ETH zürich

Introduction to moisture relationships in biobased materials

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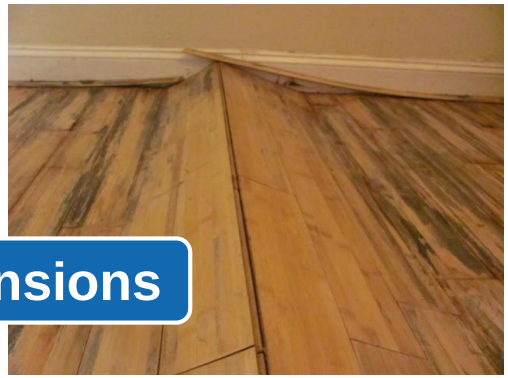
EMPA
Materials Science & Technology

Effects of moisture

Short-term mechanical performance

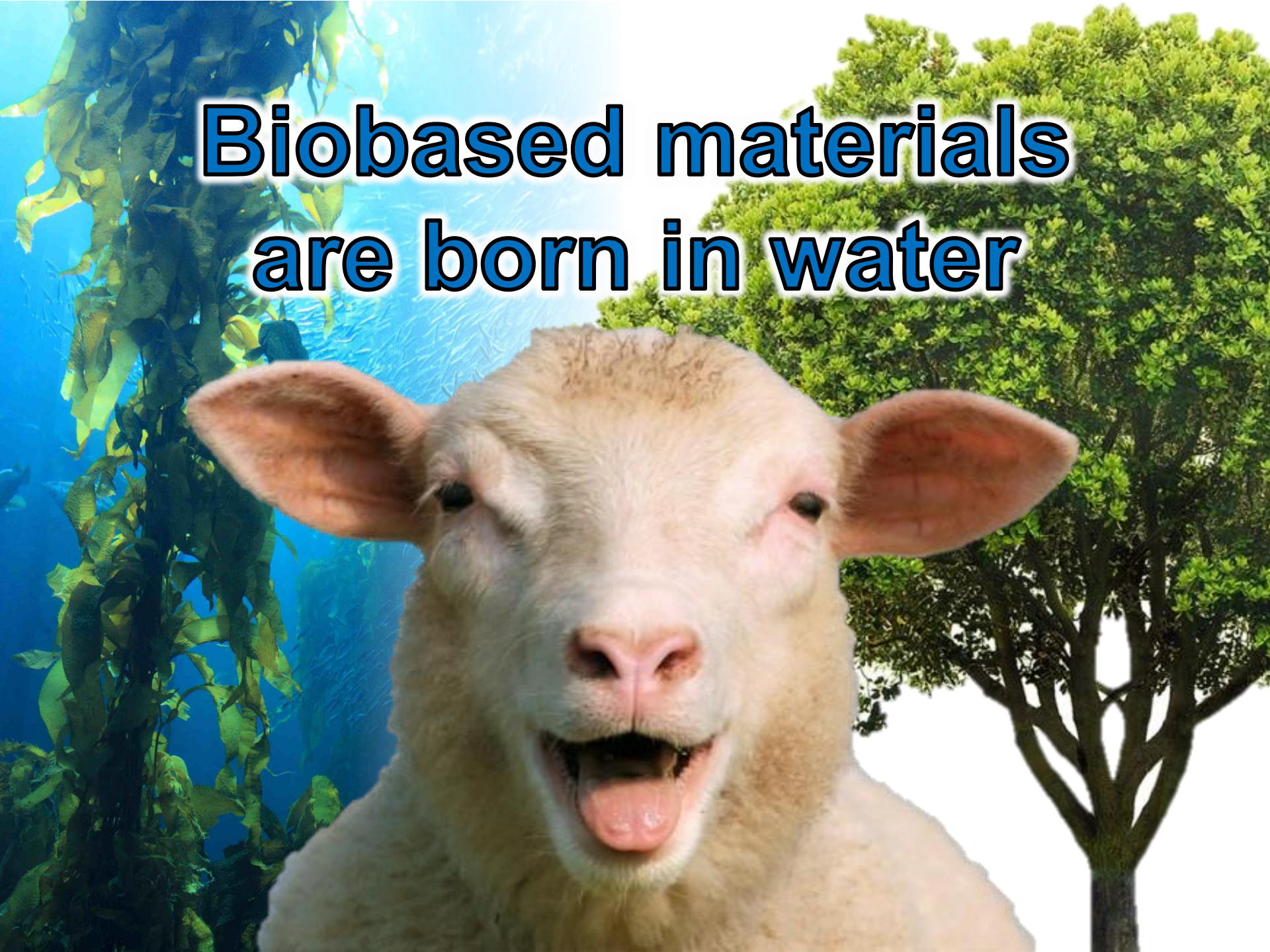
Long-term mechanical performance



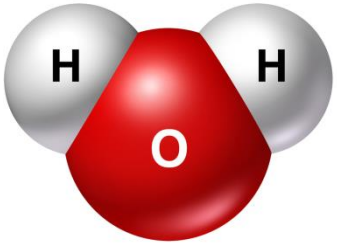
Dimensions

Durability

Biobased materials are born in water



Aqueous birthmarks



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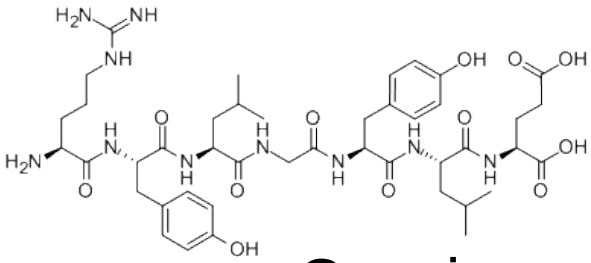
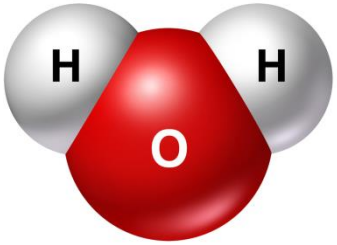
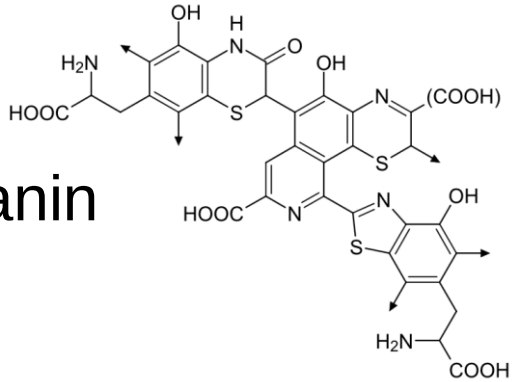
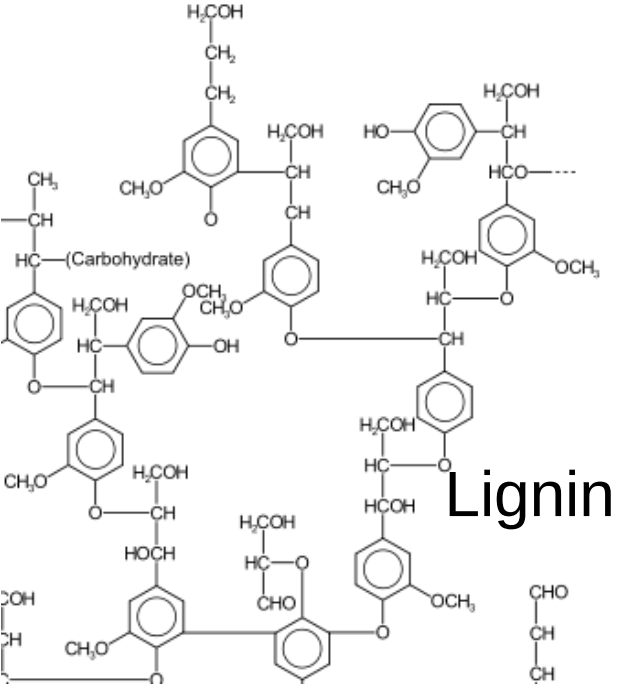


Casein

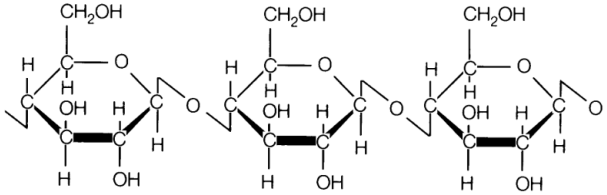


Melanin



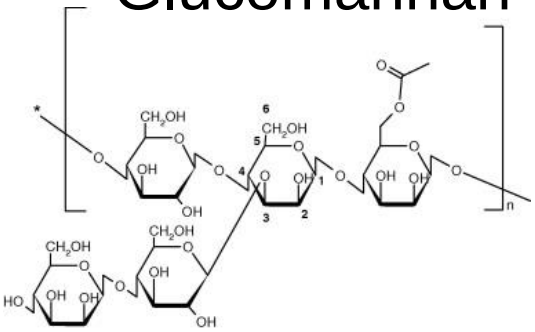


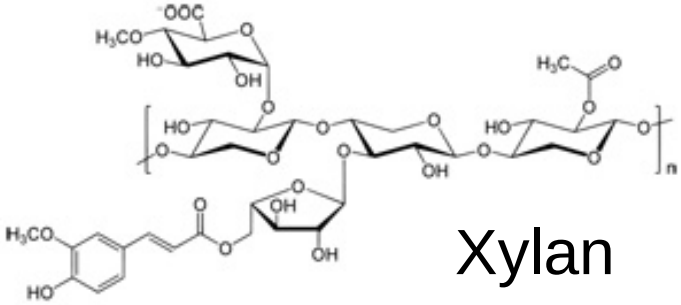
Lignin



Cellulose

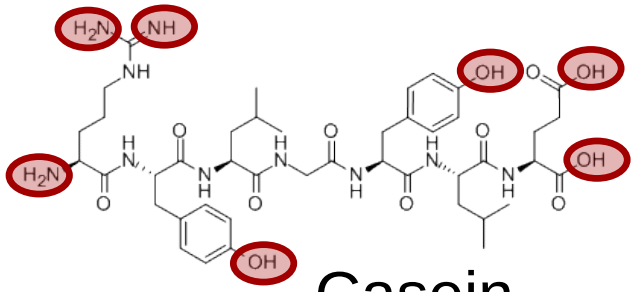
Glucomannan



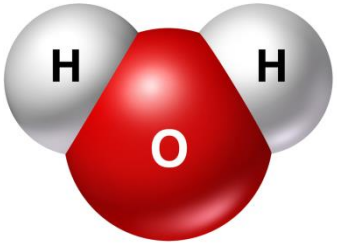


Xylan

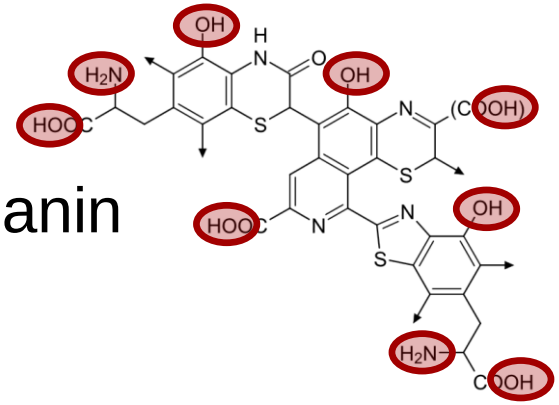
Aqueous birthmarks

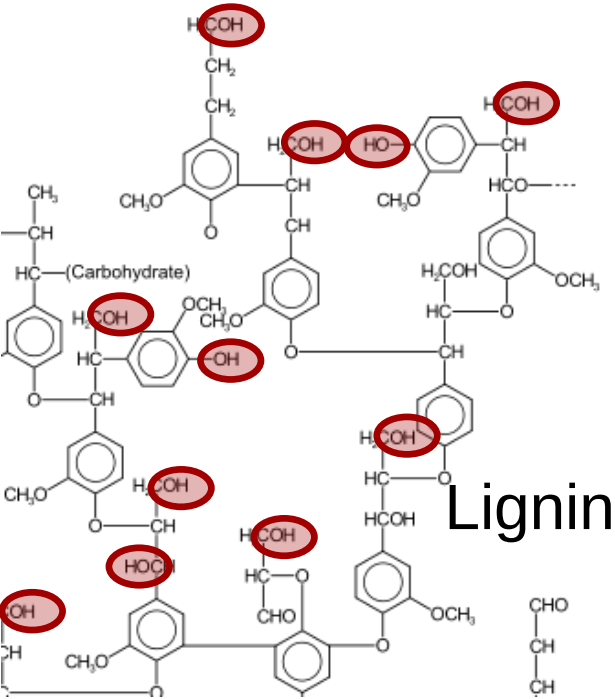


Casein

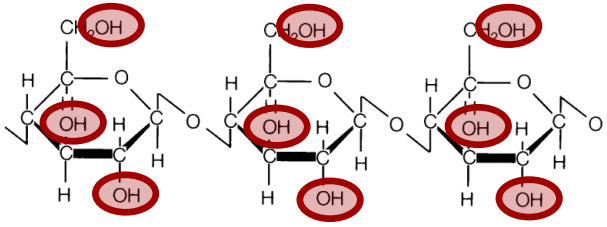


Melanin





Lignin



Cellulose

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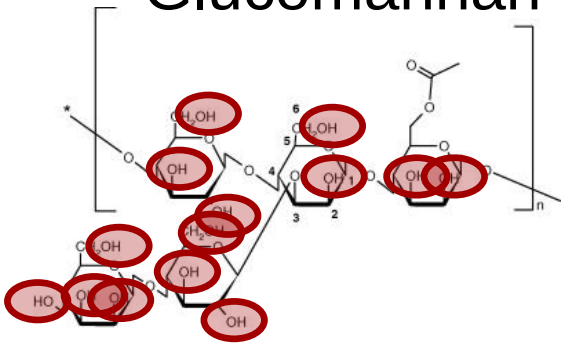
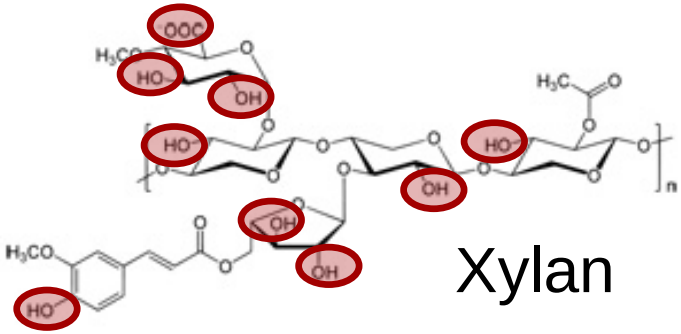
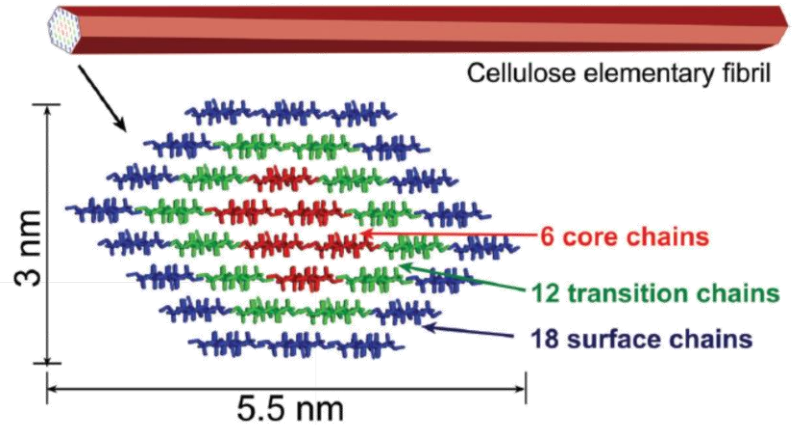


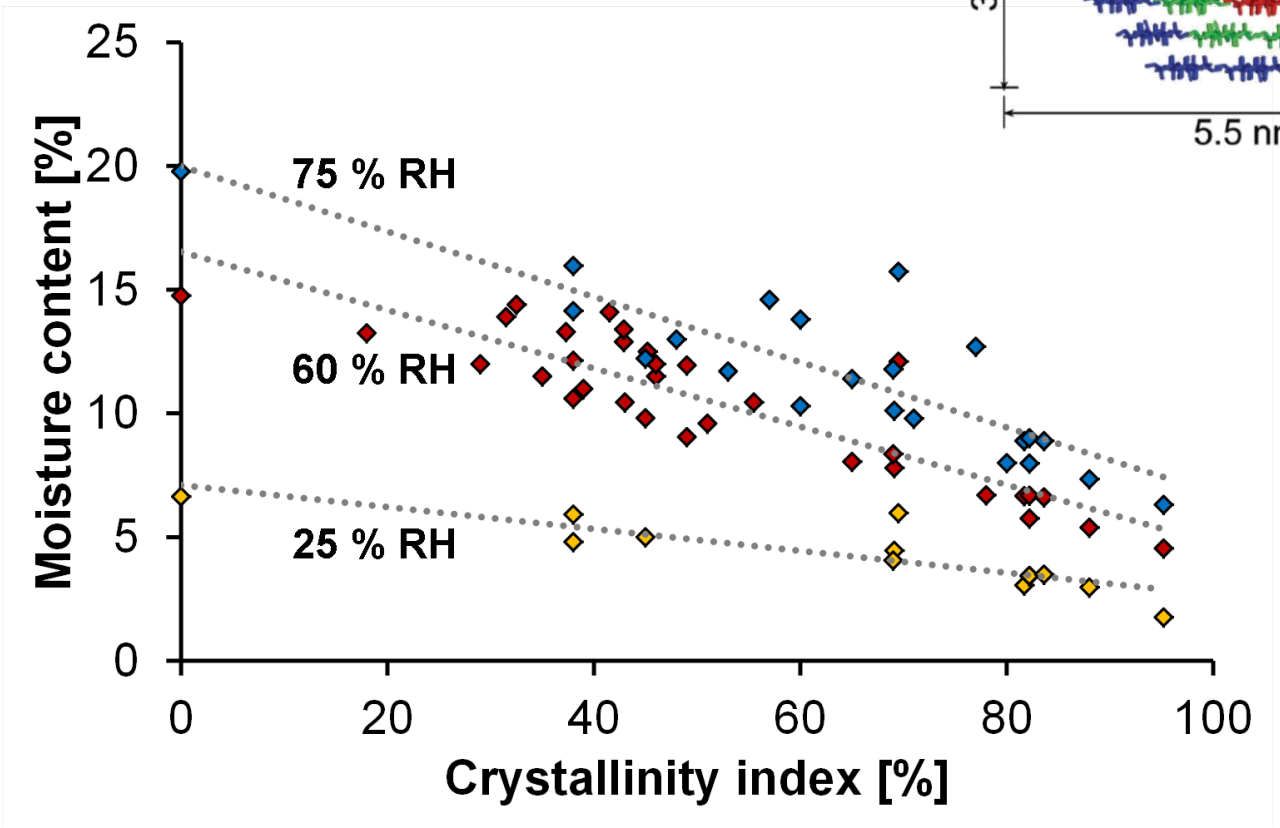


Xylan

Accessibility for water

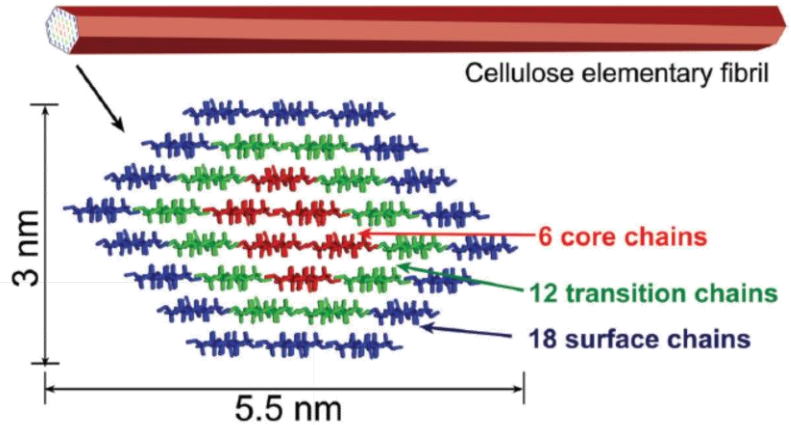


Atalla et al. (2009) Structures of plant cell wall celluloses, In: Biomass recalcitrance (Himmel ed.)



Not all polar groups can be accessed by water.

Accessibility for water



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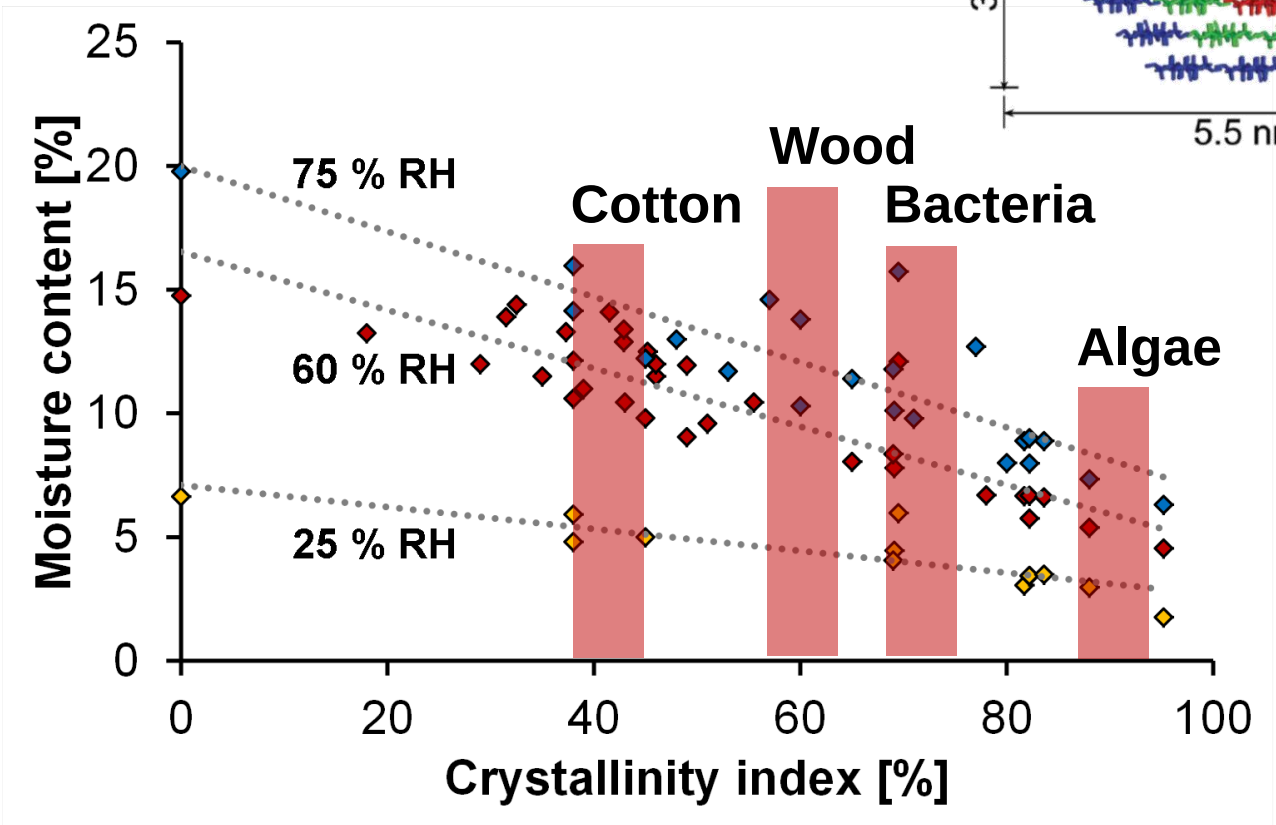
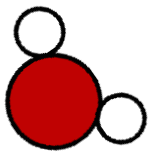
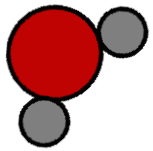


Not all polar groups can be accessed by water.

Probing the accessibility for water



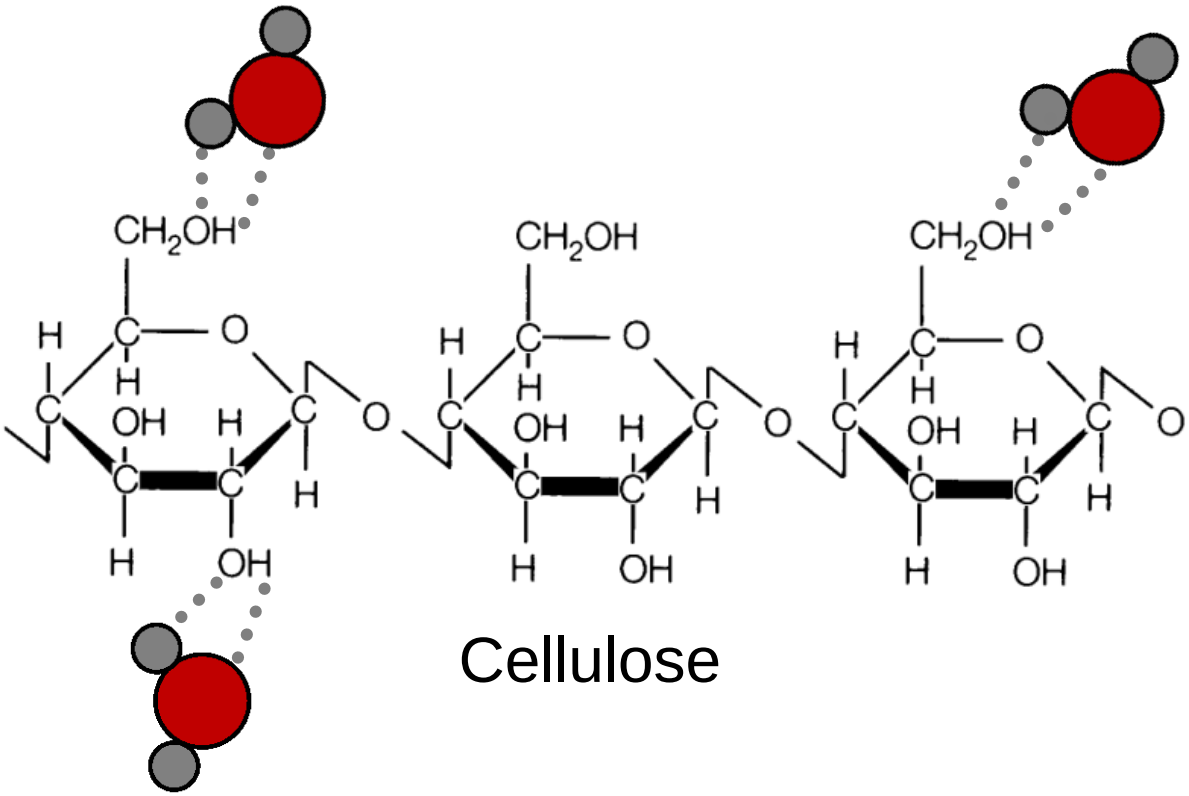
Water (H_2O), M_w = 18.01 g/mol



HEAVY WATER (D_2O), M_w = 20.03 g/mol

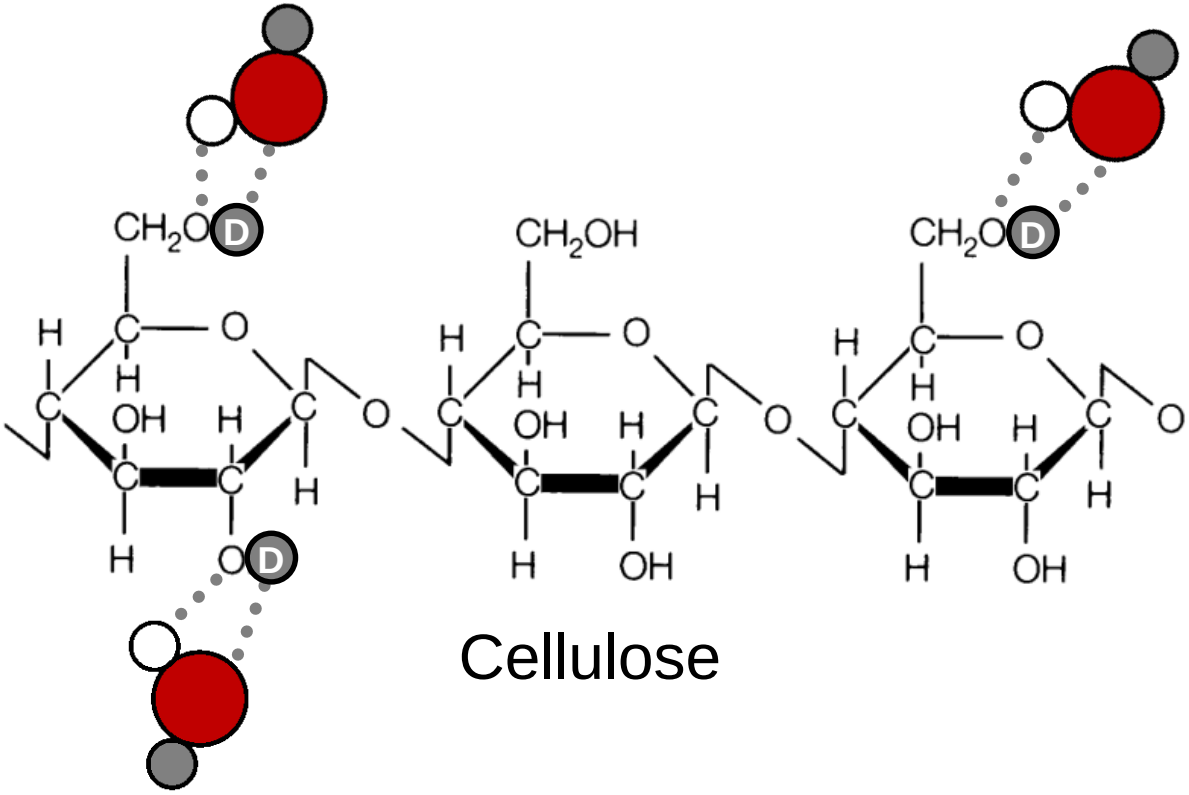
Deuterium (D) is close to twice as HEAVY as protium (H)

Probing the accessibility for water



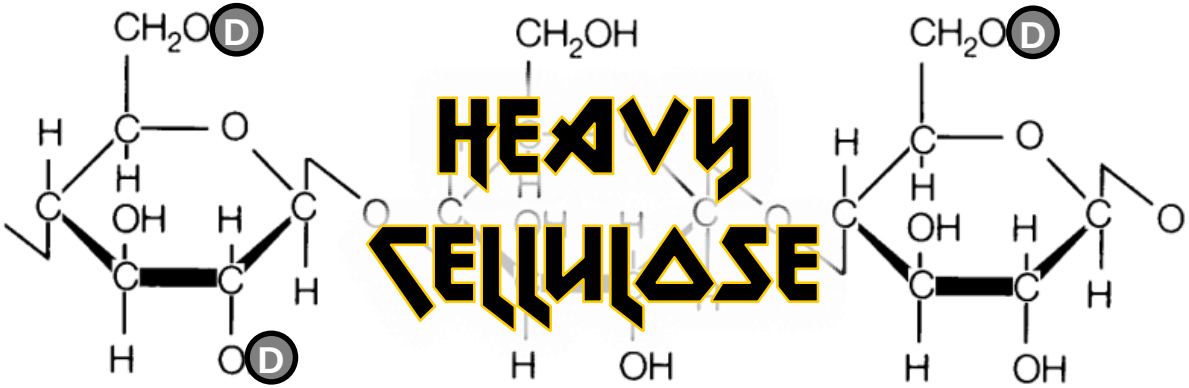
Cellulose

Probing the accessibility for water



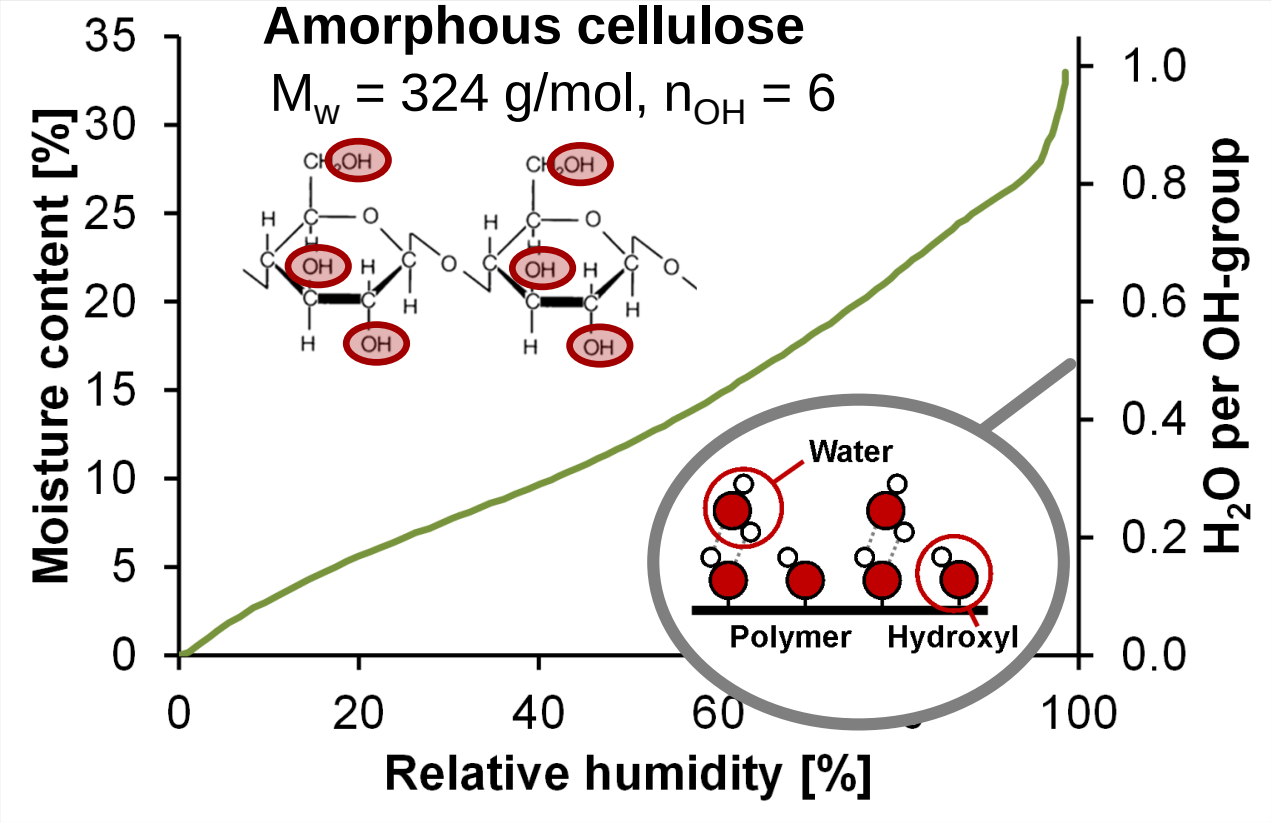
Probing the accessibility for water

For every mol H exchanged with D, mass is increased 1.006 g
Cellulose has 18.5 mmol/g OH, i.e. max. increase **18.6 mg/g**

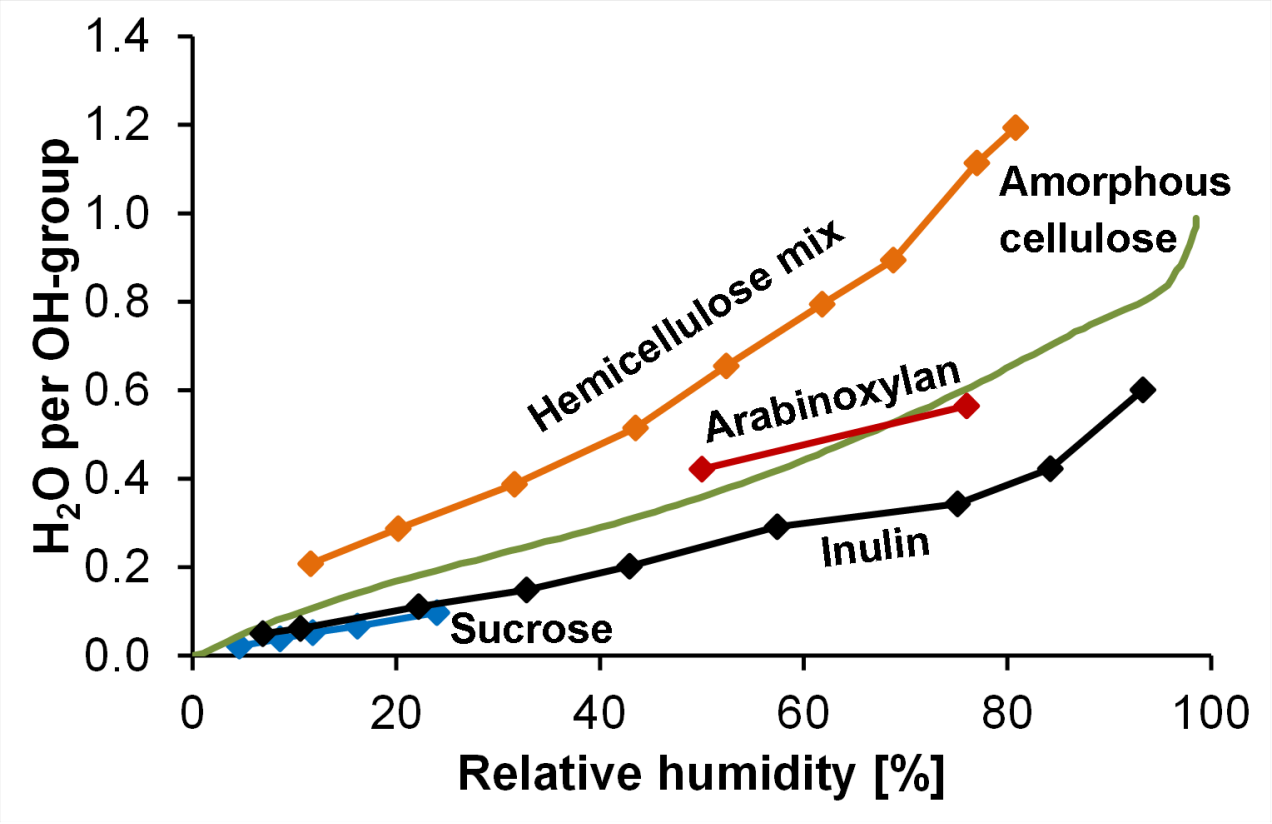


~~Cellulose~~

Average water distribution

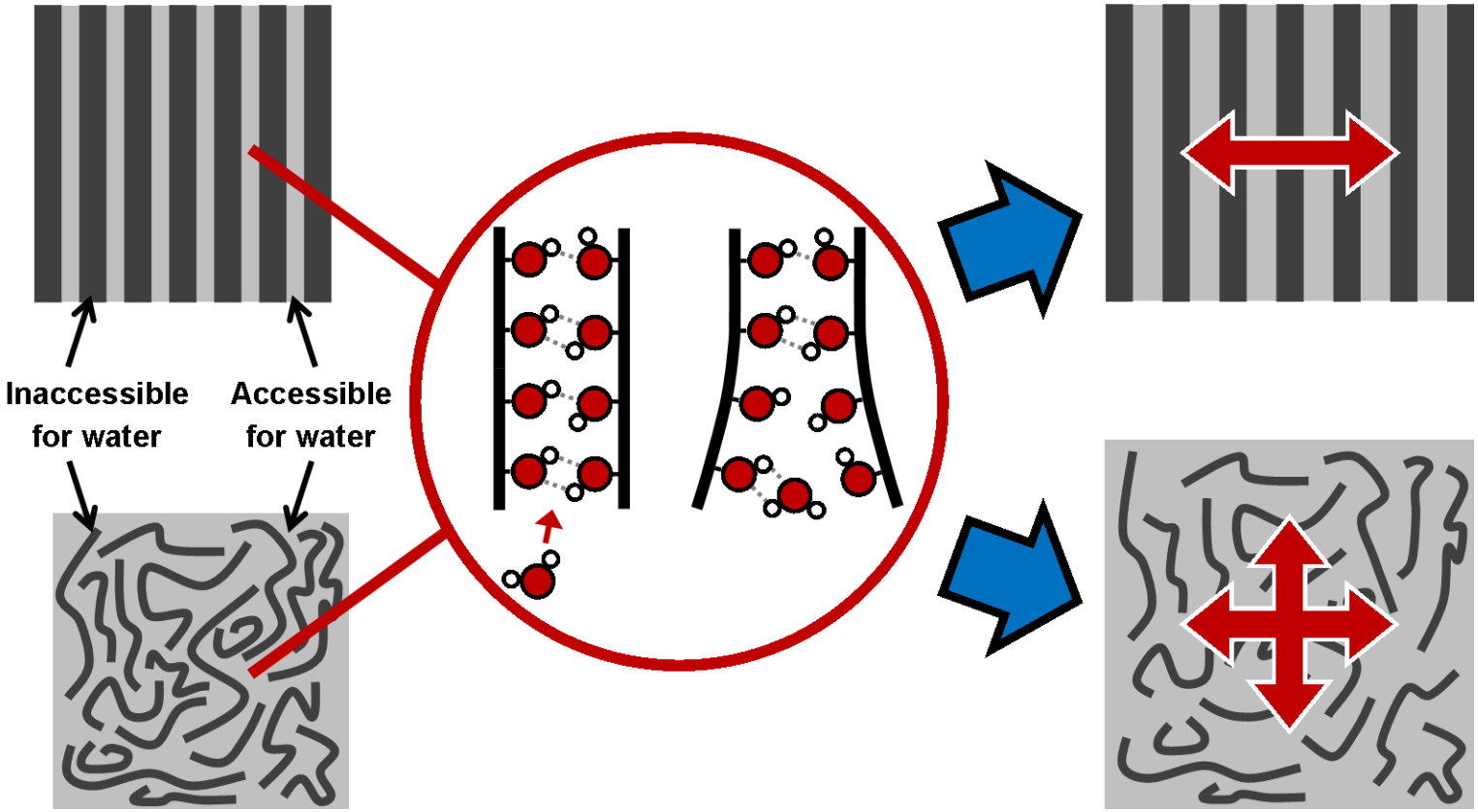


Average distribution in amorphous biomaterials

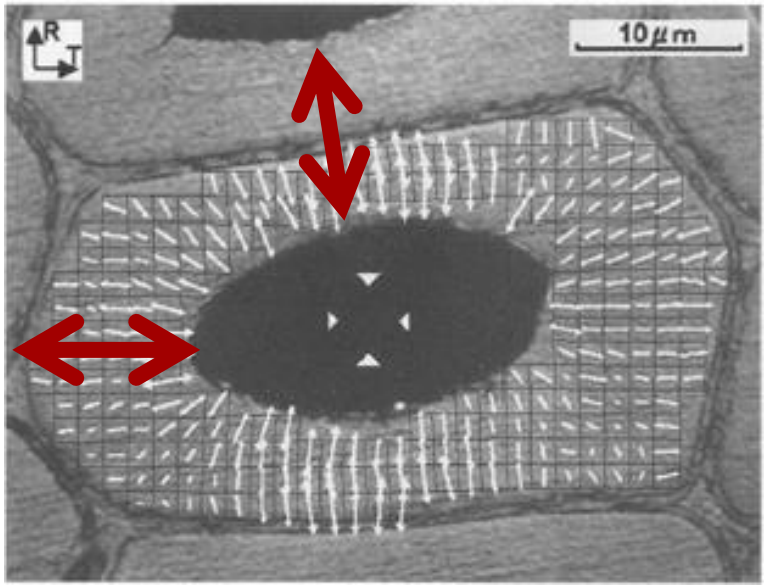


Dimensional instability of biobased materials

Water induced movements

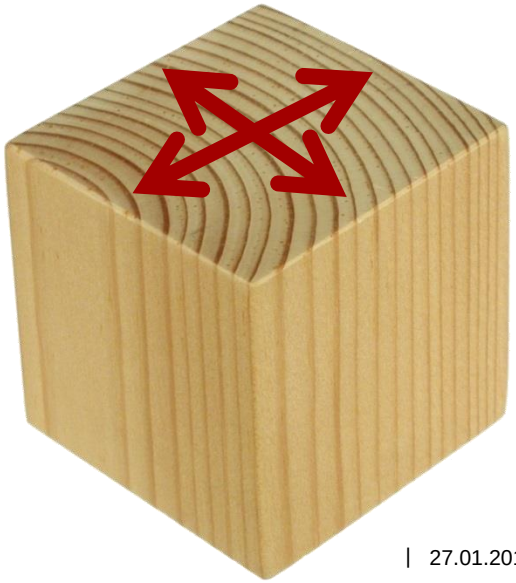


Swelling on several length scales

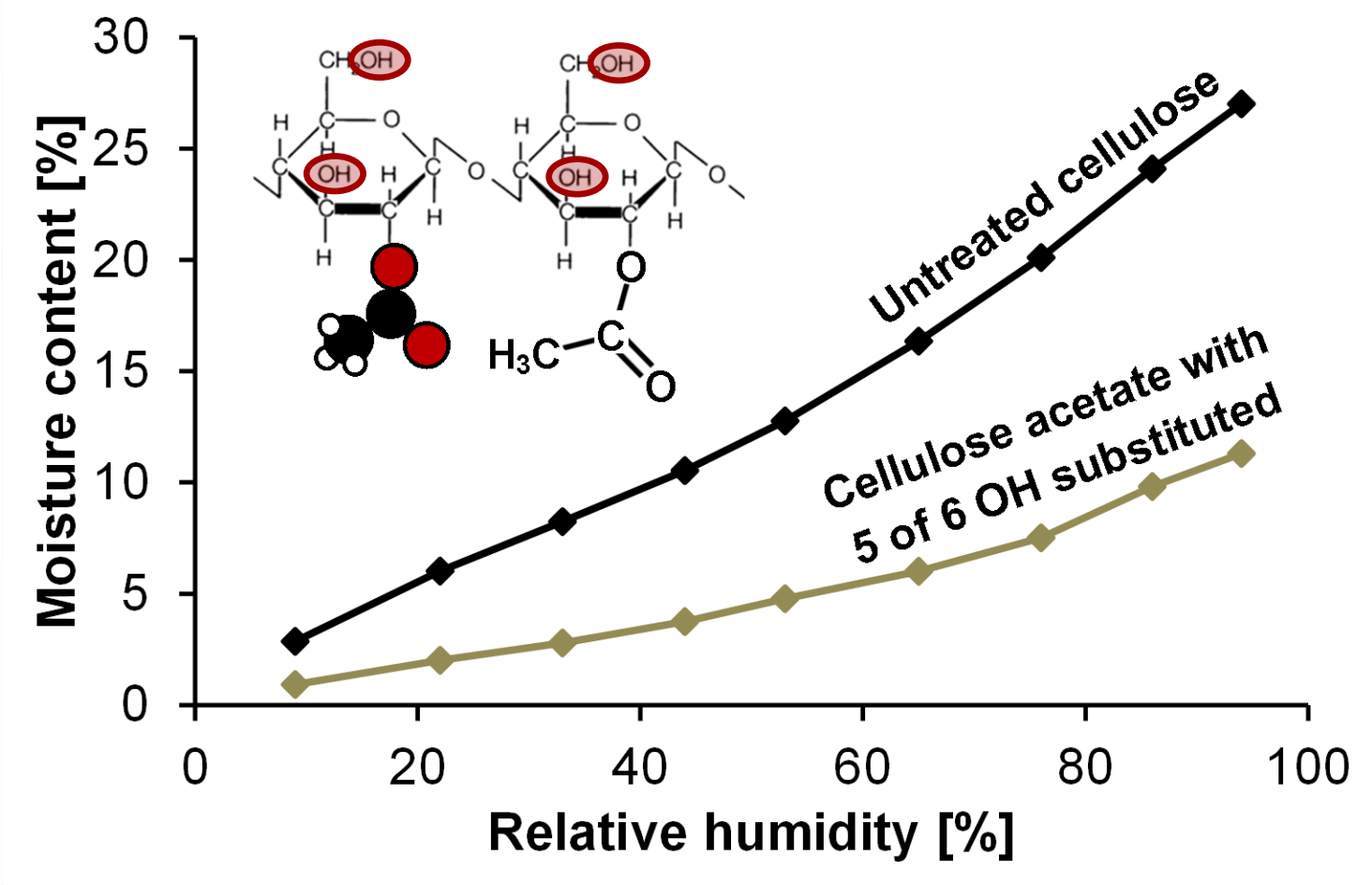


Murata and Masuda (2001) J Wood Sci, 47:507

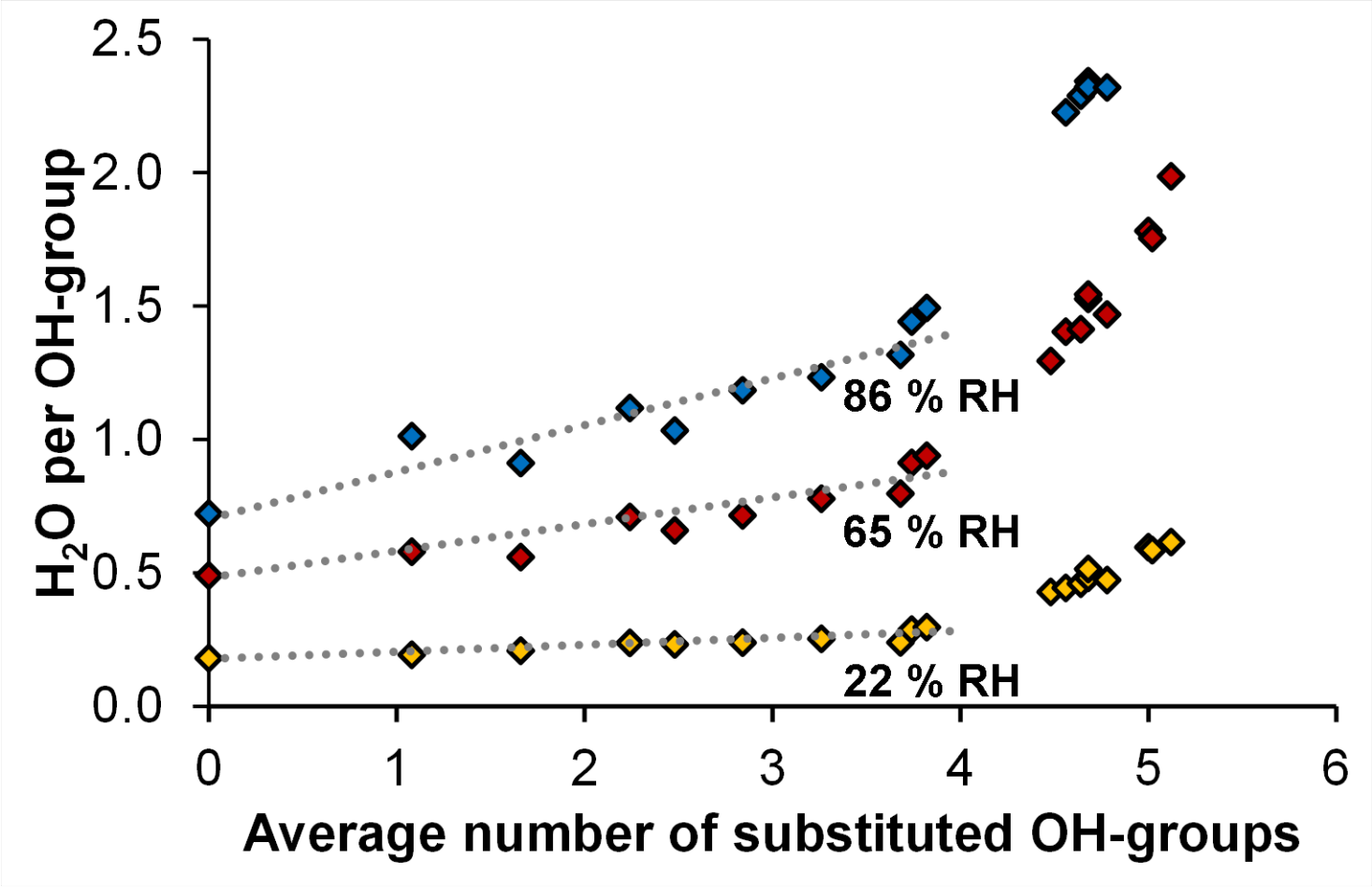
A change in moisture content will cause a change in dimensions on several scales



Controlling sorption and swelling



Controlling sorption and swelling



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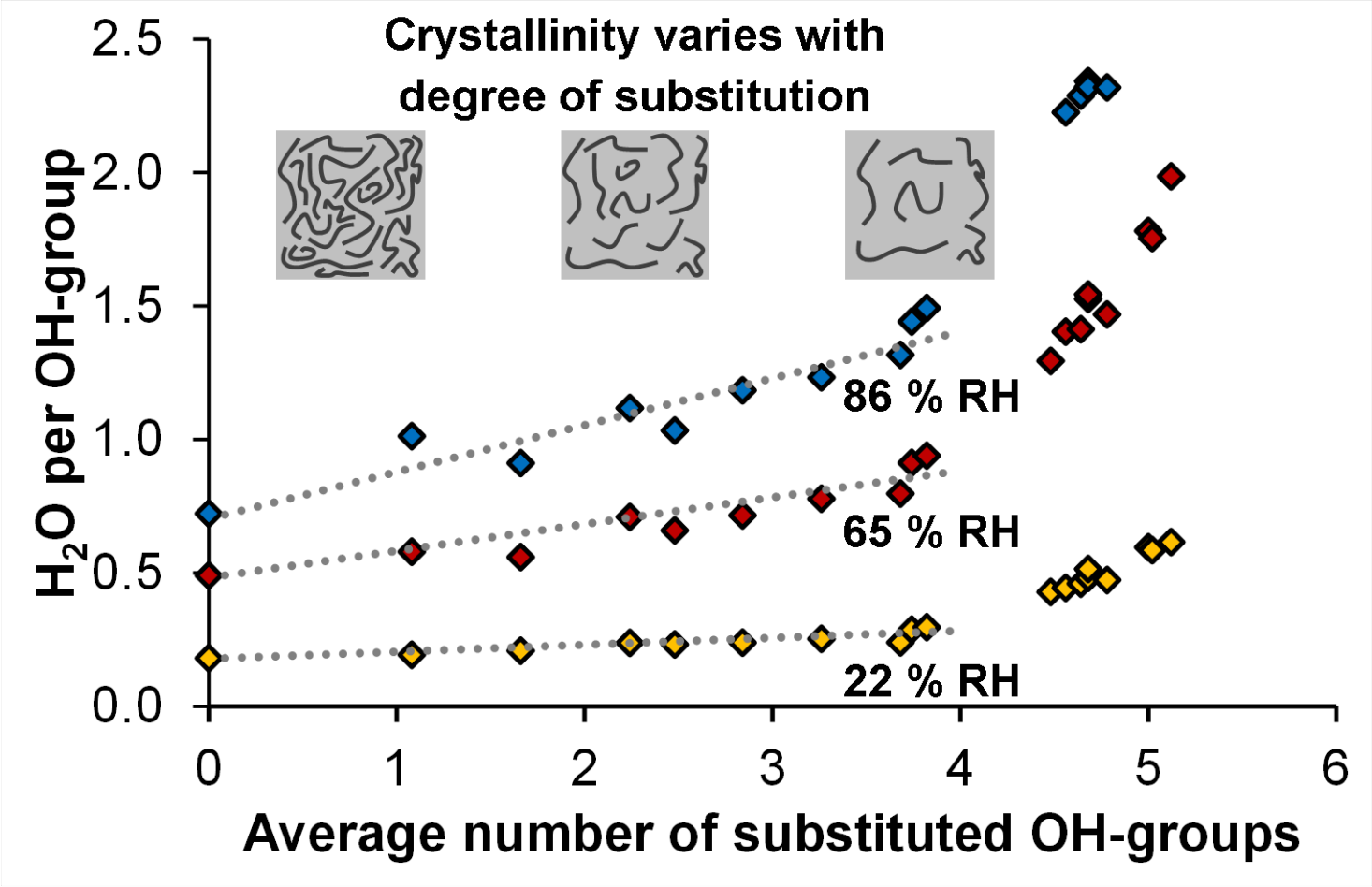
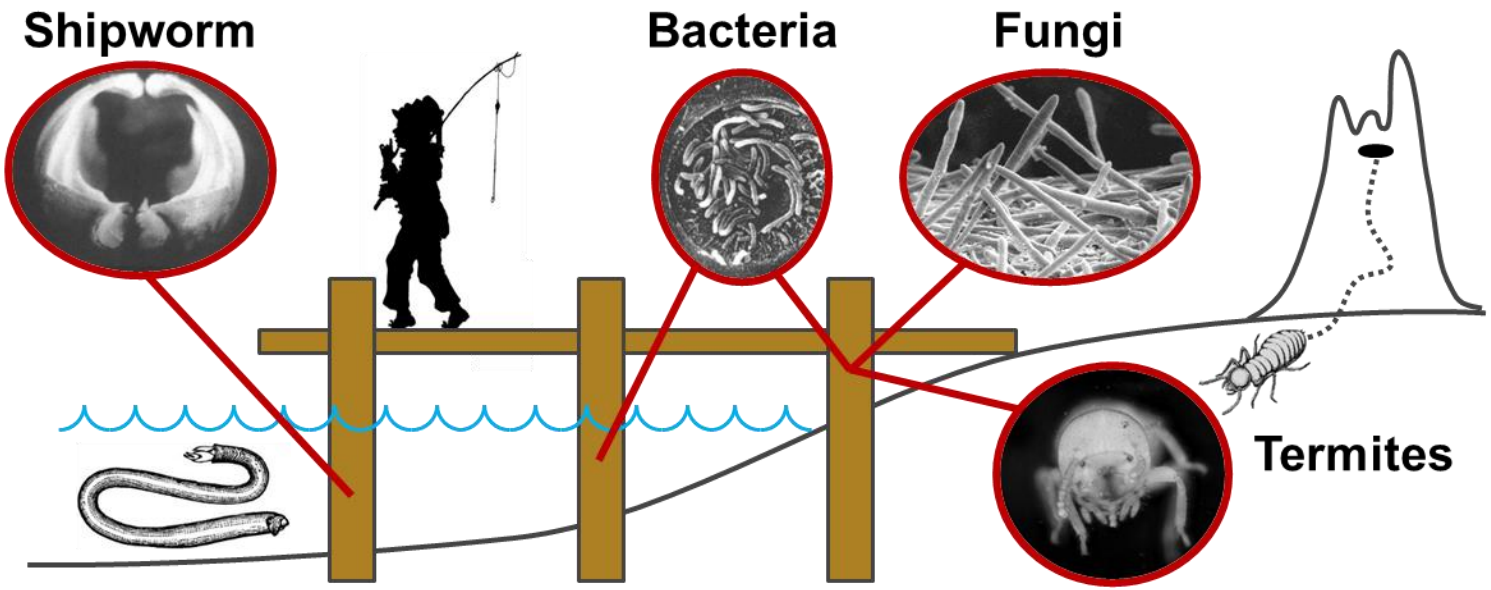
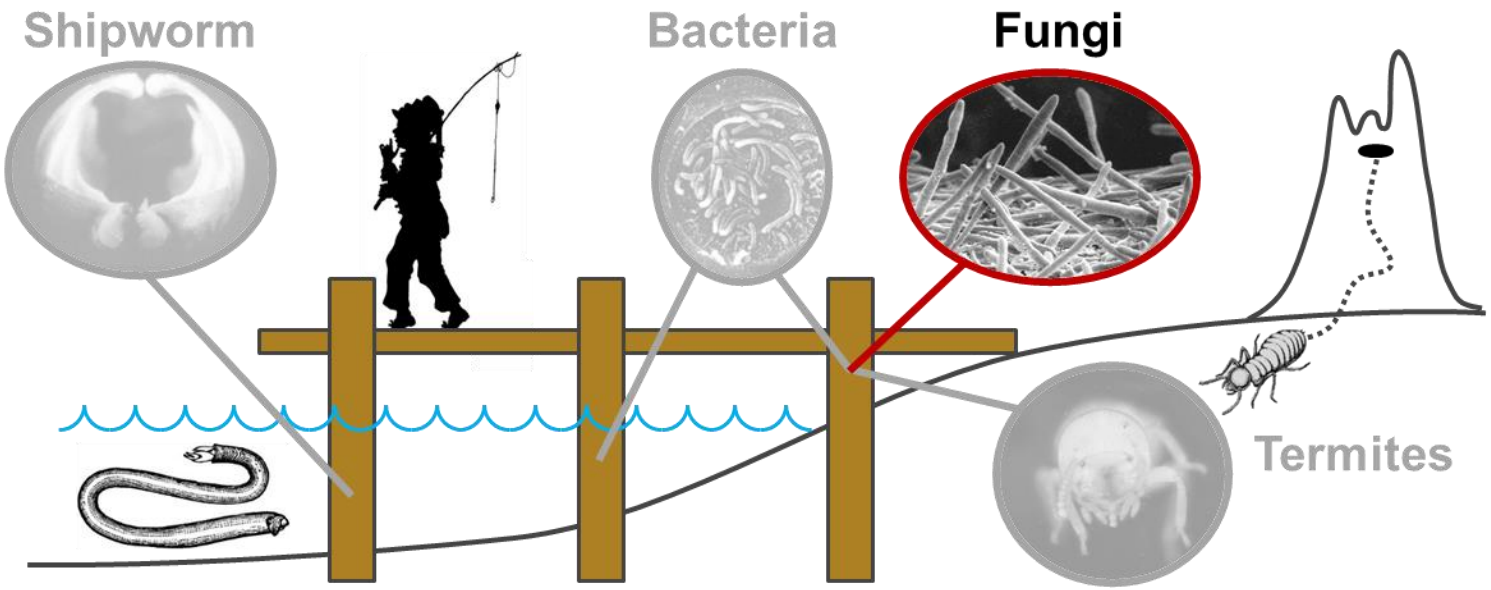


Implications for durability of biobased materials

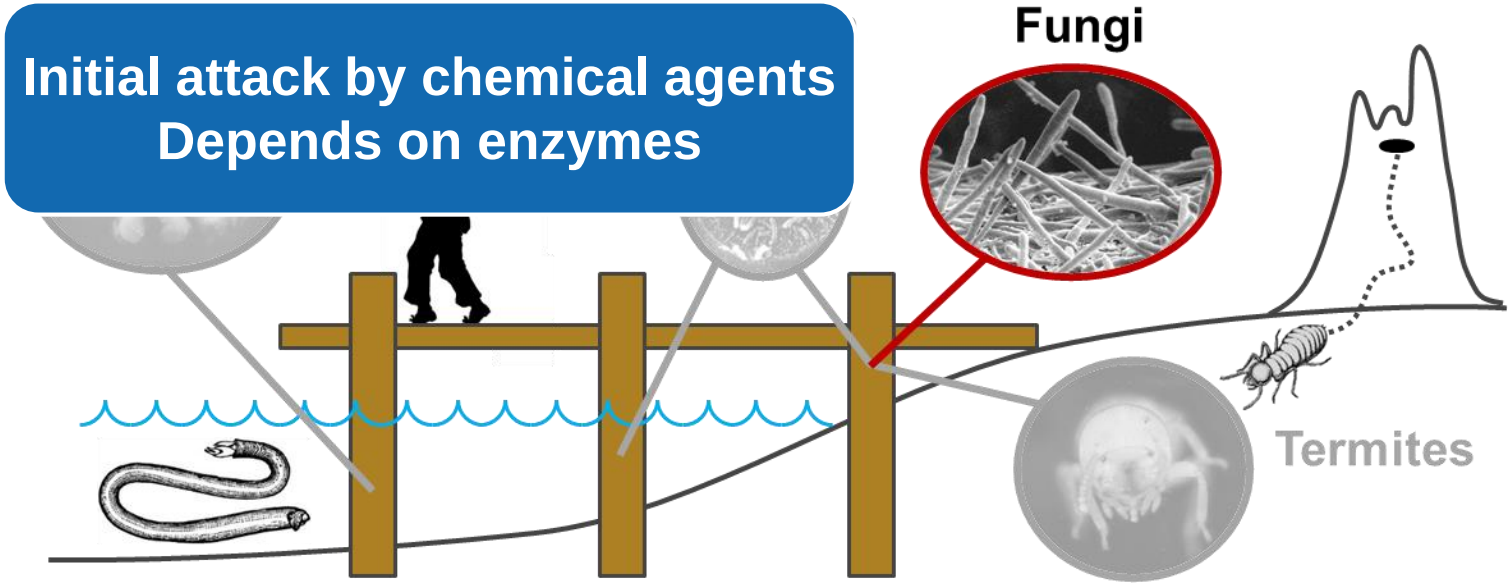
Biological degradation agents



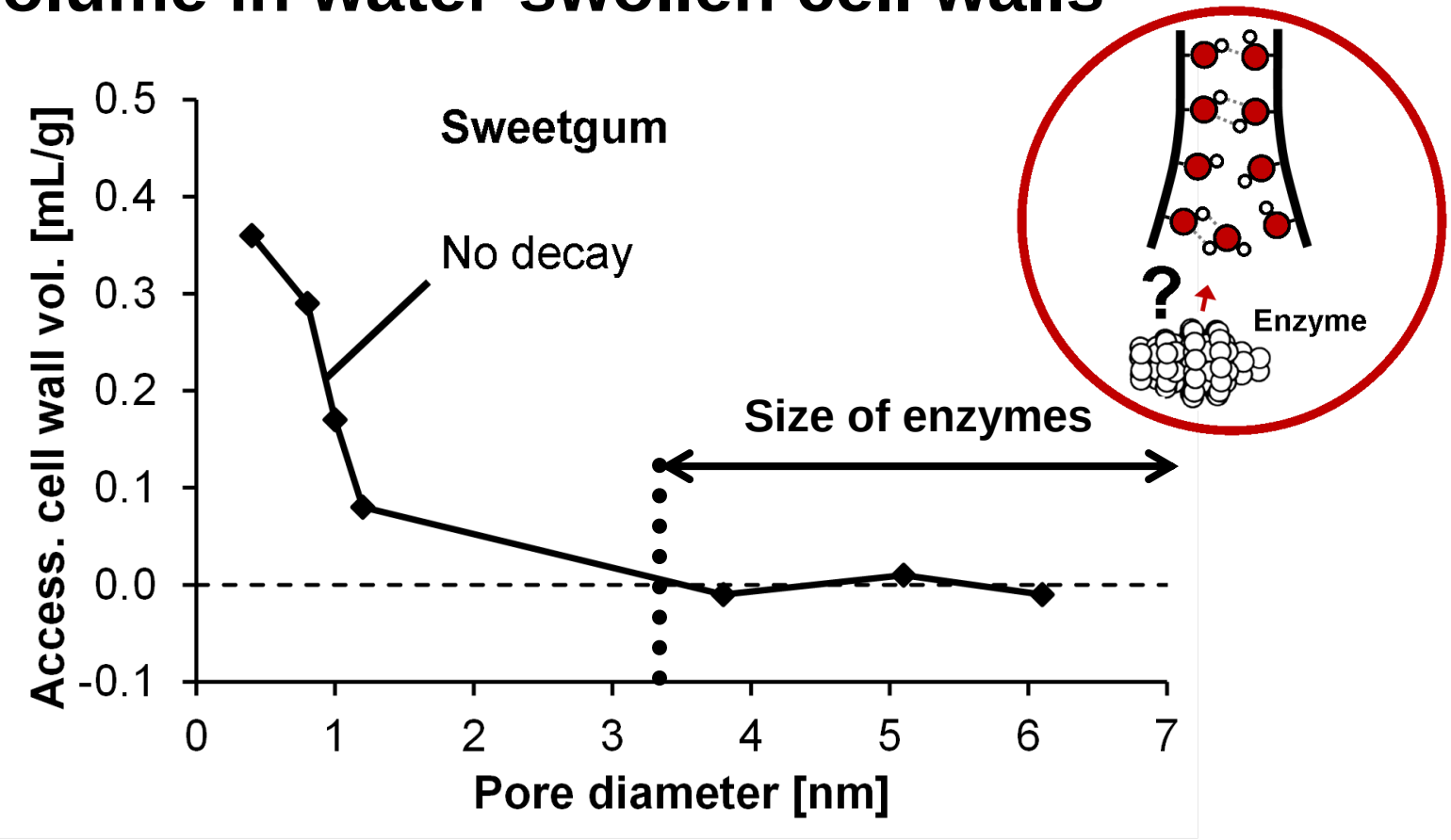
Fungal degradation of wood



Fungal degradation of wood

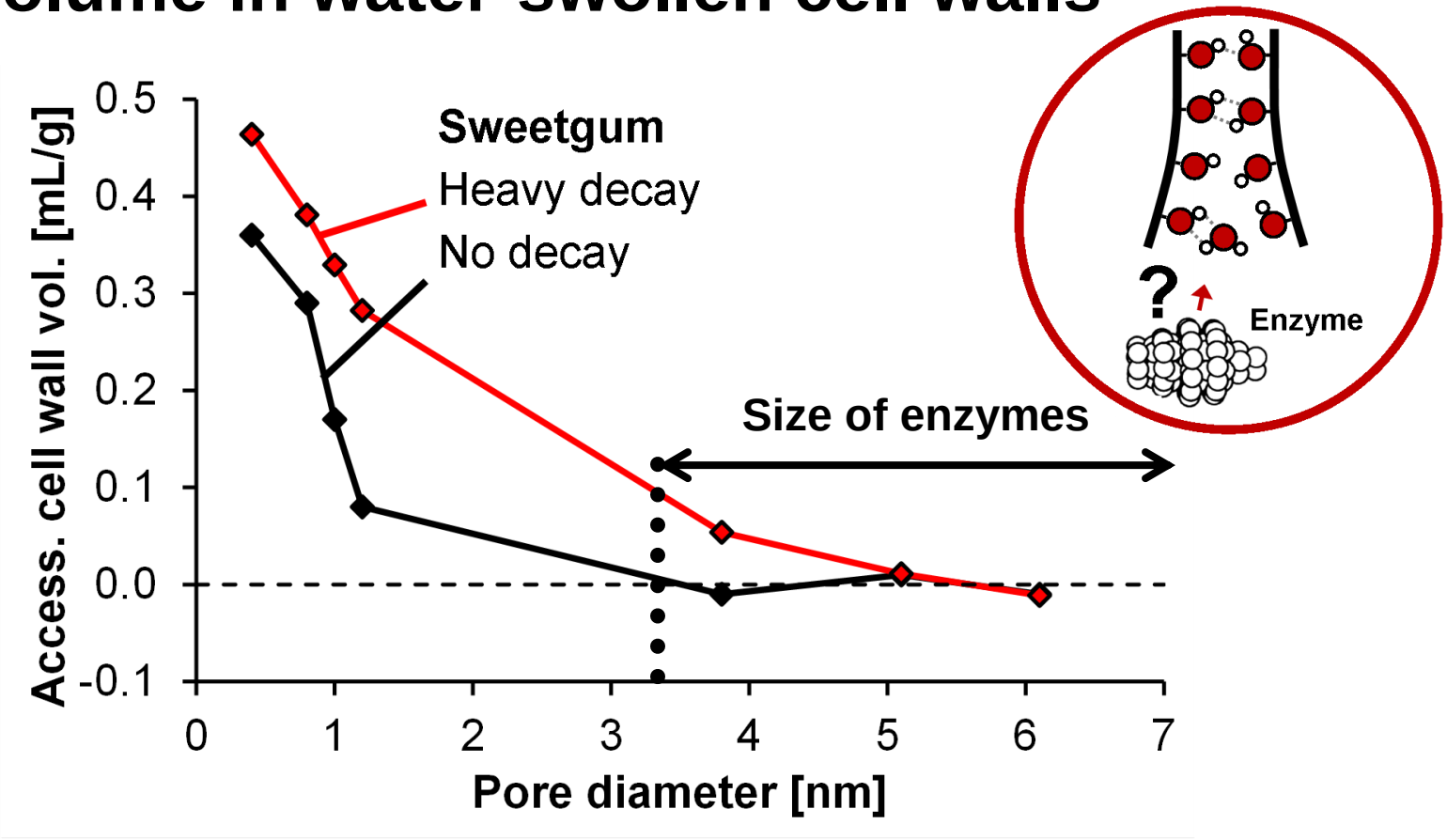


Pore volume in water-swollen cell walls



Flournoy et al. (1991) Holzforschung,45:383

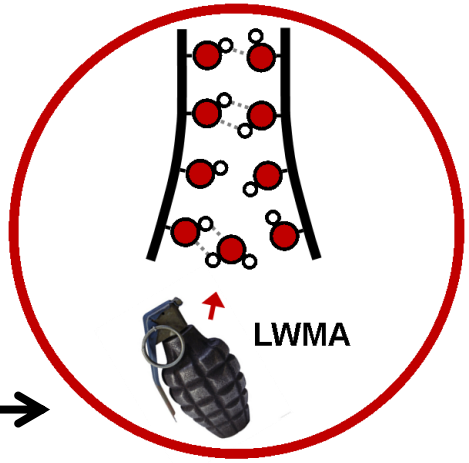
Pore volume in water-swollen cell walls

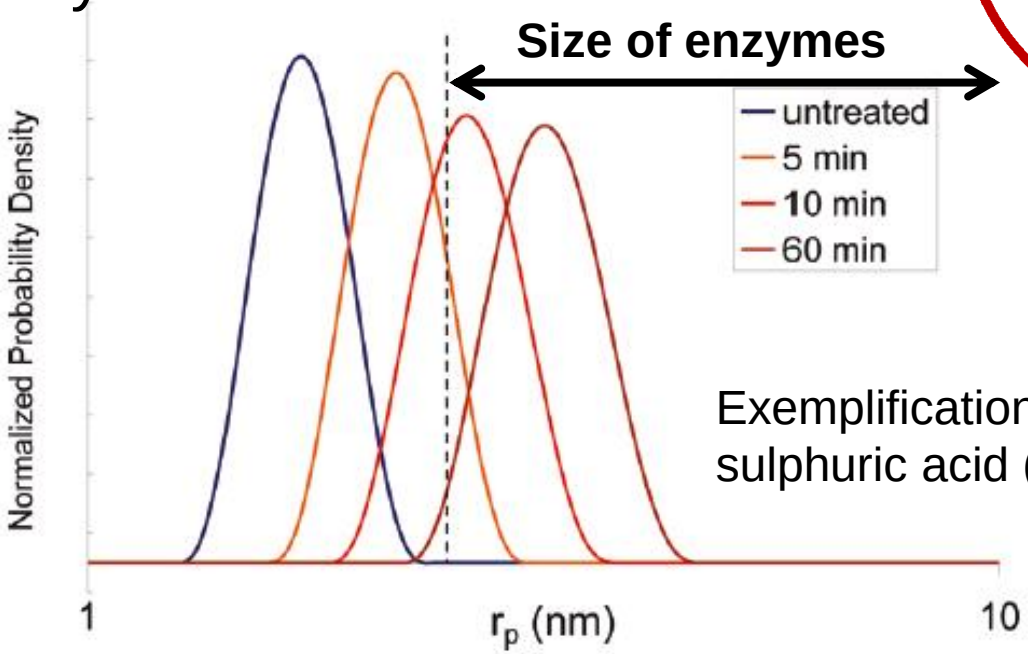


Flournoy et al. (1991) Holzforschung,45:383

Increasing cell wall nano-porosity

Fungi use low weight molecular agents (LWMA) to increase porosity and allow access for enzymes

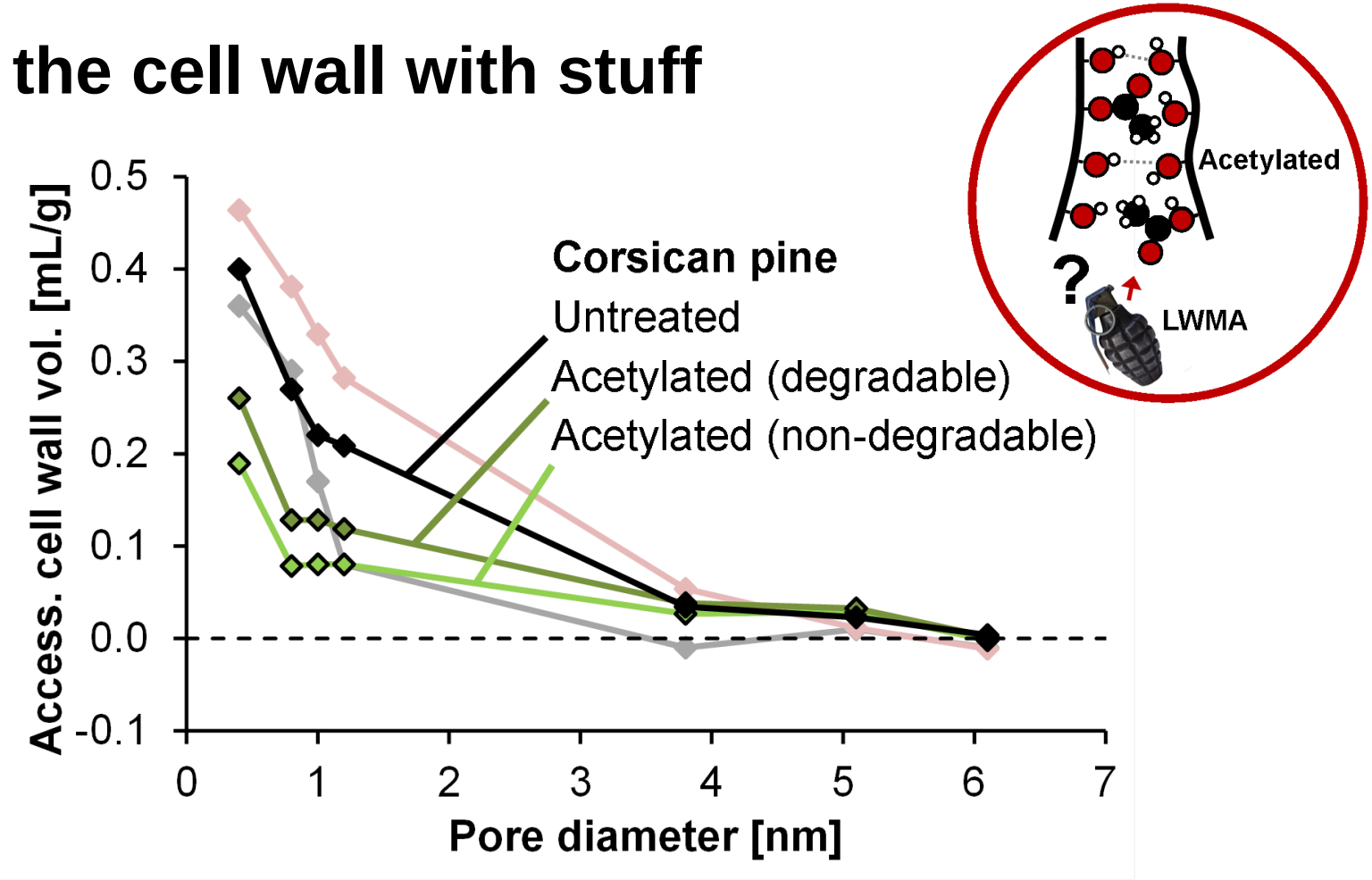




Exemplification using dilute sulphuric acid (H_2SO_4)

Foston and Ragauskas (2010) Energ Fuel, 24:5677

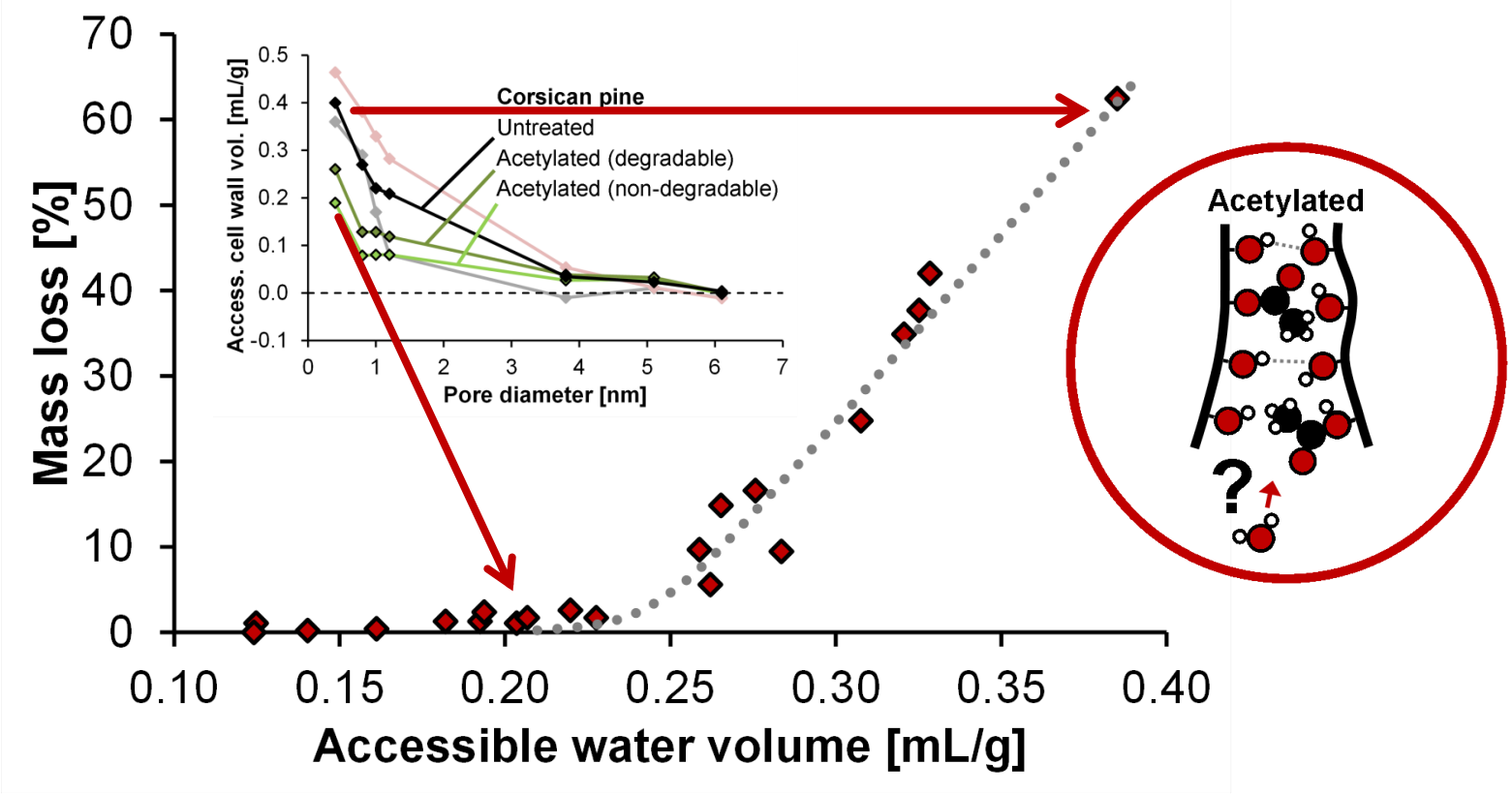
Filling the cell wall with stuff



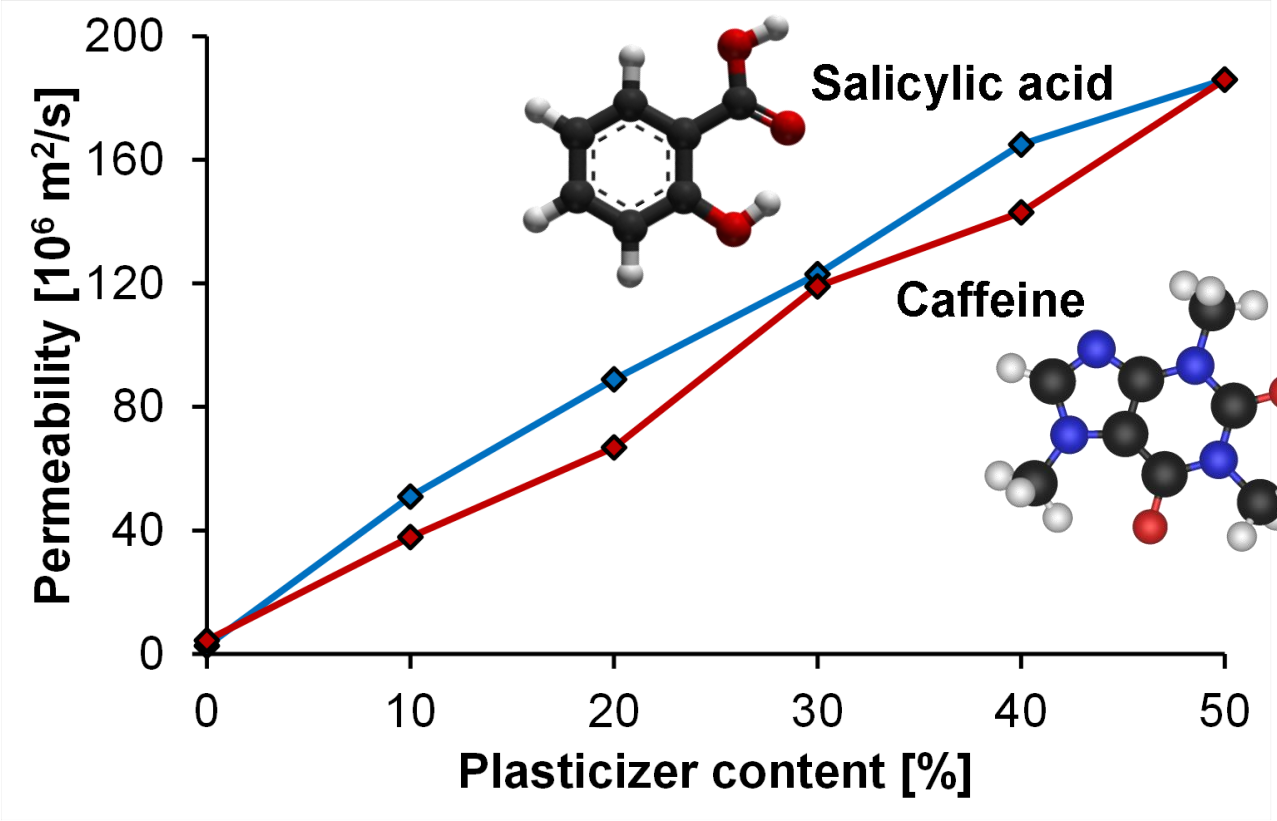
Hill (2009) Wood Mater Sci Eng, 4:37

Moisture capacity and decay limit

Differently sized anhydrides = OH-substitution **not** important



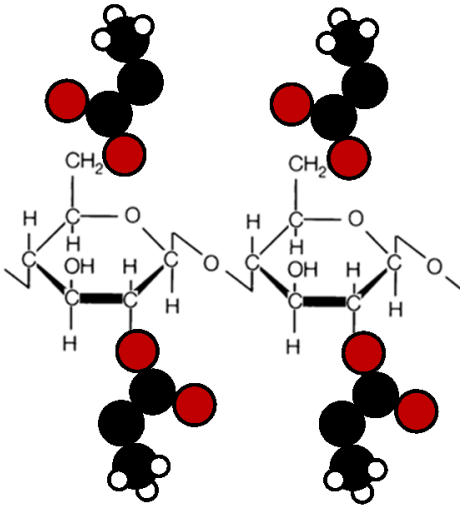
Permeability of small molecules in ethylcellulose

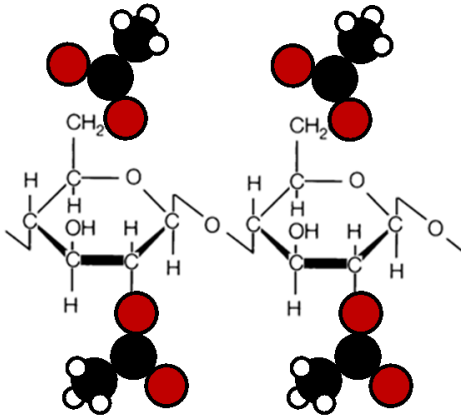


Steric hindrance in modified biobased films?

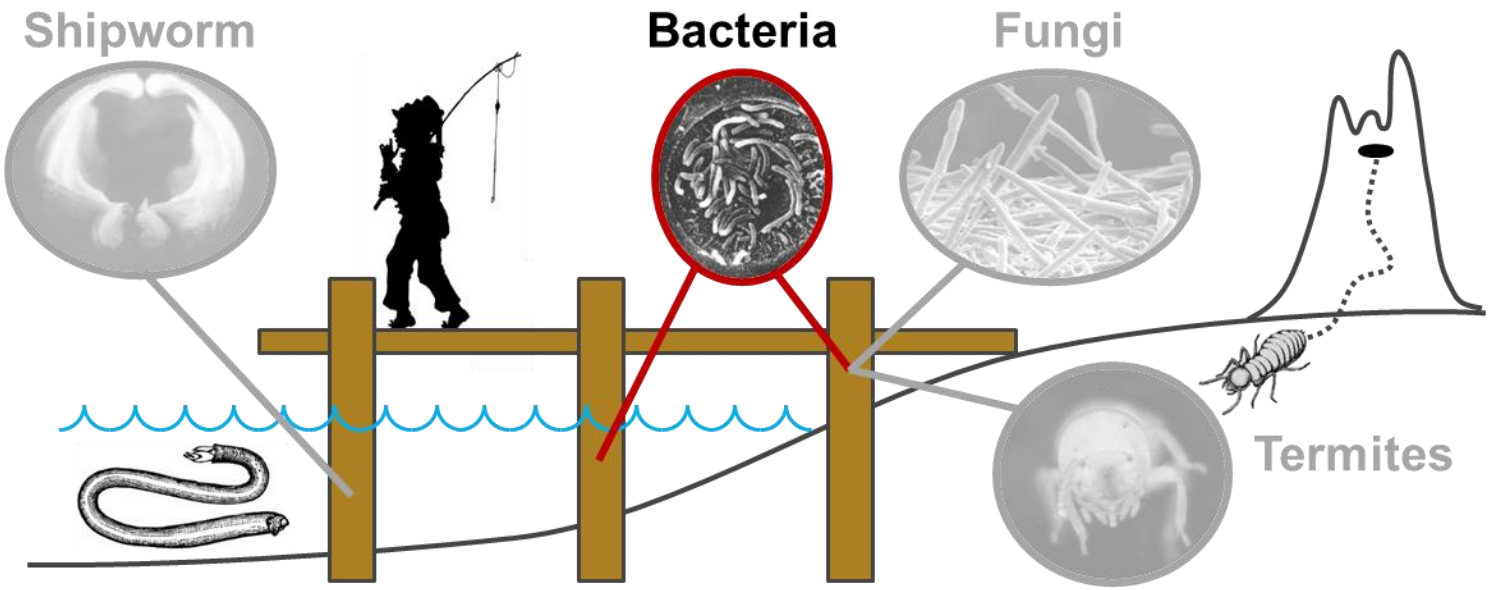
Cellulose acetate (C2) is not durable against microbial decay

Cellulose propionate (C3) is durable when > 4 OH-groups are substituted





Bacterial degradation



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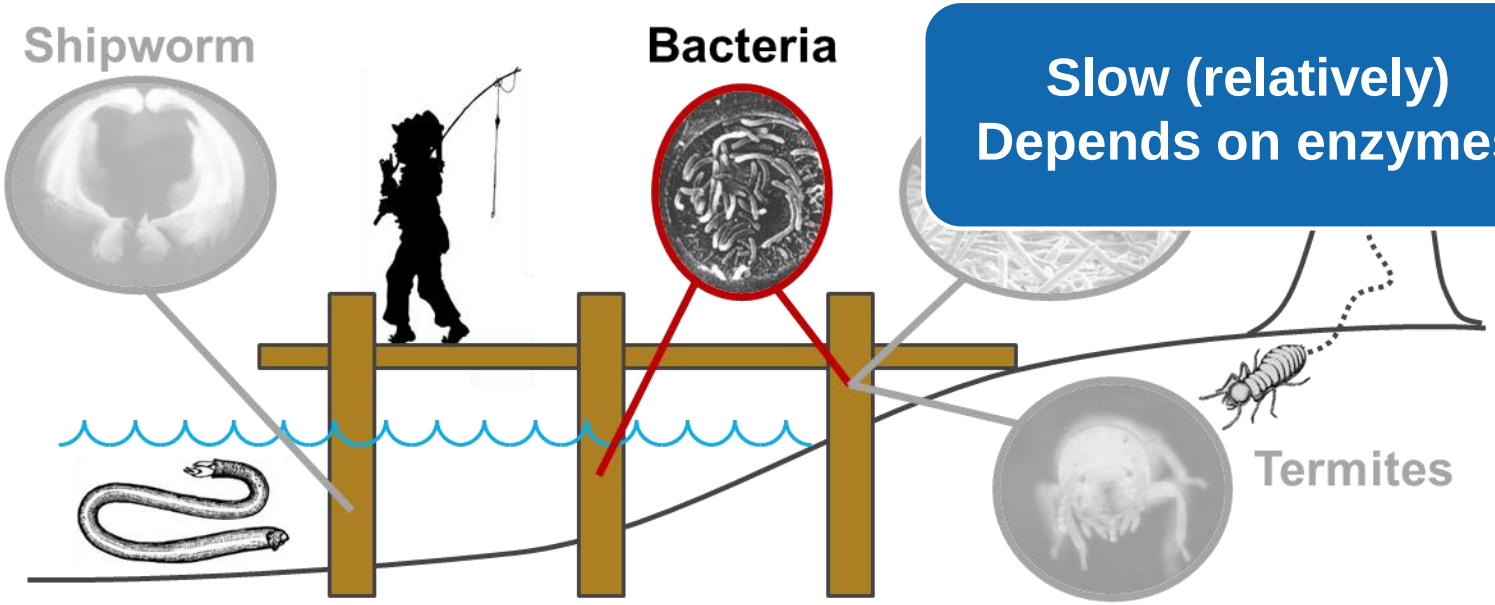
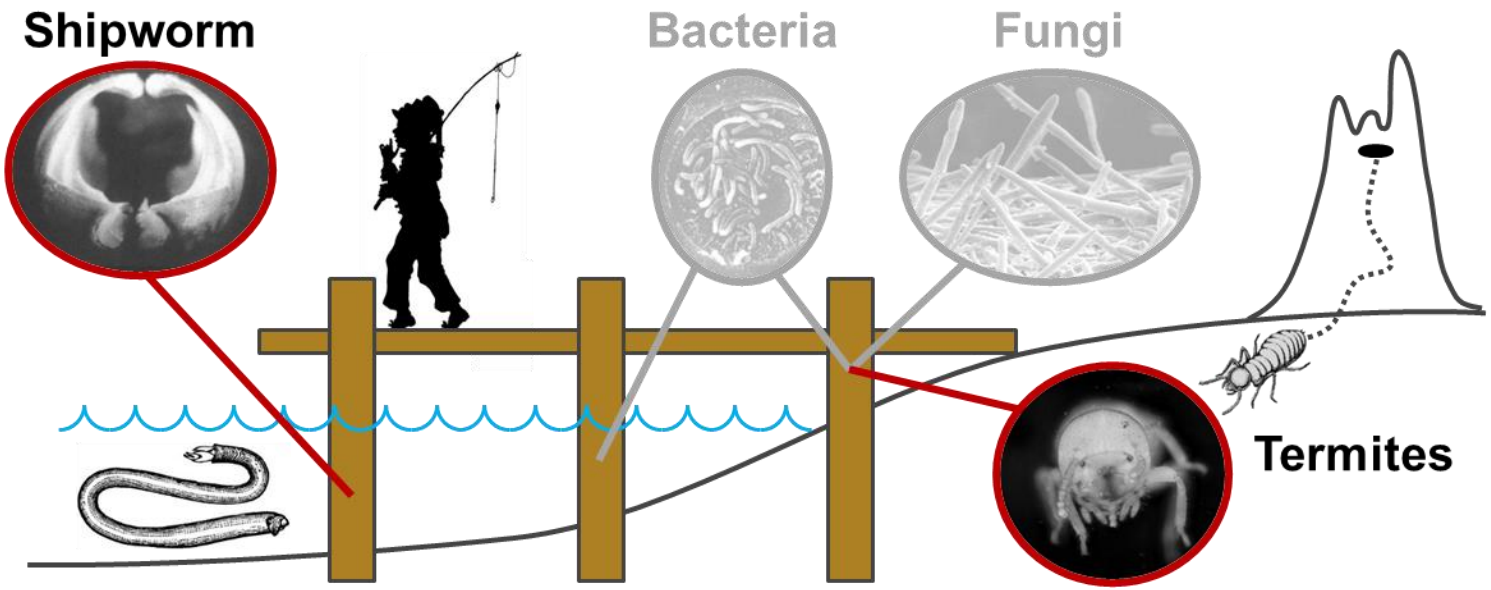
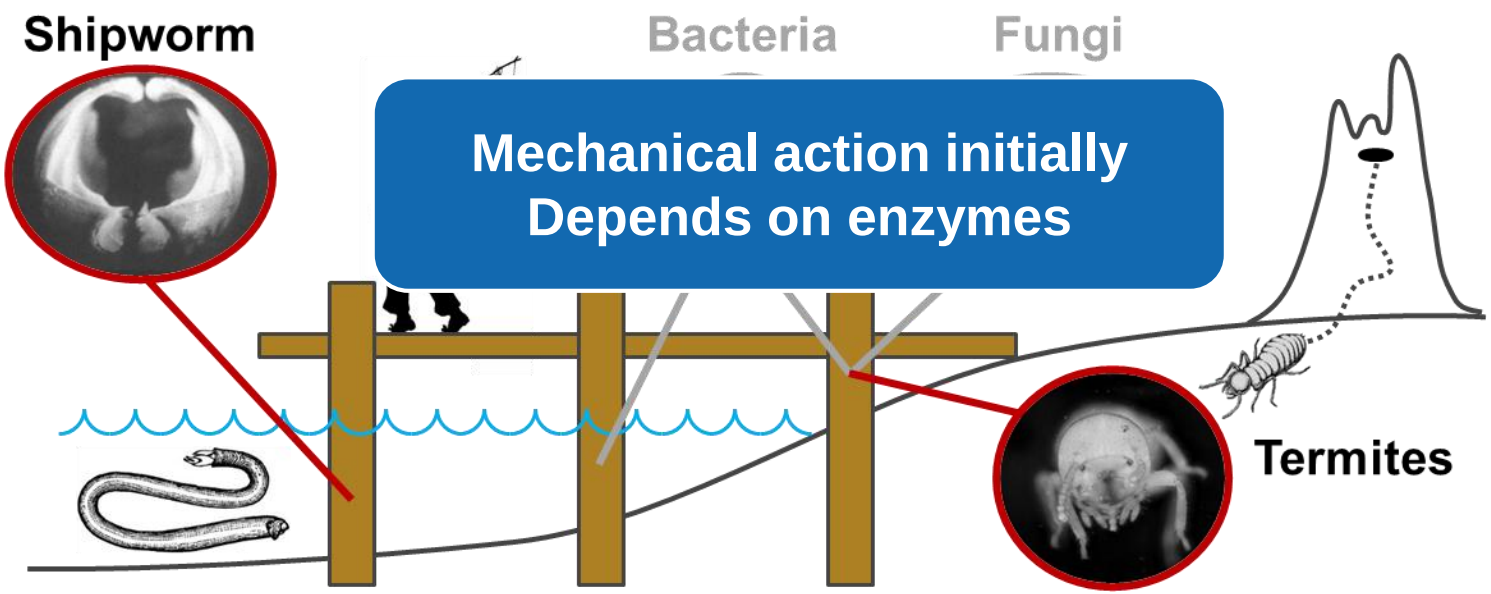


Slow (relatively)
Depends on enzymes

Shipworm and termites



Shipworm and termites



Mechanical action initially
Depends on enzymes

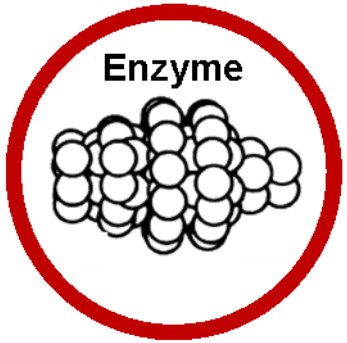
Summary

Degradation by organisms ultimately depends on enzymes

Swelling in water is not enough for dense biomaterials

Enzymes are good but

Physical / chemical violence + enzymes = better



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Thank you…