An interdisciplinary view on the strength of a fiber – fiber bond in paper

Robert Schennach
Outline

CD – Laboratory for surface chemical and physical fundamentals of paper strength

Bonding Mechanisms

The bonded Area

Measuring the bond strength between two individual paper fibers

Model system

Summary
The CD – Laboratory

Surface Chemistry
Institute of Solid State Physics
Graz University of Technology

Fiber – Fiber Bond Strength

Morphology of the Fiber – Fiber Bond and Bonded Area
Institute of Pulp and Paper Technology
Graz University of Technology

Atomic Force Microscopy of Paper Fibers and Fiber – Fiber Bonds
Institute of Physics
University of Leoben

CD – Laboratory for surface chemical and physical fundamentals of paper strength
Single Paper Fiber

The different walls are build from the cellulose microfibrils, which are ordered in S1 and S2 and not so ordered in P and T.
Bonding Mechanisms

- Interdiffusion
- Induced dipoles
Mechanical Interlocking

Mechanical Interlocking can be compared to a Velcro fastener

Mechanical properties of microfibrils will play a role

Friction between the microfibrils will play a role
Interdiffusion

A cellulose molecule from one fiber diffuses into the second fiber.

Amount of interdiffusion will depend on diffusion coefficient.

Friction will play a role.

Interdiffusion will increase hydrogen bonding and Van der Waals Bonding.
Hydrogen Bonding

12 – 16 kcal Bond strength

Evaluation of Number of Hydrogen Bonds

Area in molecular contact

Which molecules are on the outermost surface
Van der Waals Bonding

< 1 kcal Bond strength

This is true for Noble gases and small molecules

However, consider larger molecules like aromatics

\[
\begin{align*}
\text{Boiling point: } & 80 \, ^\circ\text{C} \\
\text{Boiling Point: } & 218 \, ^\circ\text{C} \\
\text{Boiling Point: } & 354 \, ^\circ\text{C}
\end{align*}
\]
Coulomb Interaction

There are charged species in paper fibers

A paper fiber has a negative charge due to acid groups

Positive counter ions of the acid groups make bonding effect

It is known that an increase in the amount of charge increases paper strength

Can coulomb interaction be the reason?

Or is the influence of the charged species on swelling the dominant effect?
Bonded Area

a) Optical microscopy
b) AFM topography
Polarization Microscopy

The proposed model from 1960 (D. H. Page) does not fit to our experimental findings.

Polarization Microscopy

- 9 reflections taken into account.

- In the approximation of isotropic surfaces only 5 nonzero reflections: $E_1, E_5, E_6, E_7, E_9$

Gilli E, Kappel L, Hirn U and Schennach R, Composite Interfaces, 16 (2009) 901
Polarization Microscopy

Fiber-fiber bond

π

Parallel crossing of fibers: The reflexes between the fibers interfere negatively, due to the phase-shift at specular reflection.
Polarization Microscopy

Dying the lower fiber restores the possibility to distinguish between bonded and crossed unbonded fibers.
Polarization Microscopy

- The colors show good congruence with the photographs
Polarization Microscopy

- Experiment and simulation: Bond intensity for crossed polarizers and a bonding angle of 90° as a function of the fiberwall thicknesses.
Measuring Bond Strength

We can determine the bonded area without destroying the bond.

If we can measure the force necessary to rupture a fiber – fiber bond, we know the specific bond strength.

In principle one can use an AFM to measure this force.

Hold one fiber fixed.

Use the AFM tip to push on the second fiber.

Measure the force necessary to rupture the bond.
Measuring Bond Strength

AFM Topography comparison of different kappa-numbers

Fiber surface is not uniform.

Fiber treatments modify fiber surfaces.

Schmied et al., submitted to JPPS
Measuring Bond Strength

Surface Investigation: Non Bonded Area vs. Formerly Bonded Area

Non Bonded Area
AFM Topography

z-scale: 0.5 µm

Formerly Bonded Area
Preliminary Results:
stitched AFM Topography

z-scale: 0.5 µm
Area in Molecular Contact

The tribology approach to area in molecular contact:

\[ M \cdot g = \sigma_c \Delta A \]

- \( M = \text{mass [kg]} \)
- \( g = 9.8 \text{ [ms}^{-2}\text{]} \)
- \( \sigma_c = \text{Indentation hardness [Nm}^{-2}\text{]} \)
- \( \Delta A = \text{Area in molecular contact [m}^2\text{]} \)

Apparently this formula is a good approximation for both smooth and rough surfaces. While there are more complicated approaches to determine the area in molecular contact, they need more unknown parameters to calculate a value.
Area in Molecular Contact

What does this mean for paper fibers?

$$\Delta A = \frac{M \, g}{\sigma_c}$$

\[ M = 0.004 \times 10^{-6} \, \text{kg} \]
\[ g = 9.8 \, \text{ms}^{-2} \]
\[ \sigma_c = 0.4 \times 10^9 \, \text{Nm}^{-2} \]

\[ \Delta A = 1 \times 10^{-4} \, \mu\text{m}^2 \]
Model System

Model System

The crystal structure of cellulose is known.

One needs to find the surfaces with the lowest surface energy.

These surfaces will be exposed in a microfibril.
Model System

top view of the (1-10) plane
top view of the (110) plane
The assignment of the exposed surfaces is not yet clear.
Model System

AFM – Surface structure, roughness, friction
IRAS – Surface chemistry
z-strength measurements

AFM – Surface structure, roughness, friction
IRAS – Surface chemistry
QCM-D – Adsorption kinetics and energetics
z-strength measurements
Summary

All five Bonding Mechanisms do play a role

We can measure the bonded Area

We can measure the bond strength between two individual paper fibers

We have access to specific bond strength

Model system to investigate the contribution of different bonding mechanisms
Acknowledgements

Eduard Gilli
Mario Djak

Lisbeth Kappel
Ulrich Hirn
Wolfgang Bauer

Franz J. Schmied
Christian Teichert

Eero Kontturi, Forest Products Chemistry
Herbert Sixta, Department of Forest Products Technology

Roland Resel, Institute of Solid State Physics