Moisture sorption in modified wood

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Outline

- Service performance and moisture sorption
- Wood modification types
- Moisture sorption isotherm
- Comparing sorption isotherms
- Modification type vs. sorption isotherm shape
- Discussion: various sorption theories
- Conclusions

Service performance and moisture

Empirical fact: moisture exclusion from cell wall substance leads to improved service performance

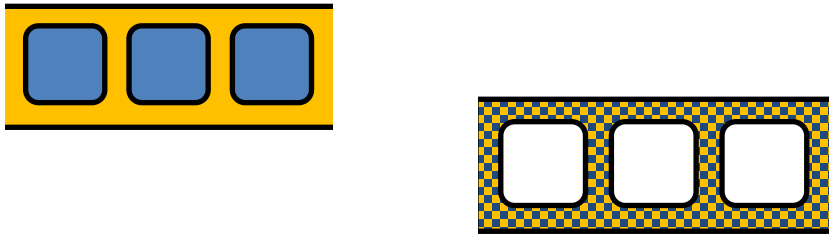
- Less movement & less degradation in service

-> Significance of reducing water sorption capacity of the fiber – only the part which is responsible for swelling.

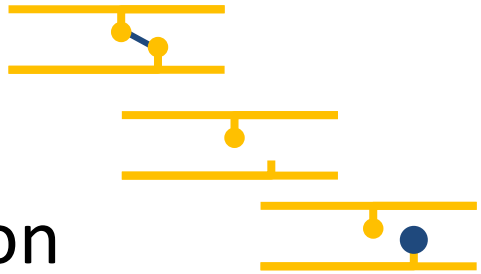
-> No fundamental improvement obtained on fiber lumen filling treatments

Wood modification types

- Lumen filling
- Cell wall bulking



- Cell wall cross-linking
- Sorption site removal
- Sorption site substitution



Modification treatments are mostly hybrid type.
Separation of types by water sorption studies?

Moisture sorption isotherm

- Describes equilibrium: EMC(RH,T)
- *or* EMC(μ,*T*)

  $\mu = RT \ln h$, h = RH/100

  chemical potential

- Physical adsorption: treat as a co-existent phase of water

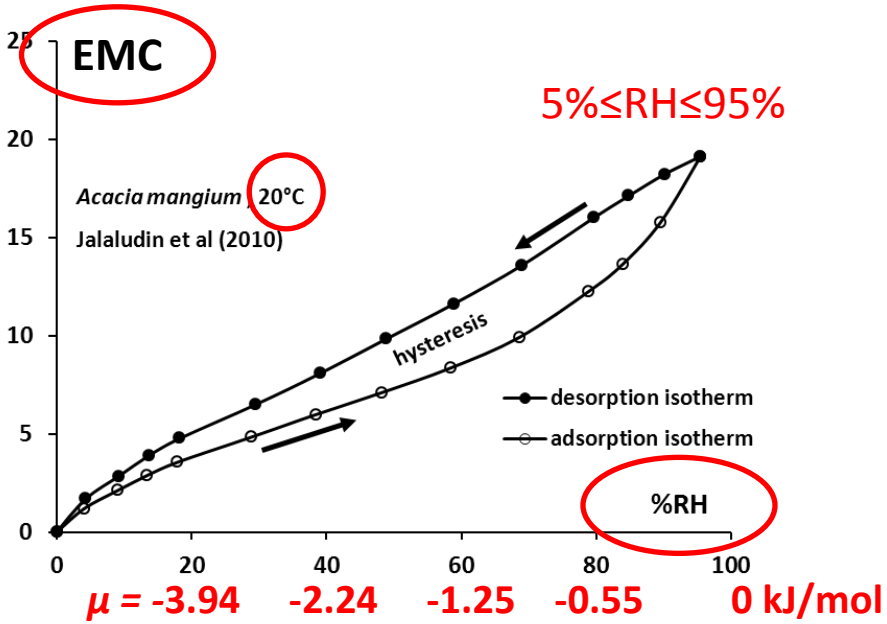
  $\mu_{ads} = \mu = RT \ln h$

  EMC = EMC(μ)

  Polanyi (1916)

Explanation:

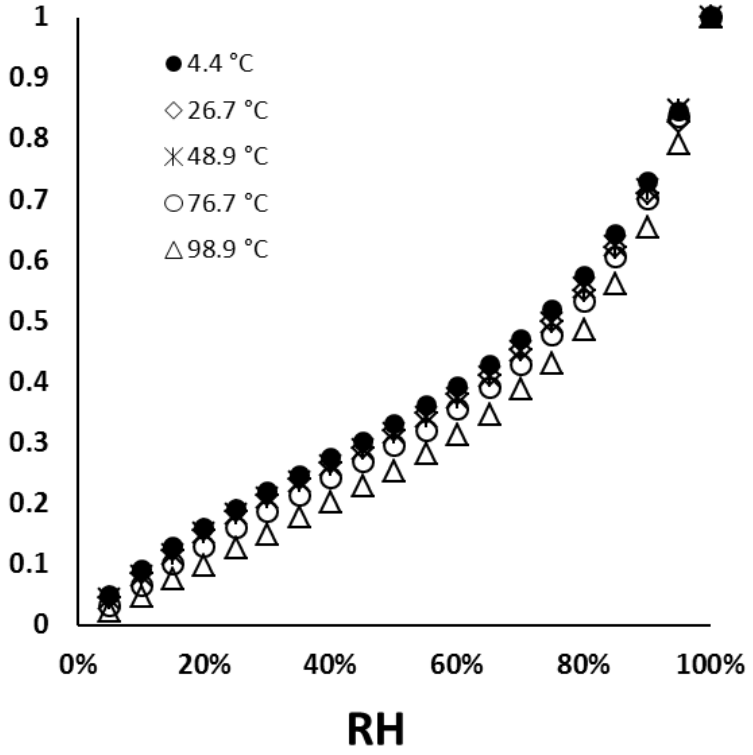
- Bulk water: no equilibrium for h<1 possible
- μ is the necessary extra free energy release by adhesion to obtain equilibrium at h<1



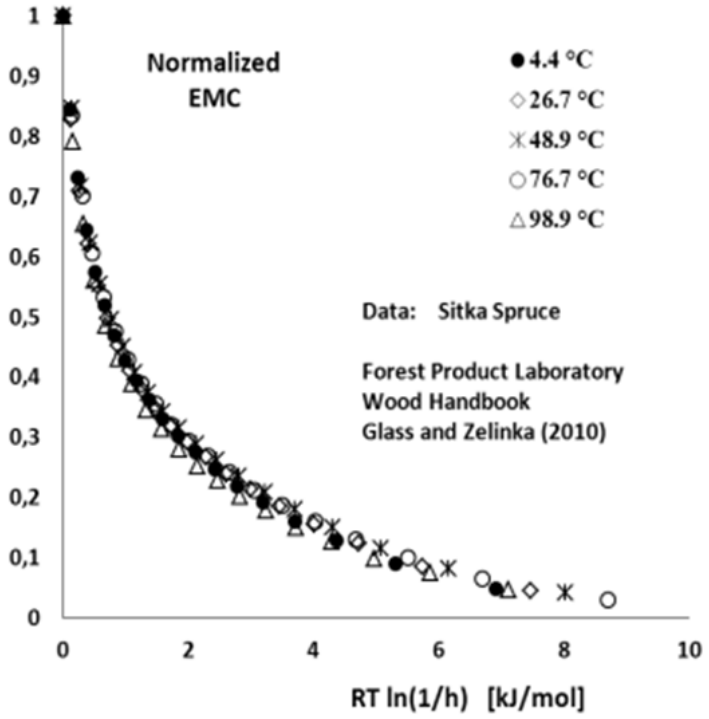
- Compare average thermal energy ≈ 2.5 kJ/mol (20°C)

Moisture sorption isotherm as a function of:

humidity



chemical potential



Origin of the sigmoid shape of adsorption isotherm:
non-linear relationship between μ and h

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Comparing Sorption Isotherms control vs. modified wood

- Make comparison at equal vapor conditions (equal $\mu = RT \ln h$), meaning equal RH at <u>one</u> temperature T.
- Beware of trivial EMC changes by dry mass increase/decrease, as a result of modification:

$$EMC = \frac{m_{adsorbed\ water}}{m_{dry\ control}\left(1+\frac{WPG}{100\%}\right)}$$

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Seborg, Tarkow, Stamm (1953):

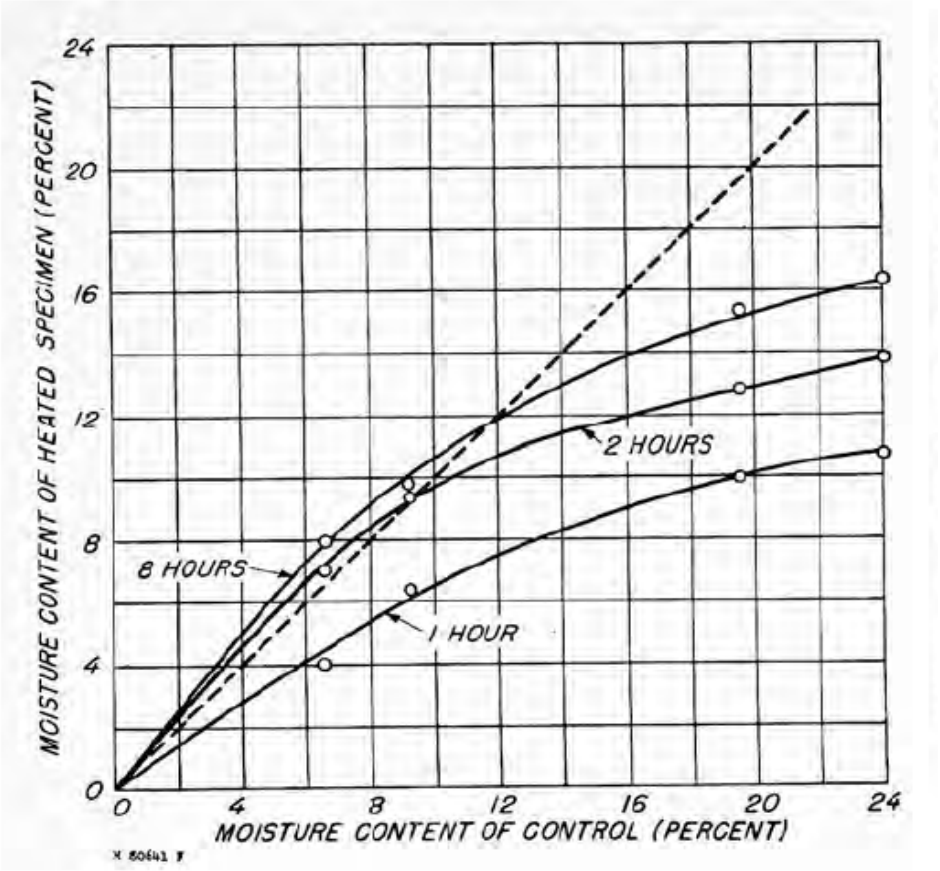


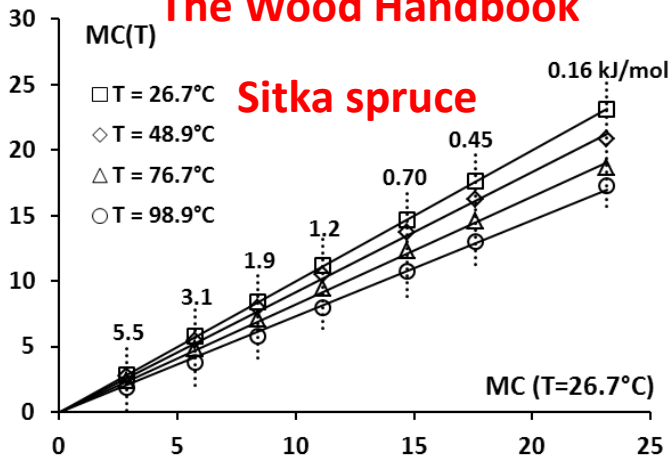
Figure 8.—Relation of equilibrium moisture content of specimens heated for 1 to 8 hours in air at 300° C. to the equilibrium moisture content of the control specimens, which had been exposed to the same relative humidities as the heated specimens.

Moderate Heating

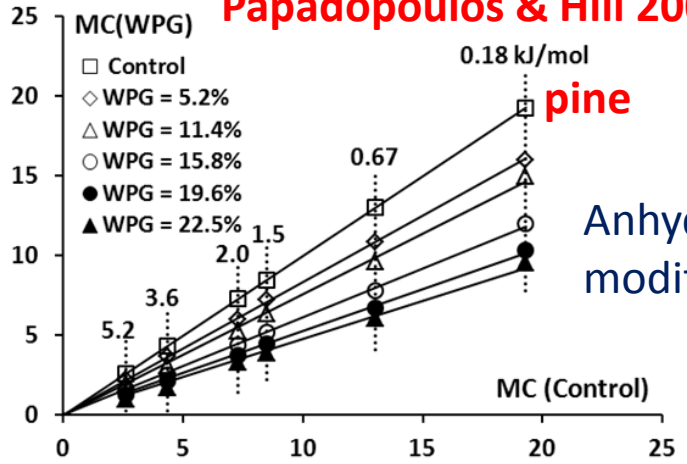
(hornification)

Thermal modification

The Wood Handbook

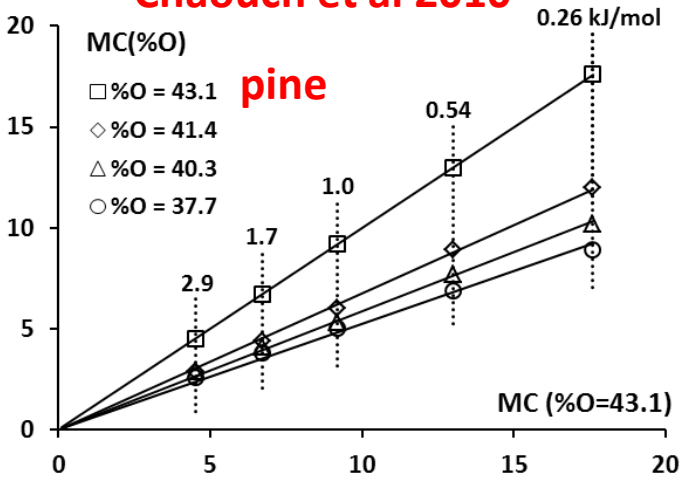


Papadopoulos & Hill 2003

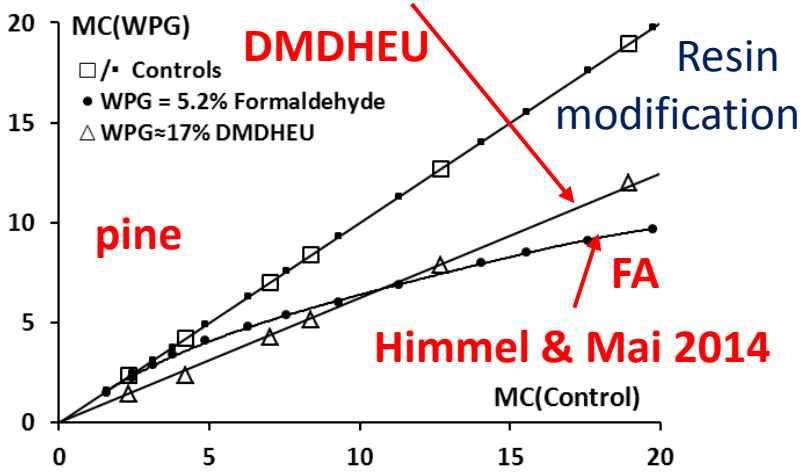


Anhydride modification

Chaouch et al 2010



Papadopoulos & Mantanis 2012



Resin modification

Himmel & Mai 2014

As an approximate empirical rule, wood modifications don't change the shape of the isotherm – only the relative sorption capacity! - exception: FA-treatment.

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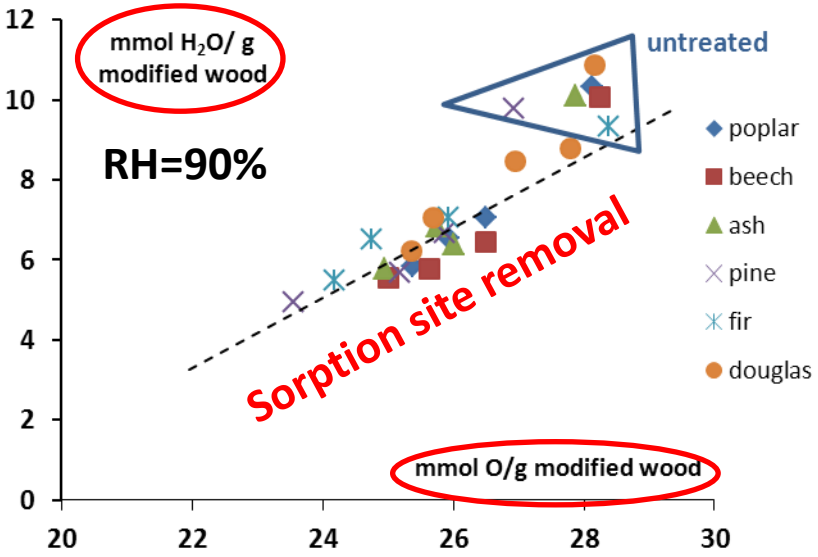
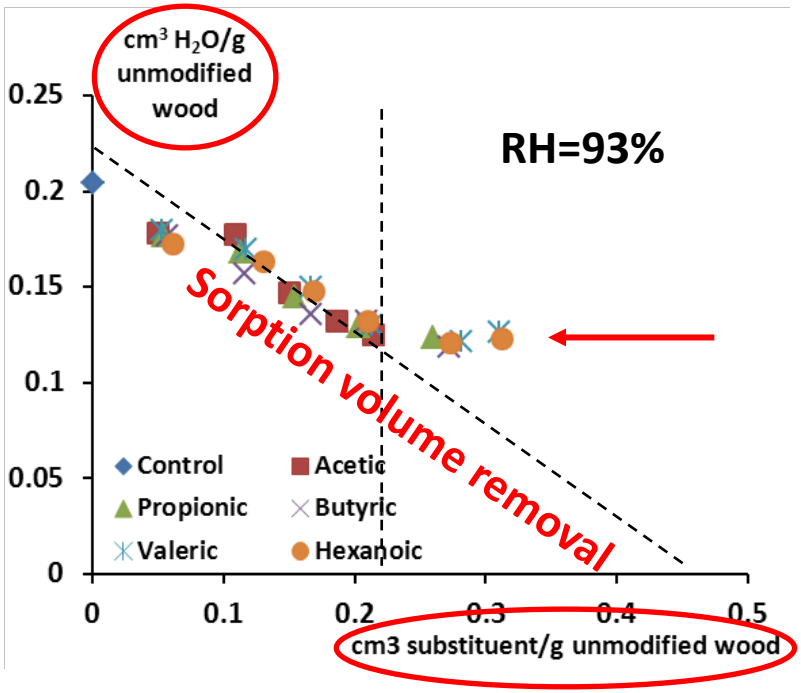
HEAT TREATMENT



Data:
Chouch et al (2010)
Lam (2011)

1 water sorption site loss per removed hydroxyl group

CARBOXYLIC ANHYDRIDES



Data:
Papadopoulos and Hill (2003)

1 cm^3 water sorption capacity loss per 2 cm^3 substituent

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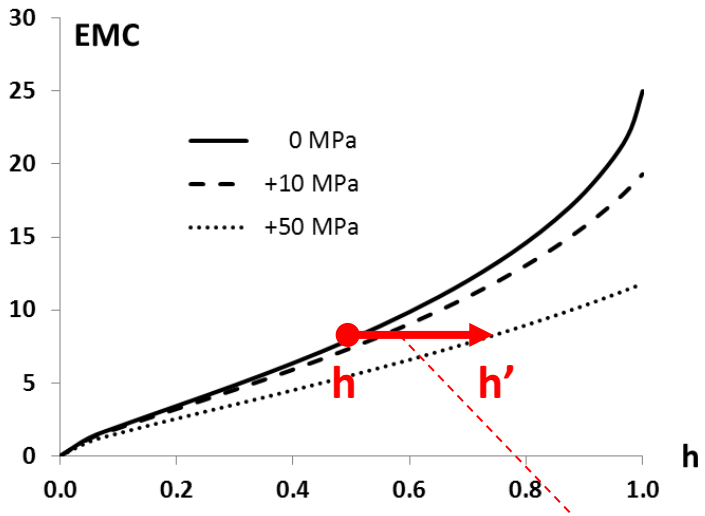
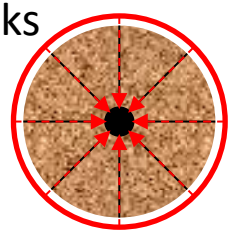
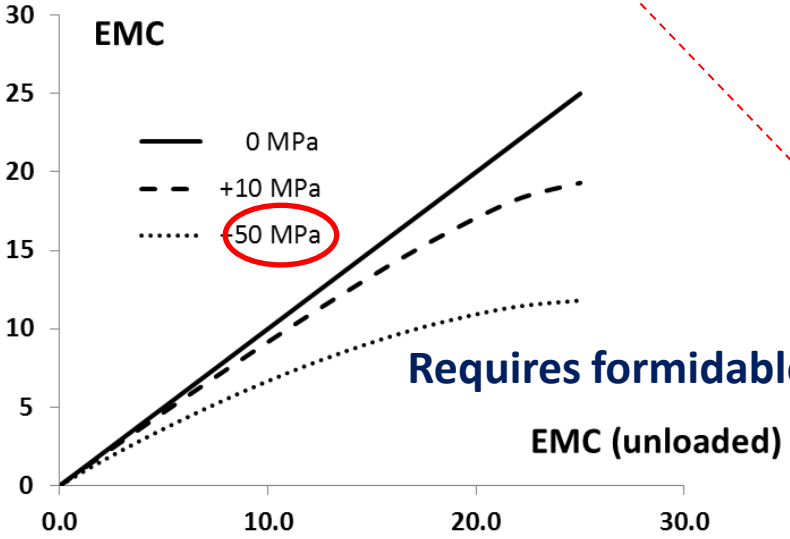
EFFECT OF STRONG CROSS-LINKING ON EMC



Cross-links



Restrained hygro-expansion
= effective compressive stress **P**



Shift by work of compression:

$RT \ln 1/h - RT \ln 1/h' = v_m P$

Requires formidable stress!

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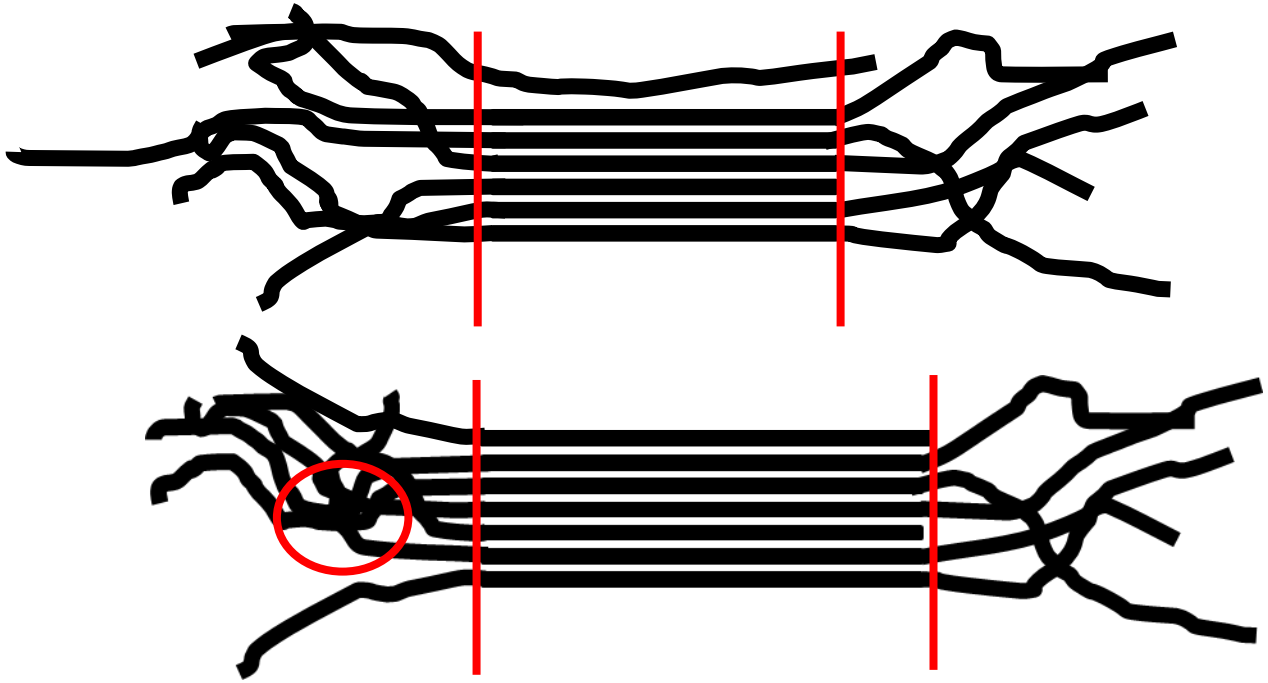
EFFECT OF WEAK CROSS-LINKING ON EMC



- Loss of sorption sites or accessible volume
- No restrained swelling effect on EMC

Discussion: various sorption theories

- For most modification treatments,

  EMC ≈ k . f $\quad$ k = sorption capacity

  f = sigmoid function of h

  or decay function of μ

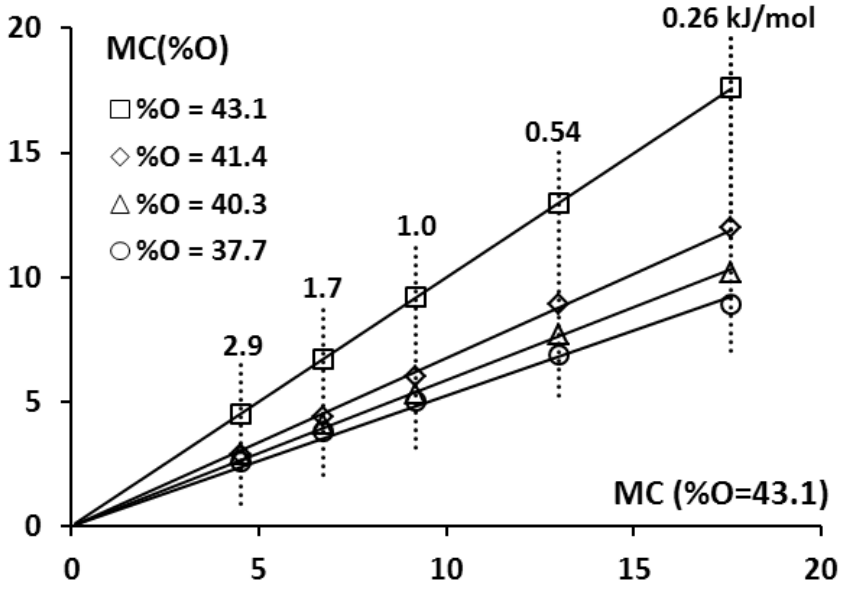
- Multilayer sorption theories have such factor "k", but were found physically unrealistic (Willems 2014).
- Free volume theory (Vrentas& Vrentas 1991) assign low vs. high h part of the isotherm to glassy vs. viscoelastic behavior – unlikely described by simple "k".

Dicussion: various sorption theories

- Recent site occupancy model Willems(2014): EMC ≈ k . f, uses $f(h)=h^{0.73}$, which is not a sigmoid function leading to $k=k(h)$ ≠ constant!
- Site occupancy model improvement with new microscopic bonding model of moisture in wood under development…..

Conclusions

- Only very strong cross-links can significantly modify the sigmoid shape of water sorption isotherm (well understood)
- All other modifications mainly change the sorption capacity (not well understood)
- Trivial effects of dry mass changes (“reduced EMC”)
- None of existing sorption theories offers full account of all wood modification effects



Thank you for your attention!

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