Modeling the interactions between cellulose and xylan at the molecular scale

Karim Mazeau
Centre de Recherches sur les Macromolécules Végétales, Grenoble, France
Motivation

• Plant biology
• Surface modification of cellulose
• Cellulose-based materials
• Second-generation biofuels
Presentation outline

- Background
- Adsorption of oligomers
  - Low surface coverage
  - Monolayer
- Interfacial effects in nanocomposites
  - Effect of moisture
  - Structural effect
Native cellulose at the molecular scale

1/ Polymorphism of the bulk structure


- View parallel to the fiber axis
- (110) $\alpha$
- (100) $\alpha$
- (1-10) $\beta$
- (010) $\beta$
- (100), (1-10) $\beta$

2/ The external morphology: the nature of the exposed surfaces

- BFDH theory:
  - 4 fundamental cleavage planes:
  - octagon

Bravais, A., Etudes crystallographiques, Paris 1913
Native cellulose at the molecular scale

3/ The external morphology: relative abundance of the exposed surfaces

4 Dominant surfaces
- moderately rough hydrophilic
  - $I_\beta (1-10)$, $I_\alpha (100)$, $I_\beta (110)$, $I_\alpha (010)$

8 potential surfaces for Xylan adsorption

2 Minor surfaces
- flat hydrophobic
  - $I_\beta (100)$, $I_\alpha (1-10)$
- rough hydrophilic
  - $I_\beta (010)$, $I_\alpha (110)$
Preferred interaction site of xylan on cellulose

Evidence from CP/MAS $^{13}$C NMR

- Direct adsorption
- Specific of (110) I$_{\beta}$

Pure cellulose vs mixture cellulose + 30 % of birch kraftpulp xylan.

P. T. Larsson *ACS Symp. Ser.* 2004
Preferred interaction site of xylan on cellulose

Enzymatic degradation of cellulose xylan complexes, evidence from WAXS

Tightly bound Xylan adsorb on (100) $I\beta$

Loosely bound Xylan adsorb on (110) and (1-10)

P. A. Penttila et al., Biores. Technol. 2013, 129, 135
Xylan: a highly heterogeneous polymer

**Skeleton:**
Xyl \(\beta(1\rightarrow4)\) Xyl

**Branches**
- Araf \(\alpha(1\rightarrow3)\)
- GlcA \(\alpha(1\rightarrow2)\)
- 4OMeGlcA \(\alpha(1\rightarrow2)\)
- Oac, O3 > O2

**Structural heterogeneity:**
- A/X, G/X ratio
- Fine structure: irregular, regular, bloc.
- What is the length of the non substituted segments?

**Structure-property relationship:**
Skeletal residues adsorb onto cellulose, the side chains inhibit the adsorption.

Nomenclature

The paradox

A priori “Incompatible” conformations of the individual chains in the crystal state:

Cellulose: $2_1$ helix, repeat 1.03 nm

Xylan: $-3_1$ helix, repeat 1.53 nm
Cellulose, the model

Periodic supercell:
- A = 4.32 nm (8 chains)
- B = very large
- C (chain axis) = 4.15 nm (8 units)

Cellulose film:
- 3 layers in the $\beta$ organisation
- Expose the (110) surface
- Surface area $2 \times 18$ nm$^2$
- Free: exposed hydroxyl groups
- Frozen: all the remaining atoms
Interaction xylan/cellulose: Low surface coverage

- Xylan adsorb flat on cellulose,
- Efficient exploration of the surface
- Reproducible results
Adsorbed conformation of Xylans

Global conformation:
Length of the end2end vector

- When adsorbed, low DP of xylan is extended: straight and curved.
- Kinks appeared at DP = 25
The PES of Xylobiose

Helical conformations run diagonally across the PES:

Helix if the sum $\Phi + \Psi$ is constant

- helix 2₁ 120°
- 3₁ left 190°
- 3₁ right 50°
Adsorbed conformation of Xylans (DP=5).

Conformational variability

$3_1$ left > non helical >> $2_1$ >> $3_1$ right
Orientation of the Xylan backbone (DP5)

- Xylan prefers to be oriented parallel, tilted and anti parallel with respect to the cellulose fiber axis.

End2EndZ : alignment with the microfibril axis.

- Orientation parameter End2Endz (Å)

Population

Time (ps)

0 100 200 300 400 500

-30 -20 -10 0 10 20 30

orientation parameter End2Endz (Å)

parallel

anti-parallel

tilted

AUF N PAS REPRODUIRE SANS AUTORISATION DE L'AUTEUR
Substitution effects (DP5)

- No significant effect of the side chains on the adsorption features
- Valid within the limit of the following assumptions
  - low DP, low surface coverage
  - vacuum
  - Enthalpies of adsorption

Backbone extension (Å)

Normalized Interaction energy (kcal/mol/unit)
Free energy of adsorption

The model:
Cellulose surface: 18 chains X 18 residues
Xylan: DP = 10, adsorbed
TIP3P water molecules
Equilibration: unconstrained MD

Free energy of dissociation by steered MD
Potential of Mean Force
Umbrella sampling
Windows 0.5 Å
Pulling rate 1m/s
WHAM analysis
Free energy of adsorption

- Different desorption mechanisms
- The parallel orientation is preferred
- Relative free energy difference of 3.8 kJ/mol/unit
Interaction hemicellulose/cellulose : monolayer

- Adsorption of 8 chains of 5 residues each

\[ Q = DP \left( \frac{M_{\text{xyl}}}{N_a} \right) \cdot \left( \frac{S_{\text{spe}}}{S_{\text{mod}}} \right) \]

- \( Q \): amount of xylan adsorbed within a monolayer
- \( DP \): number of adsorbed xylosyl units \( 5 \times 8 = 40 \)
- \( M_{\text{xyl}} \): 132 g.mol\(^{-1}\)
- \( N_a \): Avogadro number \( 6.023 \times 10^{23} \)
- \( S_{\text{spe}} \): specific surface of cellulose : 300 m\(^2\).g\(^{-1}\)
- \( S_{\text{mod}} \): 18 nm\(^2\)

- \( Q = 0.14 \text{ g xylan/g cellulose} \)
- 70 % of the cellulose surface covered
- Conformational features preserved
- Xylan roughly parallel to each other
- Tilted with respect to the fibre axis
bio-sourced nanomaterials

Cellulose/xylan multi-layer

Xylan film supported by cellulose
Interfacial effects in bio-sourced nanomaterials

Cellulose film:
- 3 layers of chains in a crystalline organization

Xylan fraction: X240
- 5 layers distant by 0.5 nm
- Average density 1.3 g.cm$^{-3}$
- Max intensity at the interface
- Interpenetration xylan-cellulose

Water:
- Exclusively within xylan
- Max intensity at the interface

$B = 4.5 \text{ nm}$
Organization of the xylan chains in the first layers

- Extended segments interrupted by kinks
- Aligned to each other
- Not aligned to the fiber axis
- 1st layer denser and more organized than the 2nd one
Intermolecular Radial Distribution Functions

Cellulose : Xylan

Cellulose : Water

Xylan : Xylan

Xylan : Water
Hydration effects

<table>
<thead>
<tr>
<th>B parameter (nm)</th>
<th>4.5</th>
<th>5.5</th>
<th>6.5</th>
</tr>
</thead>
<tbody>
<tr>
<td># H2O</td>
<td>170</td>
<td>695</td>
<td>1275</td>
</tr>
<tr>
<td>Water content (w/w)</td>
<td>8.8</td>
<td>28</td>
<td>42</td>
</tr>
<tr>
<td>Density (g.cm(^{-3}))</td>
<td>1.30</td>
<td>1.22</td>
<td>1.18</td>
</tr>
<tr>
<td>Diffusion coefficient (10(^{-5})cm(^2)/s)</td>
<td>0.0242</td>
<td>0.2755</td>
<td>0.5905</td>
</tr>
</tbody>
</table>

- 8.8% of moisture isolated molecules and small aggregates
- 28% of moisture large aggregates
- 42% of moisture continuous channels of water.
Hydration effects

Moisture influence:
- The amount of xylan in contact with cellulose
- The organization state of xylan far from the interface
- The interaction strength between cellulose and xylan

Work of adhesion:

\[ W = \frac{E_{\text{cellulose}} + E_{\text{xylan}} + E_{\text{water-xylan}} - E_{\text{total}}}{2S} \]
Structural effect: $X_{240} \text{ vs } (XXAXX)_{40}$

- Less Ara\textit{f} at the interface than in the xylan phase
- Ara\textit{f} are detrimental for adhesion.
Summary

• Xylan adsorb on cellulose as extended $3_1$ helical segments interrupted by kinks

• It is oriented aligned (low surface coverage) and tiled (high surface coverage) to the cellulose fiber

• $E = -3.8 \text{ kJ/mol/monomer}$

• Moisture uptake decreases the interaction strength at the interface

• Side chains are detrimental for adhesion.