Modeling the interactions between cellulose and xylan at the molecular scale

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Motivation

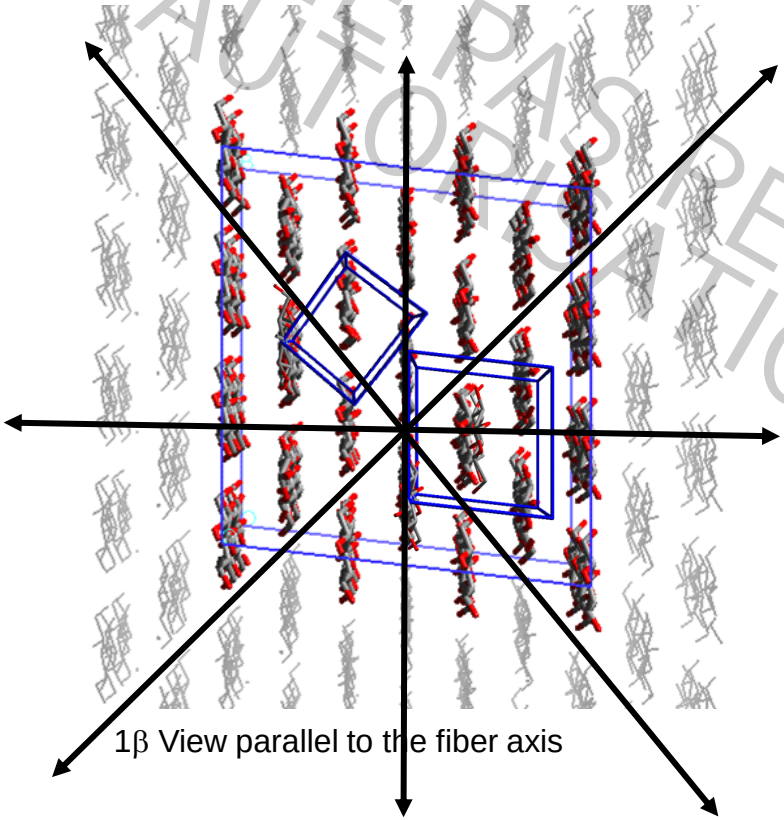
- Plant biology
- Surface modification of cellulose
- Cellulose-based materials
- Second-generation biofuels

Presentation outline

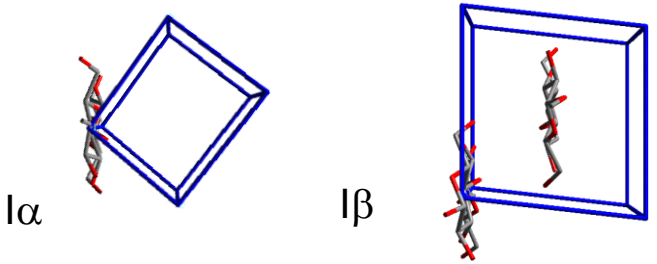
- Background
- Adsorption of oligomers
  - Low surface coverage
  - Monolayer
- Interfacial effects in nanocomposites
  - Effect of moisture
  - Structural effect

Native cellulose at the molecular scale

1/ Polymorphism of the bulk structure



1β View parallel to the fiber axis



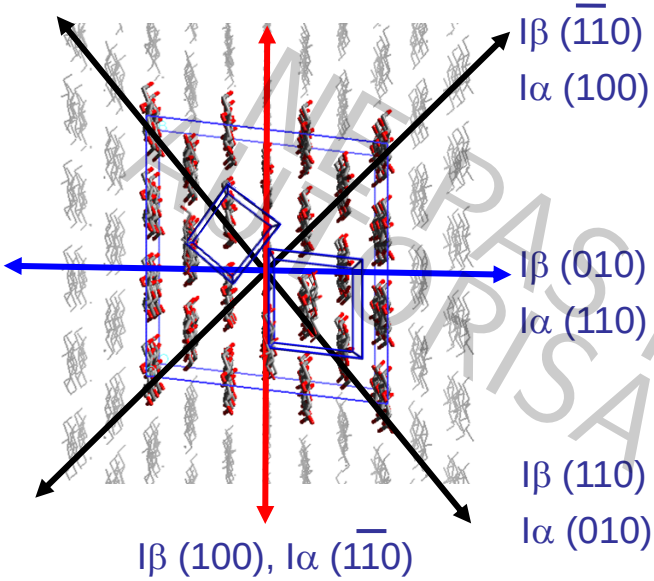
Iα : Y. Nishiyama, et al, JACS (2003)
Iβ : Y. Nishiyama, et al, JACS (2002)

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

BFDH theory :
4 fundamental cleavage planes : octogon

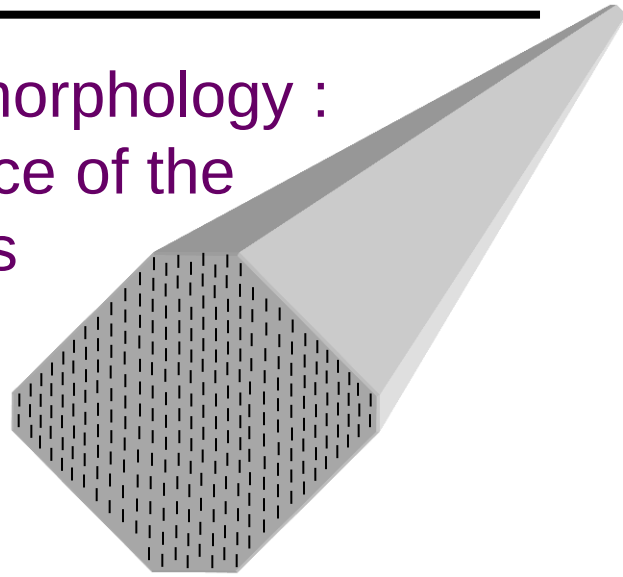
Bravais, A., Etudes crystallographiques, Paris 1913
Friedel, G., Bull. Soc. Fr. Mineral., 30, 326, 1907
Donnay, J.D.H., Harker, D., Am. Mineral., 22, 463, 1937

Native cellulose at the molecular scale



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

8 potential surfaces for Xylan adsorption

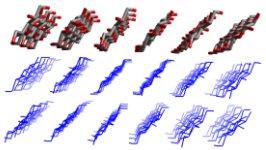


Irregular octogon

4 Dominant surfaces

moderately rough hydrophilic

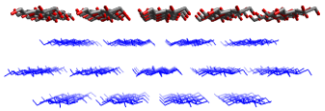
Iβ (1-10), Iα (100) Iβ (110) , Iα (010)



2 Minor surfaces

flat hydrophobic

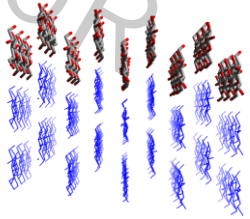
Iβ (100), Iα (1-10)



2 Minor surfaces

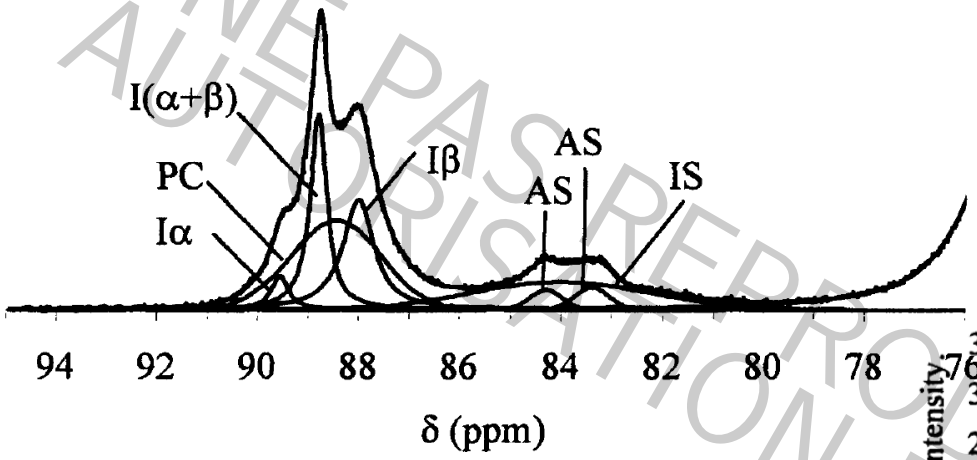
rough hydrophilic

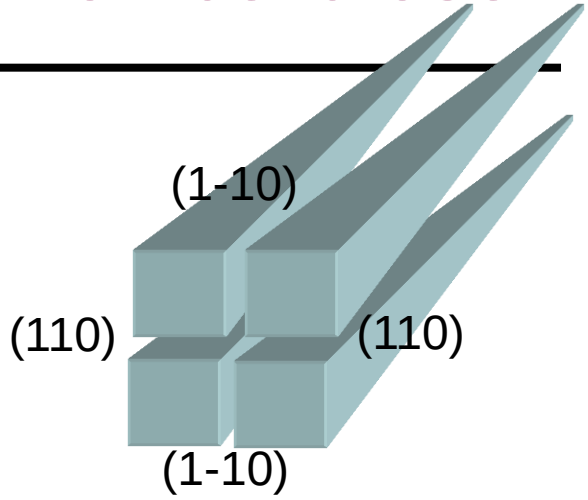
Iβ (010), Iα (110)

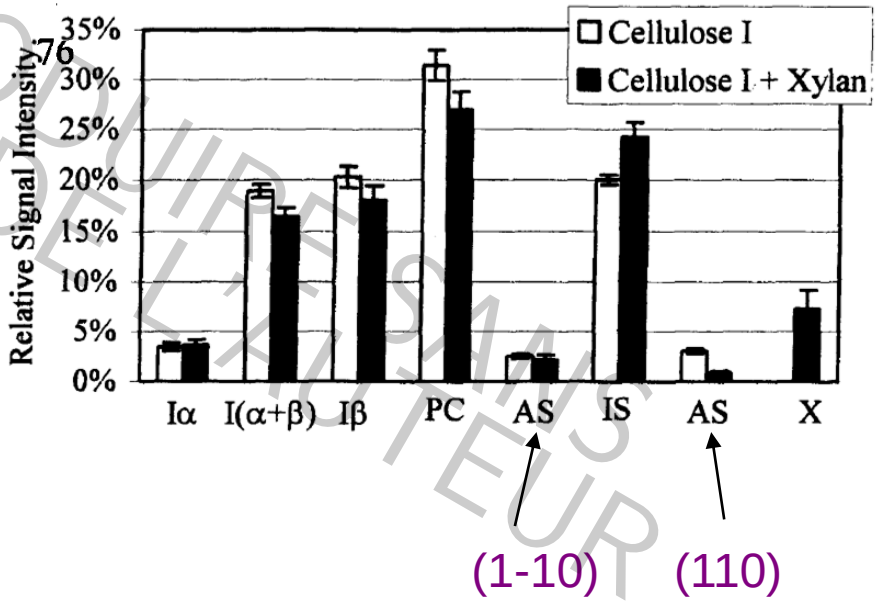


Preferred interaction site of xylan on cellulose

Evidence from CP/MAS ^{13}C NMR







- Direct adsorption
- Specific of (110) Iβ

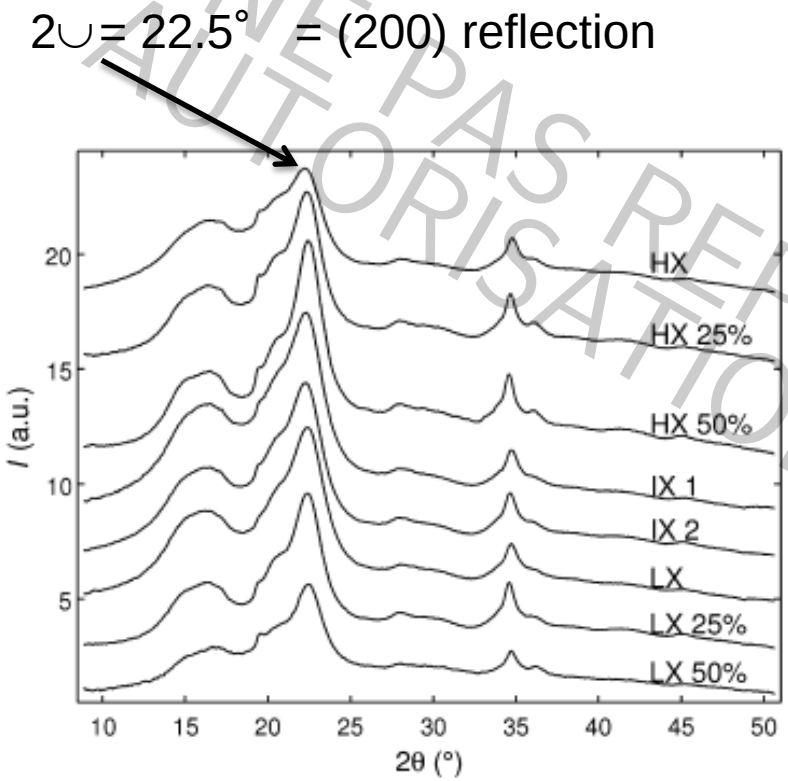
Pure cellulose vs mixture cellulose + 30 % of birch kraftpulp xylan.

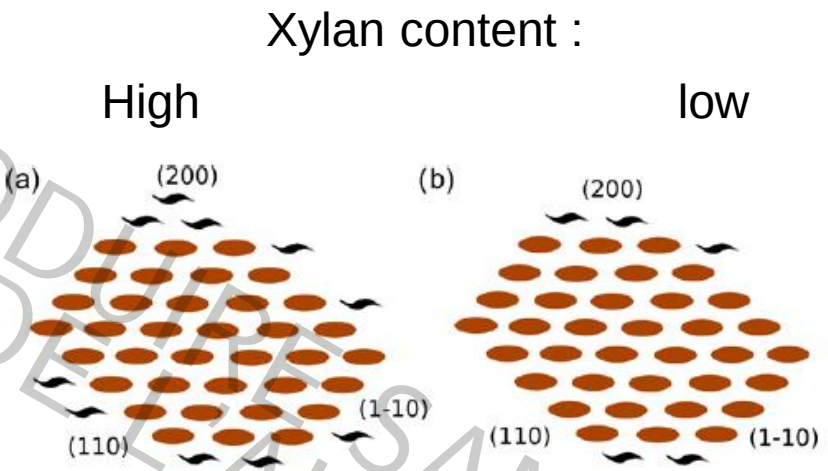
P. T. Larsson *ACS Symp. Ser.* 2004

P. T. Larsson *et al*., *Solid State Nucl. Magn. Reson.* 1999

Preferred interaction site of xylan on cellulose

Enzymatic degradation of cellulose xylan complexes, evidence from WAXS





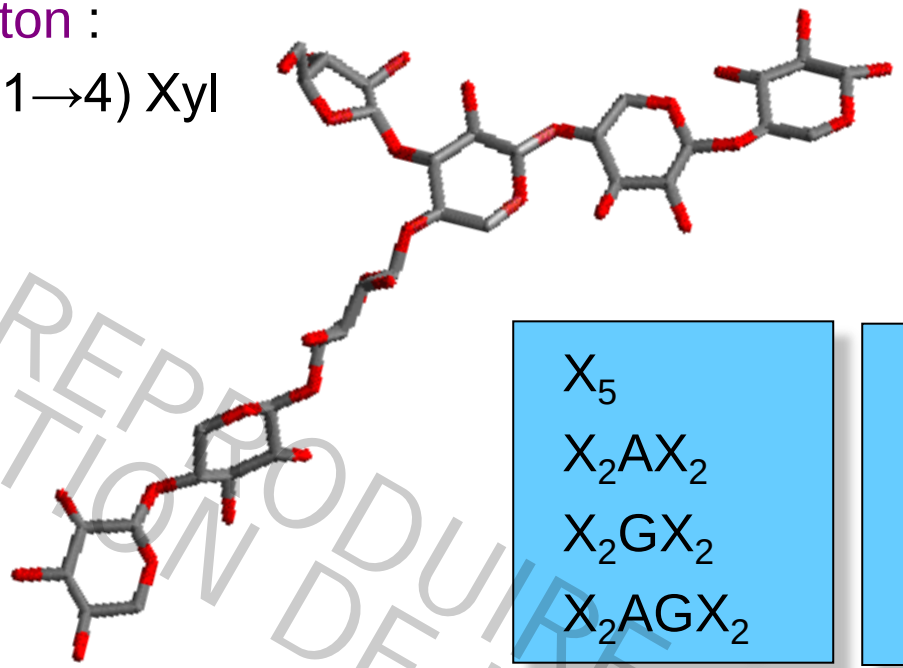
- Tightly bound Xylan adsorb on (100) Iβ
- Loosely bound Xylan adsorb on (110) and (1-10)

P. A. Penttila *et al*., *Biores. Technol.* 2013, 129, 135

Xylan : a highly heterogeneous polymer

Skeleton :

Xyl β(1→4) Xyl



Branches

Araf α(1→3)

GlcA α(1→2)

4OMeGlcA α(1→2)

Oac, O3 > O2

…..

Structural heterogeneity :

A/X, G/X ratio

Fine structure : irregular, regular, bloc.

What is the length of the non substituted segments?

X_5	X_{10}
X_2AX_2	X_{15}
X_2GX_2	X_{20}
X_2AGX_2	X_{25}

X_{240} $(XXAXX)_{40}$

Nomenclature

R. Faure *et al.*, *Aust. J. Chem.* 2009

Structure-property relation ship :

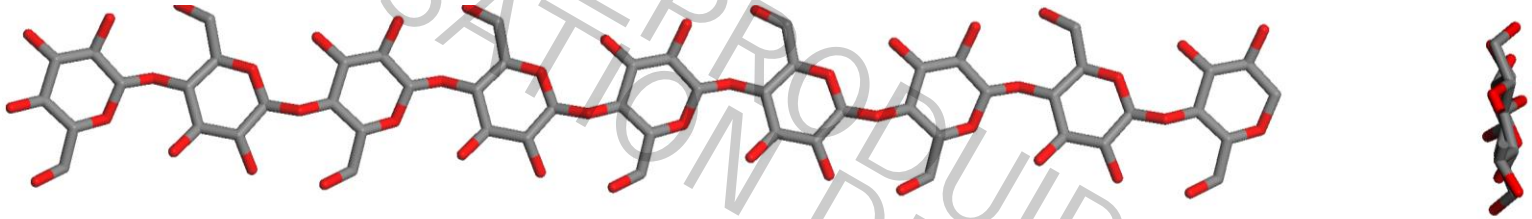
Skeletal residues adsorb onto cellulose, the side chains inhibit the adsorption.

M. A. Kabel *et al*, *Carbohydr. Polym.* 2007

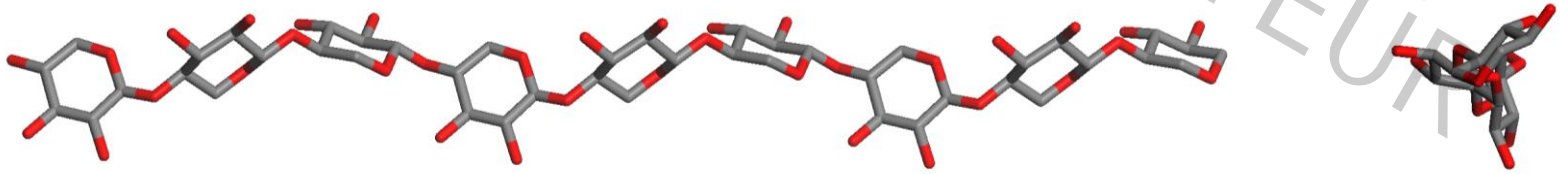
The paradox

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

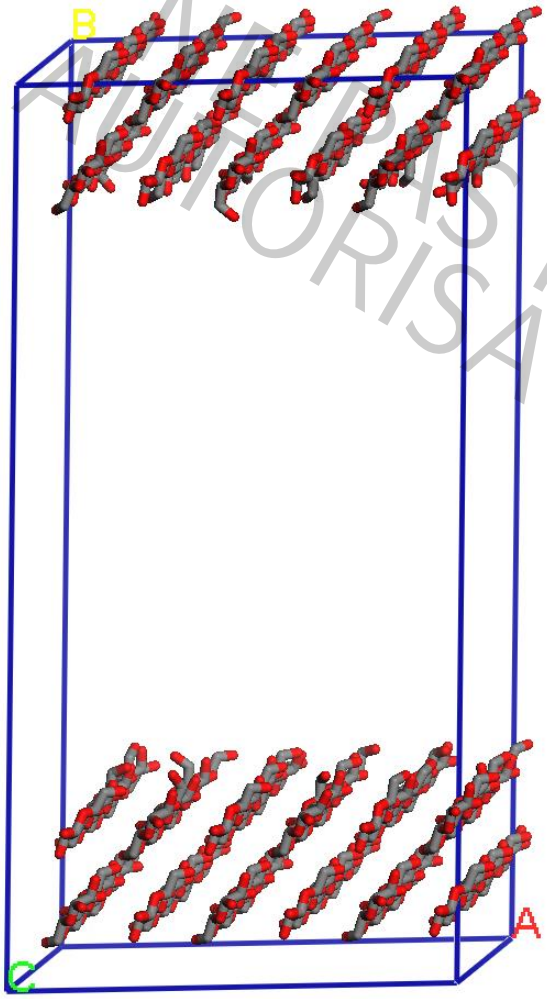
Cellulose : 2_1 helix, repeat 1.03 nm



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 Iβ organisation

Expose the (110) surface

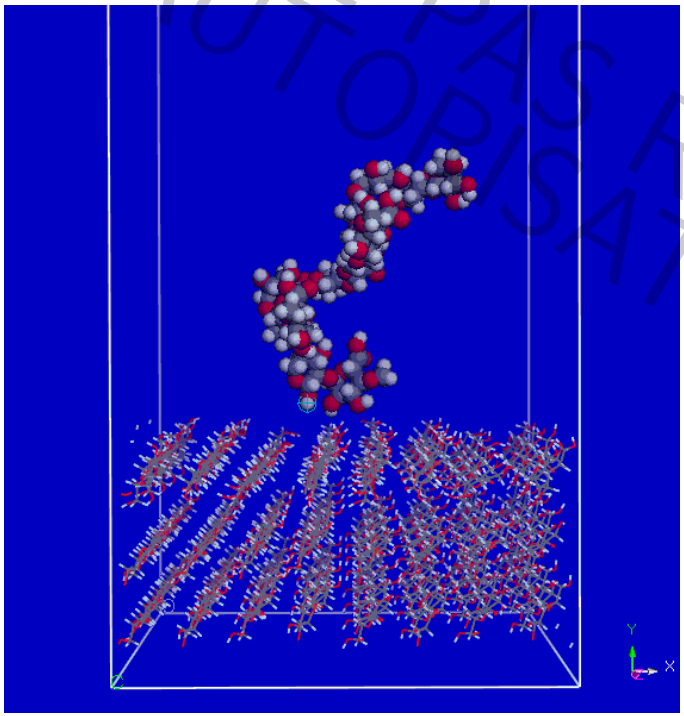
Surface area 2x18 nm^2

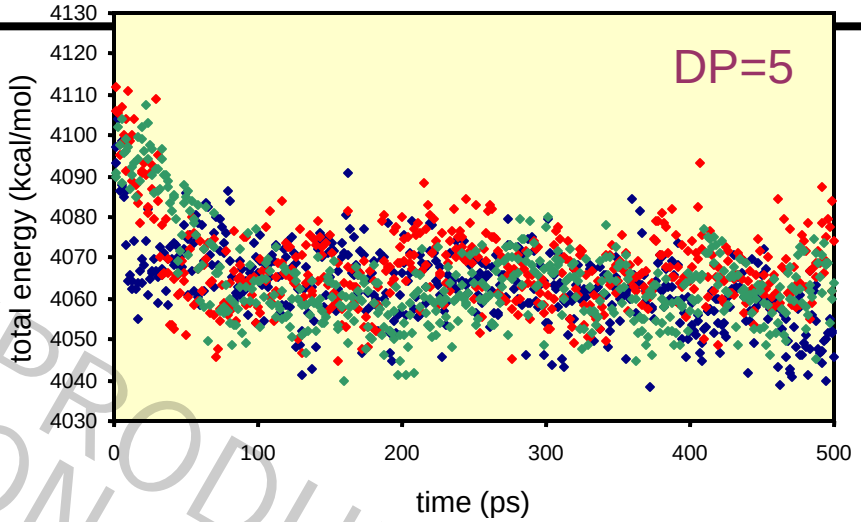
Free : exposed hydroxyl groups

Frozen : all the remaining atoms

Interaction xylan/cellulose : Low surface coverage

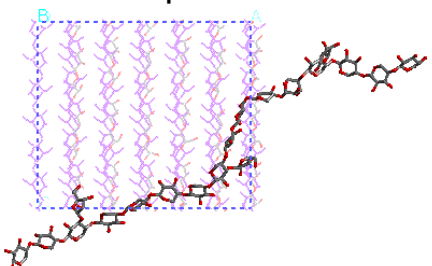
MD, NVT 400 K, ε=10



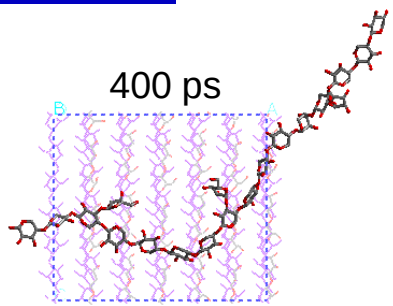


- Xylan adsorb flat on cellulose,
- Efficient exploration of the surface
- Reproduction

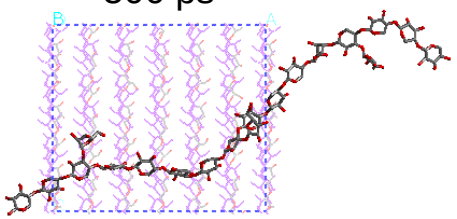
300 ps



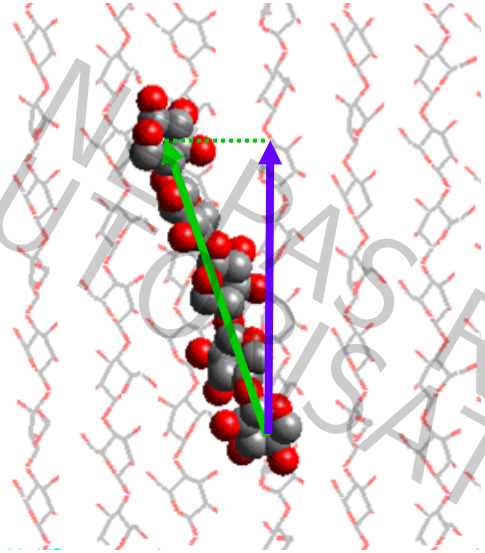
400 ps



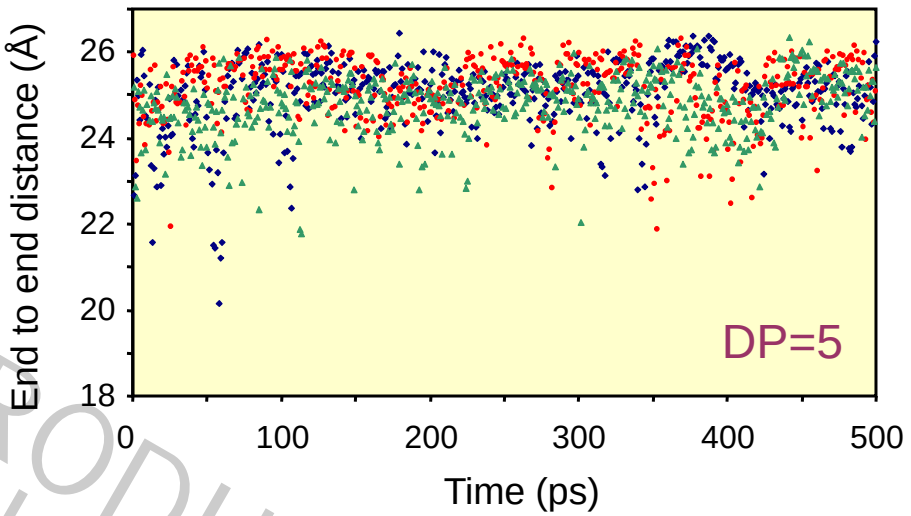
500 ps

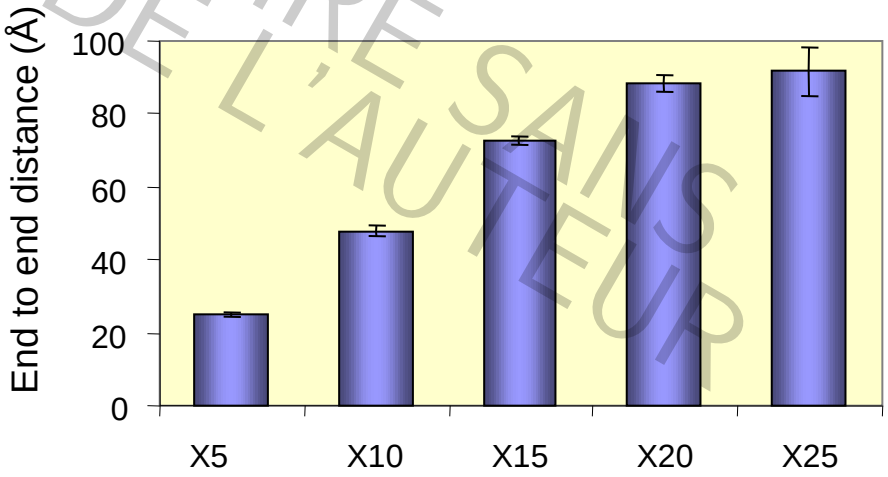


Adsorbed conformation of Xylans



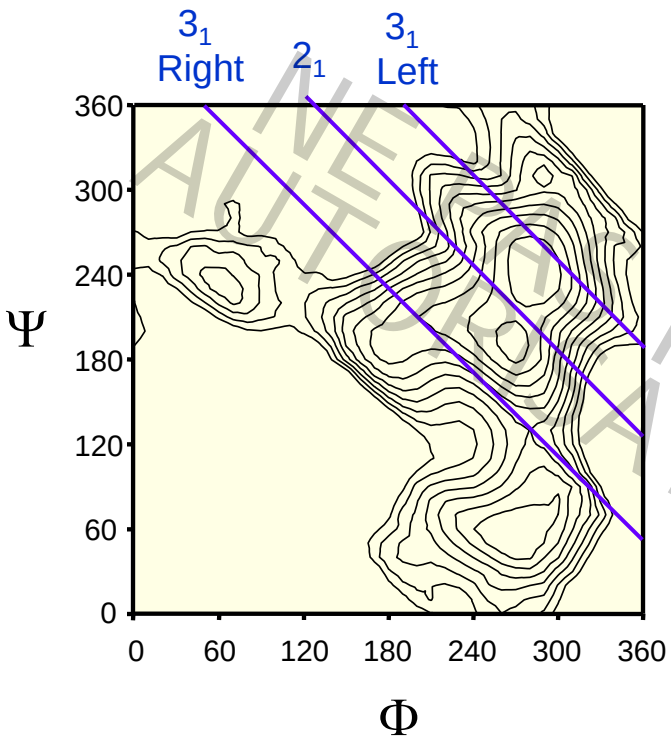
Global conformation :
Length of the end2end vector

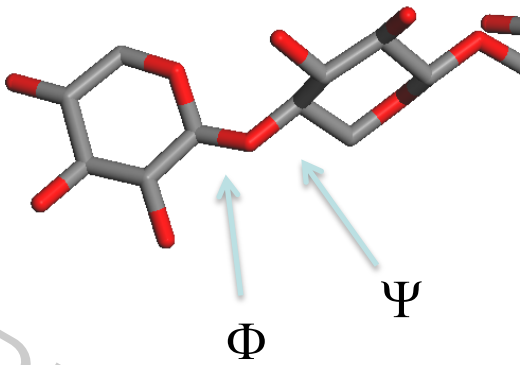




- When adsorbed, low DP of xylan is extended : straight and curved.
- Kinks appeared at DP = 25

The PES of Xylobiose





Helical conformations run diagonally across the PES :

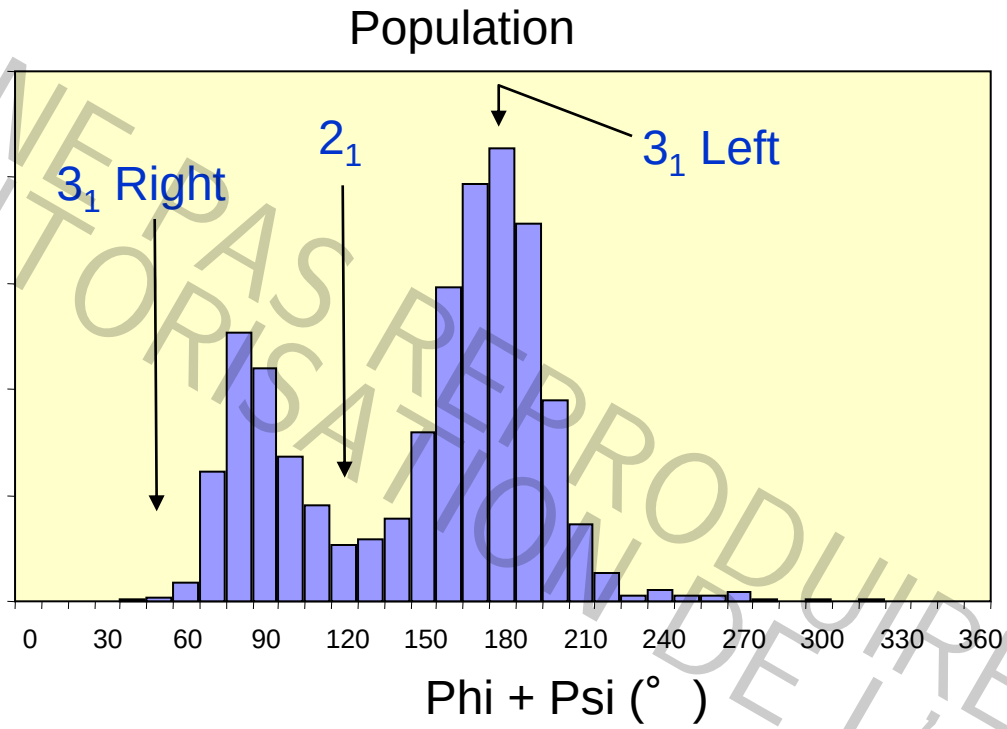
Helix if the sum Φ+Ψ is constant

helix 2_1 120°

3_1 left 190°

3_1 right 50°

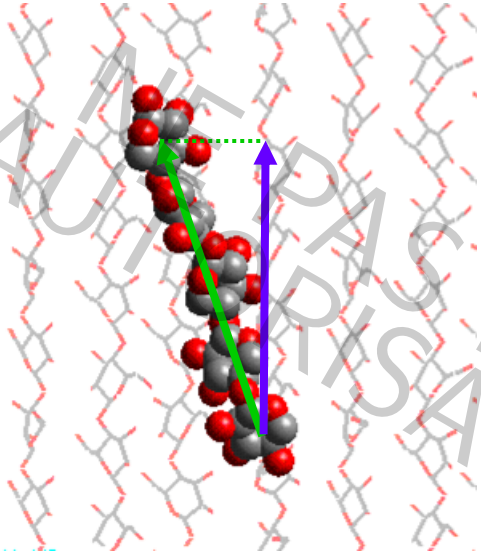
Adsorbed conformation of Xylans (DP=5).



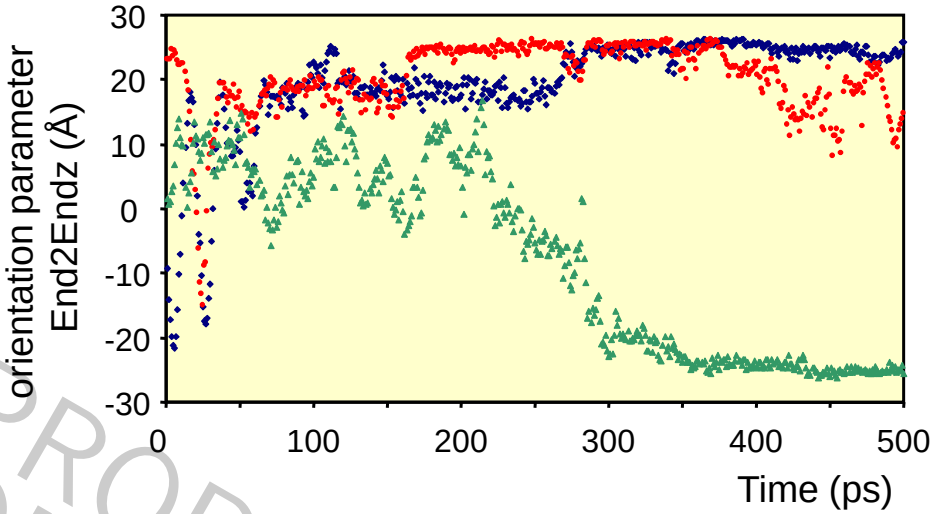
Conformational variability

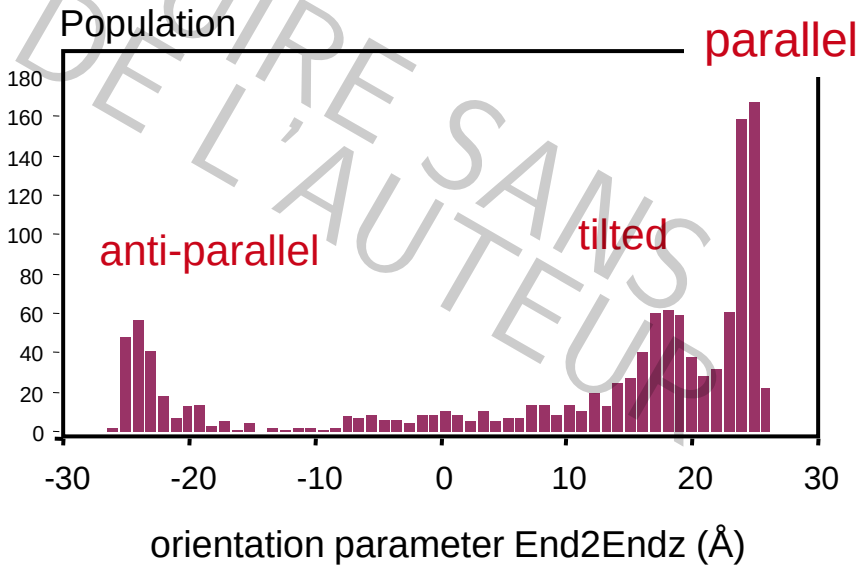
3_1 left > non helical >> 2_1 >> 3_1 right

Orientation of the Xylan backbone (DP5)



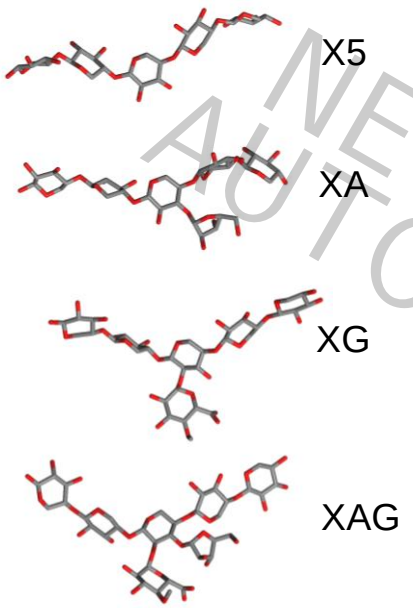
End2EndZ : alignment with the microfibril axis.

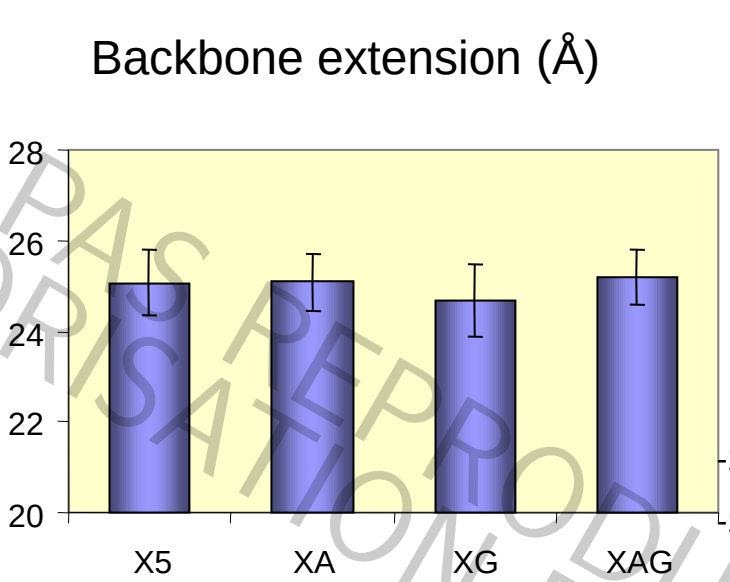


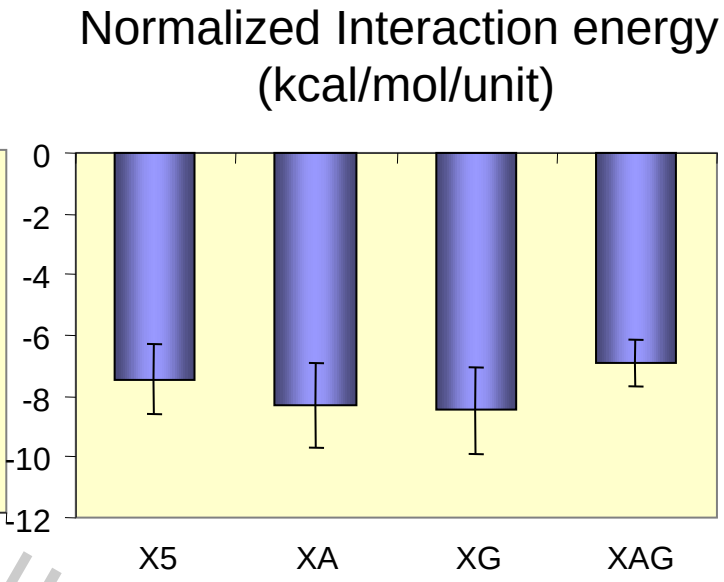


➢ Xylan prefers to be oriented parallel, tilted and anti parallel with respect to the cellulose fiber axis.

Substitution effects (DP5)

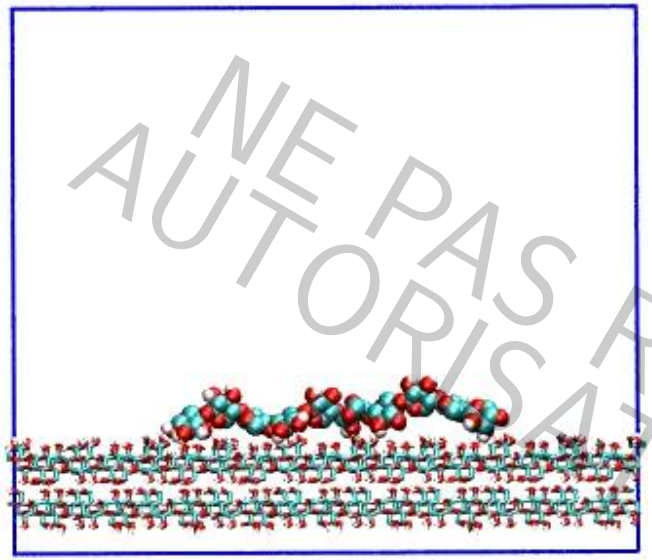


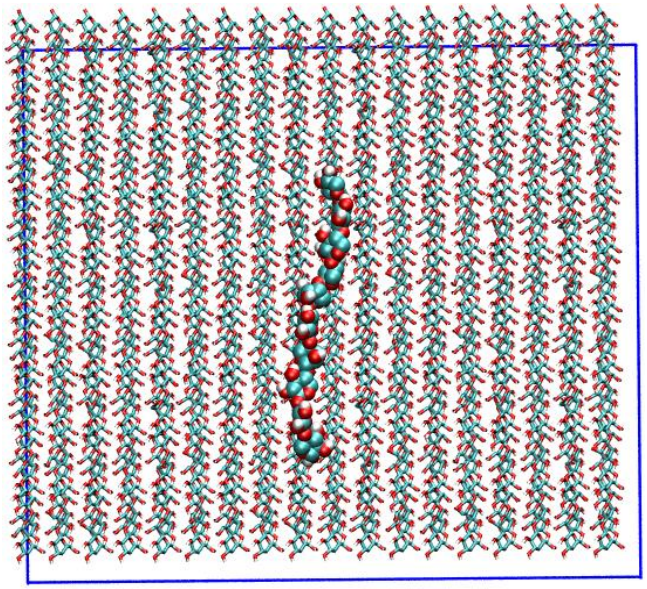




- No significant effect of the side chains on the adsorption features
- Valid within the limit of the following assumptions
  - low DP, low surface coverage
  - vacuum
  - Enthalpies of adsorption

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

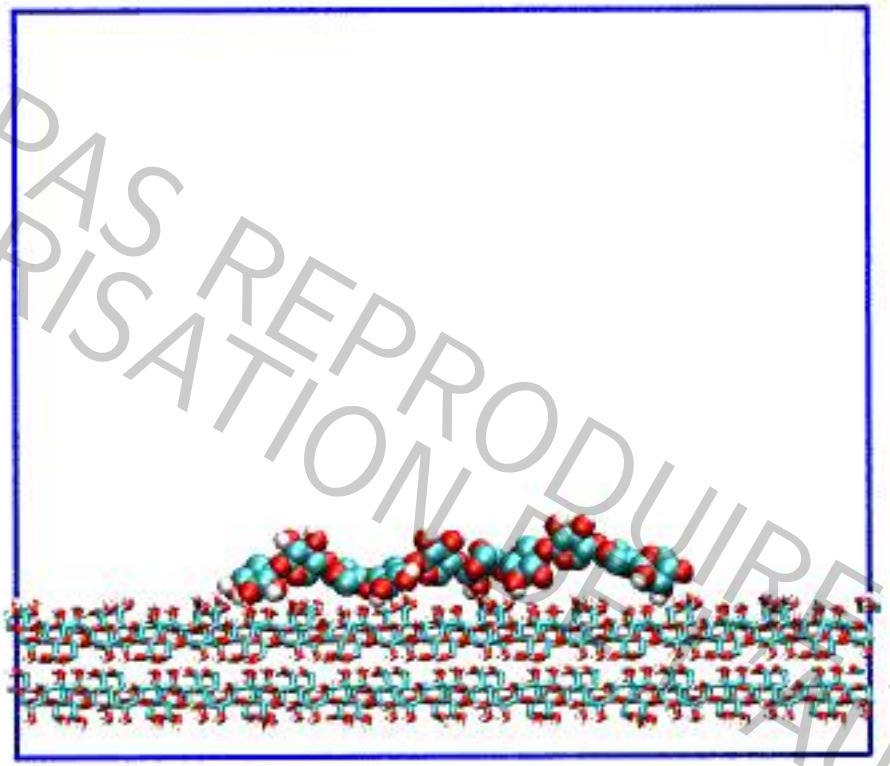
Potential of Mean Force

Umbrella sampling

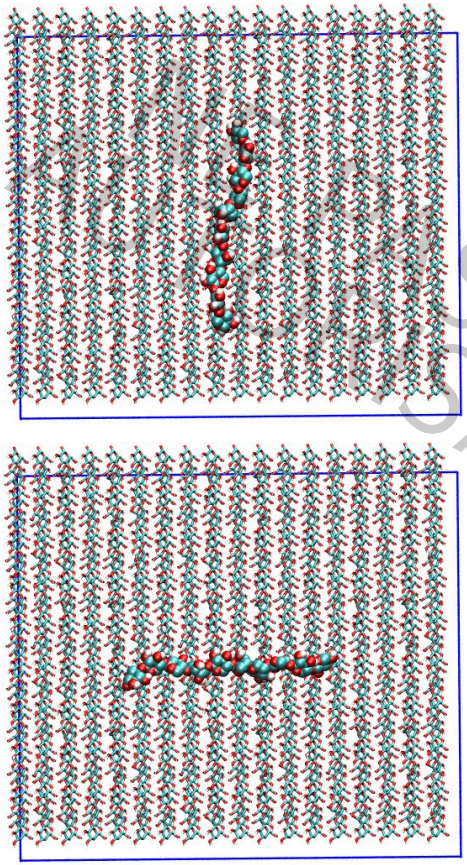
Windows 0.5 Å

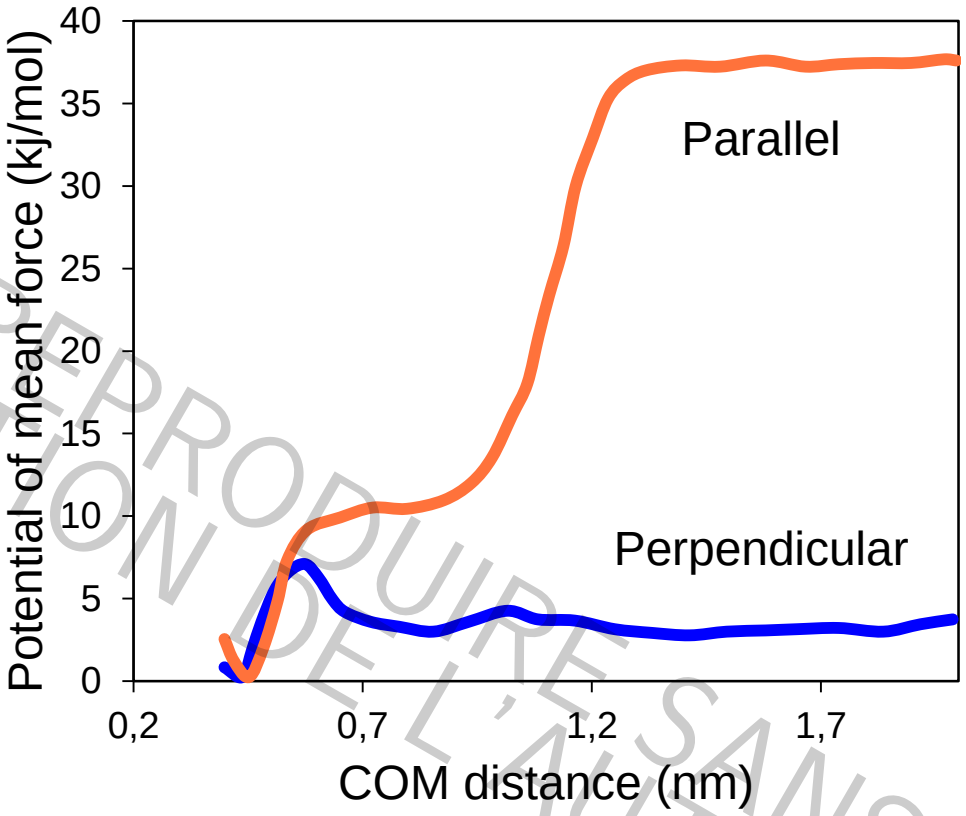
Pulling rate 1m/s

WHAM analysis



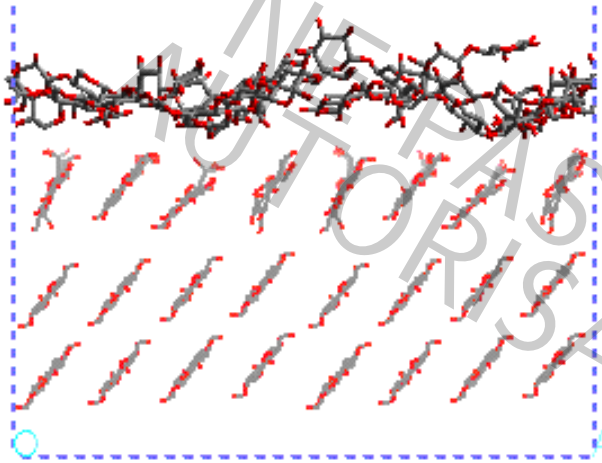
Free energy of adsorption

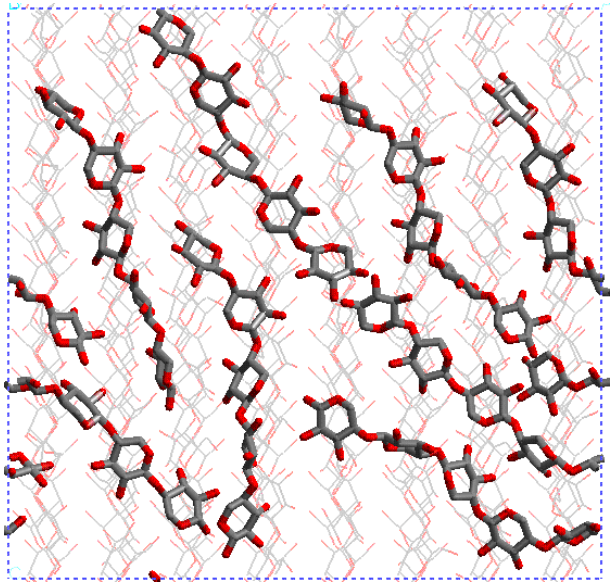




- Different desorption mechanisms
- The parallel orientation is preferred
- Relative free energy difference of 3.8 kJ/mol/unit

Interaction hemicellulose/cellulose : monolayer





- Adsorption of 8 chains of 5 residues each

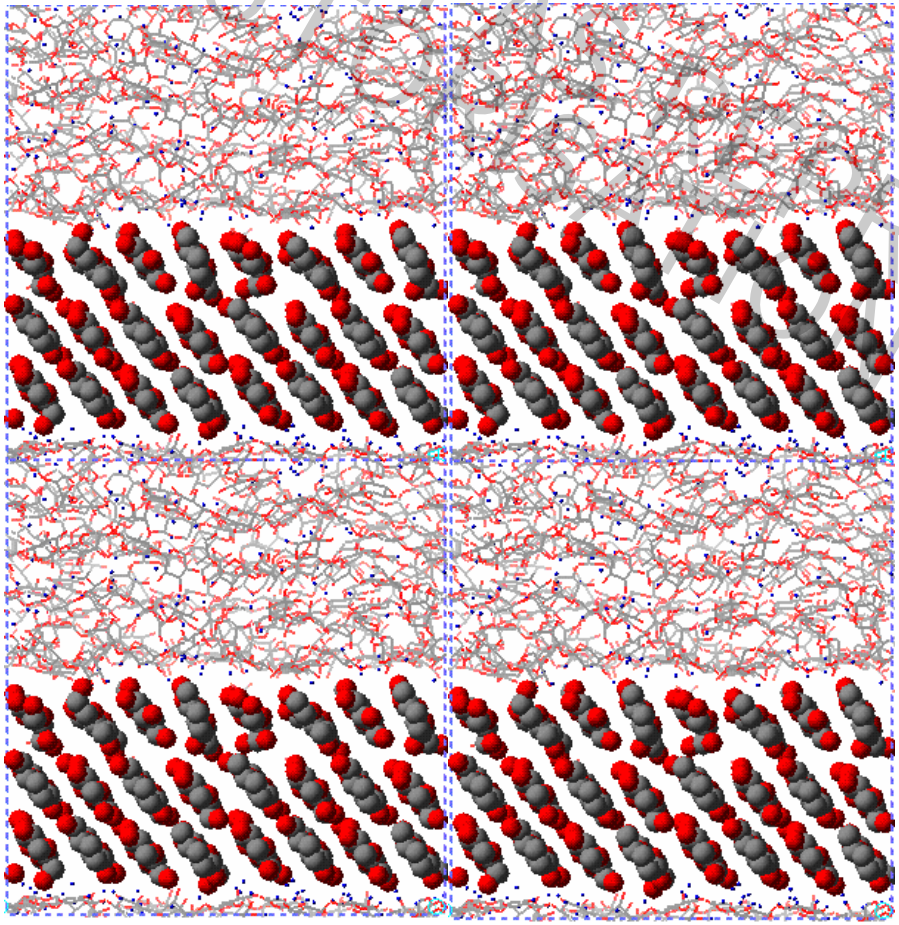
$$Q = DP\left(\frac{M_{xyl}}{N_a}\right).\left(\frac{S_{spe}}{S_{mod}}\right)$$

Q : amount of xylan adsorbed within a monolayer
DP : number of adsorbed xylosyl units 5X8=40
M_{xyl} : 132 $g.mol^{-1}$
N_a : Avogadro number $6.023\ 10^{23}$
S_{spe} : specific surface of cellulose : 300 $m^2.g^{-1}$
S_{mod} : 18 nm^2

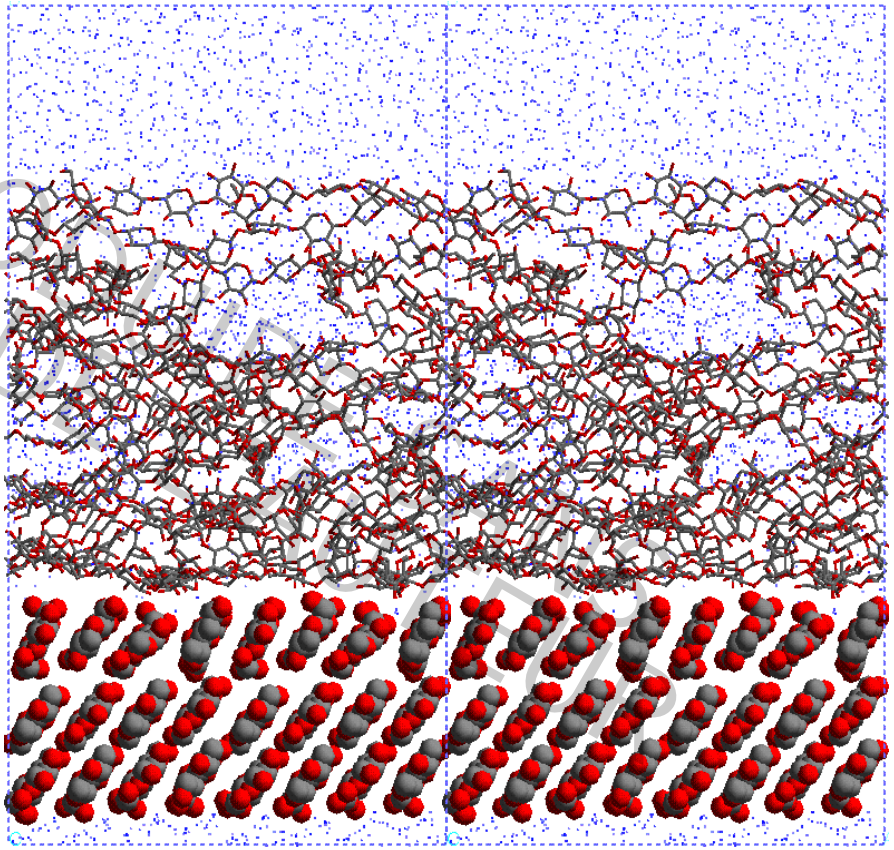
- Q = 0.14 g xylan/g cellulose
- 70 % of the cellulose surface covered
- Conformational features preserved
- Xylan roughly parallel to each other
- Tilted with respect to the fibre axis

bio-sourced nanomaterials

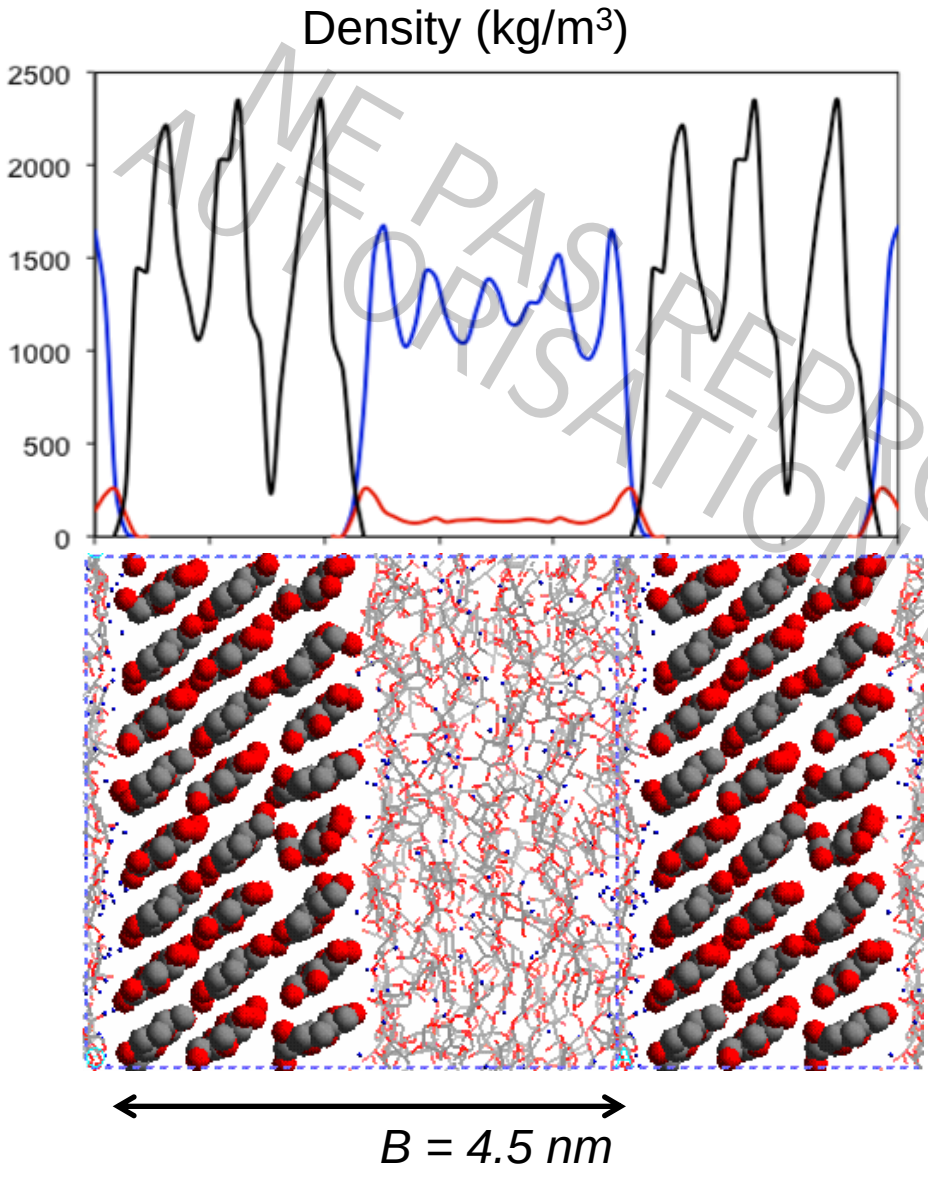
Cellulose/xylan multi-layer



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

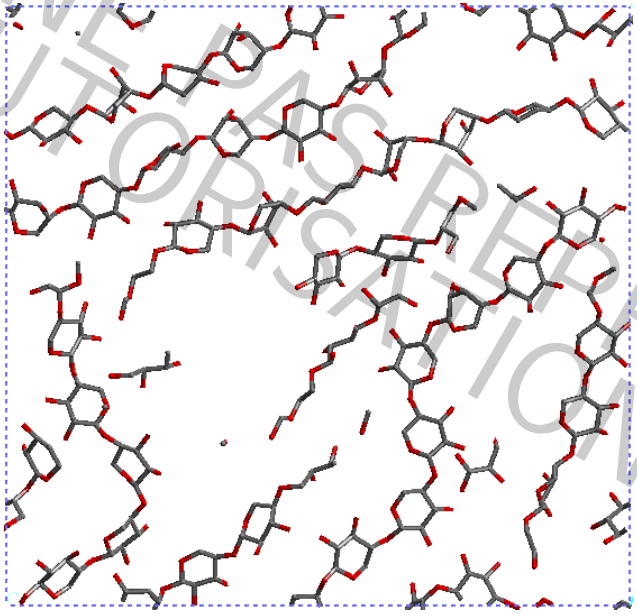
Water :

Exclusively within xylan

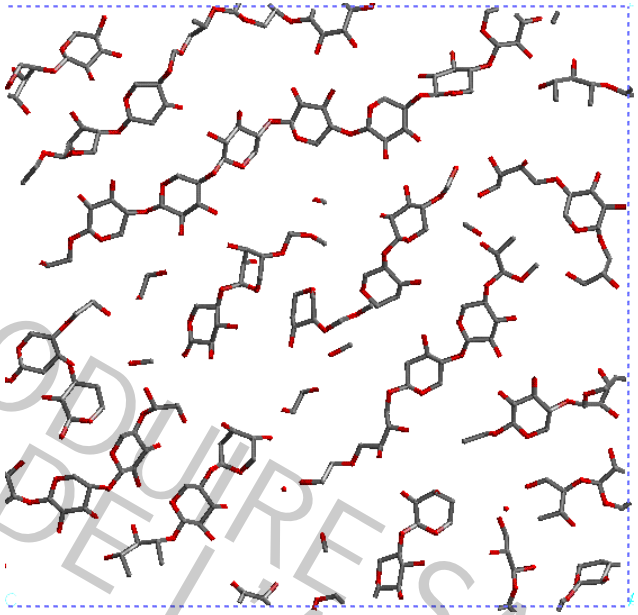
Max intensity at the interface

Organization of the xylan chains in the first layers

1st layer



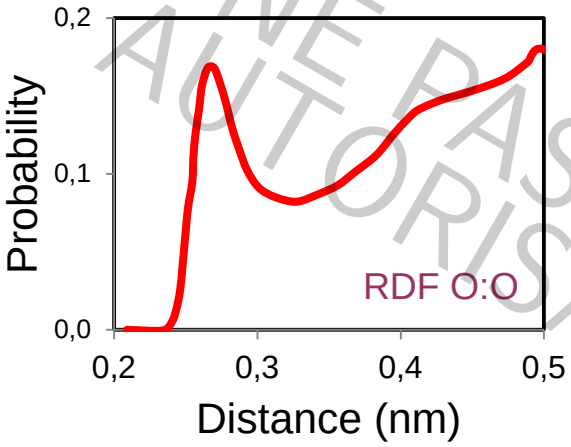
Second layer

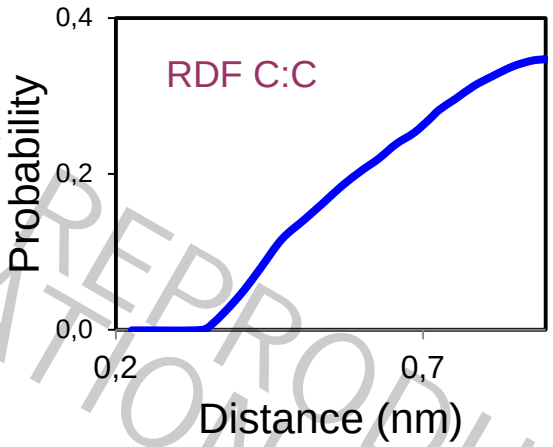


- Extended segments interrupted by kinks
- Aligned to each other
- Not aligned to the fiber axis
- 1st layer denser and more organized than the 2nd one

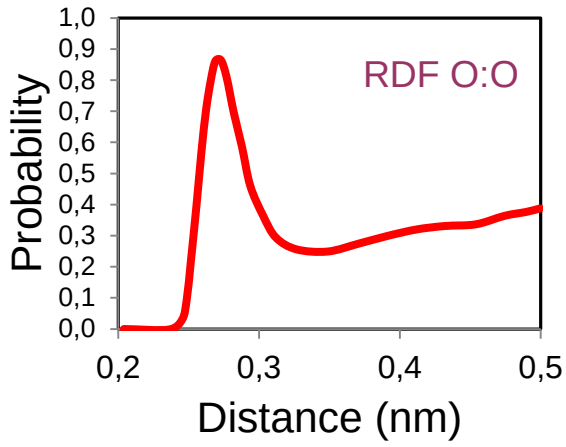
Intermolecular Radial Distribution Functions

Cellulose : Xylan

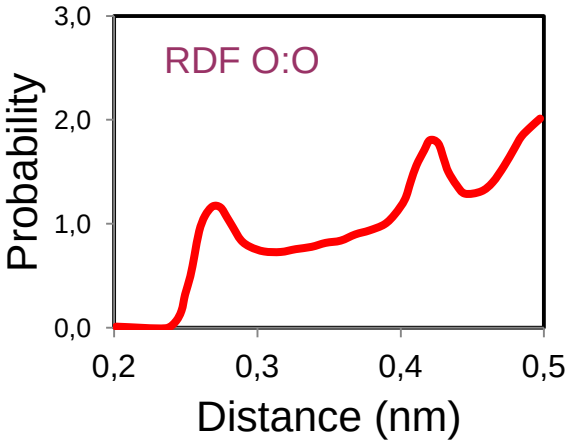


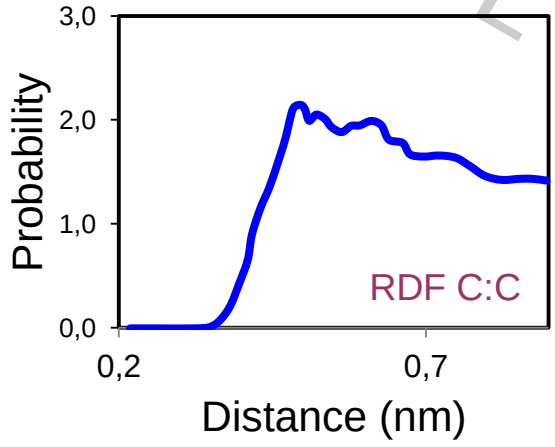


Cellulose : Water

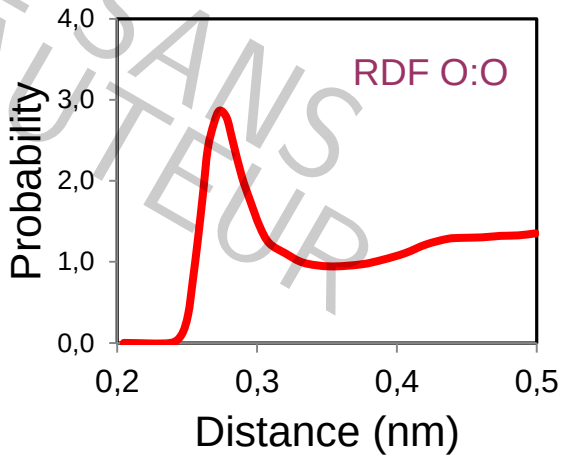


Xylan : Xylan

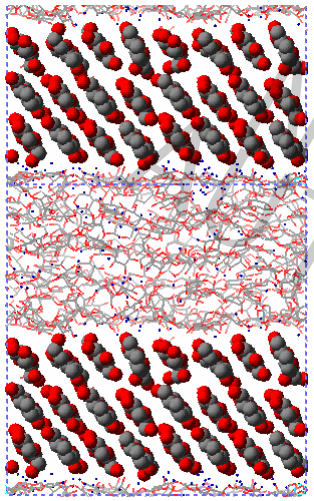




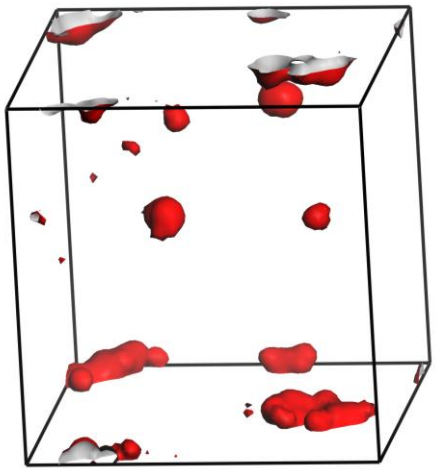
Xylan : Water



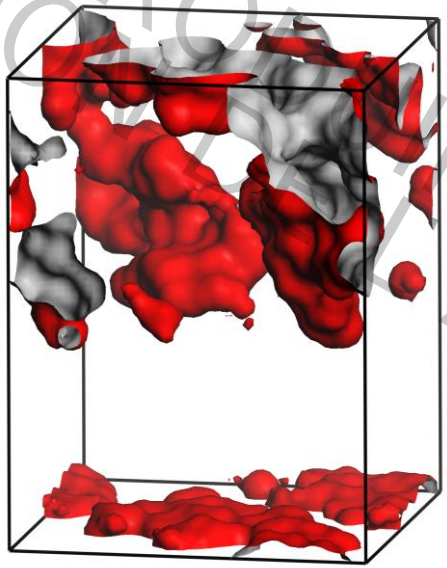
Hydration effects



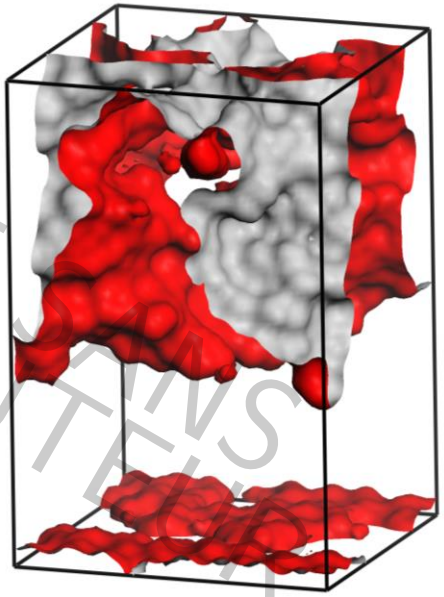
B parameter (nm)	4.5	5.5	6.5
# H2O	170	695	1275
Water content (w/w)	8.8	28	42
Density ($g.cm^{-3}$)	1.30	1.22	1.18
Diffusion coefficient ($10^{-5}cm^2/s$)	0,0242	0,2755	0,5905



8.8 % of moisture
isolated molecules
and small aggregates

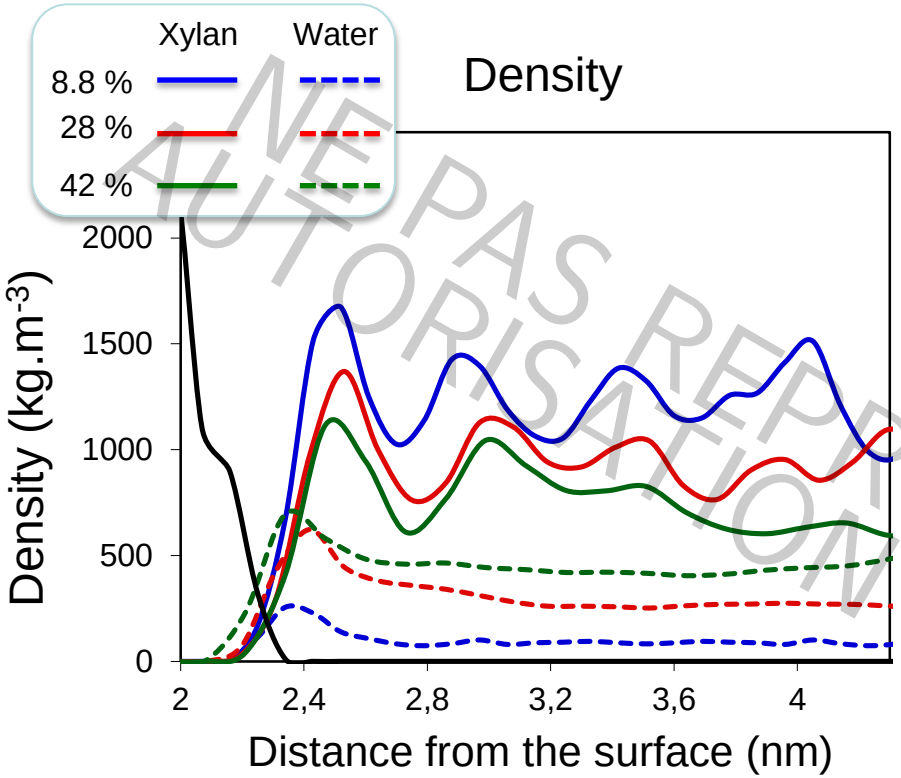


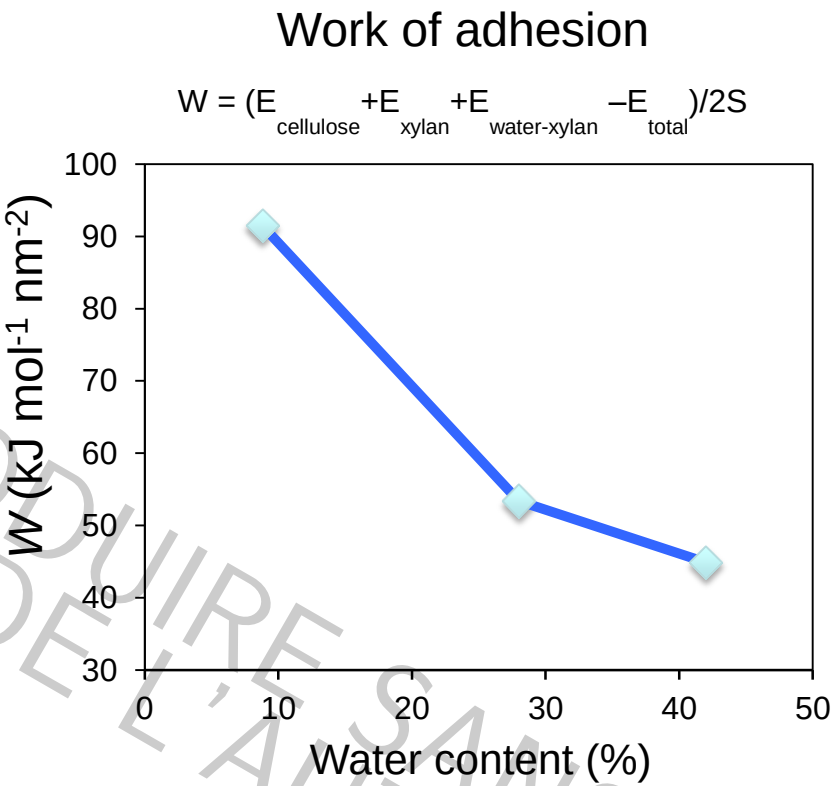
28 % of moisture
large aggregates



42 % of moisture
continuous channels of
water.

Hydration effects



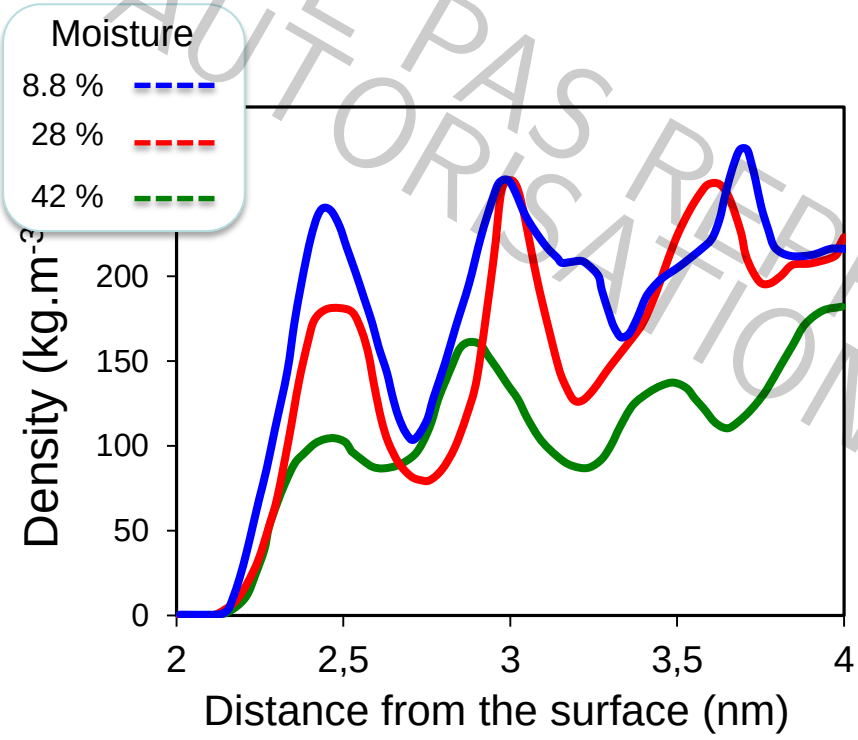


Moisture influence :

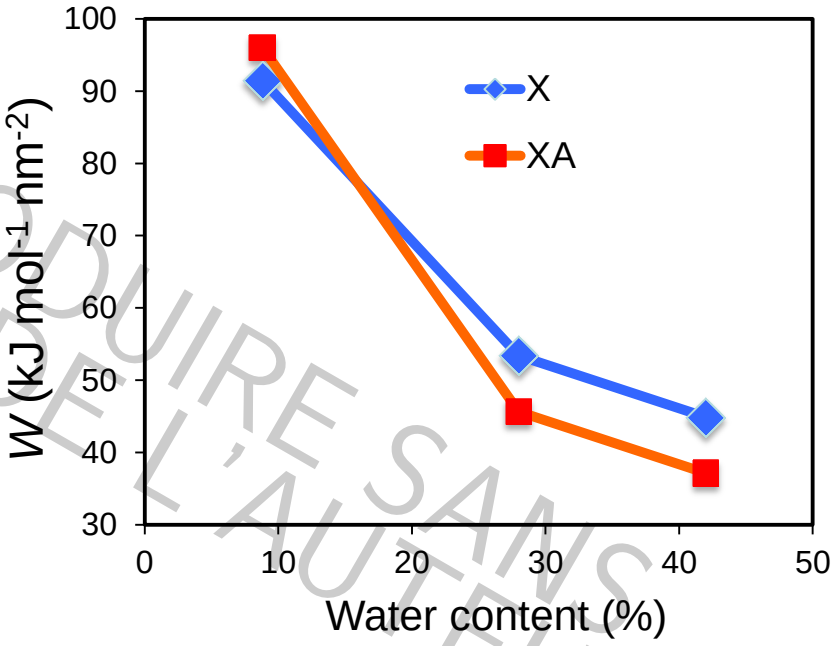
- The amount of xylan in contact with cellulose
- The organization state of xylan far from the interface
- The interaction strength between cellulose and xylan

Structural effect : X_{240} vs $(XXAXX)_{40}$

Location of the Ara*f* residues



Work of Adhesion



- Less Ara*f* at the interface than in the xylan phase
- Ara*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 kJ/mol/monomer
- Moisture uptake decreases the interaction strength at the interface
- Side chains are detrimental for adhesion.