EG60411 Bio-Material Science

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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	6/10	Recent trend of paper science and technology
9,10	6/17, 24	Pulping science and technology by Professor Hiroshi Ohi

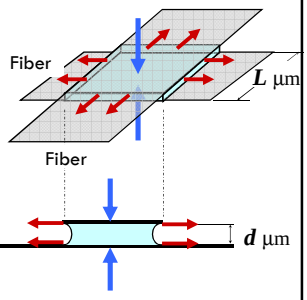
Types of chemical bond

- 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

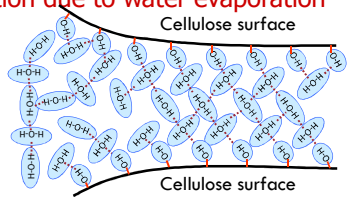
Q. Suppose two crossing flat fibers with a square , length L on a side at the crossing point. As they dry and the interfiber distance d comes to 1 mm, How much contraction stress develops between the two fibers?



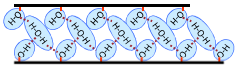
- The attractive force is called Campbell force.

Inter-fiber bond

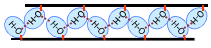
- Interfiber approach and hydrogen bond formation due to water evaporation



Loose hydrogen bond mediated by water



Firm hydrogen bond with a water monolayer



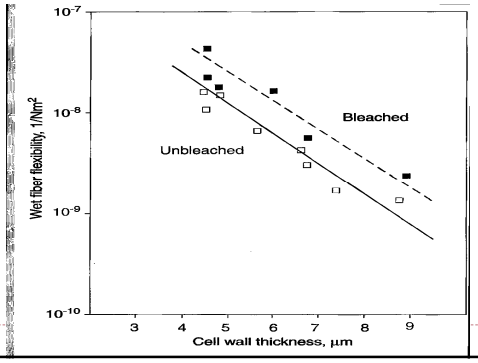
Direct hydrogen bond

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(=O)-CH$_3$**

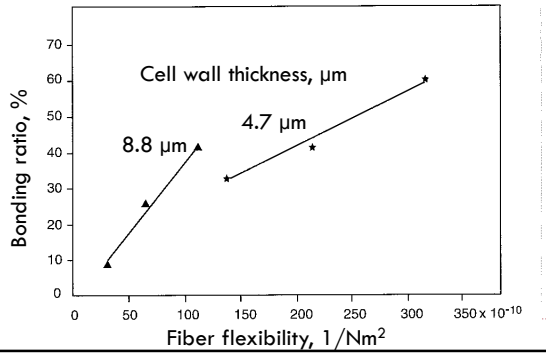
Inter-fiber bond

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

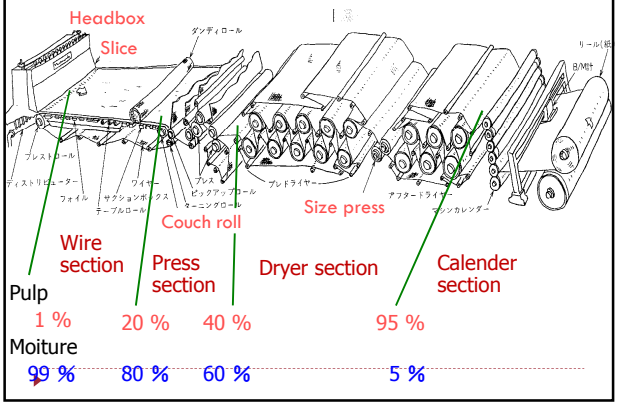


Inter-fiber bond

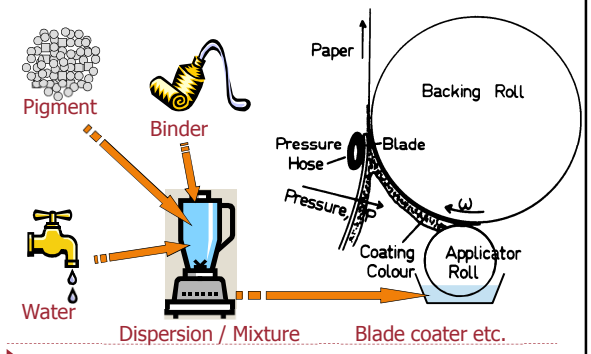
- Effect of fiber flexibility on Relative Bonded Area



Forming (Wire section) – Moisture content



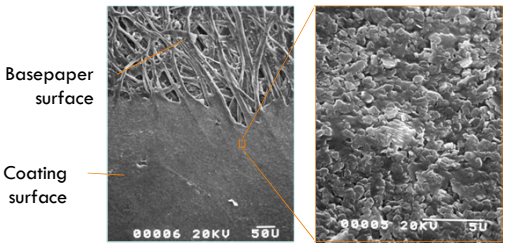
Pigment coating



Pigment coating

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

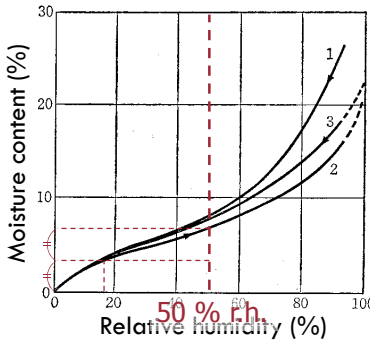


図 98 亜硫酸パルプシートの水分収着等温線 (Seborg, C. O. et al., 1938)

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

50 % rh

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)

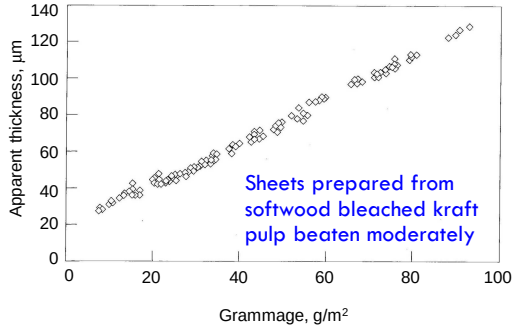
Paper structure – basic properties

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

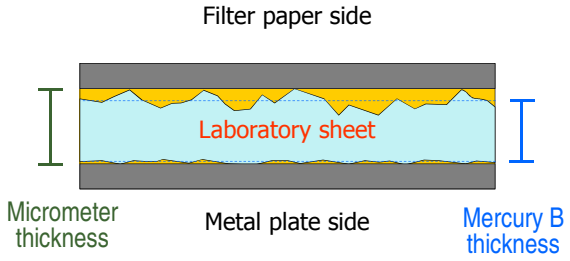
- Density
  - Mass per unit volume in g/cm^3 calculated from grammage divided by thickness

Paper structure – basic properties

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

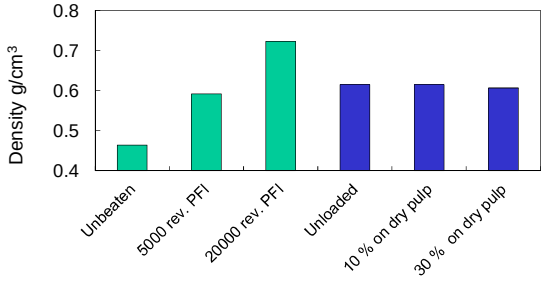


Paper structure – Why is the thickness different between the two methods?



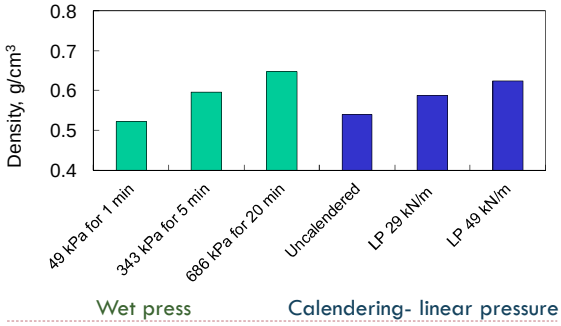
Paper structure – Factors affecting density

- Beating and filler loading

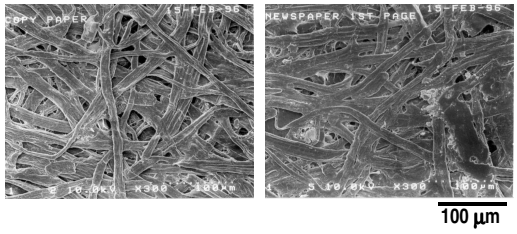


Paper structure – Factors affecting density

- Wet press and calendering

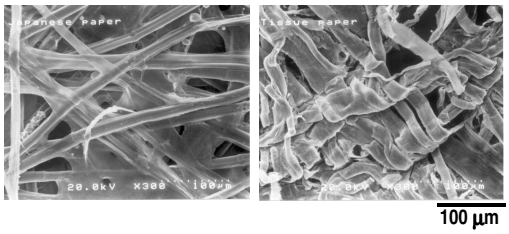


Paper structure-Scanning electron microscope(1)



Copy paper Newspaper

Paper structure-Scanning electron microscope(2)



Japanese paper Tissue paper

Paper structure – Smoothness

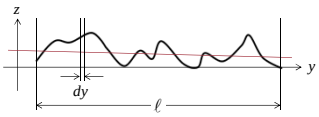
- Air leak method
  - Air flow rate through a gap between paper surface and smooth metal plate
- Surface profile (Microscopy)
  - Surface shape measured using profilometry such as stylus profilometry, confocal optical microscope.
  - Several ways of expressing surface roughness

Paper structure – Smoothness

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

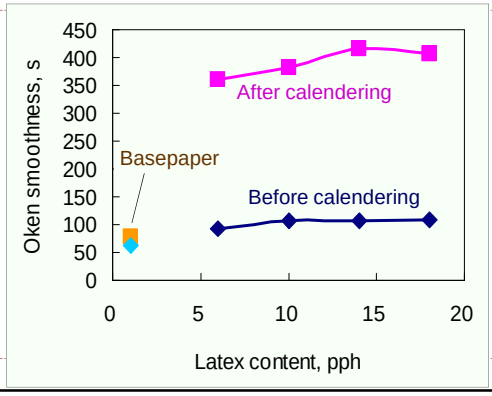
$$R_a = \frac{1}{\ell}\int_0^{\ell} |y| dy$$

  - Root mean squared roughness



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

Paper structure –Smoothness of coated paper

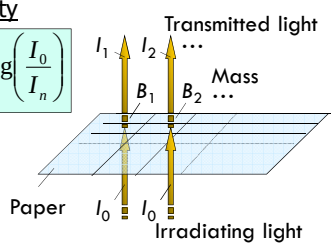


Paper structure - Formation

- 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

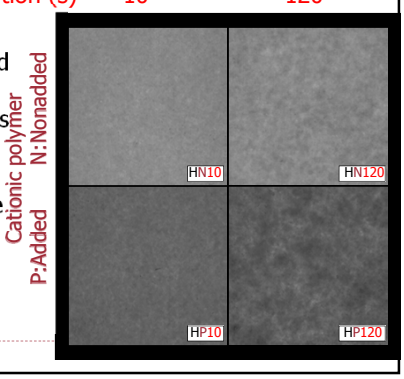


STD=Standard deviation, CV= coefficient of variation

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.

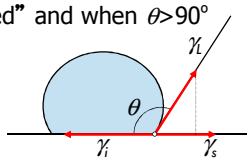


Interaction- between paper and water (liquid)

- 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 $0° < \theta < 90°$, "wetted" and when $\theta > 90°$ "unwetted".
- Young equation
  - When the contact angle is constant, horizontal components of forces are balanced.

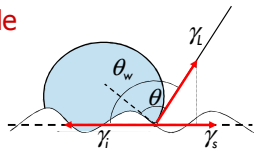


$$\gamma_i - \gamma_s + \gamma_L \cos\theta = 0$$

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

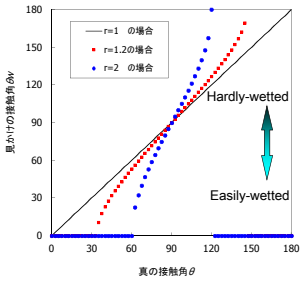
$$\cos\theta_w = r\cos\theta$$



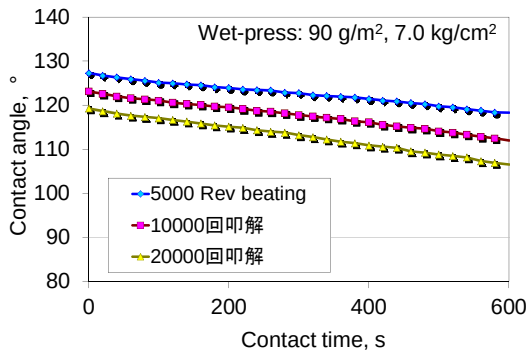
Surface chemistry - Contact angle

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

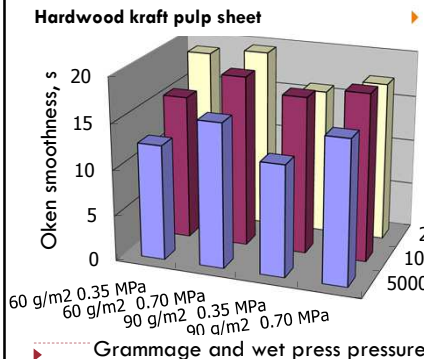
$$\cos\theta_w = r\cos\theta$$



Contact angle of paper - Beating effect



Beating and smoothness



- Surfaces smoothed by beating became easily-wetted.