Bio-Material Science

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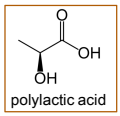
2G103, 10:10-11:25, Tuesday

Biomaterial and Biomaterial Science

- **What biomaterial is**

Materials constituting components and the structure of organisms processed to provide properties required for the use such as:

Wood, paper, cellophane, rubber, leather, polylactic acid



polylactic acid

- **What biomaterial science is**

Science and technology for providing high performance to biomaterials

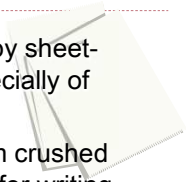
Biomaterial Science （Schedule）

#	Date	Content
1	4/16	History of papermaking
2	4/23	Pulps – Beating and fiber properties
3	4/30	Pulps – Additives and functions
-	5/7	No class (Substitute Monday classes)
4	5/14	Papermaking processes & interfiber bonding
5	5/21	Paper– Structural and absorption properties
6	5/28	Paper– Mechanical and optical properties
7	6/4	Recent trend of paper science and technol.
8-10	6/11, 18, 25	Pulping science and technology by Professor Hiroshi Ohi

Lecture information and contact

- Homepage of “Biomaterial Science (T. Enomae)”
- http://www.enomae.com/
  → Handouts in lecture(講義資料)
- E-mail address
  → t@enomae.com
  for any questions and visit to laboratory

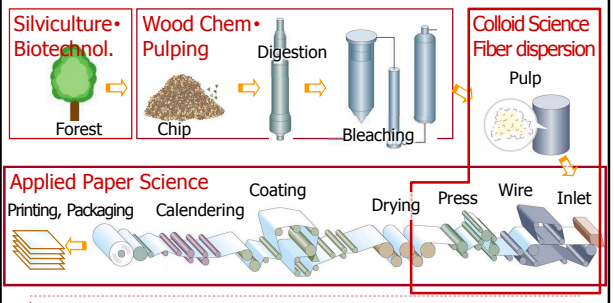
“Paper” —Definition



- “A thin, flat material obtained by sheet-forming and drying fibers especially of plants”
- “A thin, flat material made from crushed wood or cloth used especially for writing and printing on and in packaging” - Cambridge Dict.
- Plant fibers, especially wood-sourced, as a raw material of paper are called “a pulp”

Scope of Paper Science

- Colloid Sci (Fiber dispersion system) + Applied Paper Sci



Who has affected you most?

- "Who has affected you most in your life so far?" was voted in an internet site.
- Jesus Christ received the second largest numbers of votes
- (A) received the largest.
- Without paper, printing technology would not have developed, nor would wealthy life today be guaranteed.

Origin of paper

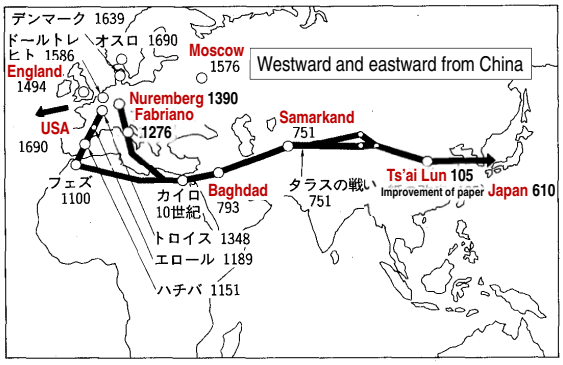
- Ts'ai Lun is traditionally regarded as the inventor of paper. Exactly, however, he invented the composition for paper along with the papermaking in A.D. 105.
- The fibrous materials used in those day were bark, hemp, silk, and fishing net.

蔡倫

Origin of paper

- The world oldest paper found in that is estimated to be between 179 and 142 BC (early Western Han 漢朝).
- It was used as a map, where mountains, waterways and roads are drawn.

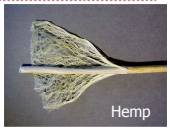
Fangmatan (放馬灘) paper



Spread of papermaking technology

History of papermaking tech. -Materials

- **Hemp**（Cannabis大麻・Linen亜麻）
  - → Cannabis has been used for cloth and fishing net in China and Japan. Linen in Europe.
- **Rags**
  - → Recycling of cloth woven originally from hemp. Cotton from the age of Industrial Revolution
- **Bast (skin) fibers**, such as Paper Mulberry etc.
- **Wood**, capable of producing on a large scale
- **Kenaf**
  - → A kind of hemp promoted for forestry preservation, but not accepted any more.
- **Plastics**, synthesized paper from polypropylene called "Yupo"



Origin of Printing technology

Gutenberg (1395? –1468)
invented a printing press in around 1445.
The invention consisted of

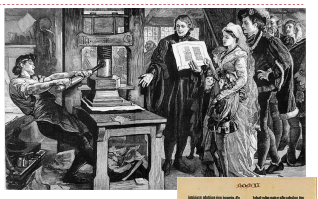
- mass-producing movable type;
- oil-based ink from linseed oil; and
- a wooden printing press similar to the agricultural screw presses

and allowed the mass production of printed books and was economically viable for printers and readers alike.

Johannes Gutenberg

Movable type

42-line Bible (42B)



- Gutenberg printed and published 180 copies of 42-line Bible.
  - → The start of the age of the printed book in the West
- Relationship with paper
  - → Increased paper demand
  - → Development of mass production of paper
  - → Use of wood as a papermaking material
  - → Invention of paper machine to produce "continuous paper".

The Greatest Inventions of the Past 2000 Years

Edited by John Brockman and published on Jan 12, 2000

- John Brockman, a novelist of USA, asked "What is the most important invention in the past two thousand years? and Why?" to famous.
- "Reading glasses" and "eraser" were unexpectedly proposed.

- Many people including Dr. Philip Anderson, a Nobel prize winner, chose "**printing technology**" because it promoted knowledge occupied by privileged people to the public.

- Another physical scientist chose "watch" for quantification of time passage that was dependent on one's sense so far.

- "Heliocentric theory", "mathematics", "differential and integral calculus", "democracy", and "religion" were also supported.

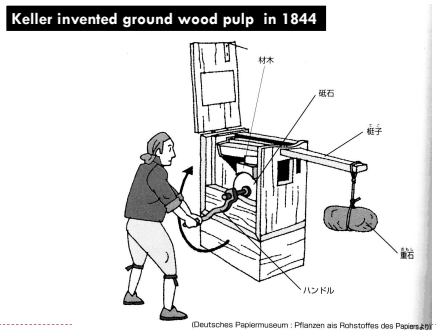
- See http://www.edge.org/documents/Invention.html

History of papermaking tech. – Machine

1670	Hollander beater invented [Holland]
1719	Reaumur submitted his invention - paper can be made from wasp hives- to the Academy [France]
1798	Louis-Nicolas Robert invented manufacture of continuous paper [France]
1844	Keller invented ground wood pulp [Germany]
1851	Burgess [USA] and Watts [England]invented soda pulping to make wood pulp.
1856	Healey received a patent of corrugated [England]
1856	Tilghman invented the sulfite pulping [USA]
1879	Dahl invented Kraft pulping [Germany]
1950	Hardwood pulping initiated[Japan]
1968	Thermo-Mechanical Pulping (TMP) Developed[Sweden]
1977	Quinone-added pulping invented [Japan]

Mechanical pulping – Groundwood pulp

- GP or SGW ([Stone] Groundwood Pulp)



Old printed material in Japan

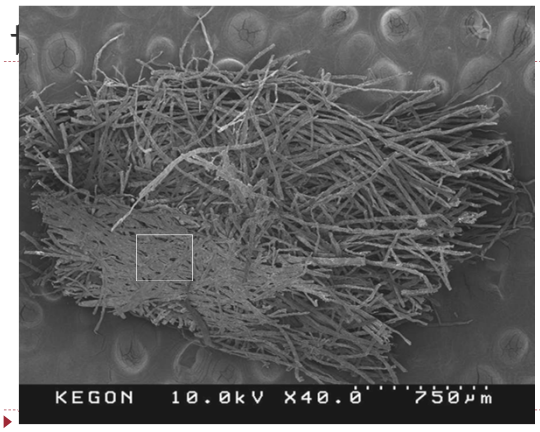
In 764, Emperor Koken had holy texts (無垢浄光陀羅尼経) printed on paper one million copies for peace of Japan, contained in one million wooden miniatures of a three story tower, and laid out in the ten great temples like Horyu-temple and Todai-temple.

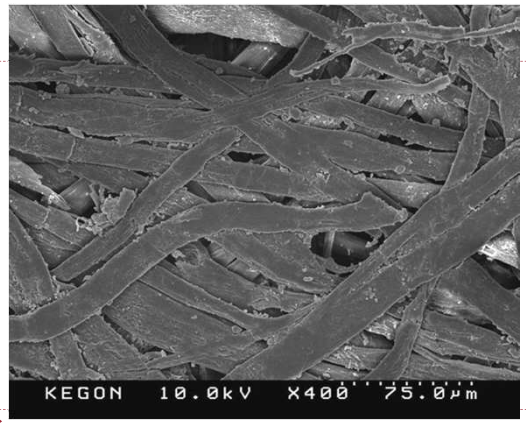
The world oldest printed material

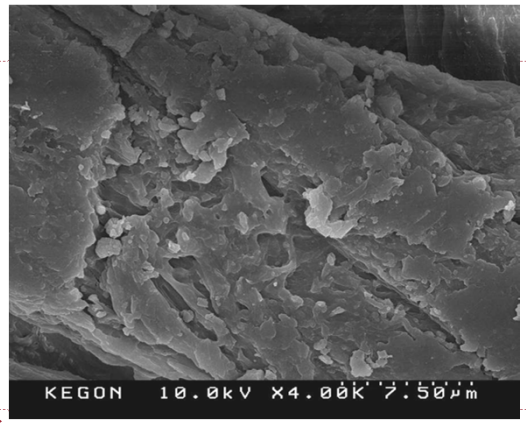
In 1966, printed holy texts was discovered in the Buddha tower of Bukkoku-temple (**仏国寺**) of Keishu, Shinra (**新羅慶州**), currelty Korea(**韓国**). This tower is known to have been built in 751.

The world oldest printed material

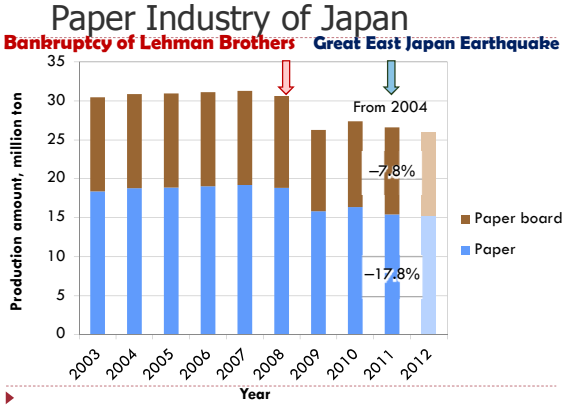
Paper with holy texts (華厳経) written in 755, Silla era (新羅) was analyzed.



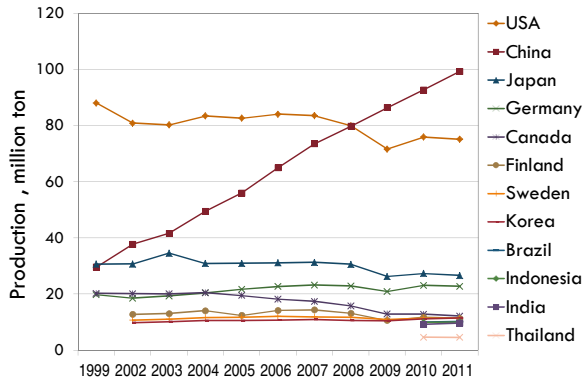




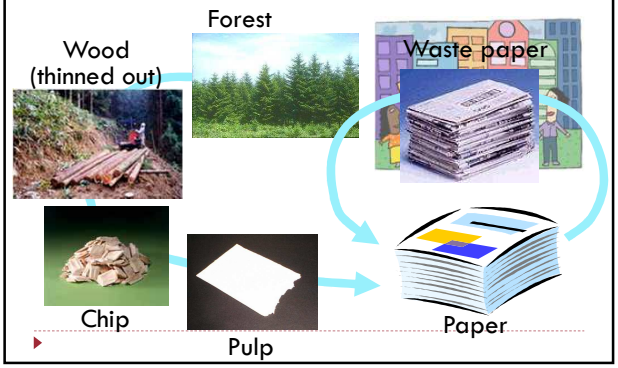
Paper Industry of Japan



Production of paper and paperboard

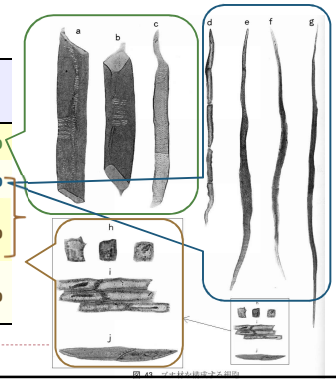


How to make paper ▸ From "wood"

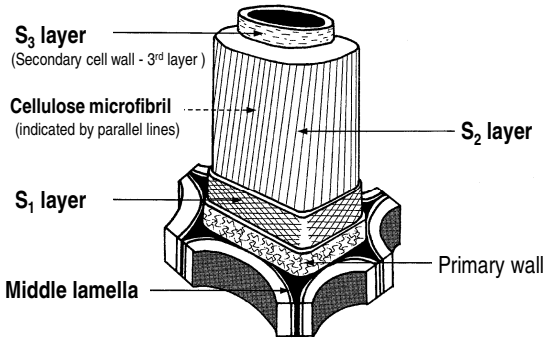


Wood tissue – cells of beech tree

Component of hardwood tissue	
Vessel	20%
Wood fiber	60%
Axial parenchyma cell	10%
Radial parenchyma cell	10%



Wood tissue – structure of cell wall

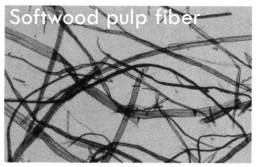


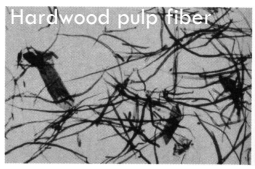
Structure of plant cell wall and axial direction of cellulose microfibrils

Kind of pulp

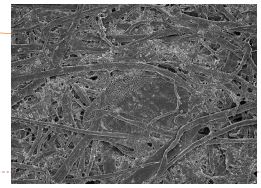
- **Pulp**
  - **Fibers mainly consisting of cellulose extracted from plant such as wood by mechanical or chemical treatment**
- Mechanical pulp [MP]
  - Fibers extracted from wood by crushing
- Chemical pulp [CP]
  - Fibers extracted from wood by dissolving lignin
- Deinked pulp [DIP] (recycled pulp)
  - Fibers extracted from waste paper by removing ink

Chemical pulp – Fiber geometry



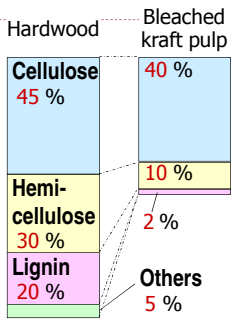


- Copy paper consists of (B) wood pulp fibers
- Observe pulps



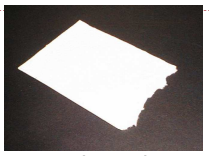
Wood composition – Major 3 components

Chemical component	Approx. ratio (%) Softwood	Hardwood
Cellulose	45	45
Hemicellulose	25	30
Lignin	25	20
Others Terpenoid Resin acid Fatty acid etc.	2 - 8	



Change of Composition by kraft pulping

Form of pulp

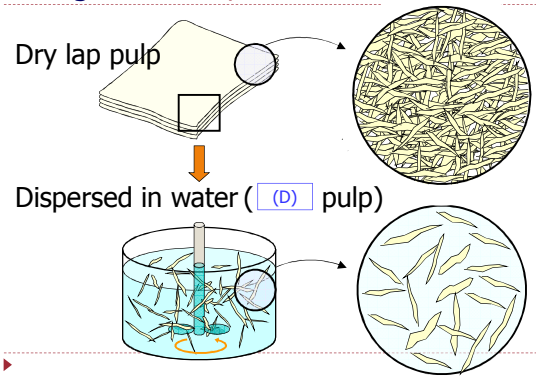


Dry lap pulp

- **Slush pulp**
  Pulp suspension with concentrations of approx. 1-4%
- **Lap pulp**
  Pulp Formed and folded by wet machine. Called "**Dry lap**" when dried
- **Bale pulp**
  A bunch of pulp sheets compressed and bound with a wire

Transported (C) pulp

Disintegration - Separation into individual fibers



Standard disintegrator (defibrator)

- Pulp is put in water in steel container with ca. 3.4 L capacity
- Stirred with a propeller mixer at 3000 min^{-1} (rpm)
- Latency of MP should be removed at high temperature (Latent=hidden)

Pulp	Dry mass	Water volume	Revol-utions
Chemical	30 g	2.0 L	30,000
Mechanical	60 g	2.7 L	60,000

Beating (refining)

- Post-disintegration process
- Process where shear stress is applied to water-containing fibers resulting in **fibrillation** (formation of small filaments or fibers) on the surface and **concentrically loose structure**

Beating (refining)

- Beating achieves large bonded area between fibers and thus higher paper strength.

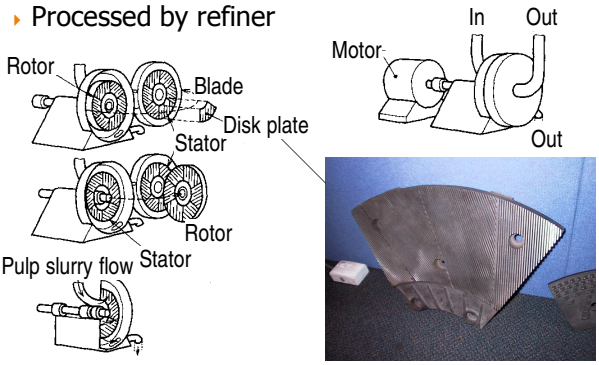
Q. Why can this breaking process increase paper strength?

Difference between disintegration and beating

- **Disintegration** is a process to separate fibers bonded or entangled, keeping fiber characteristics
- **Beating** is a process to treat mechanically individual fibers, changing fiber characteristics

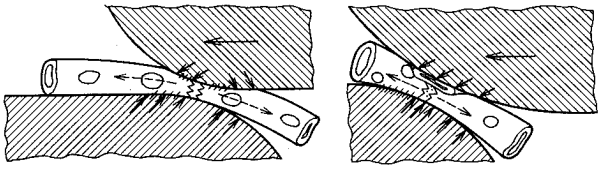
Beater – Refiner(refining)

- Processed by refiner



Beater – PFI mill (beating)

Beating – mechanism

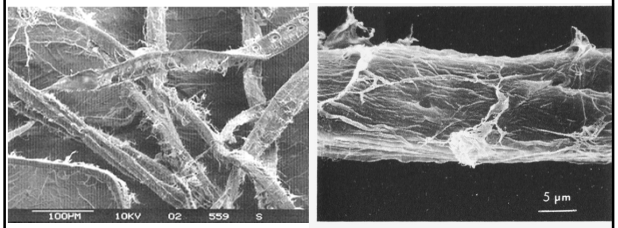


Effect of blades on pulp fibers during beating

Refining – movie – refiner

Beating – change of fibers – **external** fibrillation

{ External fibrillation
Internal fibrillation



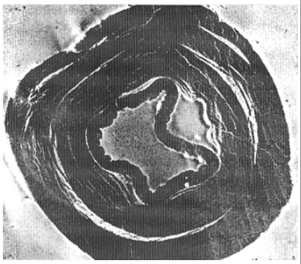
Scanning Electron Micrographs of freeze-dried softwood pulp fibers after beating

Beating – change of fibers – **internal** fibrillation

{ External fibrillation
Internal fibrillation

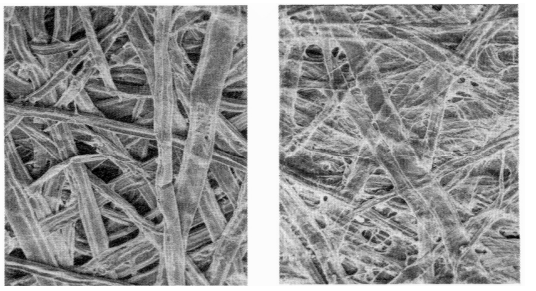
= Concentric loosening (Lamellar separation)

Connection of small pores formed by lignin removal



Lamellar separation of fiber cell wall by beating

Beating – change of paper structure



Unbeaten (left) and beaten (right) softwood pulp sheets

- **Q.** How did fibers and sheets change by beating?

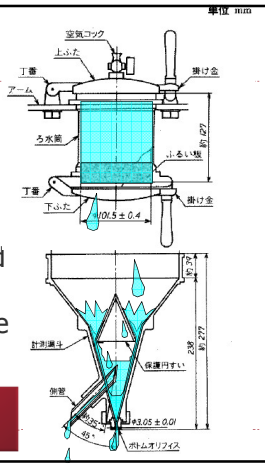
Evaluation of fiber properties

- Freeness (Drainability)
- Specific surface area
- Fiber length distribution
- Distinguishment by staining
- Fiber coarseness
- Curl index

Evaluation of Freeness

- Canadian standard freeness (mLCSF)
  - One L of pulp suspension at 0.3% and 20 °C is pored and the volume (mL) of water drained from the side pipe is measured.

- **Q.** Does CSF increase or decrease by beating?



Evaluation of Freeness

- Canadian standard freeness
  - Unbeaten pulp ca. 650 mL CSF
  - Beaten pulp ca. 400 mL CSF
  - Reasons why freeness (E) by beating are
    - More fines (small pieces of fibers)
    - Fibrillation

    make paths between fibers in a pulp mat thin, winding, and long.

Water Retention Value (WRV)

- M_w : Mass of pulp after centrifugation
  M_d : Mass of the pulp after oven drying

$$WRV(\%) = 100 \times (M_w - M_d)/M_d$$

- **Q.** Calculate WRVs to 2 decimals in percentage.

Pulp	After cent.(g)	Oven dried(g)
SBKP beaten	**0.61**	**0.23**
SBKP unbeaten	**0.59**	**0.28**
HBKP beaten	**0.54**	**0.22**
HBKP unbeaten	**0.45**	**0.24**

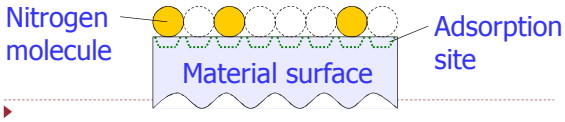
Sample	WRV, %
Bleached softwood	102
Bleached hardwood	101
TMP	139
CTMP (hardwood)	122
CTMP (50% HW + 50% SW)	124
Unbleached sulphite	104
Recycled pulp	159
Non-wood pulp	204
Never-dried Kraft pulp	114

Nitrogen adsorption method

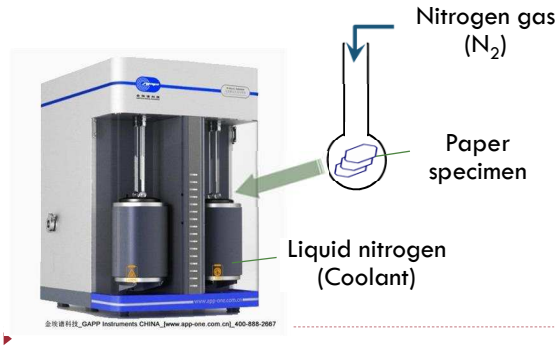
- Langmuir model
  - All the adsorption sites are equivalent and the surface is homogenous.
  - Monolayer coverage
  - No interactions between adsorbate molecules on adjacent sites

Nitrogen adsorption method

- Langmuir model (cont'd)
  - The fractional coverage of the surface θ changes at the adsorption rate proportional to gas pressure p and the number of empty sites $N(1-\theta)$.
  - The desorption rate proportional to $N\theta$.



Nitrogen adsorption method

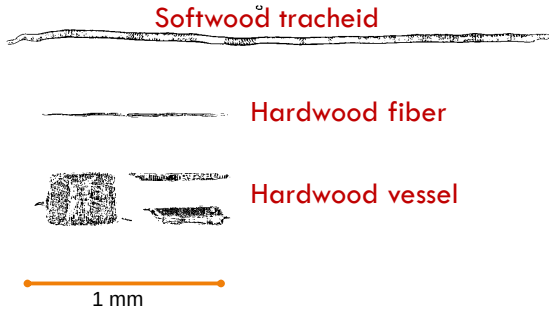


Specific surface area (SSA)

Drying method	Sample	BET SSA, m^2/g
Solvent exchange	Unbleached Spruce KP	230
	Bleached Spruce KP	185
	Spruce α-cellulose	185
	Spruce GP	25
	Birch KP	129
Evaporation at 105 °C	Unbonded pulp fibers	1.2
	Paper	0.5 – 1.0

KP=kraft pulp, GP=ground wood pulp

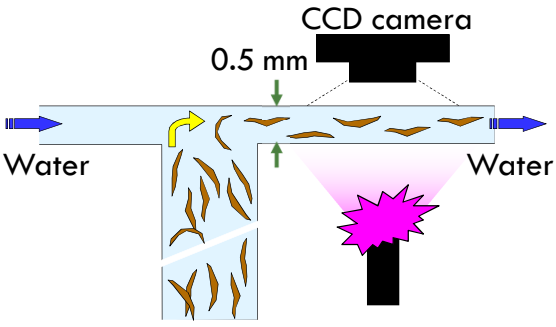
Length and width of fibers



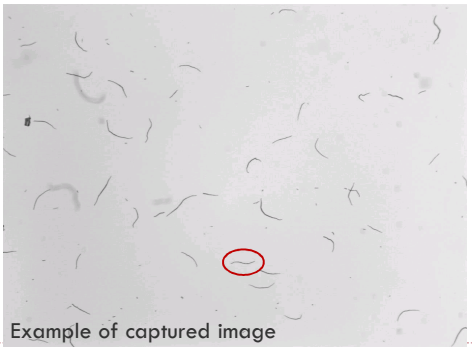
Fiber length and width distribution

Fiber tester, ABB(L&W), Sweden

Fiber length and width distribution

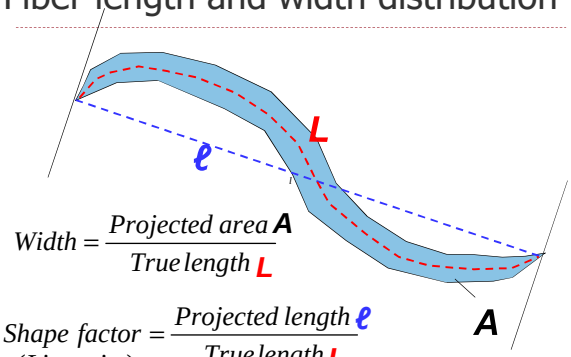


Fiber length and width distribution



Example of captured image

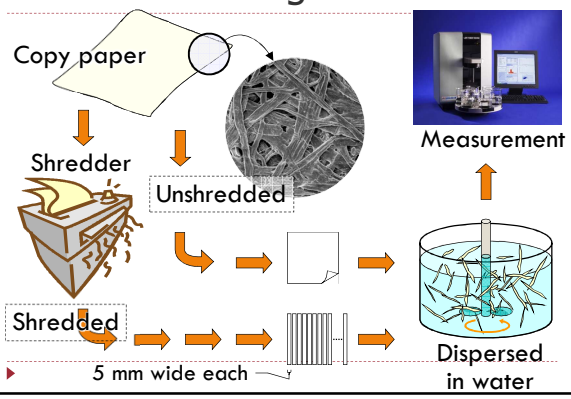
Fiber length and width distribution



$$Width = \frac{Projected\ area\ A}{True\ length\ L}$$

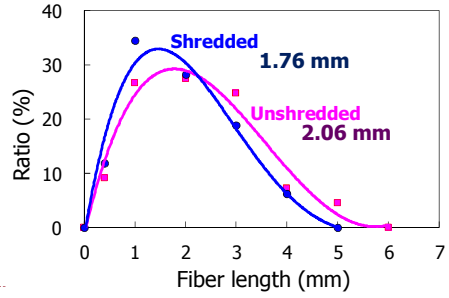
$$Shape\ factor\ (Linearity) = \frac{Projected\ length\ \ell}{True\ length\ L}$$

Mean fiber length



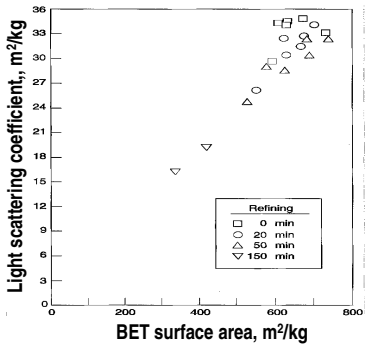
Mean fiber length

- Comparison in fiber length between shredded and unshuredded copy papers



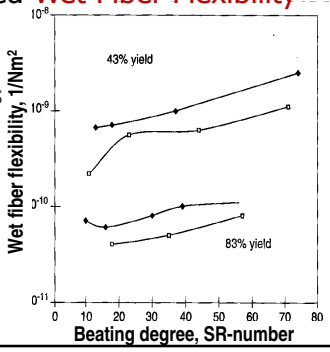
Effect of beating on paper properties

- **S**pecific **S**urface **A**rea on **L**ight **S**cattering **C**oefficient
  - LSA decreases as fiber bonding area increases.
  - Interfiber bonding area can be evaluated by SSA.
- Beating increased interfiber bonding area.



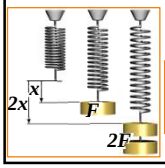
Effect of beating on paper properties

- Beating decreased Wet Fiber Flexibility (WFF)
  - Bending strength of single wet fibers was measured for determination of WFF.
  - SR = Schopper-Riegler method for determination of drainability



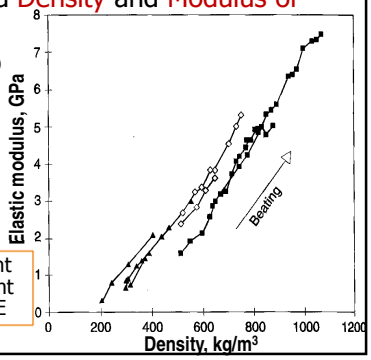
Effect of beating on paper properties

- Beating increased Density and Modulus of Elasticity (MOE)
  - Linear relationship between density and MOE regardless of beating degree



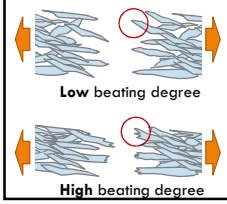
$F=kx$

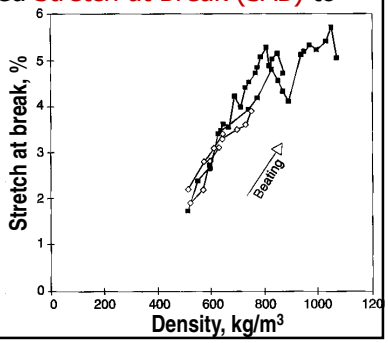
k; sprint constant = MOE



Effect of beating on paper properties

- Beating increased Stretch at Break (SAB) to certain degree
  - SAB increased with as well, but leveled off.





Stock preparation – additives

- **Paper quality** control
  - **Size (sizing agent)** - water repellency
  - **Filler** - brightness and opacity
  - **Strength agent** – dry or wet strength
  - **Dye** – optical brightening agent (OBA)
- **Paper manufacturing** control
  - **Retention aid** – ex. *aluminum sulfate* – fines, fillers, and size retained more
  - **Aintiseptic** (preservative)

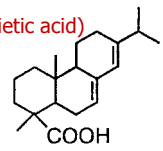
Additives – size and filler

	Acidic paper	Non-acidic paper
Size (sizing agent)	Rosin (Abietic acid)	Alkyl ketene dimer (AKD), Alkenyl succinic anhydride (ASA)
Retention aid	Alminium sulfate (alum), deteriorates paper	Cationic polymer such as Polyamine-amide epichlorohydrin (PAE)
Filler	Clay, Titan dioxide, Talk	Calcium carbonate, Titan dioxide
pH at papermaking	4.5~5.5	7.5~8.5 (7 or slightly greater)

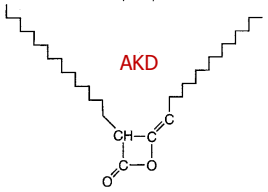
Q. Why is calcium carbonate not used for acidic paper?

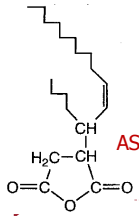
Additives – size and filler

Rosin (abietic acid)

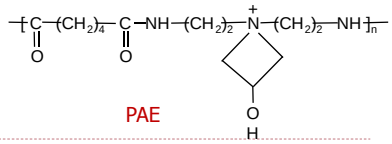


AKD





ASA



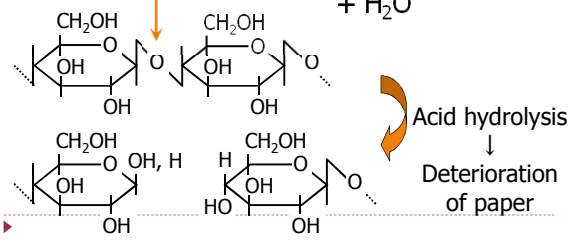
PAE

Additives – deterioration of acidic paper

Aluminum sulfate deteriorates paper.

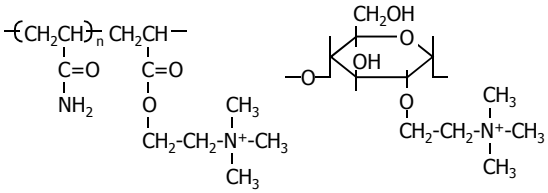
$Al_2(SO_4)_3 + 2H_2O \rightarrow 2Al(OH)^{2+} + 2H^+ + 3SO_4^{2-}$

$+ H_2O$



Additives – size and filler (2)

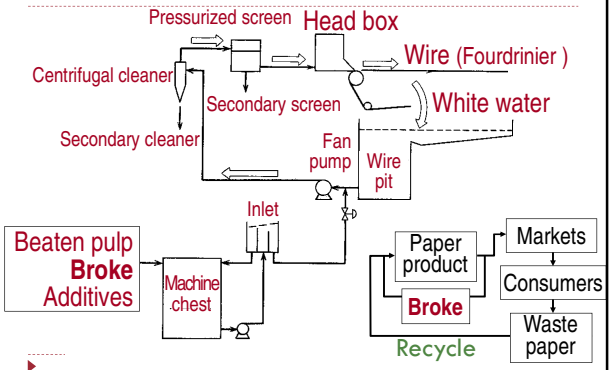
	Acidic paper	Non-acidic paper
Strength resin	Cationic polyacrylamide (C-PAM)	Cationic starch



Cationic polyacrylamide Cationic starch

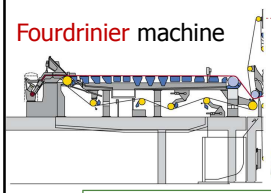
Papermaking – Additives - movie

Papermaking – approach section

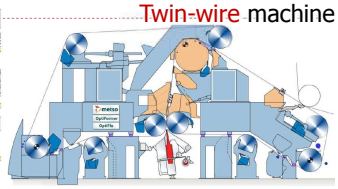


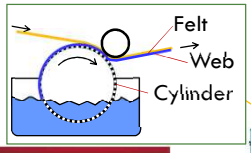
Papermaking - wire section

Fourdrinier machine

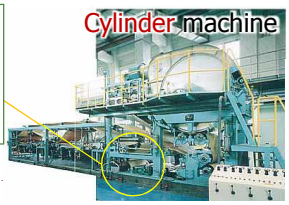


Twin-wire machine





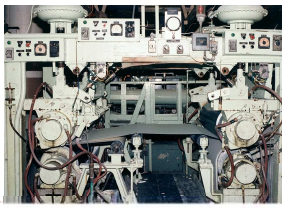
Cylinder machine



Q. What is a merit of Cylinder machine?

Papermaking – (wet) press section

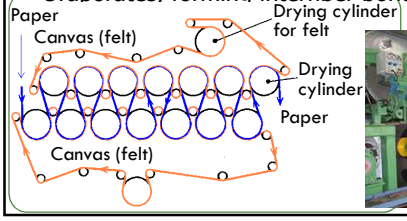
- A wet web is pressed at high pressure between large rolls to squeeze out excess water.
- Water transfers to felts that sandwich the wet web.
- Pressing increases density and wet web strength.
- The common number of nips is 3 or 4.



Kodak Historical Collection #003 (1986)

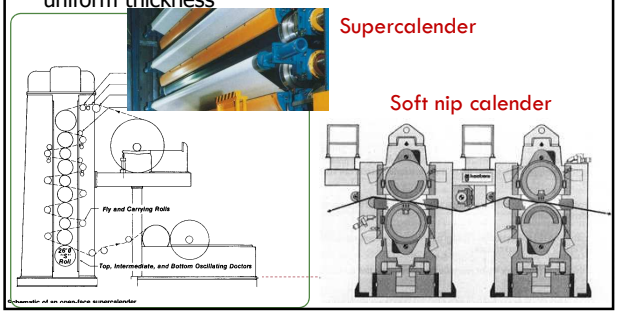
Papermaking – dryer section

- Steam-heated cylinders dry the paper with canvases.
- Free water evaporates, between fibers first , inside fibers second, and between fibrils last .
- At less than 9 % moisture content, bonding water evaporates, forming interfiber bonds.



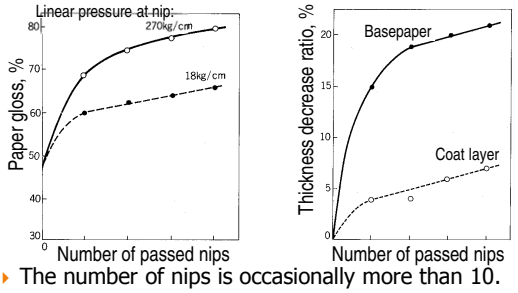
Papermaking – calender section

- A number of rolls press the passing paper.
- They make the paper surface extra smooth and glossy with friction, and provide a higher density and more uniform thickness



Papermaking – calendering effect

- Gloss improvement and compression of paper



- The number of nips is occasionally more than 10.

Q. Why is it as many as 10 although only 3 or 4 for wet press?

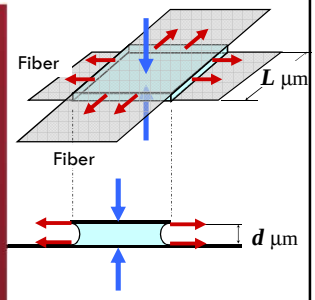
Types of chemical bond

- Ionic bond = a chemical bond in which two ions are joined together because one has a positive charge and the other a negative charge
- Covalent bond = a chemical bond in which two atoms share one or more pairs of electrons that hold them together (ca. 500 kJ/mol)
- Hydrogen bond = a weak connection that is formed between an atom of hydrogen (= a gas) and an atom of another substance such as oxygen or nitrogen (= a gas) (10∼40 kJ/mol)
- Van der Waals forces = the relatively weak attractive forces that act on neutral atoms and molecules and that arise because of the electric polarization induced in each of the particles by the presence of other particles
- Dipolar bond (coordination bond)
- Metallic bond

Inter-fiber bond

- Effect of water on interfiber bond formation

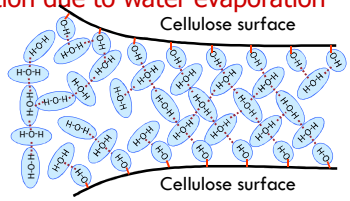
Q. Suppose two crossing flat fibers with the square , length L on a side at the crossing point. As they dry and the interfiber distance d comes to 1 mm, How much contraction stress develops between the two fibers?



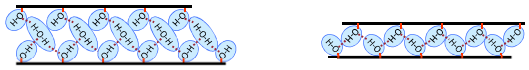
- The attractive force is called Campbell force.

Inter-fiber bond

- Interfiber approach and hydrogen bond formation due to water evaporation



Loose hydrogen bond mediated by water



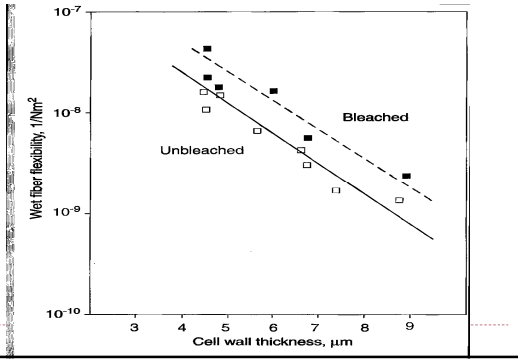
Firm hydrogen bond with a water monolayer Direct hydrogen bond

Inter-fiber bond

- Evidence of hydrogen bond
  - When paper mass was measured after allowing to stand in deuterium water (D_2O) vapor until saturation, 0.5 to 2.0 % of hydrogen of all the hydroxyl groups was not replaced with deuterium. This ratio corresponds to the percentage of hydrogen bonded hydroxyl groups.
  - Energy required for tensile breakage was calculated. 19 kJ/mol (equivalent to hydrogen bond energy)
  - Strength decreased with acetylation of carboxyl groups **Cell-OH → Cell-O-C-CH_3** (with O on the C)

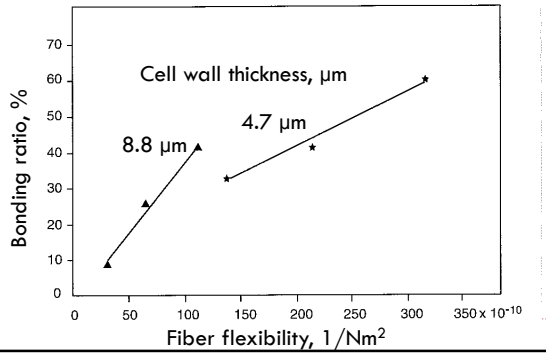
Inter-fiber bond

- Effect of **cell wall thickness** on **wet fiber flexibility**

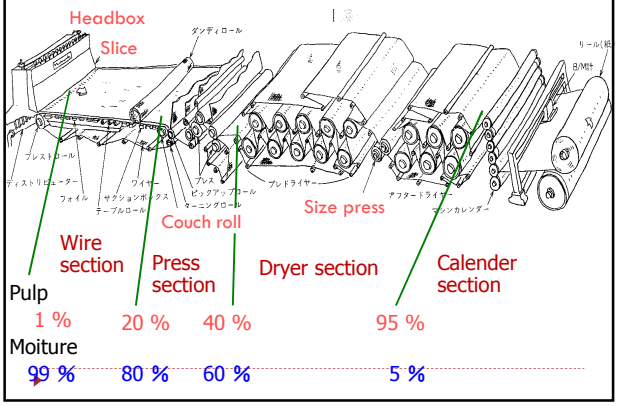


Inter-fiber bond

- Effect of fiber flexibility on Relative Bonded Area



Forming (Wire section) – Moisture content

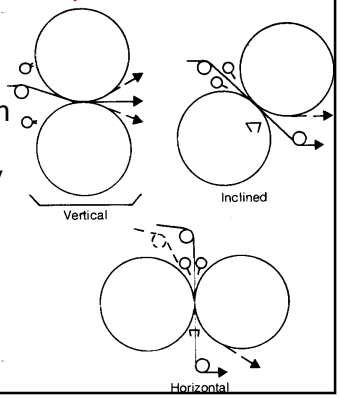


Post-forming – Size press

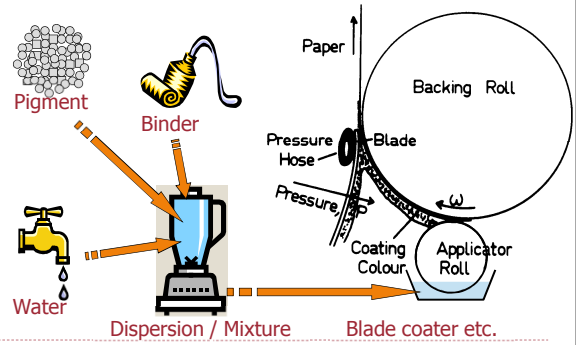
- Sizing
  - Internal sizing- addition to pulp slurry
  - External (surface) sizing – application to surface
- What is surface sizing (size press)?
  - The treatment for providing water-resistant property to paper by application of starch solution etc.
  - Other than starch, carboxymethyl cellulose, polyvinyl alcohol, polyacrylamide etc. are applied. Strong water-repellency is not required.
- Advantages over internal sizing
  - 100% retained. No deposit on walls of former or froth

Post-forming – Size press

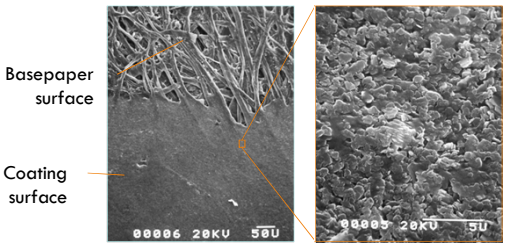
- Purpose and effect
  - Picking prevention in offset printing
  - Ink jet printability to prevent bleeding



Pigment coating

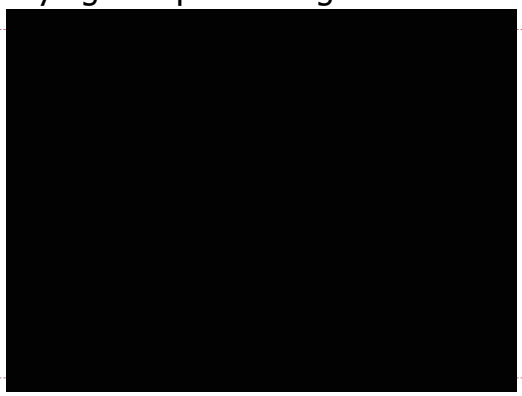


Coated paper surface - Scanning Electron Micrograph



- To increase smoothness, brightness, opacity, and gloss, and control liquid penetration

Drying and processing – movie



Paper properties – Fundamental and applied properties

- Conditioning
- Structure
- Surface chemistry
- Liquid absorption
- Mechanical properties
- Optical properties

Conditioning and test atmosphere

- 23 ºC 50% RH (Relative Humidity)
  - Paper properties depend on humidity, but less on temperature
  - although temperature difference by more than 10 ºC changes ex. tensile strength significantly.

Conditioning and test atmosphere

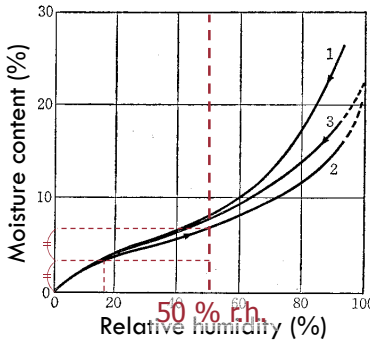


図 98 亜硫酸パルプシートの水分収着等温線 (Seborg, C. O. et al., 1938)

- Hysteresis
- Dry paper to half the equilibrium moisture content and back to 50% RH for testing
- Moisture content is affected by crystallinity

Paper structure – basic properties

- Grammage (g/m^2)
  - Mass (g) per square meter at 23 ºC and 50%RH
  - ⇔ **Grammage (oven-dry basis)** is based on the constant mass attained when kept at 105 ºC
- Thickness (mm)

  - **Single sheet thickness**, distance between two parallel planes holding a sheet at 100 kPa
  - **Bulking thickness**, thickness per sheet, calculated from that of 10 superimposed sheets
  - Includes surface roughness (dents)

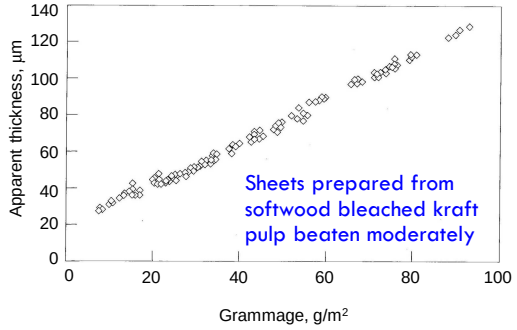
Paper structure – basic properties

Q. Which is higher, single sheet thickness or bulking thickness?

- Density
  - Mass per unit volume in g/cm^3 calculated from grammage divided by thickness

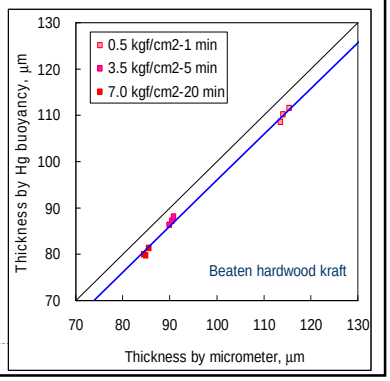
Paper structure – basic properties

- Density (grammage/thickness) affected by grammage!?

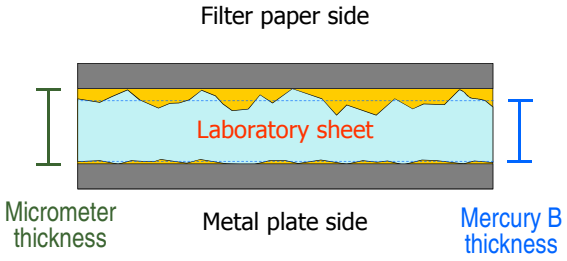


Paper structure – thickness measurement

- Micrometer
- Mercury buoyancy method

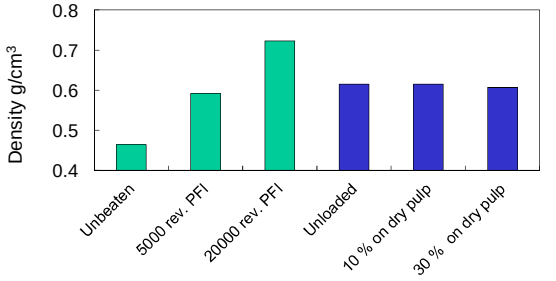


Paper structure – Why is the thickness different between the two methods?



Paper structure – Factors affecting density

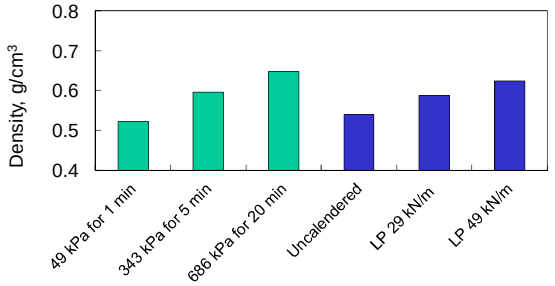
- Beating and filler loading



Beating rev. (PFI mill) Calcium carbonate addition

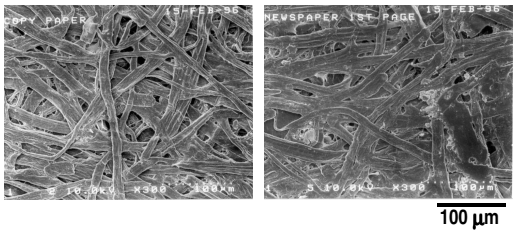
Paper structure – Factors affecting density

- Wet press and calendering



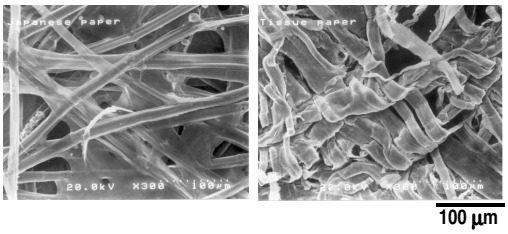
Wet press Calendering- linear pressure

Paper structure-Scanning electron microscope(1)



Copy paper Newspaper

Paper structure-Scanning electron microscope(2)



Japanese paper Tissue paper

Paper structure – Smoothness

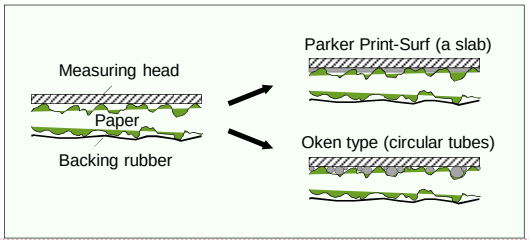
- Air leak method
  - Air flow rate through a gap between paper surface and smooth metal plate
- Surface profile (Microscopy)
  - Measurement method
    - Stylus profilometry
    - Scanning Probe Microscope
    - Confocal Optical Microscope
    - Interferometric Optical Microscope
    - Multi-detector Scanning Electron Microscope
  - Expression of surface roughness

Paper structure – Smoothness

- Air leak method
  - Air flow rate through a gap between paper surface and smooth metal plate
- Surface profile (Microscopy)
  - Surface shape measured using profilometry such as stylus profilometry, confocal optical microscope.
  - Several ways of expressing surface roughness

Paper structure – Smoothness

- Air leak method
  - Print surf roughness (µm)
  - Bekk smoothness, Oken smoothness (s)

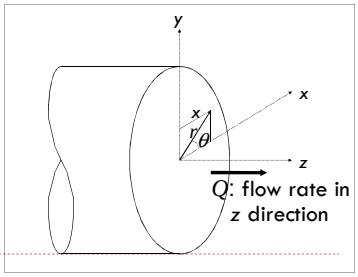


Paper structure – Smoothness

- Theory of air leak method
  - Hagen-Poiseuille flow

$$Q=\frac{\pi\Delta P}{8\mu}\frac{r^4}{l}$$

Q: volumetric flow rate
ΔP: pressure difference
μ: dynamic viscosity
r: radius of tube
l: length of tube



Paper structure – Smoothness

- Surface profile can be measured in 2D or 3D.
- Stylus, light beam, electron beam, or probe
  - Centerline average roughness (arithmetic average)

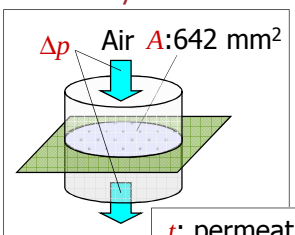
$$R_a = \frac{1}{\ell}\int_0^{\ell} |y| dy$$

  - Root mean squared roughness

$$RMS = \sqrt{\frac{1}{\ell}\int_0^{\ell} y^2 dy}$$

Paper structure – Air permeance

- Method
  - Gurley tester



Air permeance

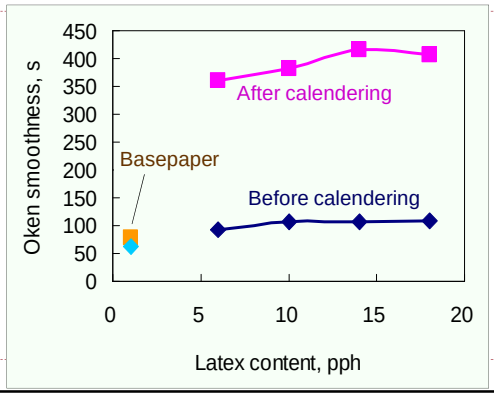
P [mm/(Pa·s)]

$$P = \frac{V}{1000 \times A \Delta p t}$$

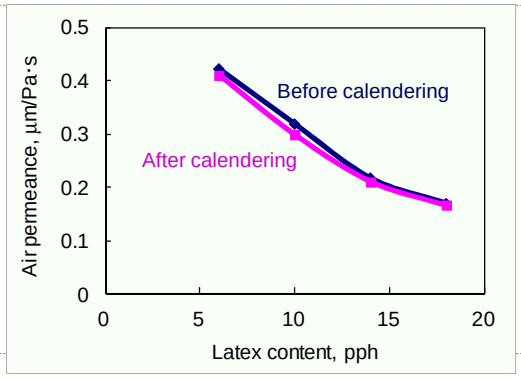
Universal air permeance

t: permeation time (s) = Air resistance (Gurley)

Paper structure –Smoothness of coated paper



Paper structure –Air permeance of coated paper

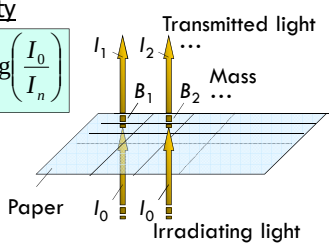


Paper structure - Formation

- Formation
  - [Definition 1] Unevenness sensed visually when white light is transmitted through paper – STD or CV of optical density

$$\log\left(\frac{I_0}{I_n}\right)$$

  - [Definition 2] Distribution of local mass B_n – STD or CV of local mass

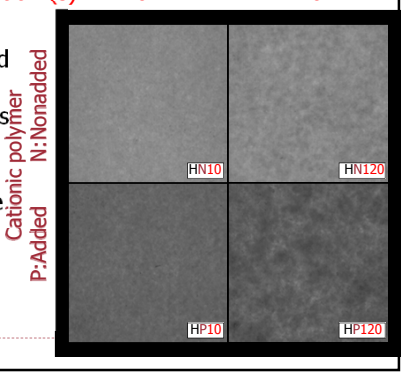


STD=Standard deviation, CV= coefficient of variation

Paper structure - Formation

Time until dehydration (s) 10 120

- Transmitted light images of softwood pulp sheets
- Formation becomes (F) by cationic polymer addition and increased time until dehydration
- Cationic polymers increases fiber retention.

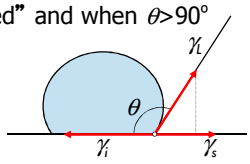


Interaction- between paper and water (liquid)

- Wetting
- Contact angle
- Surface energy
- Sizing degree
- Liquid penetration
- Swelling

Surface chemistry - Contact angle

- Contact angle (θ)
  - The angle made by the solid and liquid surfaces when a liquid droplet is placed on a solid surface.
  - When $0^\circ < \theta < 90^\circ$, "wetted" and when $\theta > 90^\circ$ "unwetted".
- Young equation
  - When the contact angle is constant, horizontal components of forces are balanced.

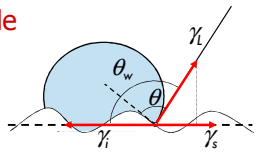


$$\gamma_i - \gamma_s + \gamma_L \cos\theta = 0$$

Surface chemistry - Contact angle

- Contact angle on a rough solid surface
  - Supposed that the area including microscopic structure is ***r*** times larger than the apparent one,
  - Wenzel's contact angle

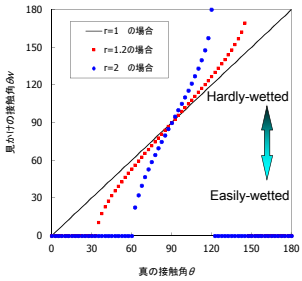
$$\cos\theta_w = r\cos\theta$$



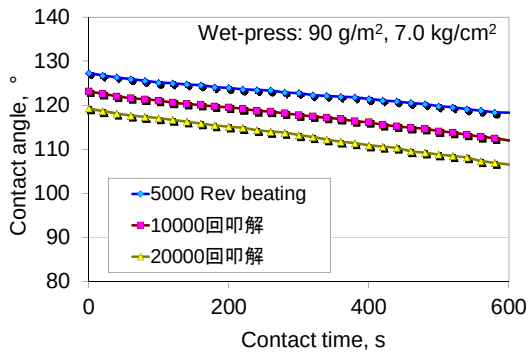
Surface chemistry - Contact angle

- Wenzel's equation
  - On a rough surface, when $\theta_w < \theta$ at $\theta < 90^\circ$, easily-wetted surfaces become more easily-wetted. But, when $\theta_w > \theta$ at $\theta > 90^\circ$, hardly-wetted surfaces become more hardly-wetted.

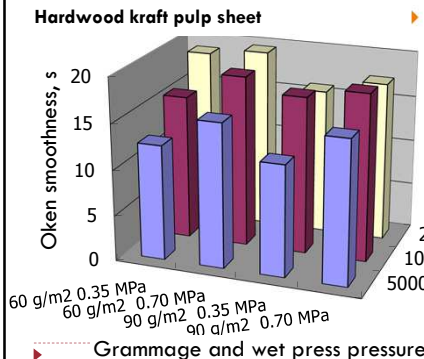
$$\cos\theta_w = r\cos\theta$$



Contact angle of paper - Beating effect



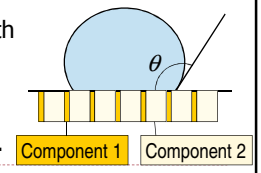
Beating and smoothness



- Surfaces smoothed by beating became easily-wetted.

Surface chemistry - Contact angle

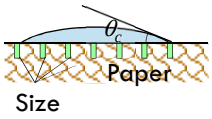
- On composite surfaces
  - The effective contact angle θ_C is dependent on the areal ratio of each component.
- Cassie's law
  - is stated as $\cos\theta_C = Q_1\cos\theta_1 + Q_2\cos\theta_2$, where θ_1 is the contact angle for component 1 with areal fraction Q_1 and θ_2 is the contact angle for component 2 with areal fraction Q_2 ($Q_1 + Q_2 = 1$).



Surface chemistry - Contact angle

Q. What is the contact angle θ_c of sized paper?

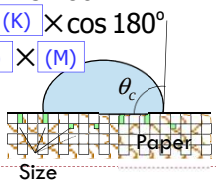
- Sizing agent need not cover the whole surface of fibers for repelling water. If a sizing agent covers 5% of the whole surface, what is the contact angle θ?
- Assume that θ is 0° for unsized fibers and 120° for the covering size.
- $\cos\theta_c =$ (G) × cos 0° + (H) × cos 120°
  $\cos\theta_c =$ (I) = 0.925
  $\theta_c =$ (J)



Surface chemistry - Contact angle

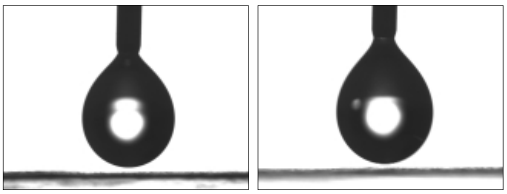
Q2. What is the contact angle θ_c of sized paper?

- Half the volume of paper is air. If 50% of paper surface is air, what is the θ_c?
- Assume that θ_c of a true surface of sized paper is 22.3° and θ of air is 180°.
- $\cos\theta_c =$ (K) × cos 22.3° + (K) × cos 180°
  $\cos\theta_c =$ (K) × (L) + (K) × (M)
  = (N)
  $\theta_c =$ (O)



Surface chemistry - Contact angle

- **Comparison in Water absorption**



Parchment **Wood-containing paper**

"wood-containing" means "made from mechanical pulp"

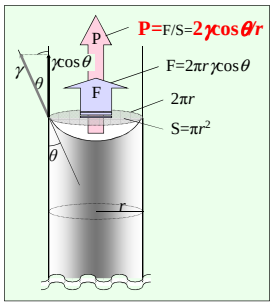
Liquid absorption theory - Capillary model

- Force developing around a meniscus of a liquid in a capillary (pipe)
- Steady flow in a pipe

$$Q = \frac{\pi P r^4}{8\eta l}$$

l: **Capillary length**
r: **Capillary radius**
η: **Liquid viscosity**
Q: **Volumetric flow rate**

(Hagen-Poiseulle equation)



Liquid absorption theory - Capillary model

Q. Substitute the relation represented in the figure into the H-P equation and develop the Lucas-Washburn equation.

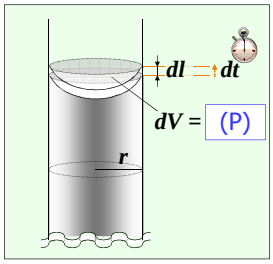
- H-P equation

$$Q = \frac{\pi P r^4}{8\eta l}$$

Substitute

$$P = \frac{2\gamma\cos\theta}{r}$$

$$Q = \frac{dV}{dt} = \text{(Q)}$$



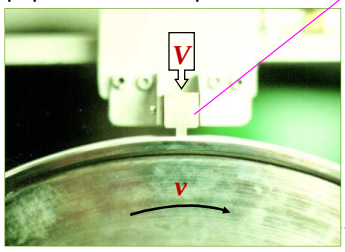
- Lucas-Washburn equation

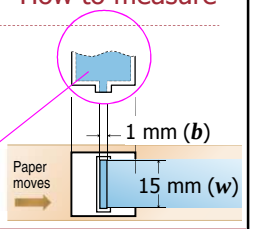
$$l = \sqrt{\frac{r\gamma\cos\theta \cdot t}{2\eta}}$$

Water absorption rate - How to measure

- Bristow's apparatus

A liquid supply head filled with a liquid of volume V scans paper at various speeds v.

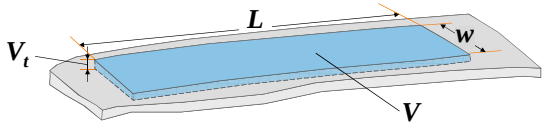




- Contact time $t = b / v$
  - Scan speed v
  - Slid width b
- Transfer Vol $V_t = V/(wL)$
  - Liquid volume V
  - Slit width w
  - Trace length L

Water absorption rate – How to measure

- Calculate transferred volume per unit area V_t



- **Contact time $t = b/v$**
  - Scan speed v
  - Slid width b
- **Transfer Vol $V_t = V/(wL)$**
  - Liquid volume V
  - Slit width w
  - Trace length L

Water absorption rate – Water and oil

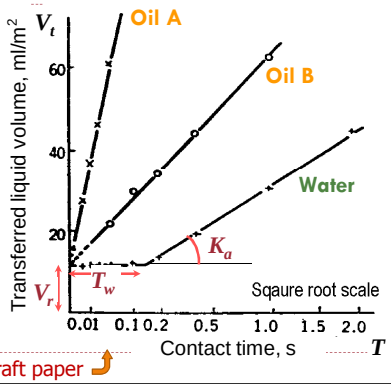
- For water,

$$V_t = V_r + K_a\sqrt{T - T_w}$$

V_r Roughness index
T Contact time
T_w Wetting delay
K_a Absorption coeff.

- For oil, $T_w = 0$. Then,

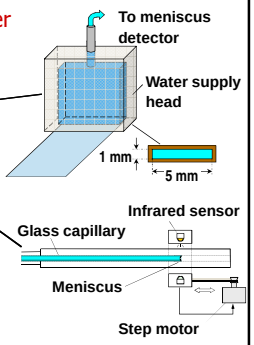
$V_t =$ (Q)



- Bristow's plot of kraft paper

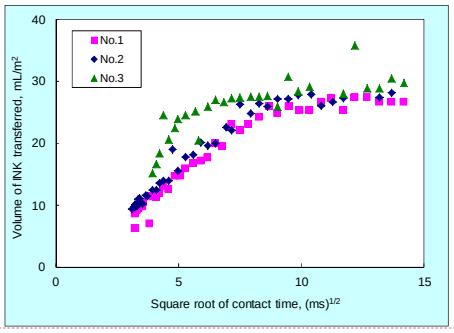
Water absorption rate - How to measure

- Automatic Scanning Absorptometer (Spiral-scan Bristow's apparatus)
  - Scanning speed changes stepwise during measurement

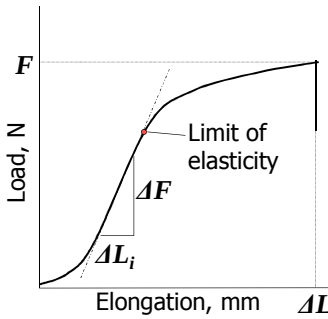


ASA

Water absorption rate of ink jet paper -ASA



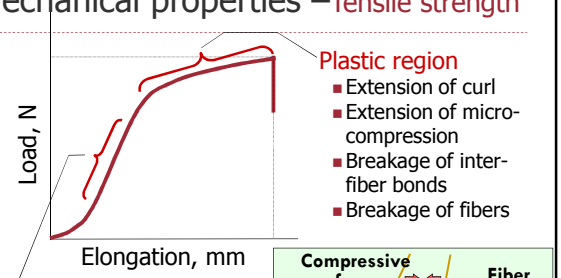
Mechanical properties –Tensile strength



Load-elongation curve

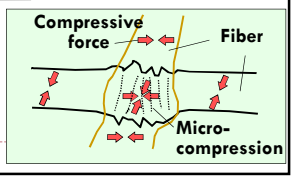
- Method
  - 15 mm in width
  - 100 mm in span
  - 10 mm/min elong speed
- Tensile index I
  - $I = \frac{F}{wg}$ (w: width g: grammage)
- Strain at break ε_T
  - $\varepsilon_T = \frac{\Delta L}{L}$
- Modulus of elasticity E^*
  - $E^* = \frac{\Delta F}{\Delta L i w T}$ (T: thickness)

Mechanical properties –Tensile strength

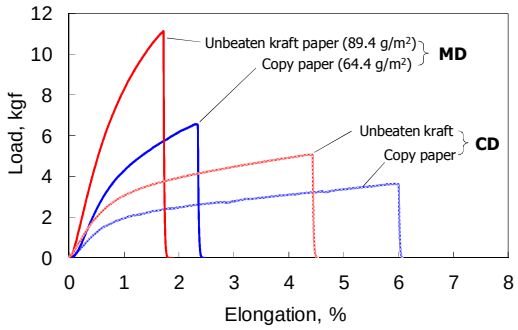


Plastic region
- Extension of curl
- Extension of micro-compression
- Breakage of inter-fiber bonds
- Breakage of fibers

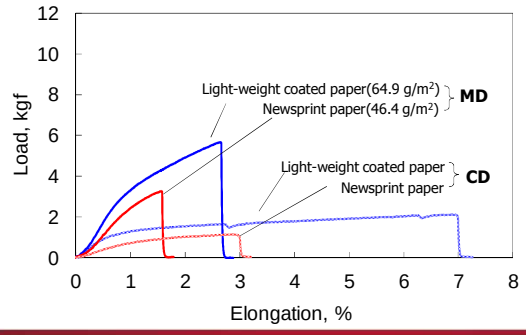
Elastic region
- Elastic elongation of fibers
- Elastic elongation of fiber network



Anisotropy–Tensile strength



Anisotropy–Tensile strength



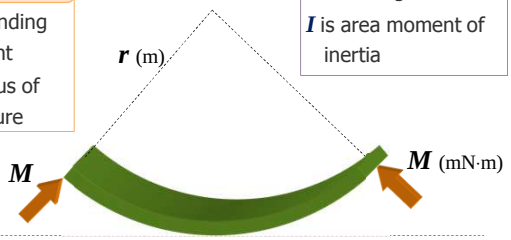
Q. Why does light-weight coated paper elongate greatly?

Mechanical properties – Stiffness

- (Bending) stiffness ***S*** represents the degree to which paper resists bending

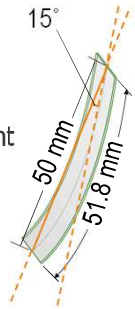
S=Mr
- ***M*** is bending moment
- ***r*** is radius of curvature

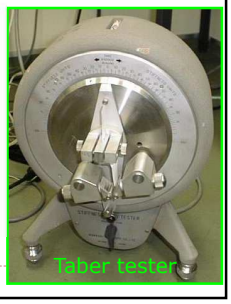
S=EI
- ***E*** is Young's modulus
- ***I*** is area moment of inertia



Mechanical properties – Stiffness

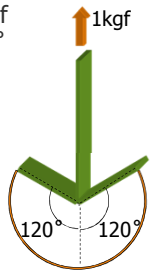
- Taber Stiffness
  - Bending moment when a test piece 38mm wide is bent to 15° and load length 50 mm
  - The unit is mN·m





Mechanical properties – Folding endurance

- Folding endurance
  - logarithm number of double folds at 120° on both sides that are required to make a test piece break
  - Longer fibers tend to show higher values.



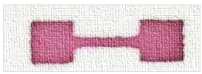
Paper devices

Paper absorbs water.

Paper substrate

- Capillary force due to porous structure

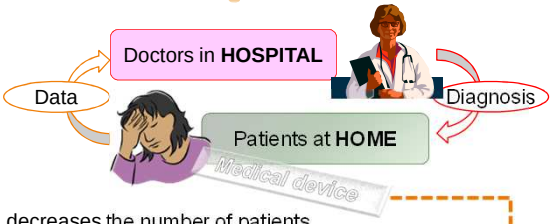
- Liquid transport
  designed channel



Lab-on-paper as a medical check-up sensor

Lab-on-paper as a medical check-up sensor

Self-diagnosis at home



- decreases the number of patients
- shortens hospital stay
  →Secure appropriate medical service in hospital

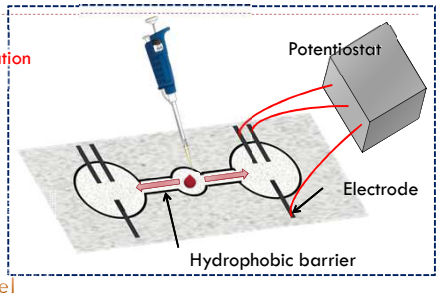
Affordable & easy-to-handle device is required

Electrochemical Lab-on-Paper

Paper
- Liquid transportation

Fabrication
- Ink jet

Microchannel
- Multiple test
- Small amount of liquid required



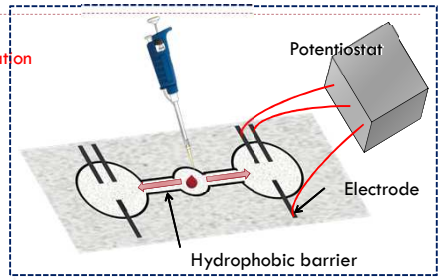
Electrochemical analysis
- Quantitative analysis

Electrochemical Lab-on-Paper

Paper
- Liquid transportation

Fabrication
- Ink jet

Microchannel
- Multiple test
- Small amount of liquid required



Electrochemical analysis
- Quantitative analysis

Paper Preparation

Improve printability

- Decrease pore size→ prevent ink bleeding
- Materials…cotton pulp→almost none of impurities

#	Beating (Revolution, PFI mill)	Density of paper (g/cm^3)
1	10000	0.568
2	20000	0.622
3	30000	0.641

Beating increases paper density

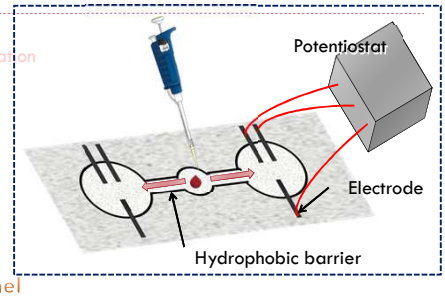
Paper substrate was successfully designed

Electrochemical Lab-on-Paper

Paper
- Liquid transportation

Fabrication
- Ink jet

Microchannel
- Multiple test
- Small amount of liquid required



Electrochemical analysis
- Quantitative analysis

UV curable ink for hydrophobic barrier

180

- Polymerized by UV-light irradiation
- Monomers, oligomers, initiators in **ethanol** → VOC-free

Ingredients of UV ink

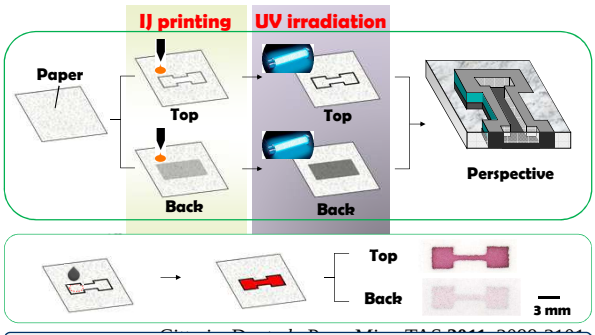
Octadecyl acrylate	1,10-decanediol acrylate	Irgacure 819
59.5%	25.5%	15.0%

(m/m)

Solvent-free & Green Material

Citterio, D. *et al.*, Proc. MicroTAS **2011**, 2099-2101

Microchannel Fabrication



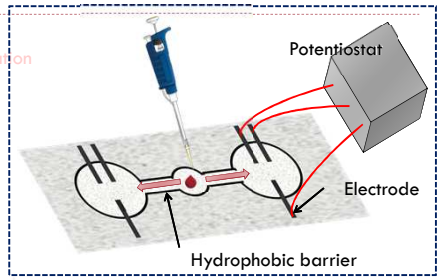
Microchannel was successfully fabricated

Electrochemical Lab-on-Paper

Paper
- Liquid transportation

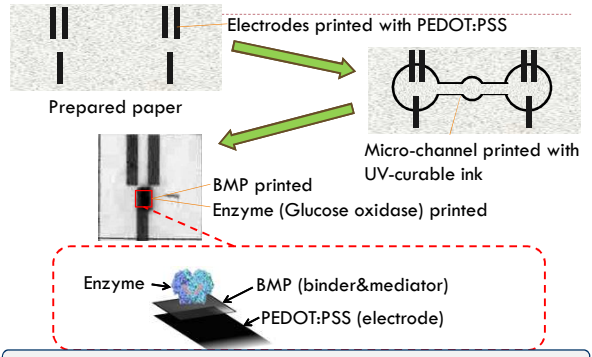
Fabrication
- Ink jet

Microchannel
- Multiple test
- Small amount of liquid required



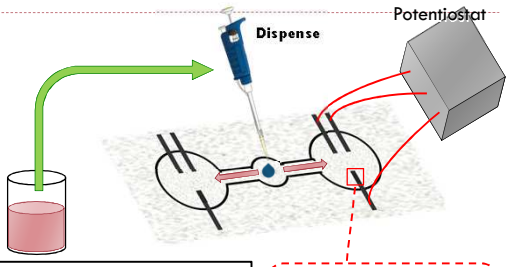
Electrochemical analysis
- Quantitative analysis

Fabrication Processes of electrodes



Lab-on-Paper was successfully fabricated

Glucose concentration



Tested glucose solution
- 1 M **KCl**
- 1 M **PBS** buffer
- Various amounts of **glucose**

Gluconic acid + H^+

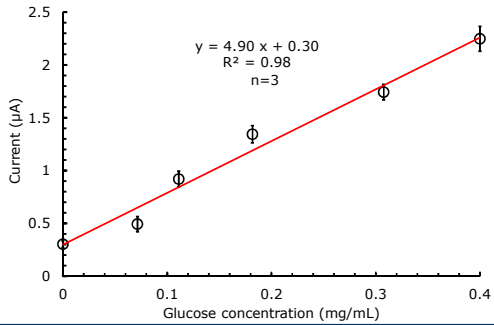
Glucose oxidase

Glucose+O_2 → e^-

Chronoamperometry for Glucose Test

Current value at 0.5 V

(vs. printed pseudo reference electrode)



Glucose conc. was successfully measured