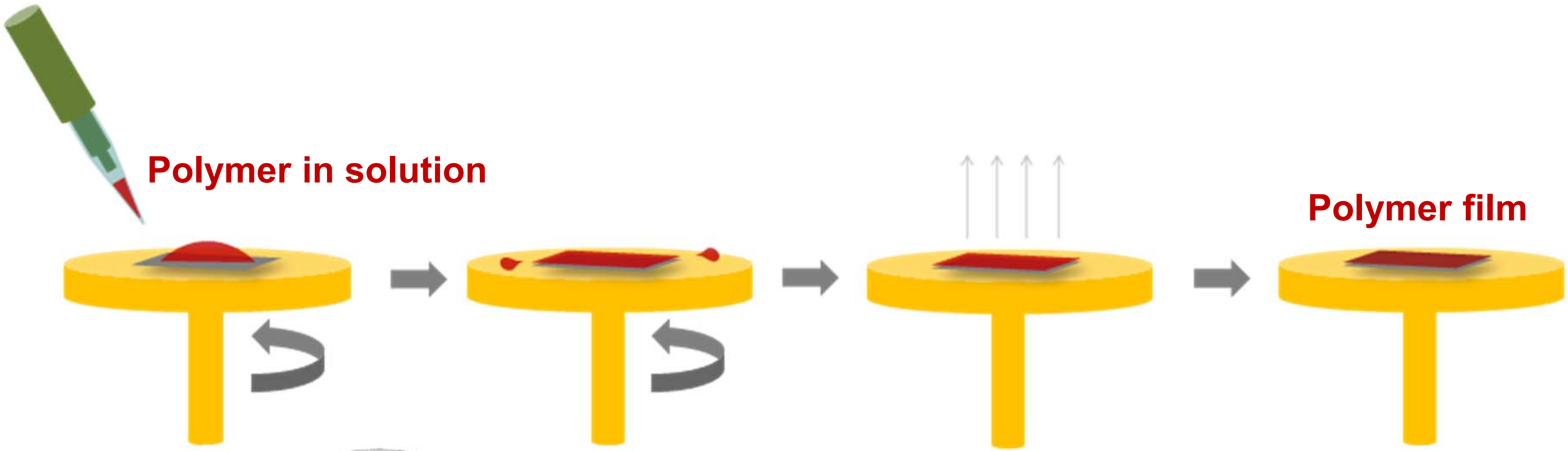
PF…primary fines
SF…secondary fines



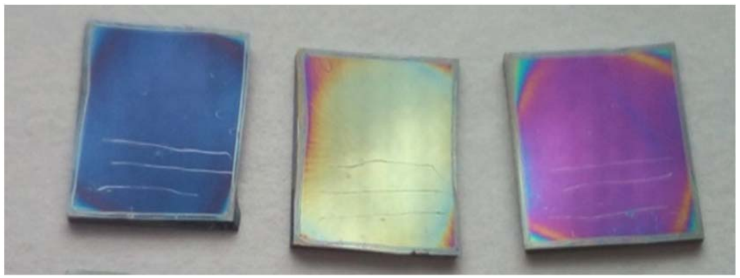
Stress strain curve of fines and NFC

Spin Coating (SC)

Coating of flat substrates with polymers yielding films with a thickness of 10 nm – 1 µm.



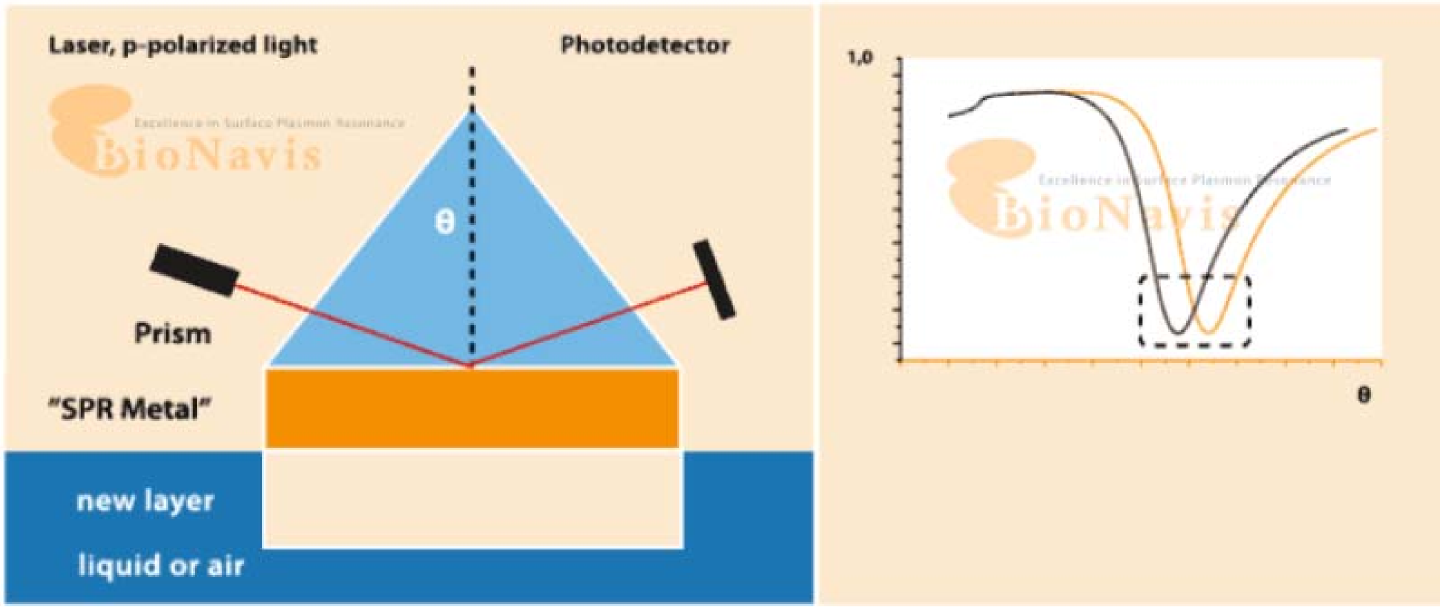
a ≈ 2500 rpm/s
v ≈ 4000 rpm
t ≈ 60 s



Multi-Parameter Surface Plasmon Resonance Spectroscopy

Provides information about layer properties: thickness and refractive index of thin film

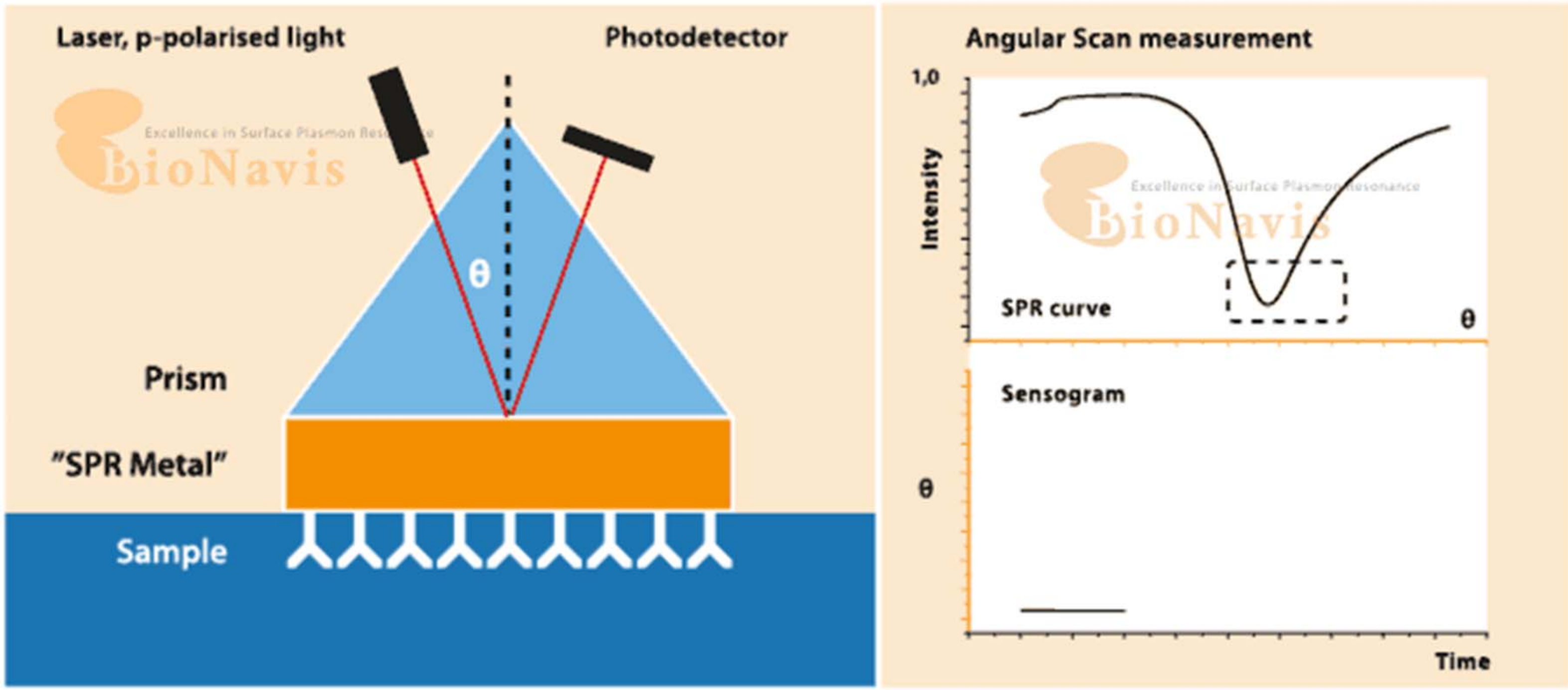
e.g. investigate swelling behavior of biobased thin films



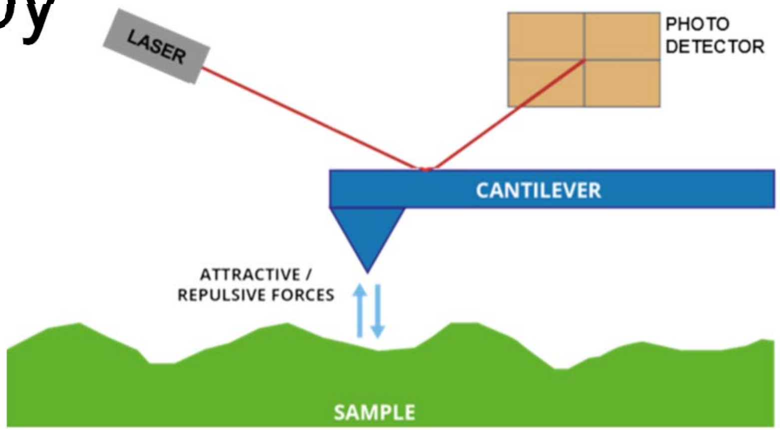
Multi-Parameter Surface Plasmon Resonance Spectroscopy

Monitor real-time label-free biomolecular interactions

e.g. investigate adsorption behavior BSA on Cell-Blend films

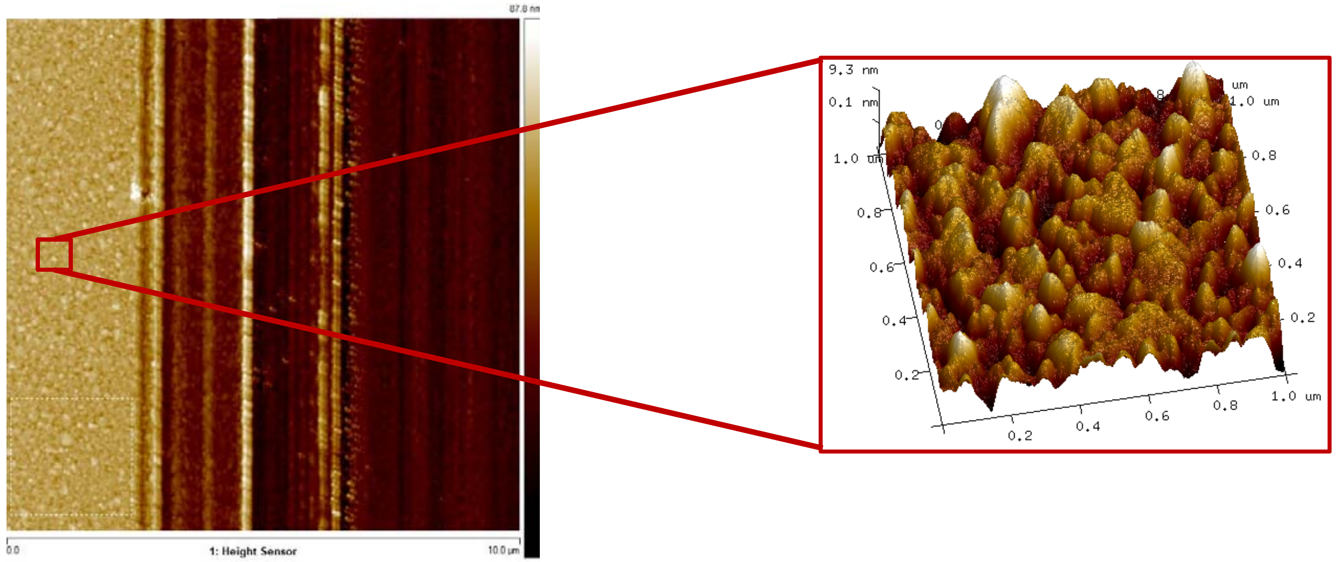


Atomic Force Microscopy



Imaging technique based on scanning of sample surface with a ultra-sharp AFM tip which is attached to a flexible canitlver.

→ Records interactions between tip and surface



Handsheet making
Paper coating
Barrier Properties

Paper making procedure

pulp from pulp mill

→

PFI refining
- 3000 rev

→

Filling into distribut

Handsheet Forming (1)

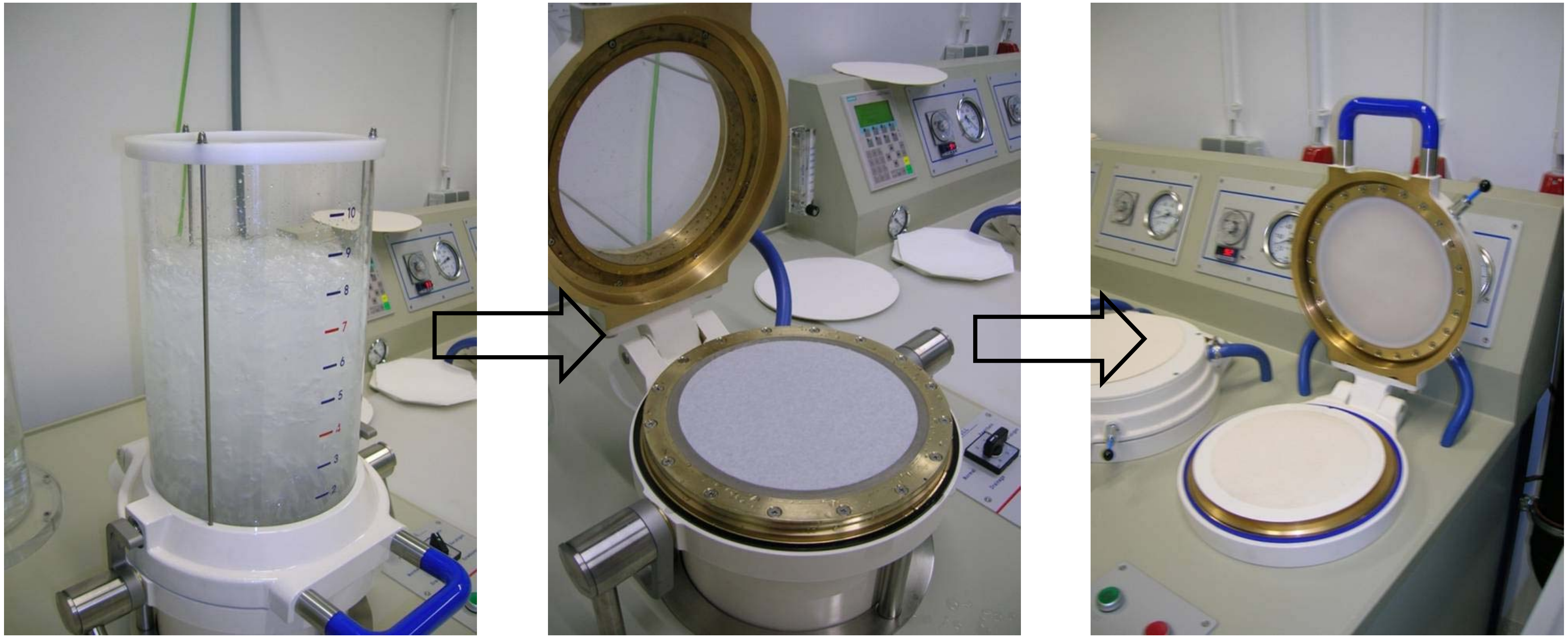
Dry Pulp

Pulp Suspension in Water

PFI refining

- 3000 rev

Handsheet Forming (2)



Coating: upscaling scheme

Industrial application

Lab Coating

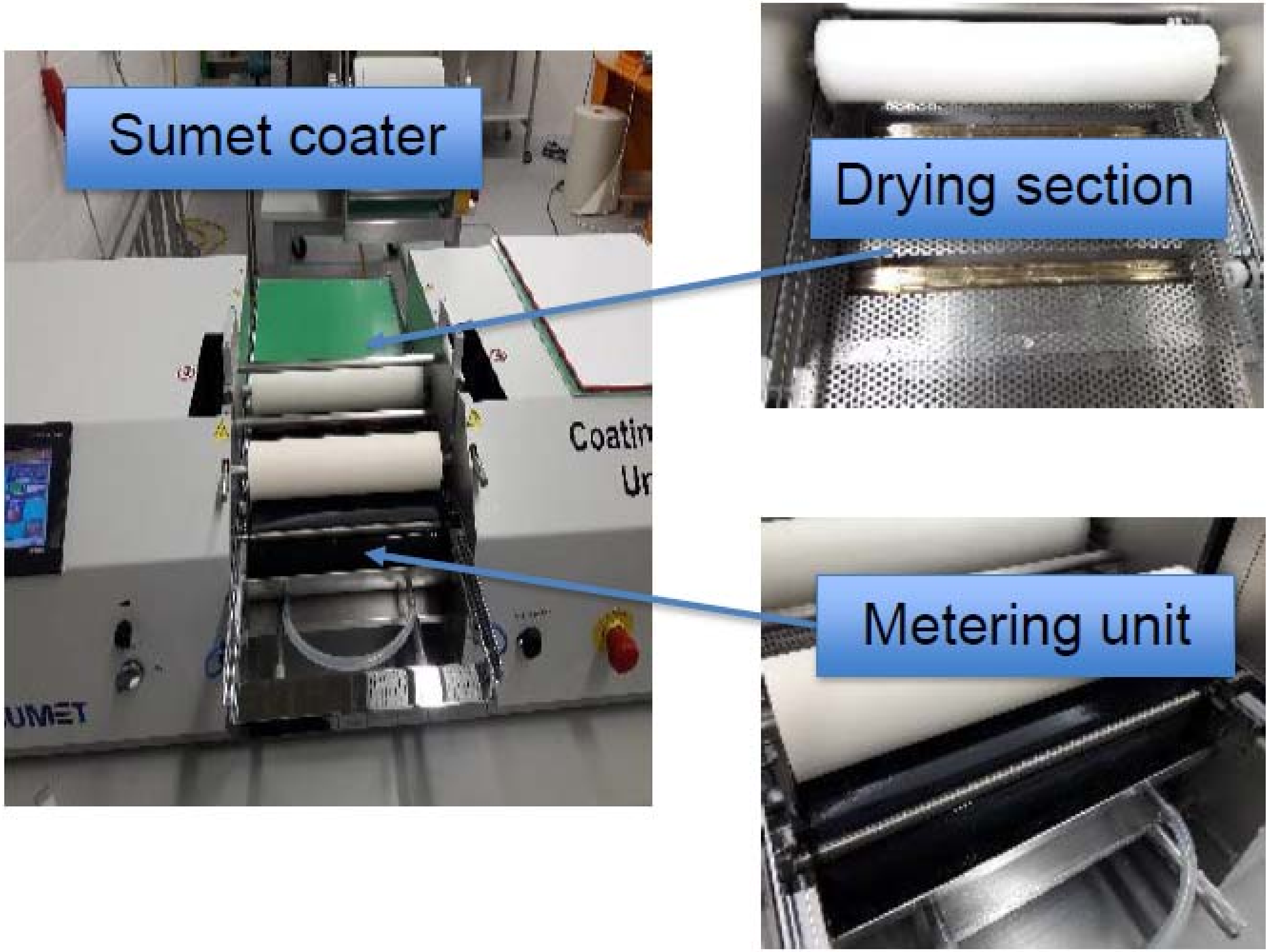
Proof of concept

Fundamental barrier testing

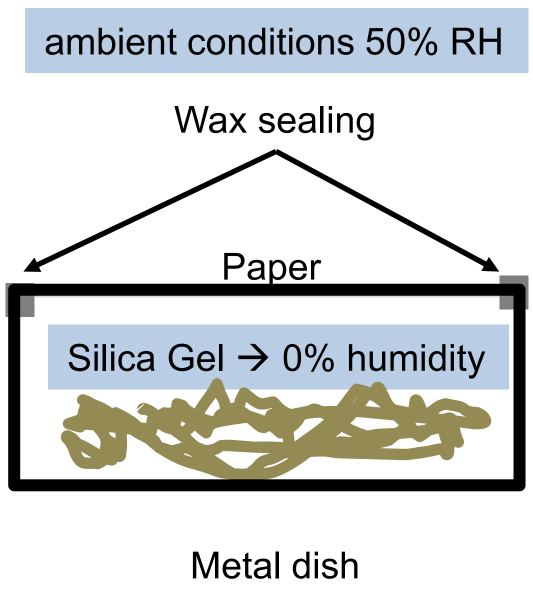
Roll to Roll Blade Coating

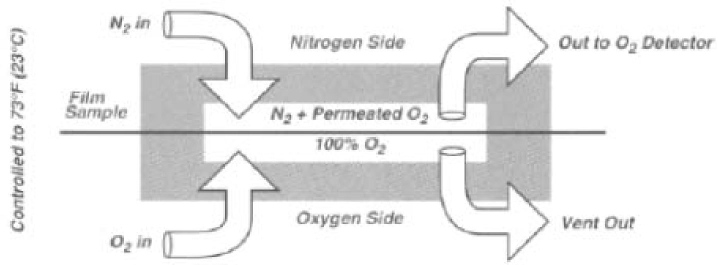
- Reel to reel coating
- IR and air dryer

Sheet Film Press Coating



Water vapor permeability
Oxygen transmission rate

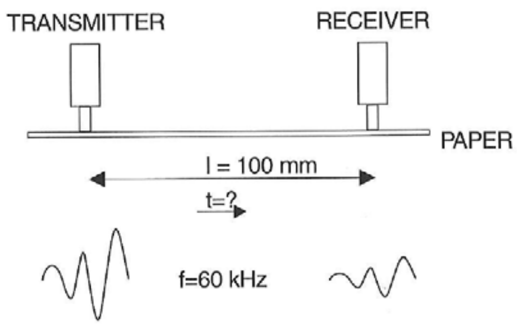


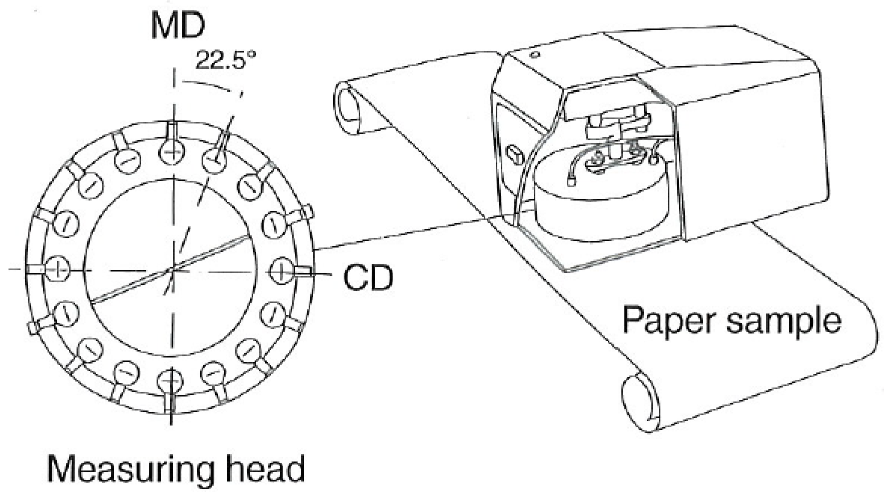


Ox-Perm 230 Device

Fiber orientation in paper
Hygro- and Hydroexpansion

Ultrasonic Tensile Stiffness Testing





Ultrasonic Tensile Stiffness Testing: Fiber Orientation

TSO_{Angle} - The angle between the maximum tensile stiffness index and the machine direction is called the tensile stiffness orientation angle or polar angle.

TSI_{MD} - Tensile stiffness index in machine direction

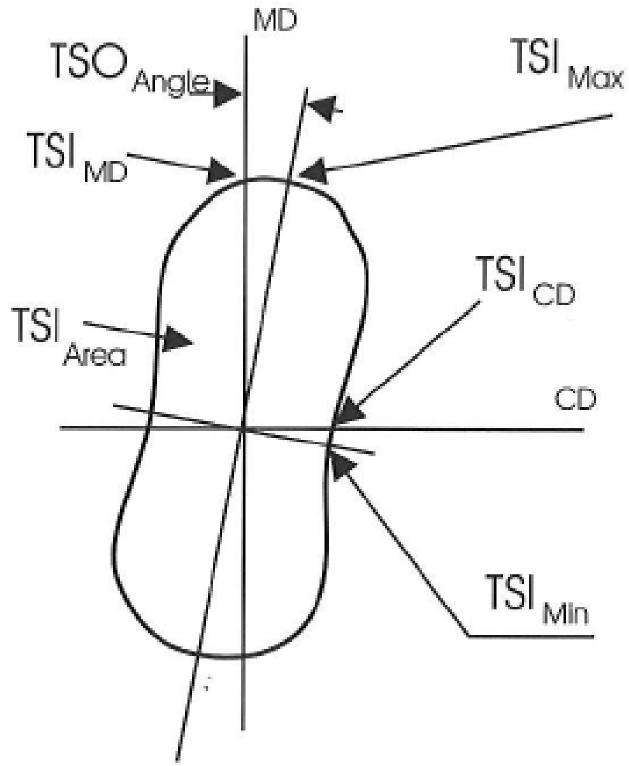
TSI_{CD} - Tensile stiffness index in cross machine direction

$TSI_{MD/CD}$ -The ratio between TSI_{MD} and TSI_{CD} - anisotropy

TSI_{Min} - Minimum value measured

TSI_{Max} - Maximum value measured

TSI_{Area} - Area of the "peanut" ellipse



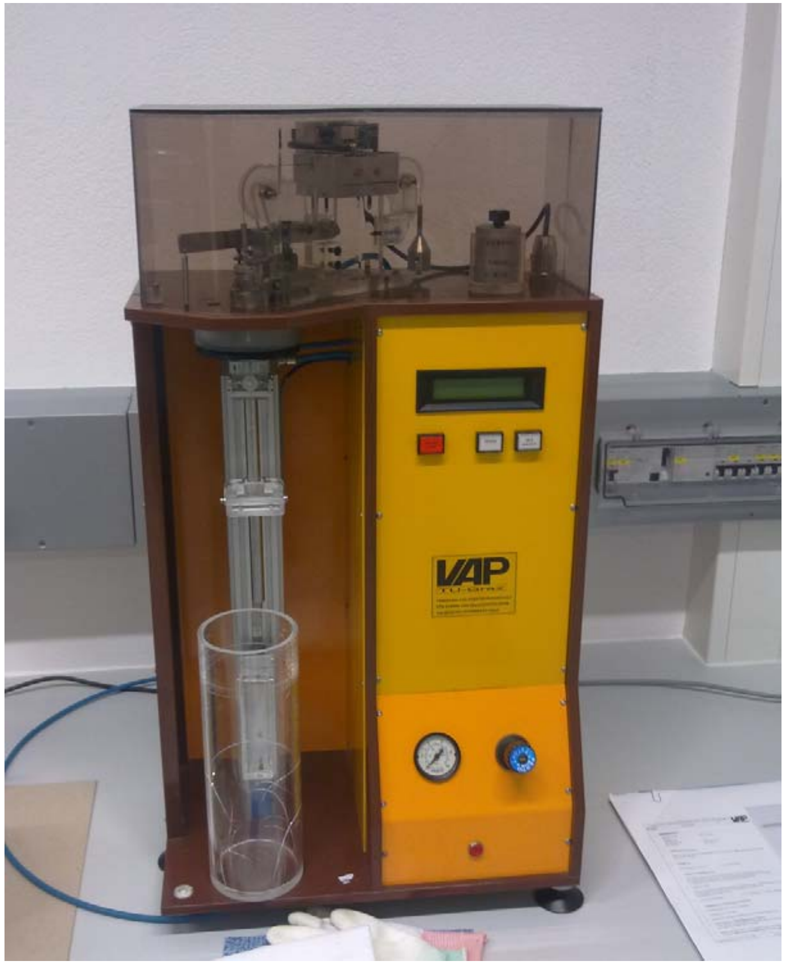
Cyclic testing of temperature and humidity

- Temperature 40ºC- 90ºC
- RH 10%-90%
- Programmable cycles for Temperature and RH

- Accelerated Ageing
- Dried in curl relaxation

Hygroexpansion tester

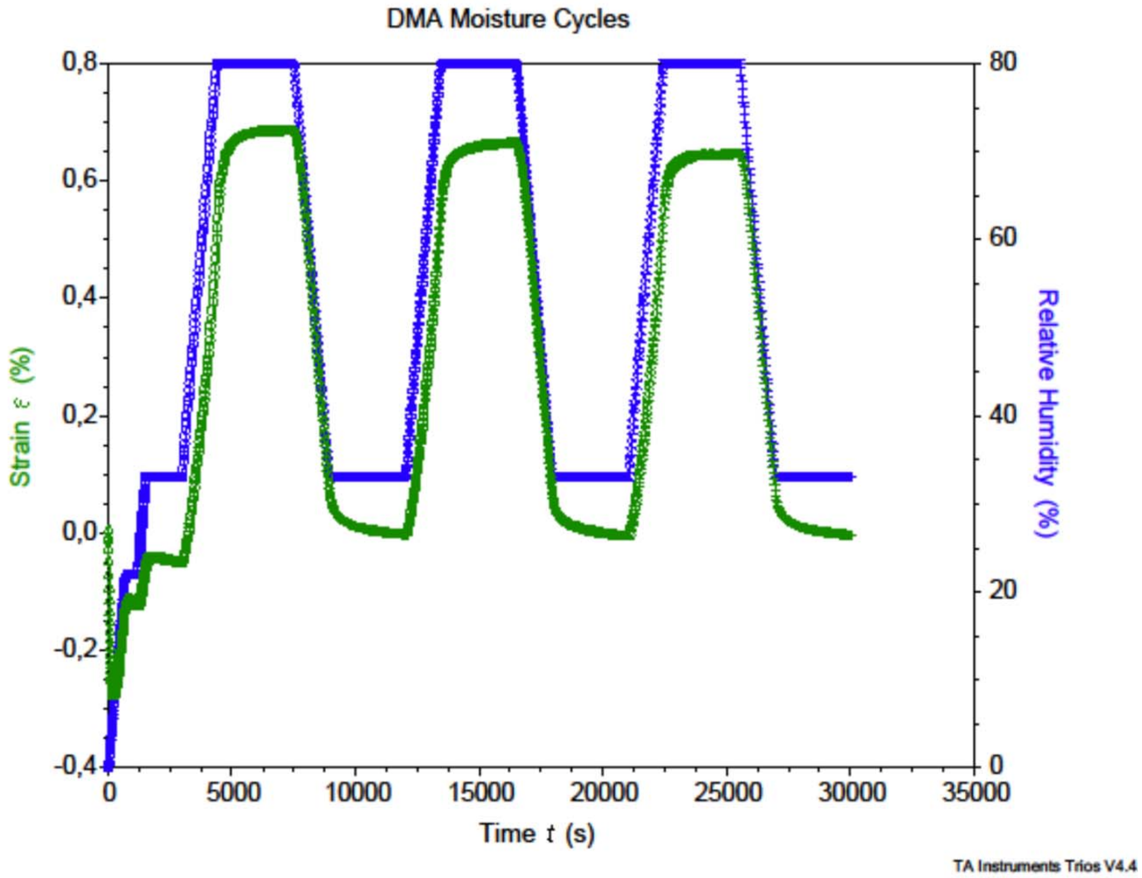
- Measures deformation upon wetting of paper
- Time resolution 0.2s



Hygroexpansion

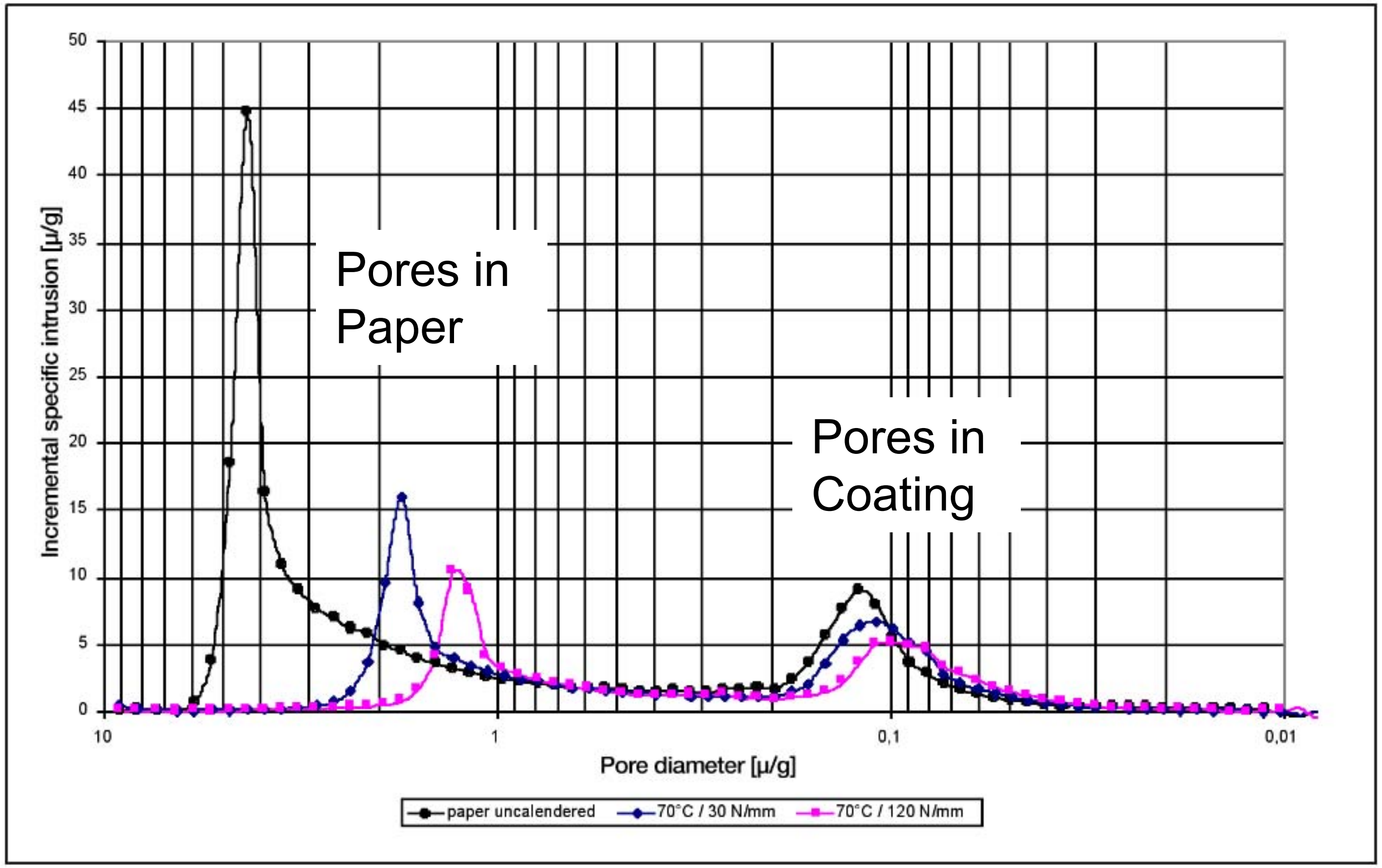
- Cycling of moisture from 33 % to 80 %
- Recording of strain

→ Hygroexpansion



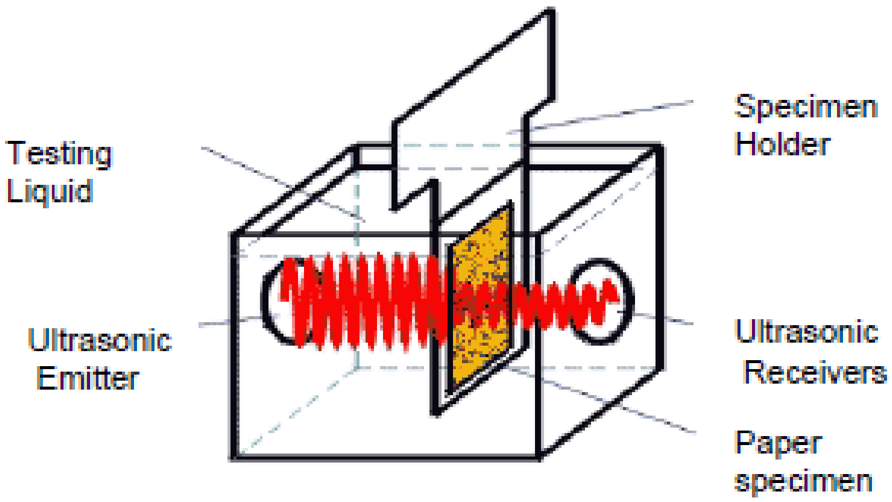
Liquid absorption and wetting

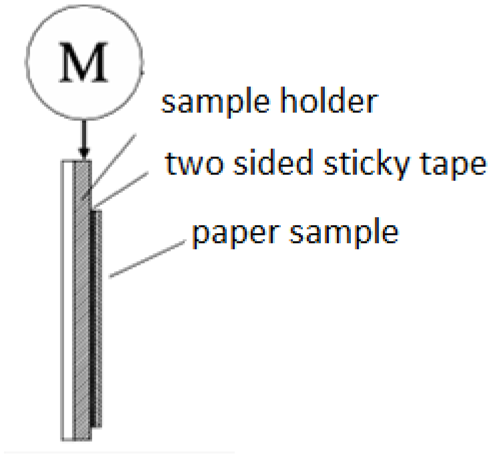
WFC Paper pore size distribution: Mercury Porosimetry

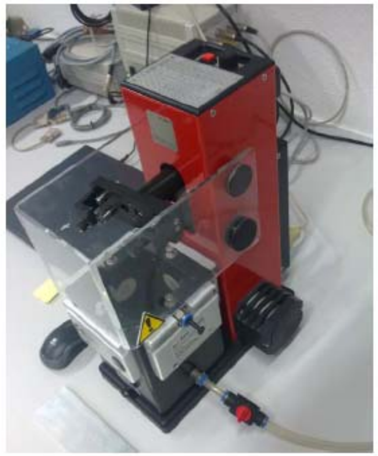


5. Series 3: The influence of nip load on pore structure (mercury porosimetry).

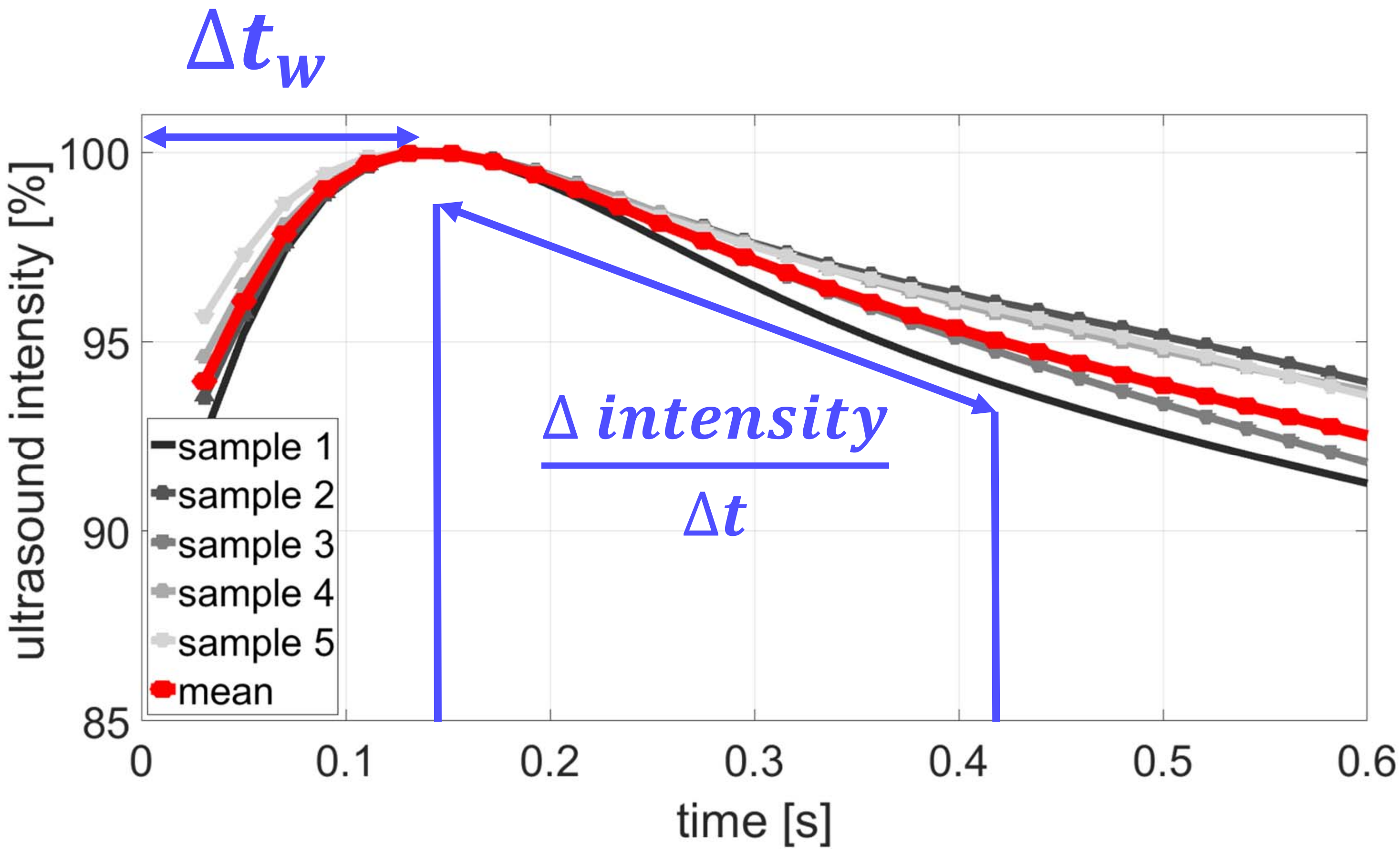
Ultrasonic penetration testing





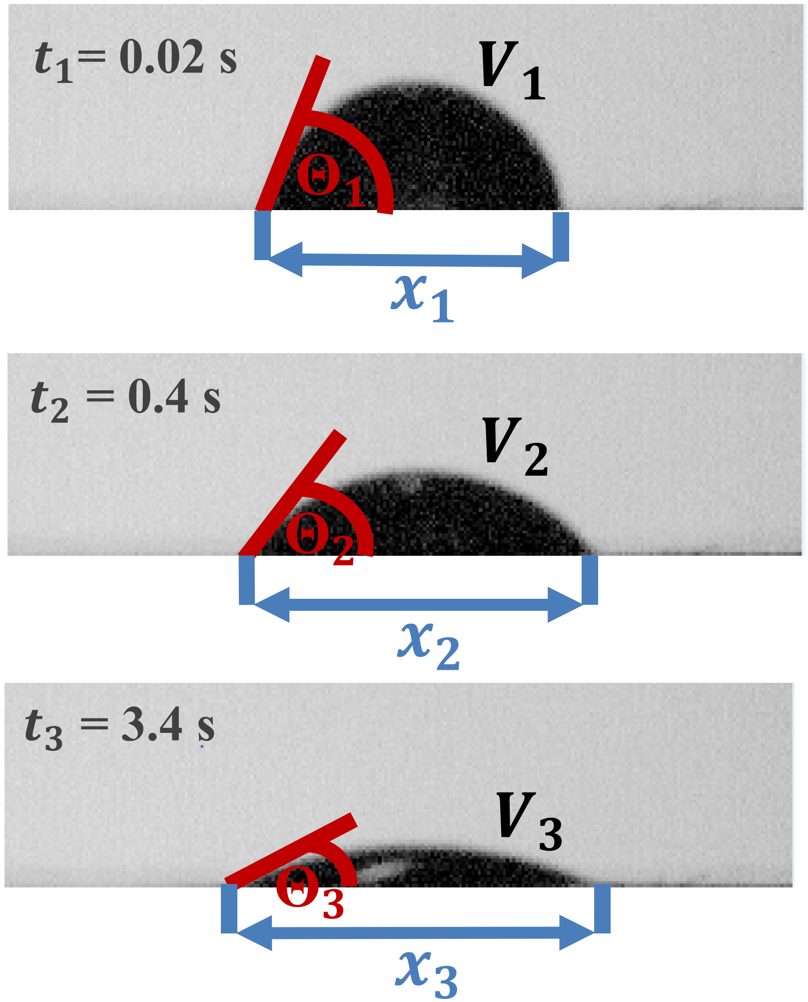


Ultrasonic penetration testing

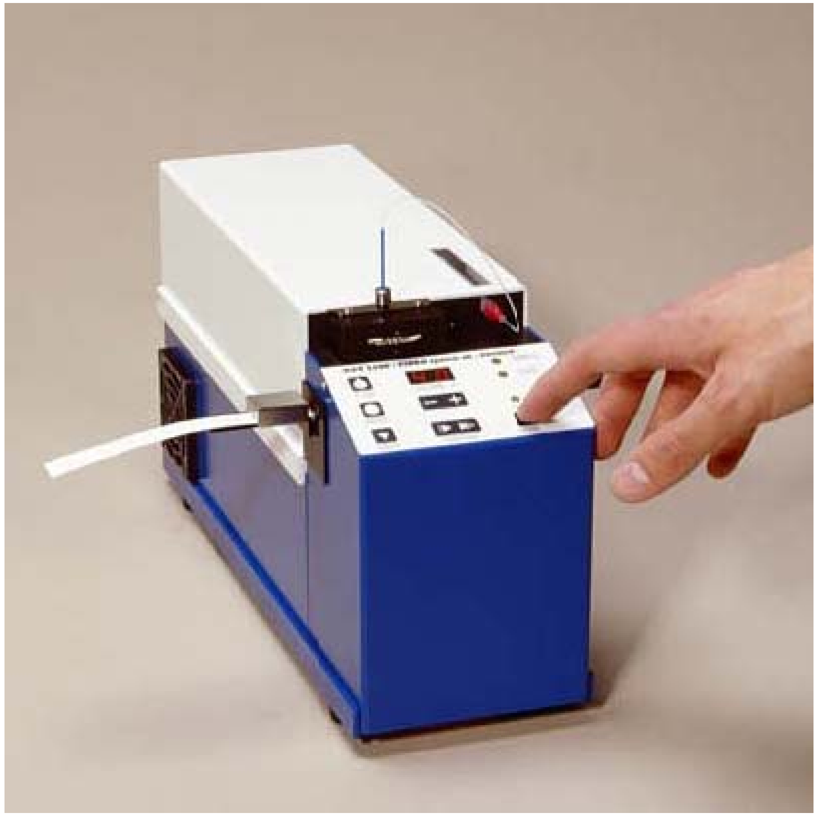


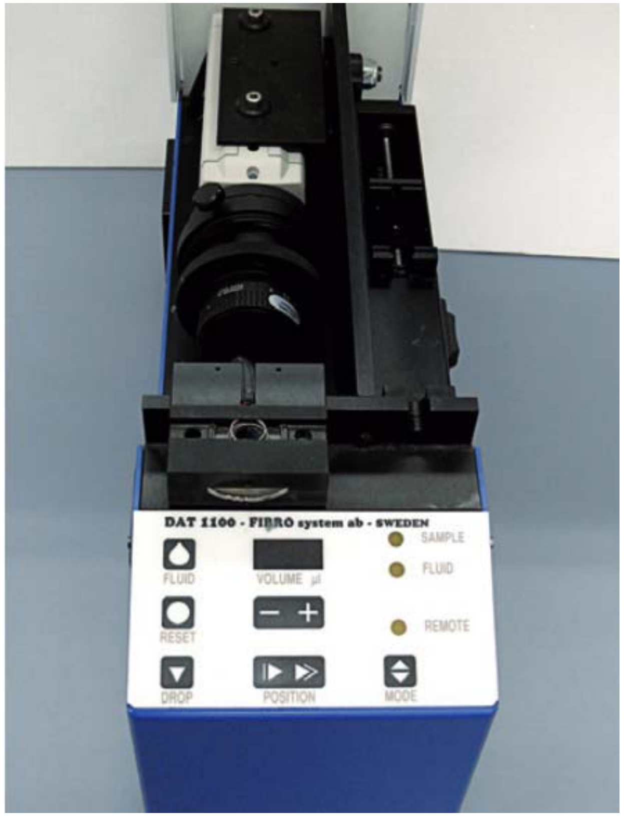
Wetting
Contact angle measurement

Contact angle measurement

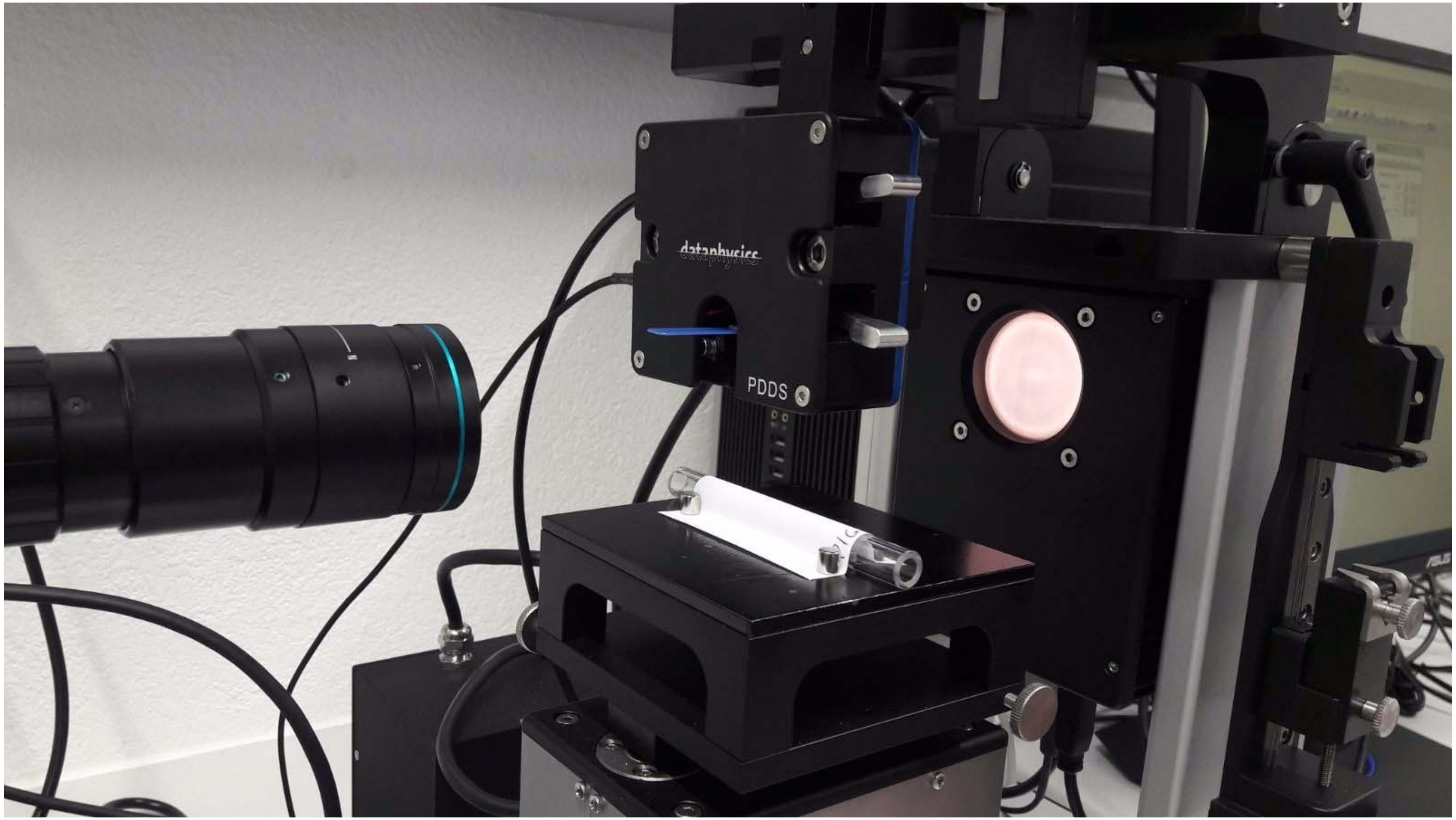


Microliter drop setup



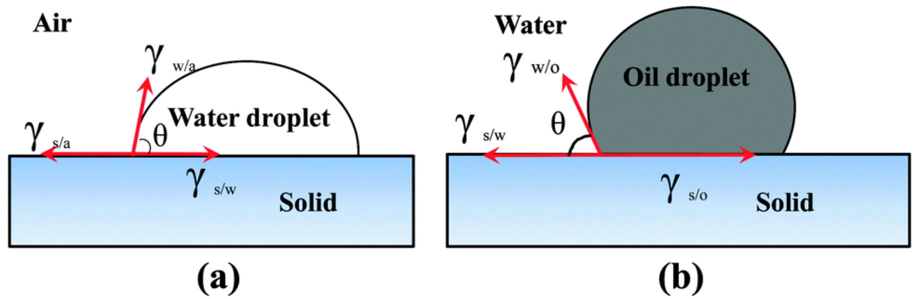


Picoliter drop setup



Polar and dispersive surface energy σ_s : testing contact angle with polar/apolar liquids

$$\sigma_S = \sigma_S^P + \sigma_S^D$$

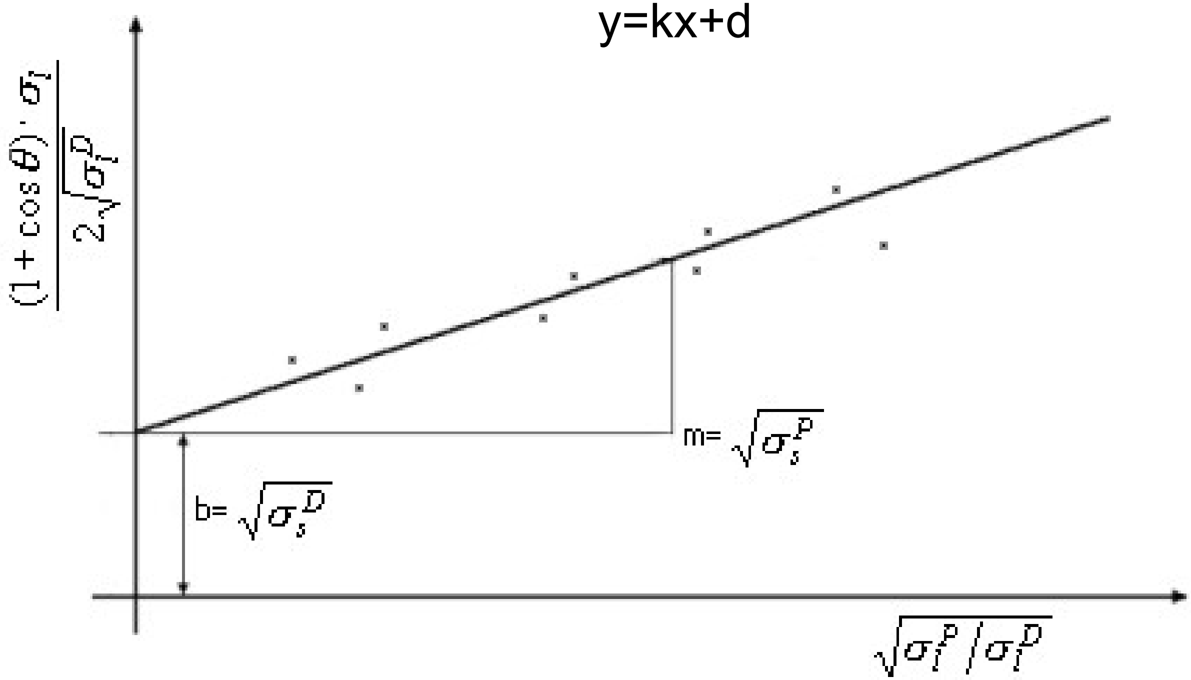


	σ_l mN/m	σ_l^D mN/m	σ_l^P mN/m	ρ g/cm³	η mPa·s	T °C
Water	72,8	21,8	51	0,988		25
Diiodomethan	50,8	50,8	0	3,325	2,762	20
Ethylenglykol	47,7	30,9	16,8	1,109	21,81	20
1-Bromnaphthalin	44,6	44,6	0	1,483	5,107	20

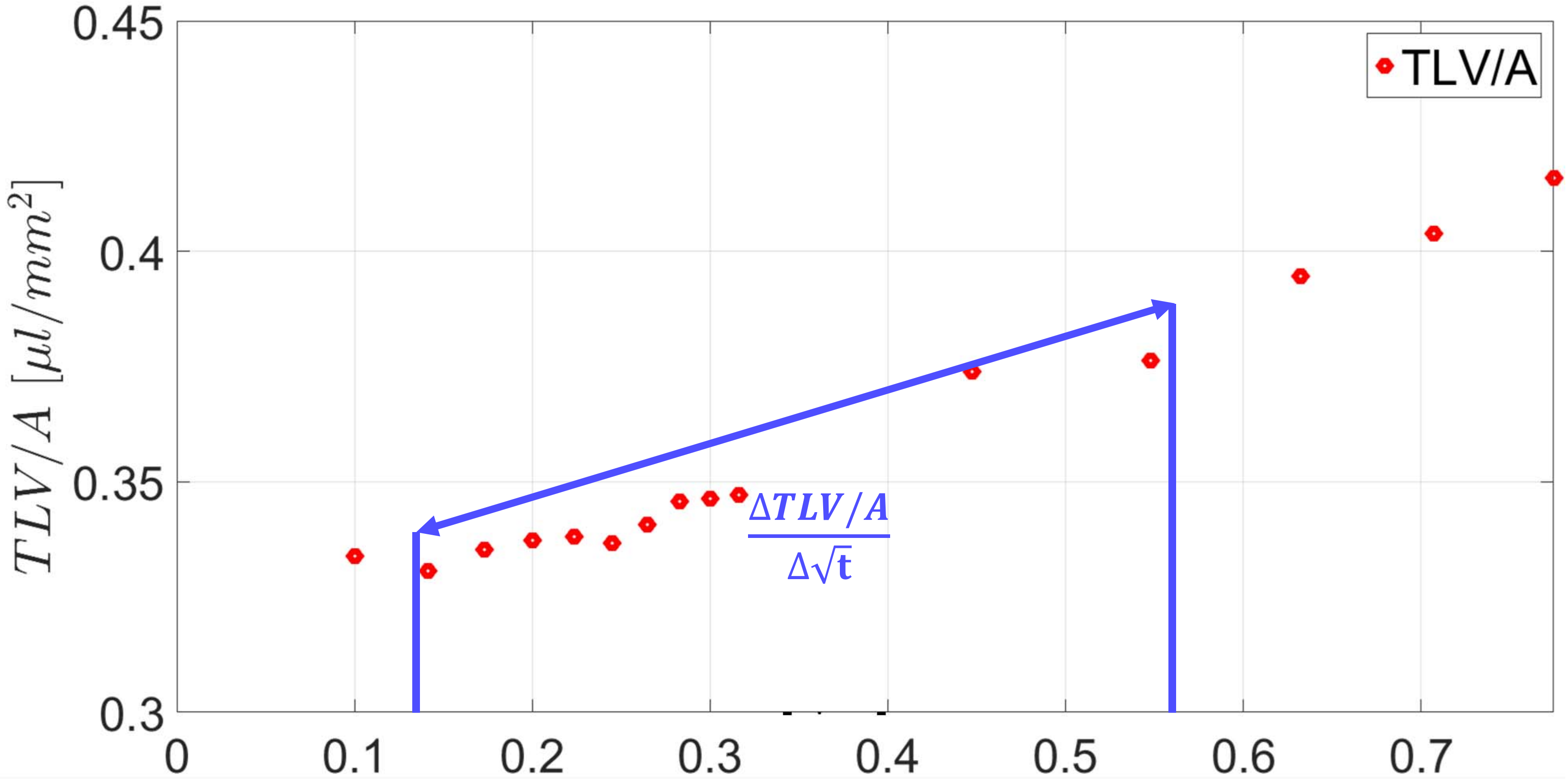
Owens, Wendt, Rabel, Kälble (OWRK) Polar and dispersive free surface energy

$$\underbrace{\frac{(1+\cos\Theta)\,\sigma_l}{2\sqrt{\sigma_l^D}}}_{y} = \underbrace{\sqrt{\sigma_s^P}}_{k}\underbrace{\sqrt{\frac{\sigma_l^P}{\sigma_l^D}}}_{x} + \underbrace{\sqrt{\sigma_s^D}}_{d}$$

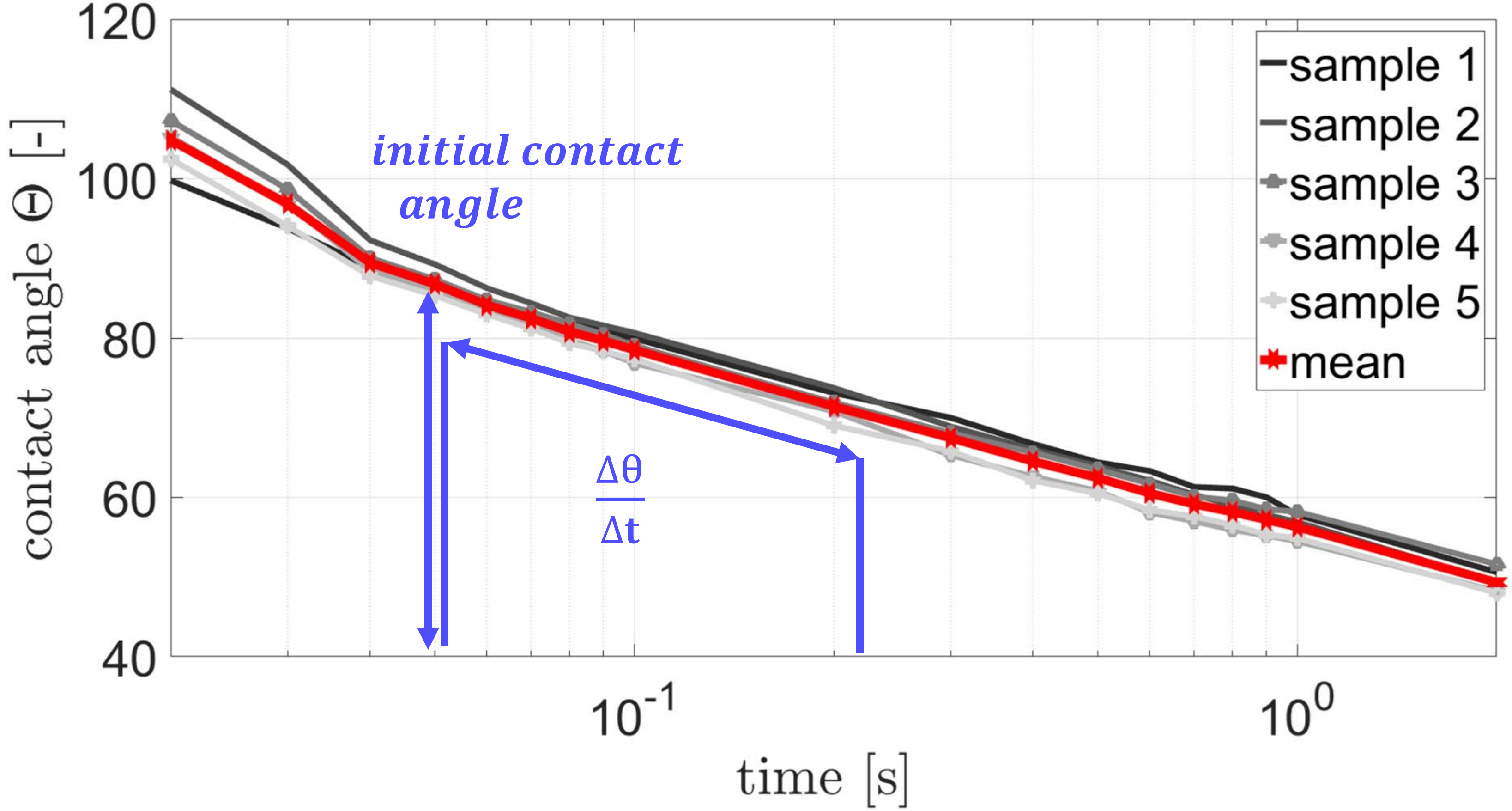
y=kx+d



Penetration depth from contact angle measurement

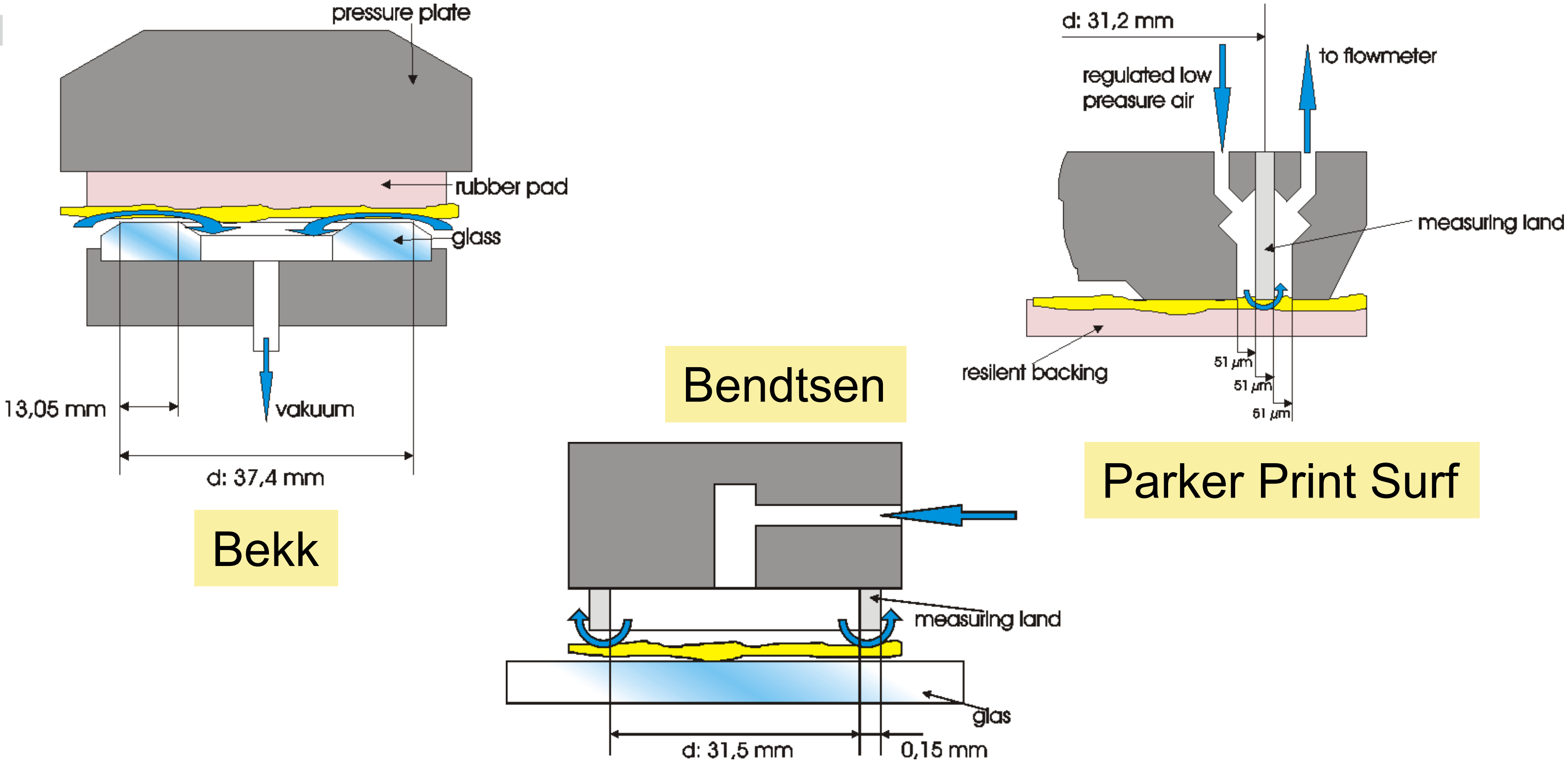


Contact angle measurement

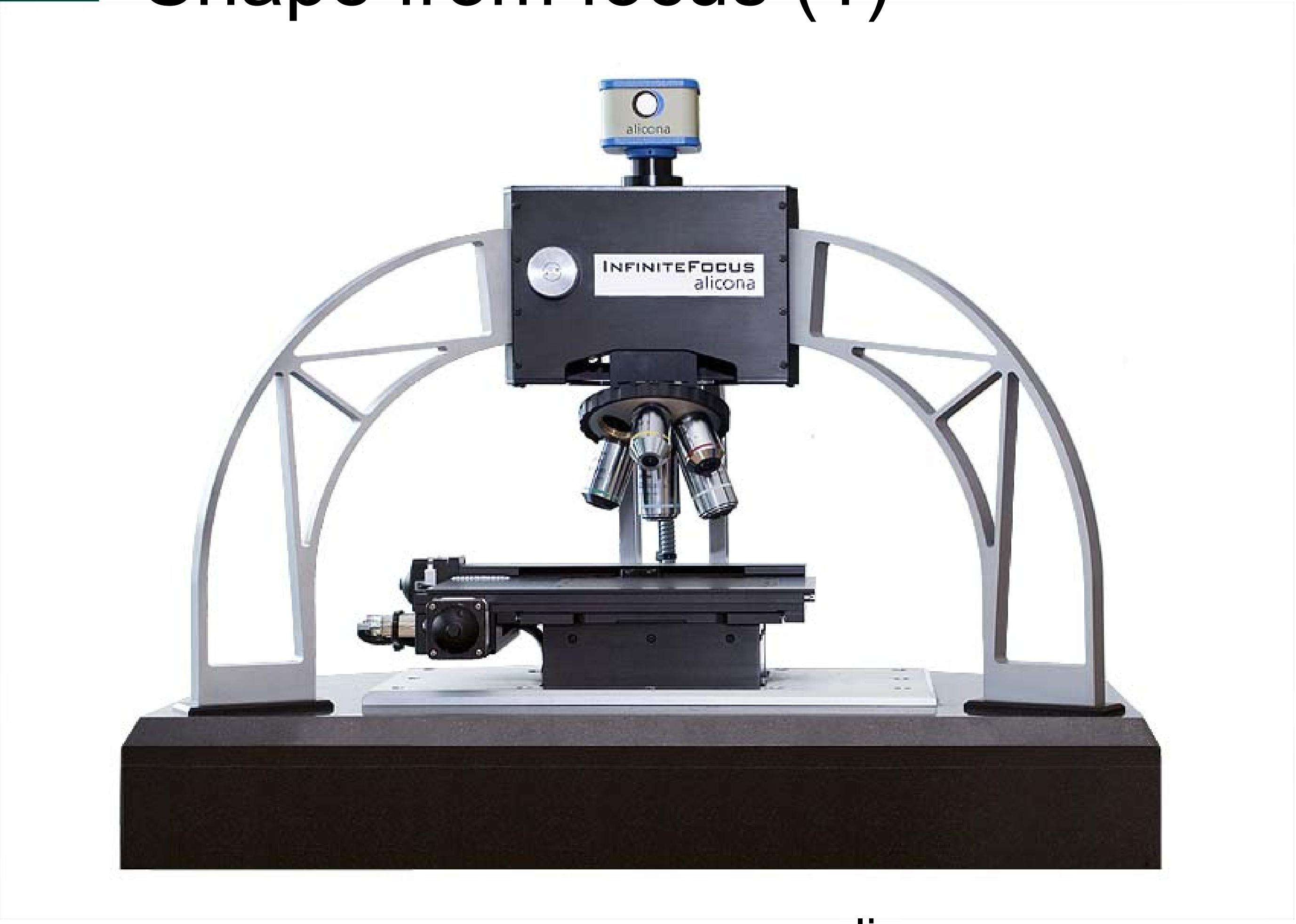


Paper Roughness

Air leakage methods

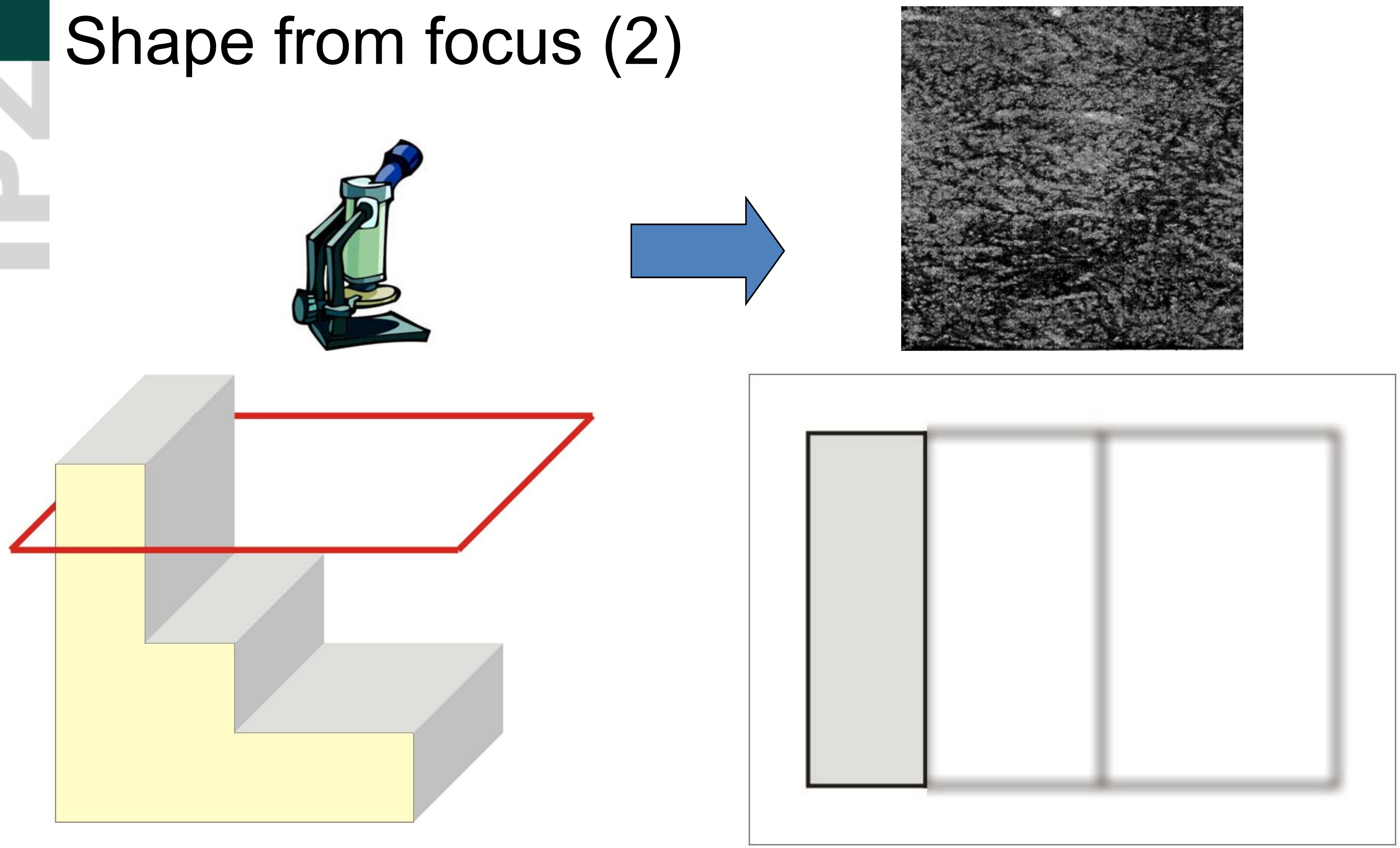


Shape from focus (1)



www.alicona.com

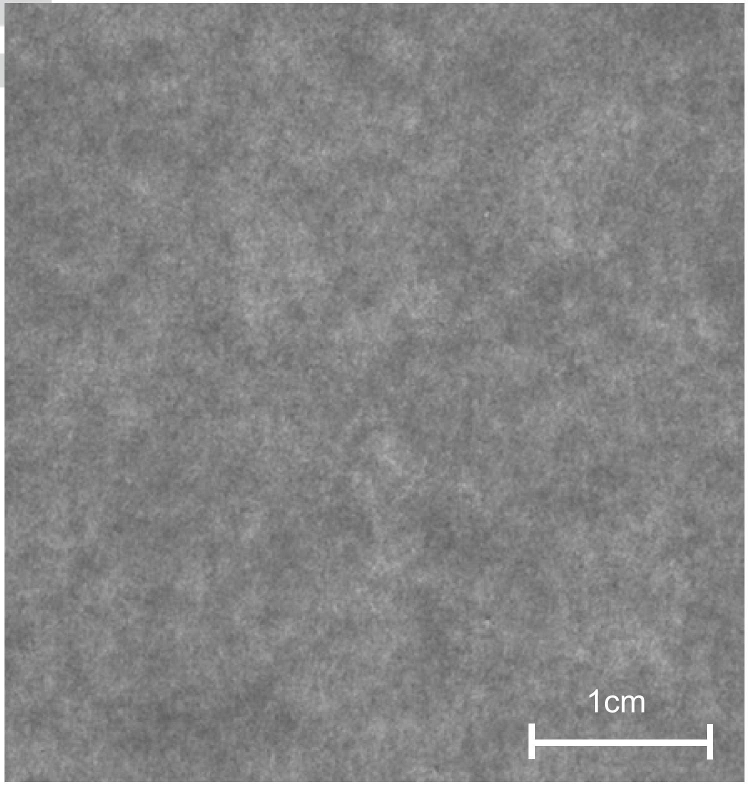
Shape from focus (2)



Paper structure
Paper mechanical testing

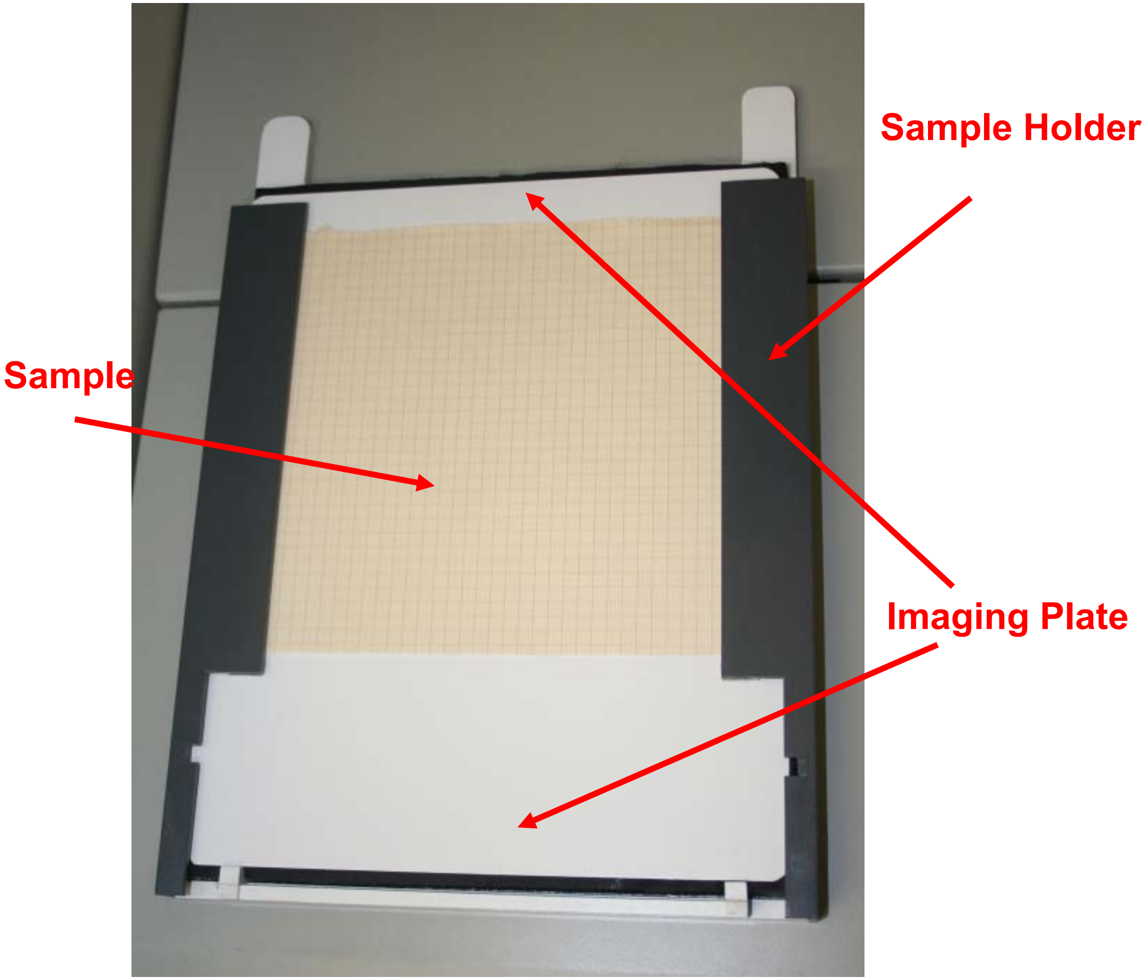
Formation

Light transmission ≠ local grammage



- Different opacities of fibers, filler,
- Densification (Calendaring)
- Not possible to convert optical image to g/m²

Beta Radiography

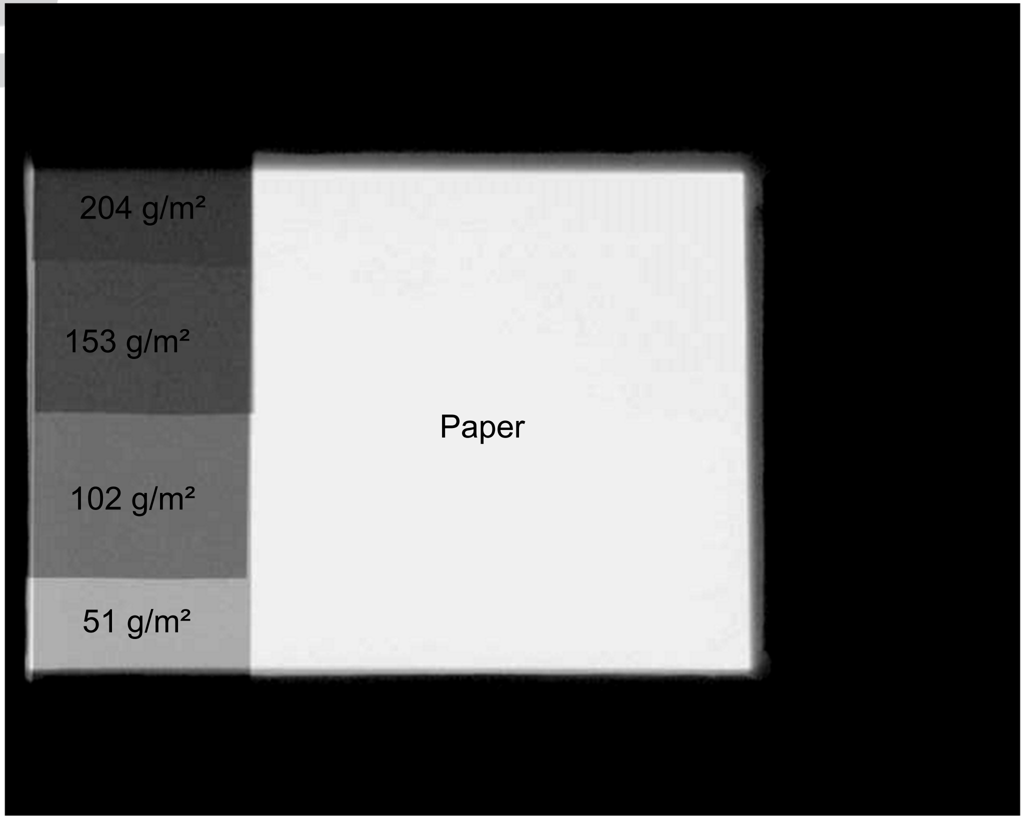


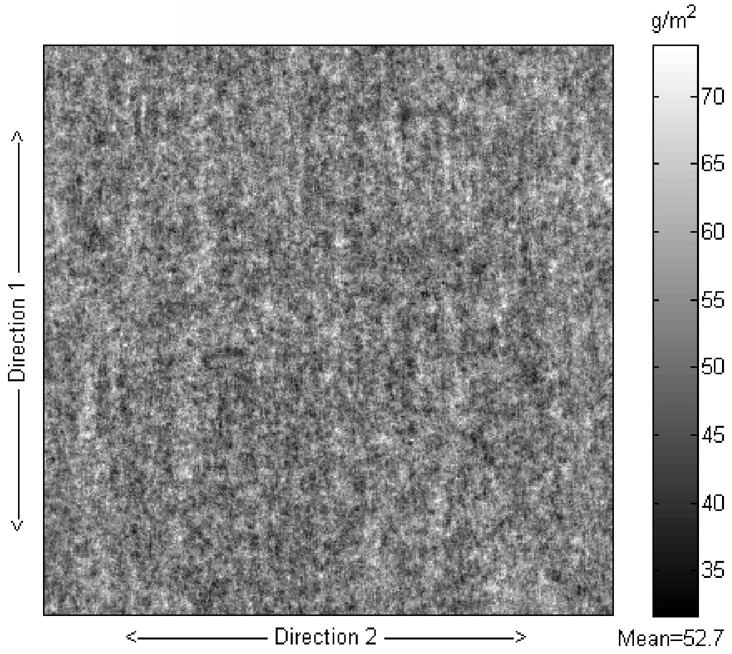
Beta Radiography

Beta Radiation unit

Scanner for imaging plate

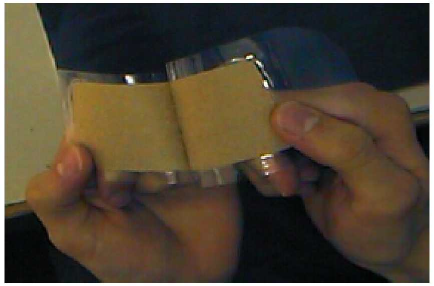
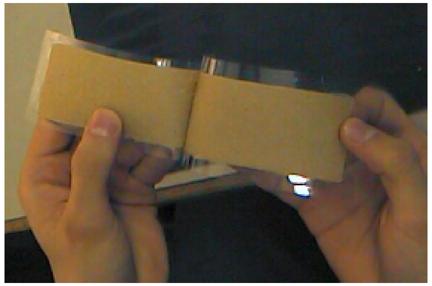
Convert image to g/m²

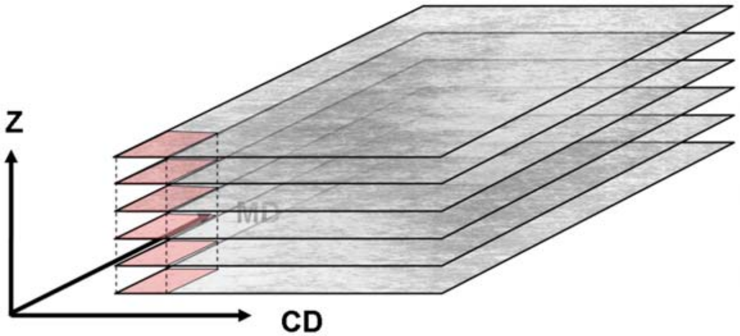


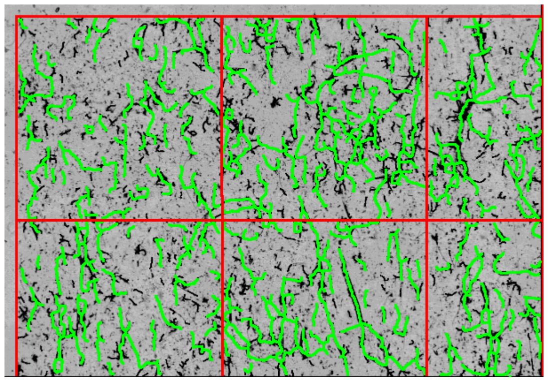
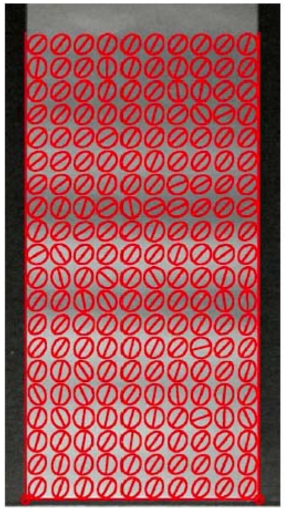


Pixel size = 50µm

Local + z-directional fiber orientation (Sheet Splitting)

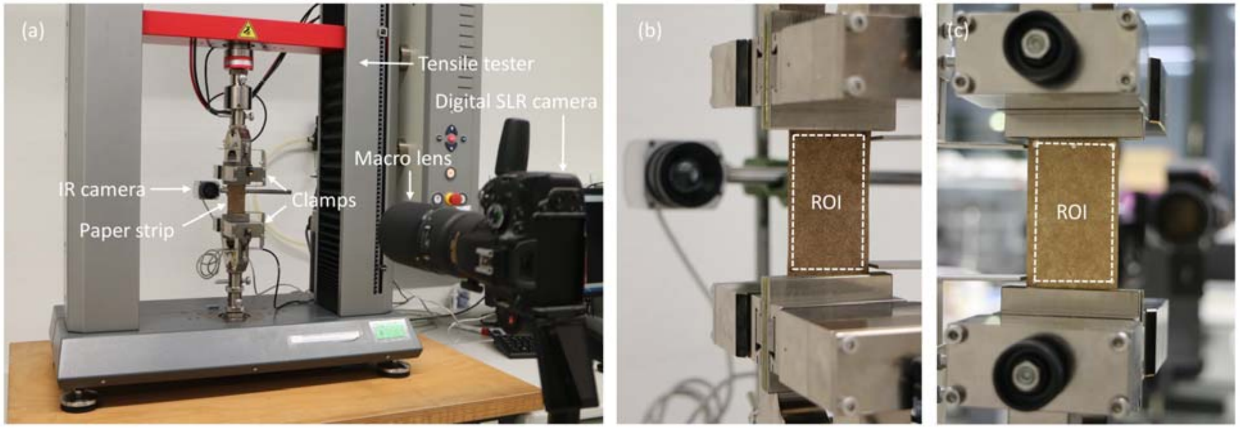


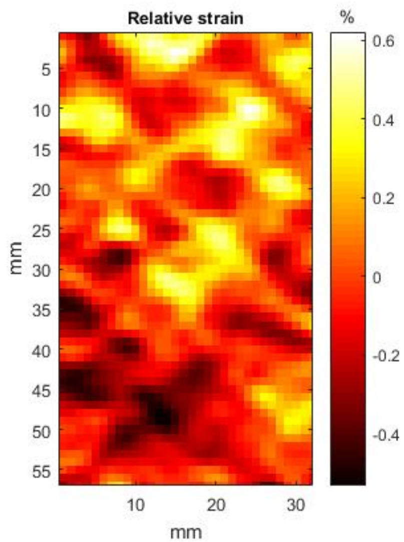



[HIRN & BAUER, 2007]

Measurement of local tensile strain & temperature increase

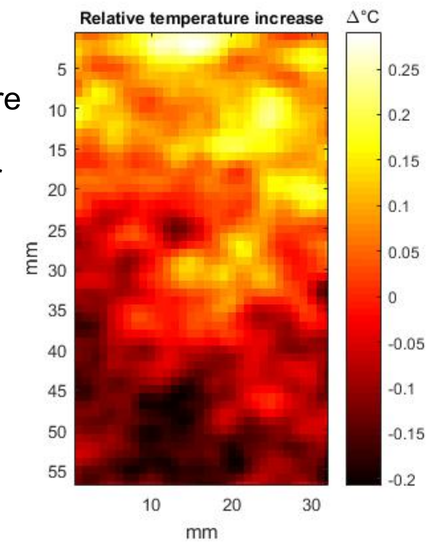
Simultaneous measurement of local strain and temperature increase during tensile test



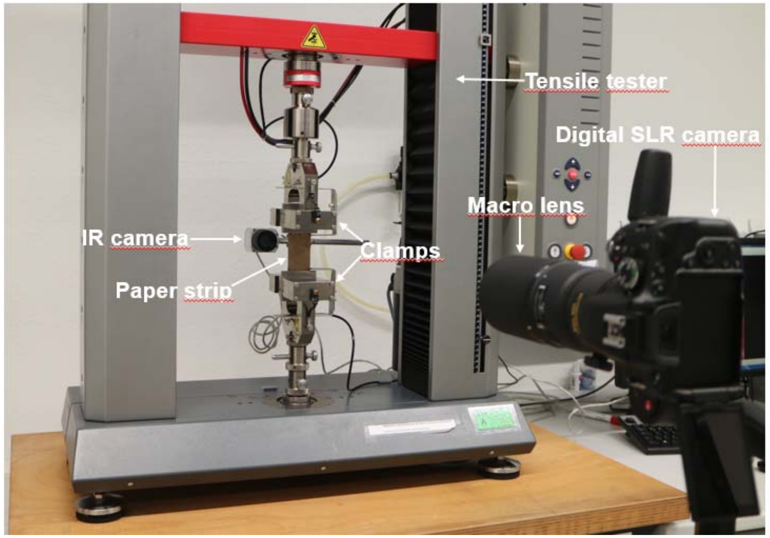


Front side
Local strain with DIC just prior to rupture

Back side
Local temperature increase with IR camera just prior to rupture

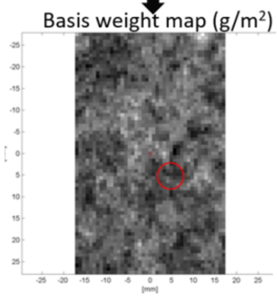


Structural Reasons for Failure



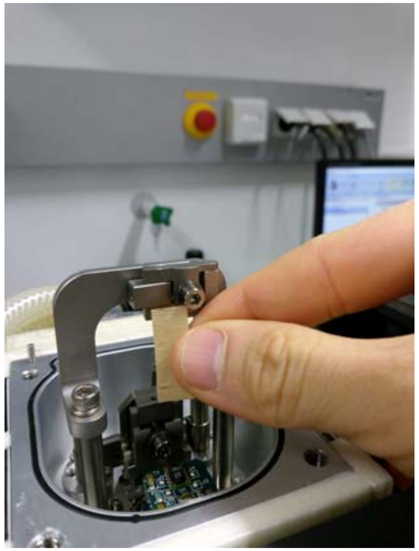
Paper structure

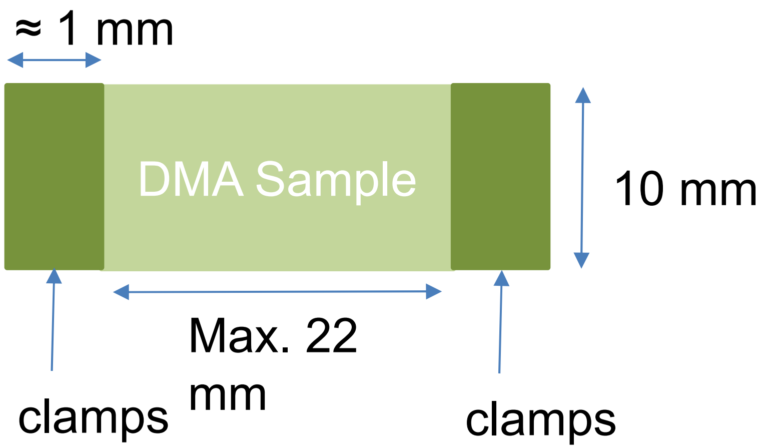
1. **Basis weight map**
2. Thickness map
3. Density map
4. Layered fiber orientation map



DMA (Dynamical Mechnical Analyser)

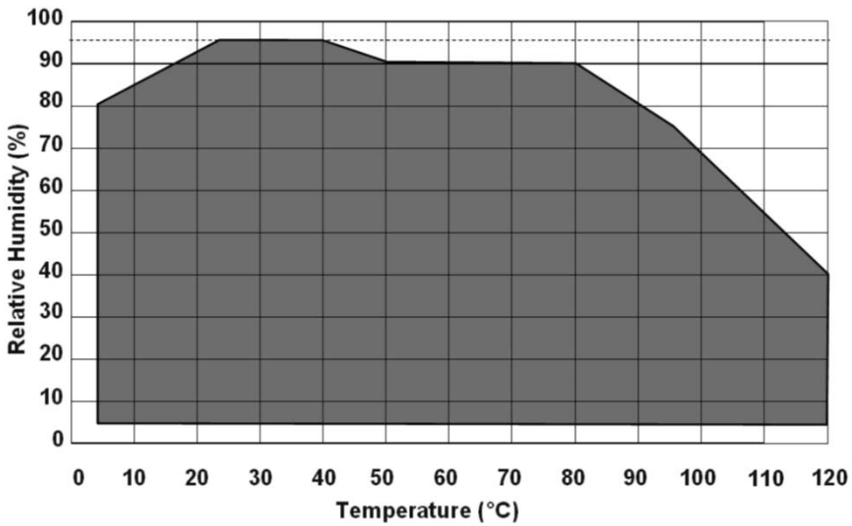
- Dynamic Testing
- Humidity Cycling
- Temperature cycling



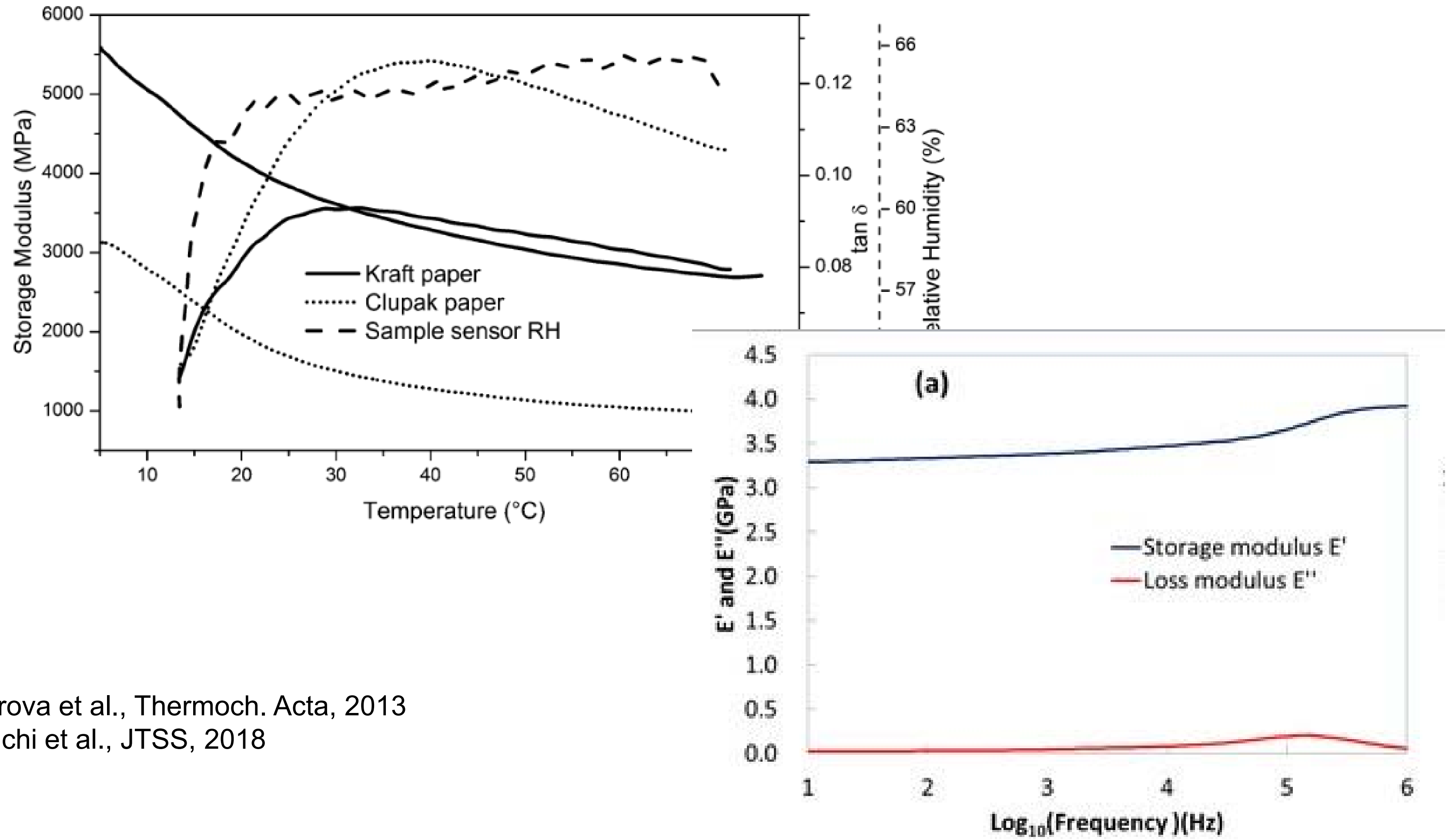


DMA (Dynamical Mechnical Analyser)

Temperature Range	5 – 120 °C
Temperature Accuracy	0.5 °C
Heating/Cooling Rate	1 °C/min
Humidity range	See figure
Humidity accuracy	3-5 %
Humidity Ramp Rate	2 % RH/min



Storage and Loss Modulus

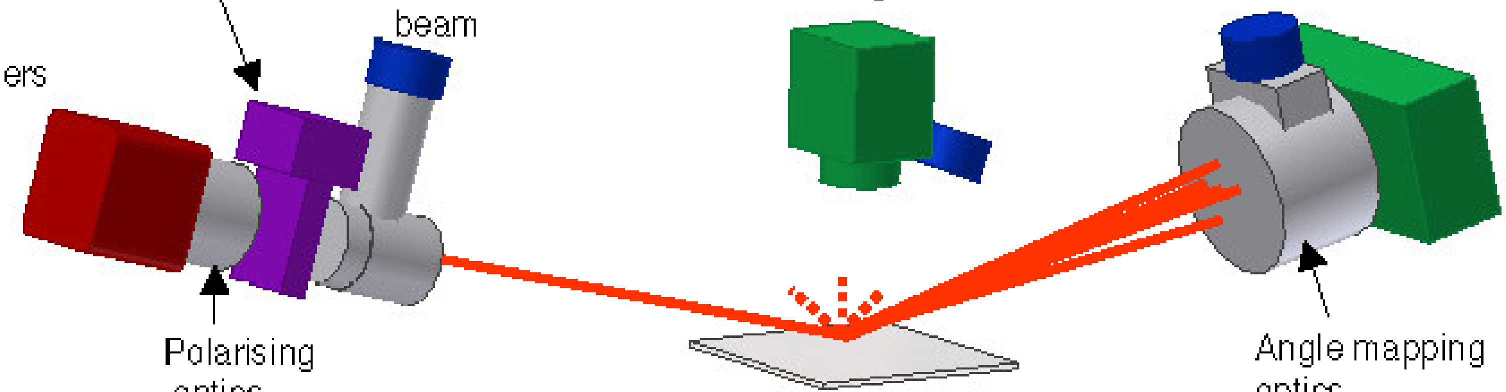


Gregorova et al., Thermoch. Acta, 2013
Horiguchi et al., JTSS, 2018

Paper Surface Analysis under High Resolution

→ printing applications

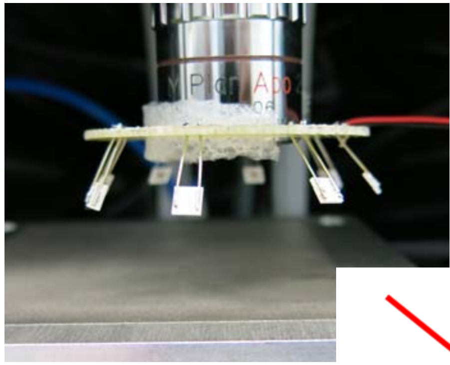
Surfoptics System:
Refractive Index, Gloss, Roughness

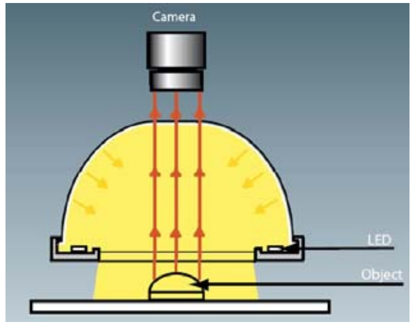


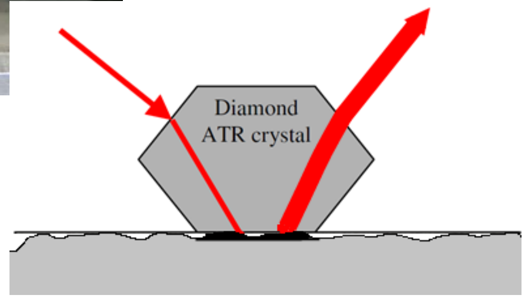
High Resolution Paper Analysis

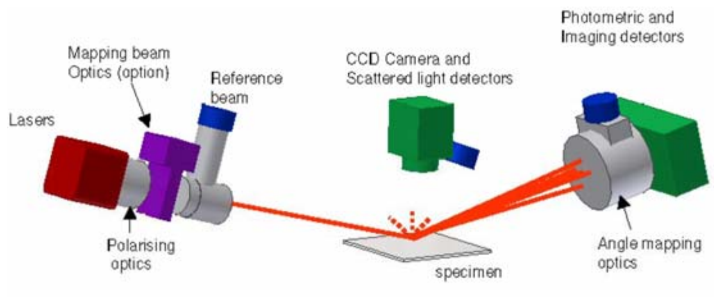
- Resolution
  50 - 200µm/pix

- **<u>Local</u>** high resolution measurement of
  - Formation
  - Optical Properties
  - Gloss
  - Refractive Index
  - UV Coating Coverage
  - Topography
  - Spectroscopy

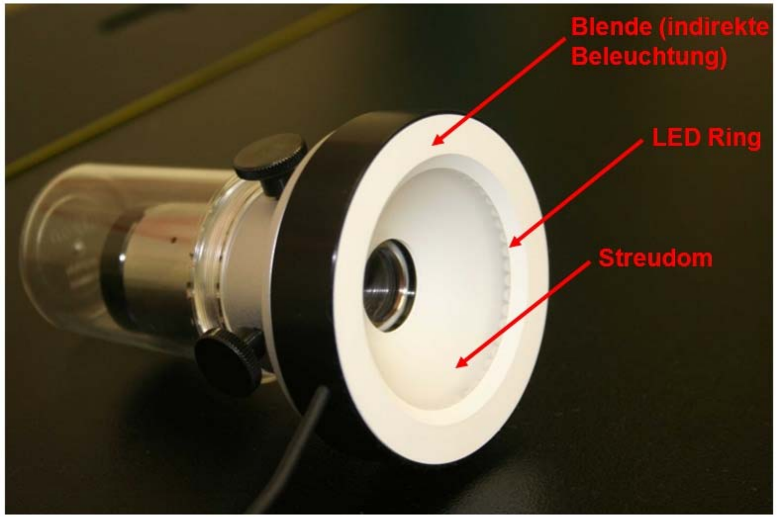


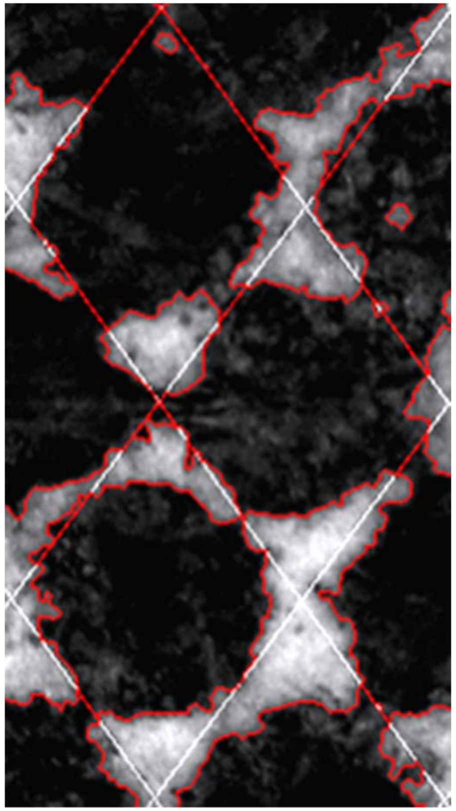




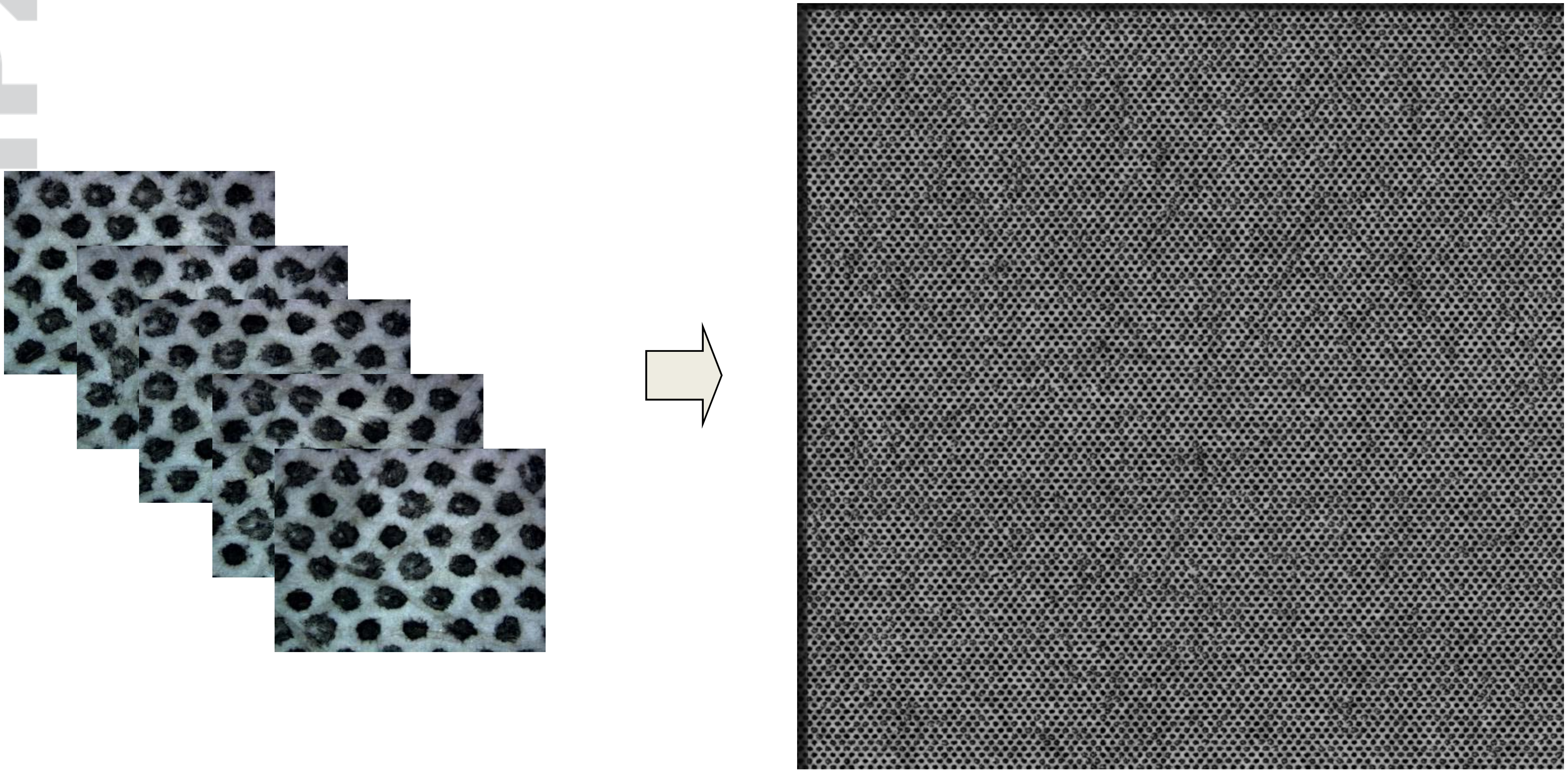


Printing Dot Image Analysis

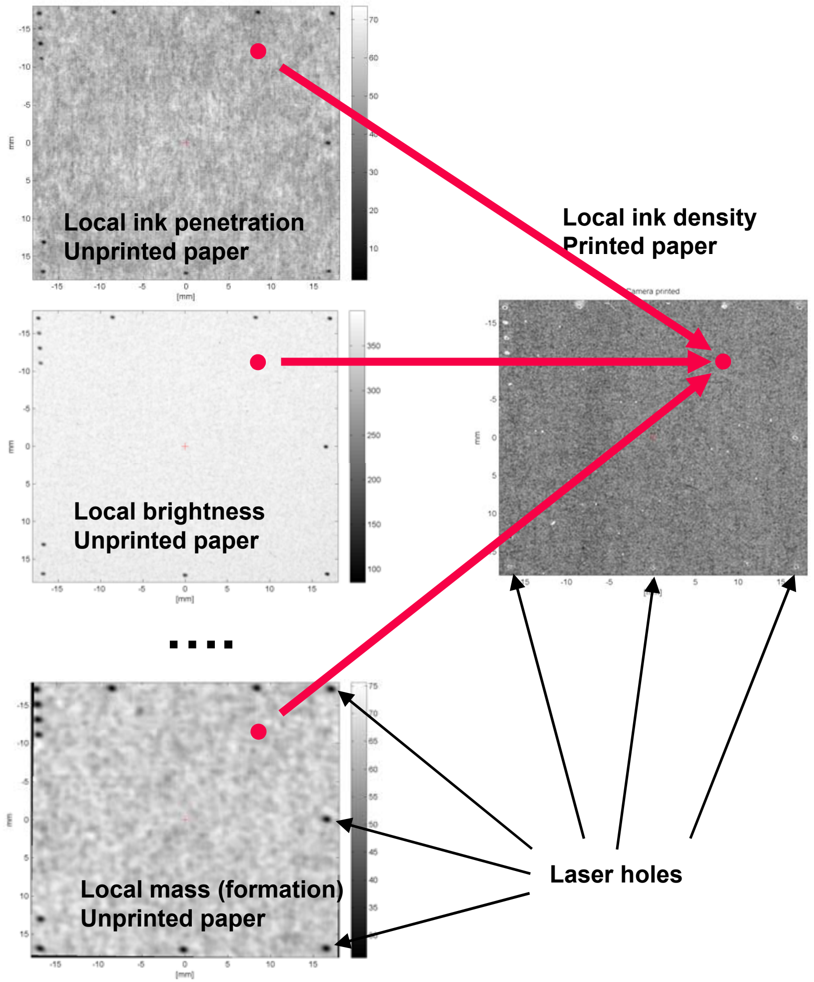




Building Large Maps



Printability: Interrelation between local paper properties and local print appearence



Training Plan

Which Testing Method	Where	Who
Surface Plasmon resonance (SPR) Atomic Force Microscopy (AFM)	**Meeting point: 11:00 at Paper Institute**, departure to the chemistry building	Carina Sampl
Spin Coater & Dynamic Light Scattering		Werner Schlemmer
Dynamic mechanical testing & Hygroexpansion		Georg Urstöger
Fluorimetry and FRET Microscopy	**Meeting point: 11:00 at Paper Institute,** departure to the Physics Building	Monica Simoes
Fiber micromechanical analysis	Climate Room	Marco Zizek
contact angle ultrasonic liquid penetration	Climate Room	Johann Schwarzl + Sarah Krainer
Sheet splitting	Climate Room	Johann Schwarzl
Film coater, blade coater and oxygen transmission rate	Blade Coater (Basement) Roll Coater (Coating Lab)	Samir Kopacic
Fines separation and analysis (pressure screen, flotation) & fiber morphology (FiberTester)	Basement Lab (Flotation) Climate Room	Daniel Mandlez
Microtomy of paper and fibers	**please attend between 10:00-12:00!** Microtome Room	Angela Wolfbauer
IR camera and tensile tester Beta radiography	Climate Room	Jussi Lahti
Laboratory papermaking	Wet Lab 1 / 2	Roman Poschner
mechanical and optical paper testing	Climate Room	Sarah Krainer + Heidi Bakhshi
IFM and Surfoptics	Climate Room	Ulrich Hirn + Heidi Bakshi

Chemistry building (green)
Physics building (blue)
Inst. Paper & Pulp Tachnology - Inffeldgasse 23 (yellow)

Please ask at the paper institute (Inffeldgasse 23) how to find the different rooms!