Solid state NMR as a tool for measuring pore sizes in water swollen cellulose fibre walls

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Co-authors

- Prof. Lars Wågberg, Fil. Lic. Anna Svensson
Why supramolecular structure?

- Supramolecular properties of cellulose I influences fibre product properties
- Fibres for new purposes
- Structure – Accessibility – Reactivity
Fibril (4 – 5 nm)

Fibril aggregate (15-40 nm)
NMR at Innventia AB

Hybrid 1990

Solution 2010

Solids 2011
The interpretation - C4 region

Accessible Surfaces

InAccessible Surfaces

Crystalline

Para-Crystalline

δ (ppm)
Nomenclature and validation

- LFD = Lateral Fibril Dimension
- LFAD = Lateral Fibril Aggregate Dimension

- Validate LFD: compare NMR and X-ray diffraction
- Validate LFAD: compare NMR and AFM or TEM
- Wet chemistry impact on spectra
- Lab-frame spin-lattice relaxation time measurements
- MD-simulations
Lateral dimensions – fibrils and fibril aggregates

\[ q_{\text{fibril}} = \frac{I_{AS} + I_{IS}}{I_{Tot}} \]

\[ q_{\text{aggregate}} = \frac{I_{AS}}{I_{Tot}} \]

\[ q = \frac{4n - 4}{n^2} \]

\( n \) is the number of polymers along a side

0.57 nm is the ‘thickness’ of one polymer
Specific surface area in water swollen state

Surface area per unit mass: \[ \sigma_{\text{sat}} = \frac{A}{M} = \frac{4}{\rho \langle a \rangle} \]

- Fibrils \( \langle a \rangle = 4 \text{ nm} \)
  \( \sigma_{\text{sat}} = 667 \text{ m}^2/\text{g} \)
- Fibril aggregates \( \langle a \rangle = 20 \text{ nm} \)
  \( \sigma_{\text{sat}} = 133 \text{ m}^2/\text{g} \)
Wet and dry pulp fibres

- Wet – about 100 m$^2$/g
- ’Dry’ – about 1 m$^2$/g

- The structural element of cellulose in a water swollen fibre wall is the *fibril aggregate*
CP/MAS $^{13}$C-NMR Cotton Linters

Porous

Non-porous

Wet

Dry

δ (ppm)
Cellulose models consistent with NMR spectra

Water swollen porous, separated fibril aggregates. About 100 m$^2$/g

Dry compact, one “solid block” of cellulose. About 1 m$^2$/g
Kinetics, initial rate constant

\[
R-\text{OH} + C_4O_3H_6 = R-O-C_2\text{OH}_3 + C_2O_2H_4
\]

Cellulose  Anhydrid  Acetylated Cellulose  Acetic acid

\[
\frac{\partial [R-\text{OH}]}{\partial t} = \frac{\partial [C_4O_3H_6]}{\partial t} = \frac{\partial [C_2O_2H_4]}{\partial t} \approx 0
\]

At short times:

\[
[R-\text{OH}] = \text{surfaces}
\]

\[
\frac{\partial [R-O-C_2\text{OH}_3]}{\partial t} \approx k_1 [R-\text{OH}]^a [C_4O_3H_6]^b
\]

\[
\frac{\partial [R-O-C_2\text{OH}_3]}{\partial t} \approx k_1' [R-\text{OH}]^a
\]

\[
\frac{\partial [R-O-C_2\text{OH}_3]}{\partial t} \approx k_1' K = k_1''
\]
Cellulose structure in cellulose rich fiber walls

Cotton linters cellulose

Eucalyptus
96α dissolving pulp
The reaction rate constant *ratio*

\[
\frac{\partial [R-O-C_2OH_3]}{\partial t} \approx k_1 K = k_1''
\]

Determined rate constant

\[
Ratio = \frac{k_{1,C}''}{k_{1,E}''} = \frac{k_1'[R-OH]^a_C}{k_1'[R-OH]^a_E} = \frac{[R-OH]^a_C}{[R-OH]^a_E} \approx \frac{\text{Specific surface area Cotton}}{\text{Specific surface area Eucaluptus}}
\]

Measured independently
Acetylation cellulose, initial rate constant ratios at 40 °C and 60 °C

- Aggregate surface area ratio
- Initial rate constant ratio 60 °C
- Initial rate constant ratio 40 °C

Ratio (C/E)
Why does this work?

- The results from the acetylation study indicate that the specific surface area of the fibre wall in a liquid swollen state measure by NMR is a chemically relevant measure.
- The cellulose I fibril aggregates expose the available specific surface area in a liquid swollen state.
- The specific surface area of cellulose I fibril aggregates in the liquid swollen state is accessible to the reagent, acetic anhydrid.
- Is this enough of an explanation?
- No!
- What is also necessary is that the physical dimensions of the reagent molecule (acetic anhydrid) must be smaller than the average fibre wall pore size.
Solute exclusion – measurement of Fiber Saturation Point (FSP)

J.E. Stone and A. M Scallan, Cellulose Chem. Technology, 2, 343-358 (1968)
Average pore size from NMR and FSP

\[ FSP = t \sigma_{sat} \rho_L = m \times \frac{m^2}{kg} \times \frac{kg}{m^3} = \text{dim. less} \]

\[ t = \frac{FSP}{\sigma_{sat} \rho_L} \]

FSP = the mass of water in fibre wall pores per unit dry fibre mass, measured in the presence of an excess of water

No explicit pore shape is assumed!
Liquid exchange and drying of fibres

The pictures illustrates the interior of a porous fibre wall

- Water
- Organic liquid
- Dry

- Aim is to preserve as much as possible of the water swollen fibre wall structure in the dry state
- Water – Methanol – Acetone – Pentane – Drying
- (Freezing may alter the structure)
Comparison and evaluation

- Specific Surface Area of fibre wall in water swollen state (NMR)
- Specific Surface Area of fibre wall in dry state (BET)
- Determine both and compare

Specific surface area determined in water swollen state (NMR) *should* constitute an upper bound to the BET area.
## Results – NMR average pore size

<table>
<thead>
<tr>
<th>Sample</th>
<th>FSP (g/g)</th>
<th>LFAD (nm)</th>
<th>NMR SSA (m²/g)</th>
<th>Average pore size 2t (nm)</th>
<th>BET SSA (m²/g)</th>
<th>SSA ratio BET/NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (ND)</td>
<td>0.94 (0.06)</td>
<td>16.9 (0.4)</td>
<td>158 (4)</td>
<td>11.9 (0.8)</td>
<td>75.3</td>
<td>48%</td>
</tr>
<tr>
<td>S (ND)</td>
<td>1.05 (0.03)</td>
<td>17.5 (0.4)</td>
<td>152 (3)</td>
<td>13.7 (0.5)</td>
<td>71.4</td>
<td>47%</td>
</tr>
<tr>
<td>Linters (D)</td>
<td>0.21 (0.08)</td>
<td>32.2 (1.3)</td>
<td>83 (3)</td>
<td>5.0 (2.0)</td>
<td>58.3</td>
<td>70%</td>
</tr>
</tbody>
</table>

### Average pore size

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average pore size NMR and FSP 2t (nm)</th>
<th>Average pore size BET adsorption (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (ND)</td>
<td>11.9 (0.8)</td>
<td>8.0</td>
</tr>
<tr>
<td>S (ND)</td>
<td>13.7 (0.5)</td>
<td>5.4</td>
</tr>
<tr>
<td>Linters (D)</td>
<td>5.0 (2.0)</td>
<td>5.1</td>
</tr>
</tbody>
</table>

SSA = Specific Surface Area  
LFAD = Lateral Fibril Aggregate Dimensions  
FSP = Fibre Saturation Point
Some recent results for average pore sizes

- Average pore diameter for dry S (ND) pulp from BET 5 nm
  - Expected to be smaller than 14 nm

- Typical pore diameter from NMR $^2$H $T_1$ measurements is 20 - 25 nm
  - Expected to be larger than 14 nm
Summing up

- A new method based on NMR and FSP for determining average pore size in water (liquid) swollen fibre walls
- A stable (highly reproducible) method where the specific surface area of the fibre material and the fibre saturation point are both determined on fibres in equivalent states
- Avoids arbitrary sample preparation procedures (wet pressing, WRV)
- No explicit pore shape is assumed
- Specific surface area from NMR constitute an upper bound to the BET area
- Between 50 % to 70 % of the specific surface area could be preserved in dry fibres