EG60411 Bio-Material Science

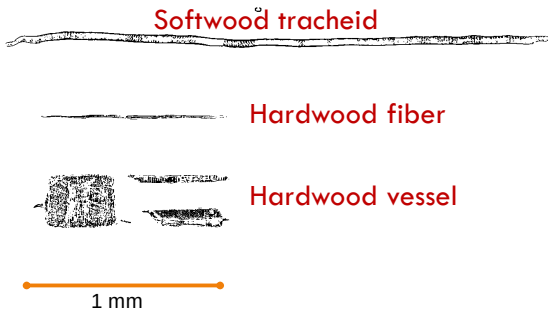
Toshiharu Enomae
Professor, PhD, Paper Device and Eco-friendly materials

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

Biomaterial Science （Schedule）

#	Date	Content
1	4/15	History of papermaking
2	4/22	Pulps – Beating and fiber properties
3	5/9, Fri	Pulps – Additives and functions
4	5/13	Papermaking processes & interfiber bonding
5	5/20	Paper– Structural and absorption properties
6	5/27	Paper– Mechanical and optical properties
7	6/3	Polysaccharide chemistry by Assoc Prof Akiko Nakagawa
8-9	6/10, 17	Pulping science and technology by Professor Hiroshi Ohi
10	6/24	Recent trend of paper science and technology

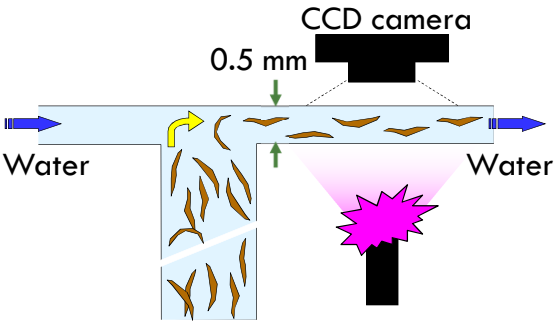
Length and width of fibers



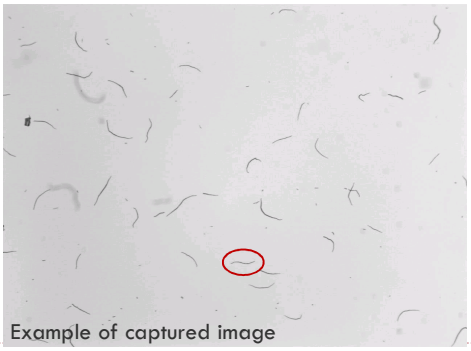
Fiber length and width distribution

Fiber tester, ABB(L&W), Sweden

Fiber length and width distribution

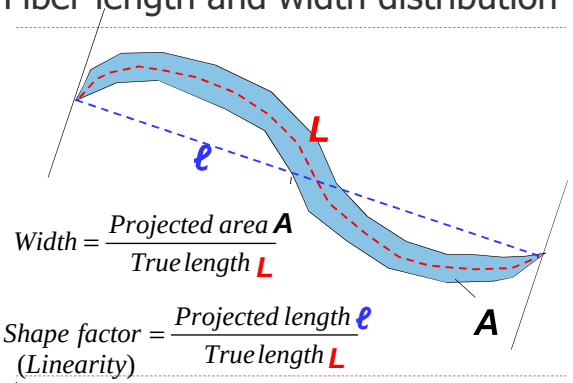


Fiber length and width distribution



Example of captured image

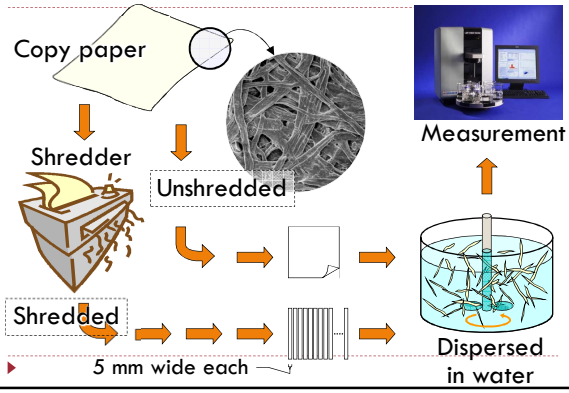
Fiber length and width distribution



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

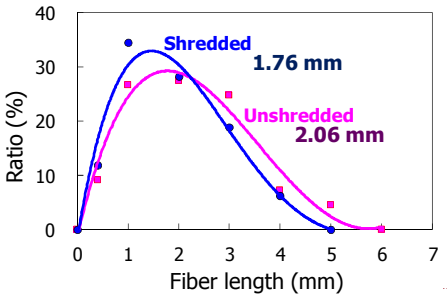
$$Shape\ factor\ (Linearity) = \frac{Projected\ length\ \ell}{True\ length\ L}$$

Mean fiber length



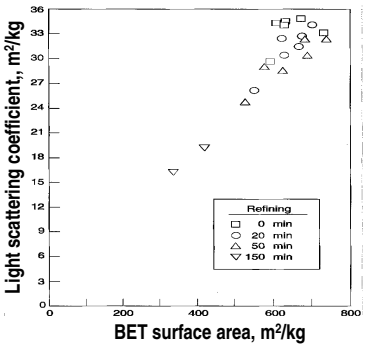
Mean fiber length

- Comparison in fiber length between shredded and unshuredded copy papers



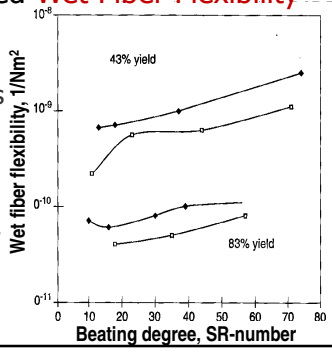
Effect of beating on paper properties

- **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.



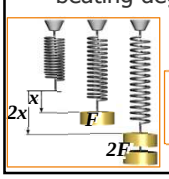
Effect of beating on paper properties

- 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



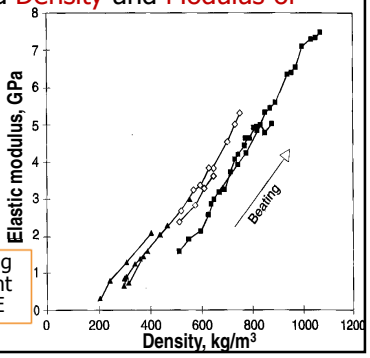
Effect of beating on paper properties

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



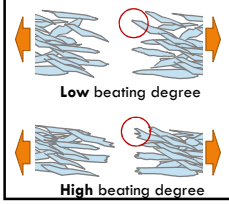
$F=kx$

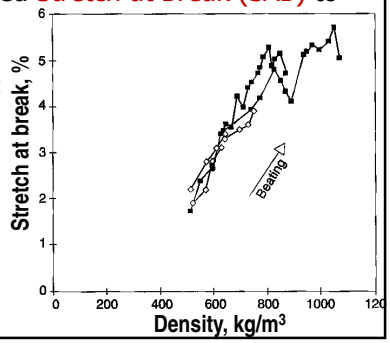
k; spring constant = MOE



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)

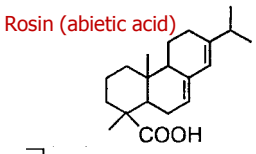
Additives – size and filler

	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)

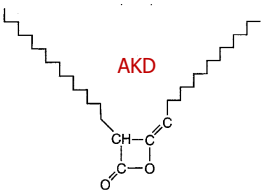
Q. Why is calcium carbonate not used for acidic paper?

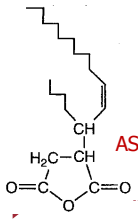
Additives – size and filler

Rosin (abietic acid)

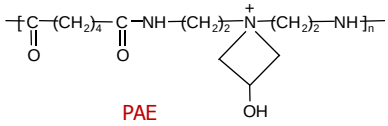


AKD





ASA

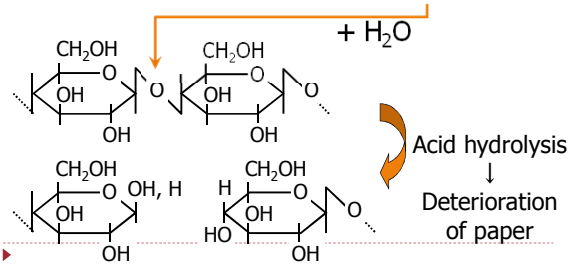


PAE

Additives – deterioration of acidic paper

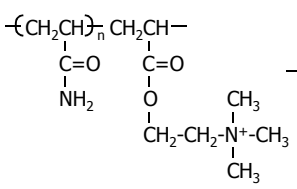
Aluminum sulfate deteriorates paper.

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

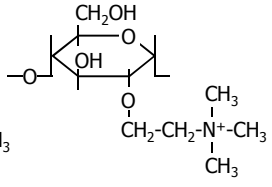


Additives – size and filler (2)

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

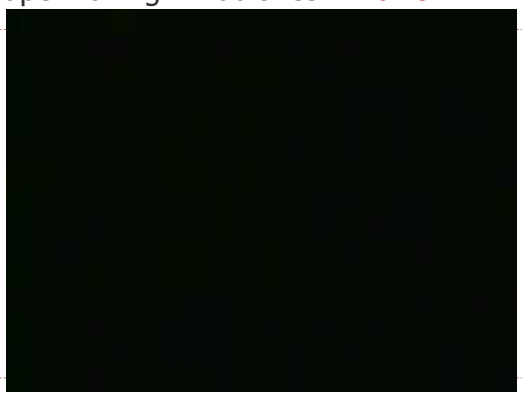


Cationic polyacrylamide

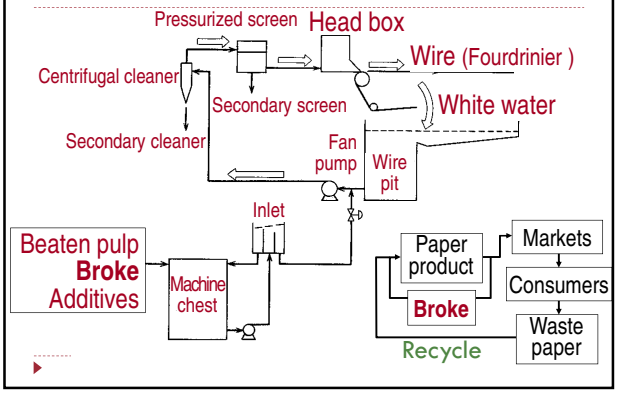


Cationic starch

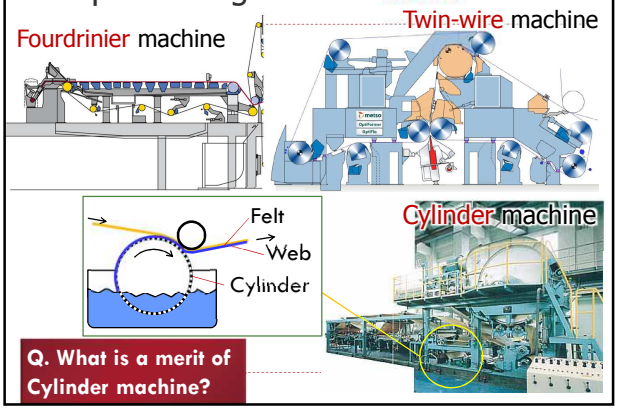
Papermaking – Additives - movie



Papermaking – approach section



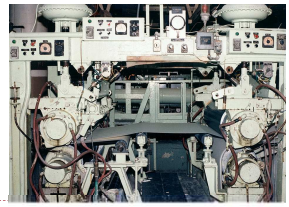
Papermaking - wire section



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.



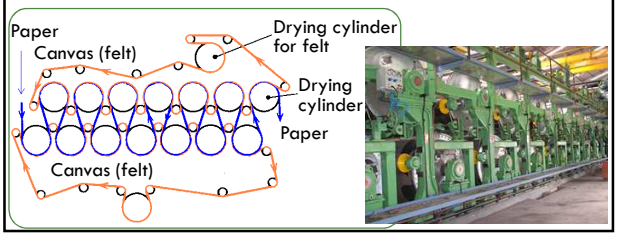
Kodak Historical Collection #003 (1986)

Papermaking – (wet) press section

Vietnam Paper Corporation (2014)

Papermaking – dryer section

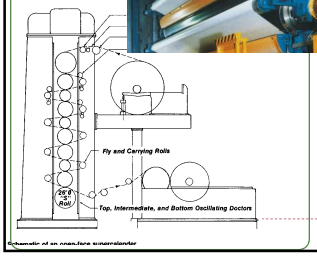
- Steam-heated cylinders dry the paper with canvases.
- Free water evaporates, between fibers first , inside fibers second, and between fibrils last .
- At less than 9 % moisture content, bonding water evaporates, forming interfiber bonds.



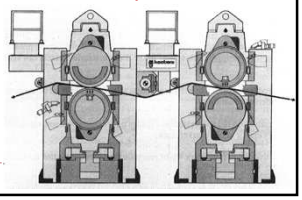
Papermaking – calender section

- 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

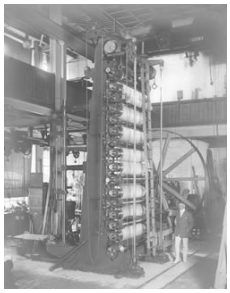
Supercalender



Soft nip calender

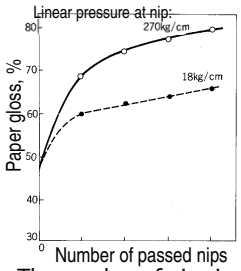


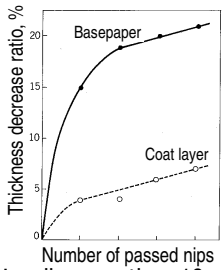
Papermaking – calender section



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?

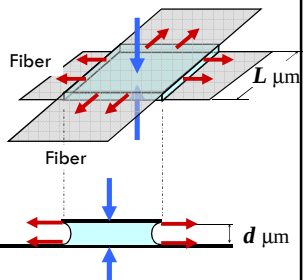
Types of chemical bond

- 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

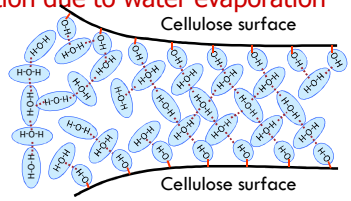
Q. Suppose two crossing flat fibers with the square , length L on a side at the crossing point. As they dry and the interfiber distance d comes to 1 mm, How much contraction stress develops between the two fibers?



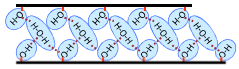
- The attractive force is called Campbell force.

Inter-fiber bond

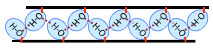
- Interfiber approach and hydrogen bond formation due to water evaporation



Loose hydrogen bond mediated by water



Firm hydrogen bond with a water monolayer



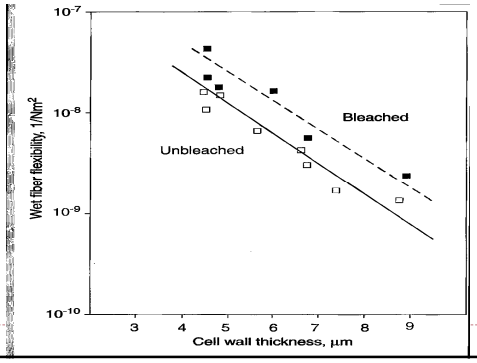
Direct hydrogen bond

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** (O)

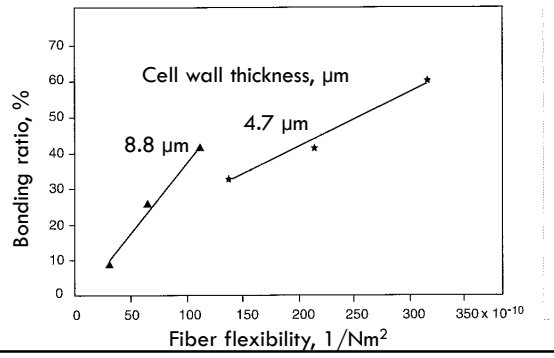
Inter-fiber bond

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

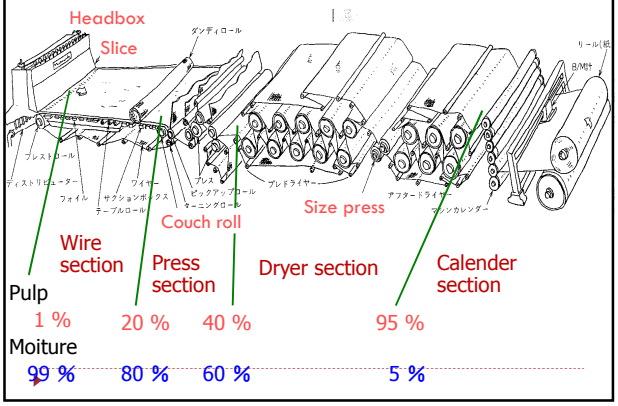


Inter-fiber bond

- 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