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VirginiaTech

Application of small-specimen rheology and ^2H quadrupolar interaction in biomass analysis

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Virginia Tech

Global research objective

"Develop and optimize analytical techniques to investigate the morphology of in-situ lignocelluloses."

Techniques:

– Submersion-Torsion Rheology

– Nuclear Magnetic Resonance (NMR)

Submersion-Torsion Rheology

Objective:

Develop a novel solvent submersion rheological technique, with very small specimens.

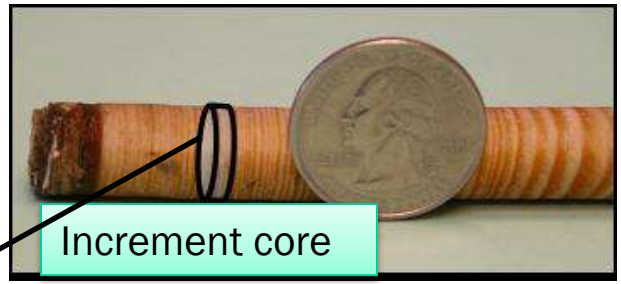
- Effect of tissue maturity.
- Effect of fungal degradation.
- Effect of wood modifier.

Rationale

Smallest possible DMA specimen

A sapling stem can be rheologically tested

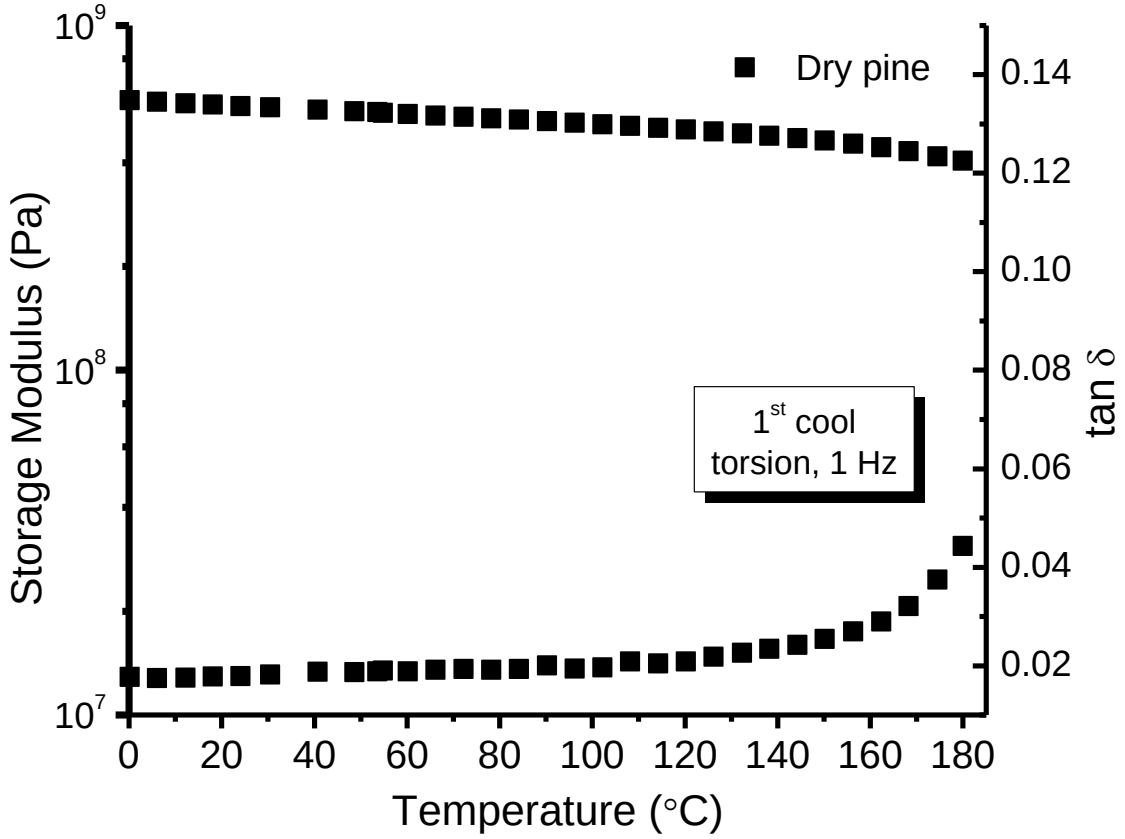
8 mm



Specimens can be excised from tree increment core

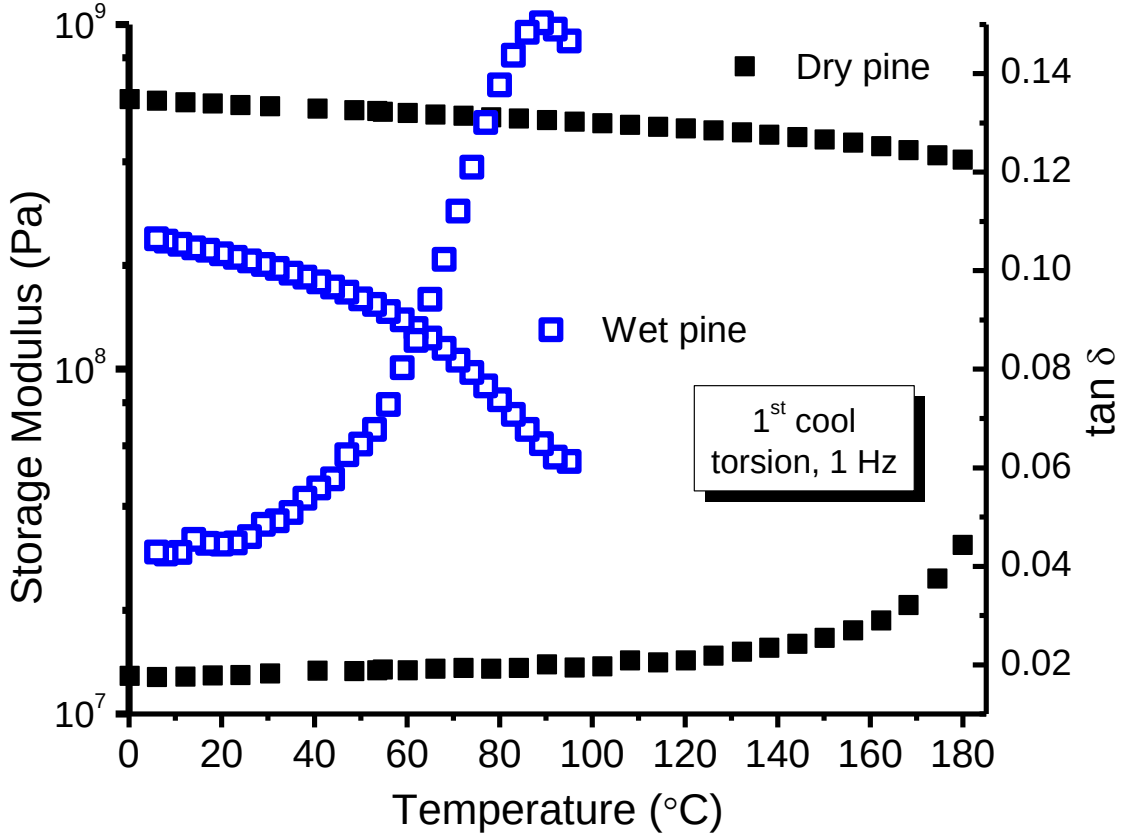
Polymer mobility of treated biomass can be tested

Why solvent submersion?



- Dry specimens exhibit weak relaxations.
- Major softening occurs with thermal degradation.

Why solvent submersion?

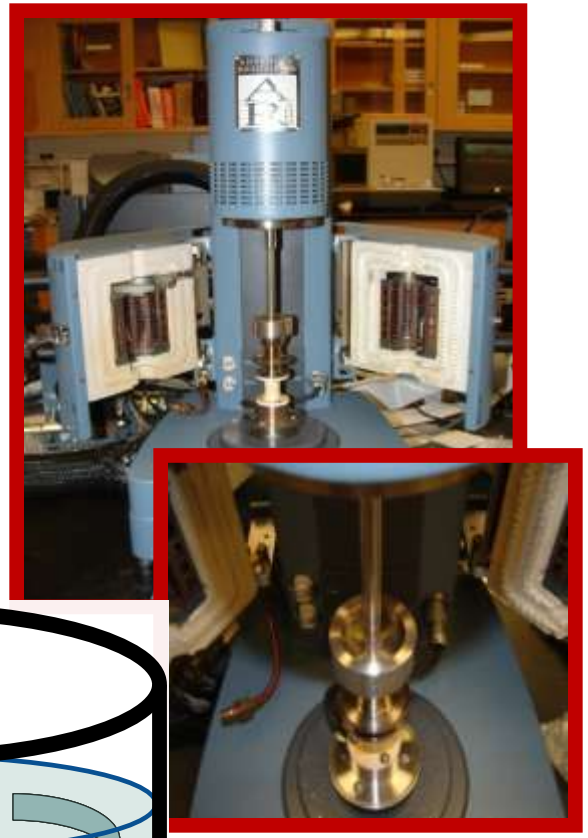


- Dry specimens exhibit weak relaxations.
- Major softening occurs with thermal degradation.
- Plasticizer immersion reveals more information,
- With narrow temp. range.

Submersion-Torsion Rheology

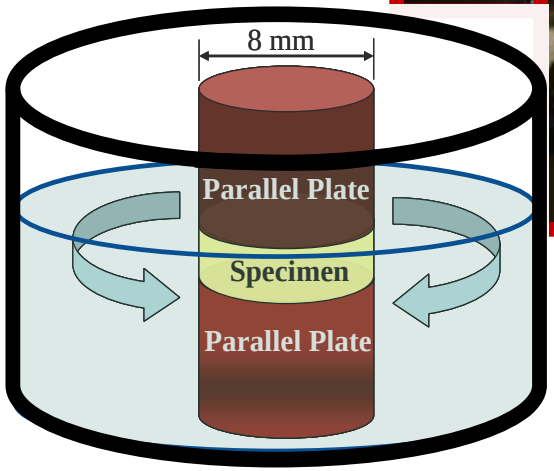
- Cylindrical discs:
  - 8 mm dia. 100μm to 6 mm thick.

- Discs impregnated with plasticizers.

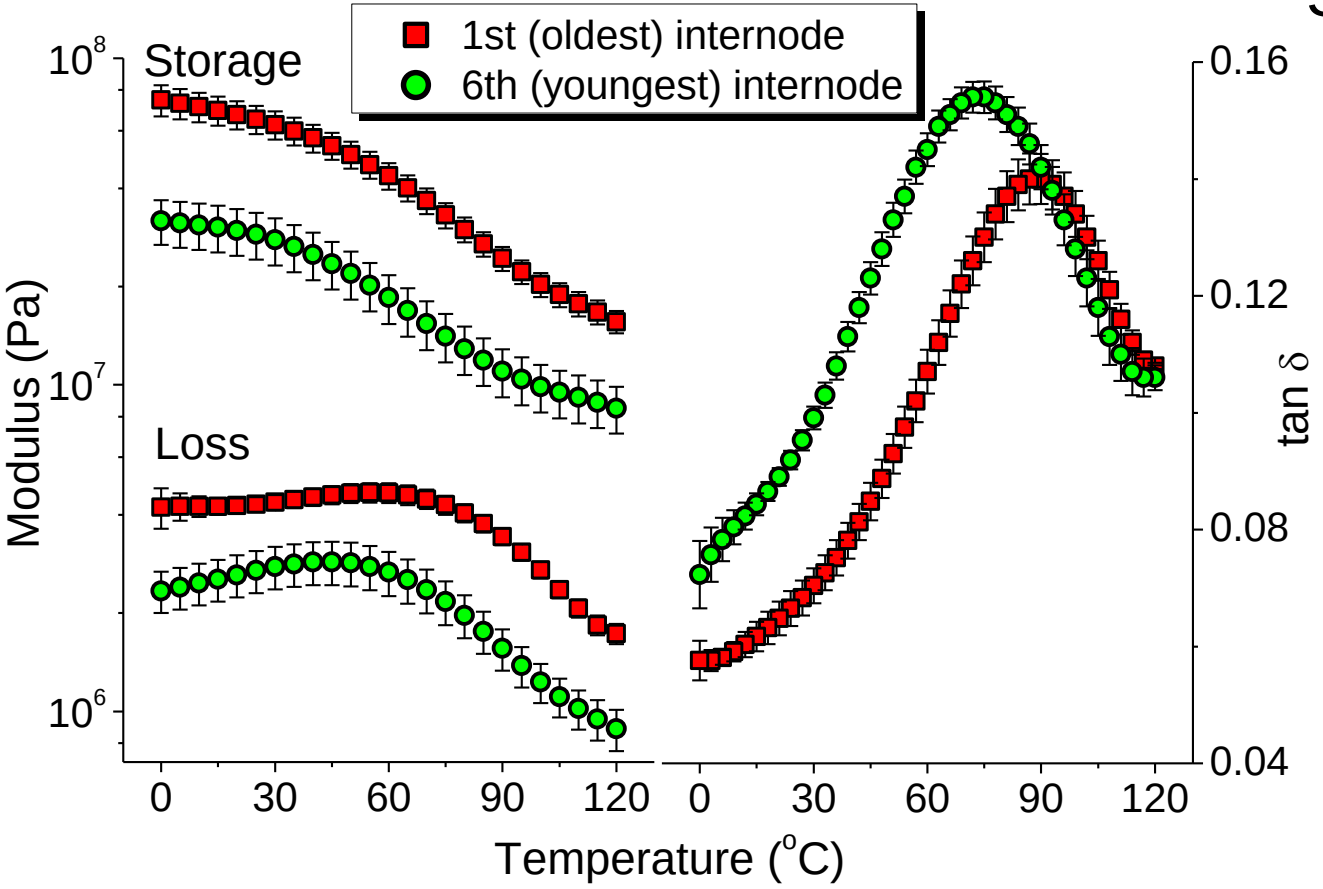


Compressive normal force holding specimens between the plates.

Dynamic/static torsion while under the solvent.

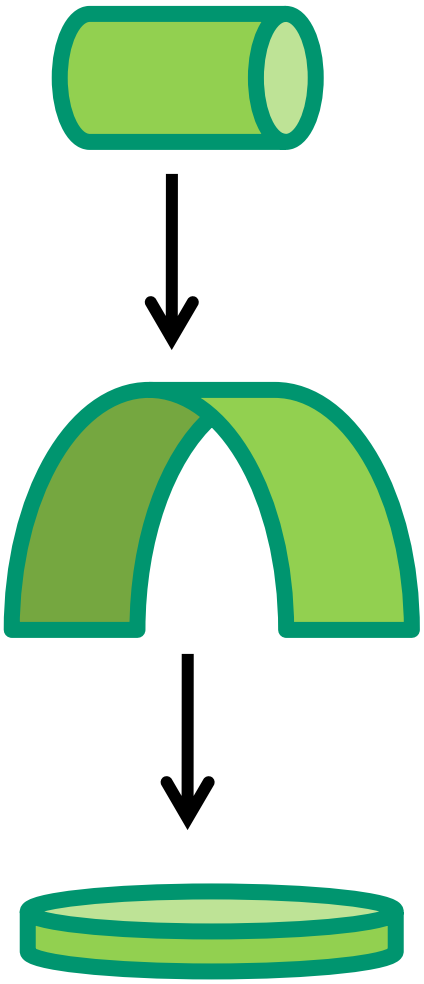


Compressive-torsion excels with very small specimens



Avg. cooling scans of switchgrass stem as a function of tissue maturity as indicated (In ethylene glycol, 2°C/min, 1 Hz); error bars = ± 1 standard deviation, n=3.

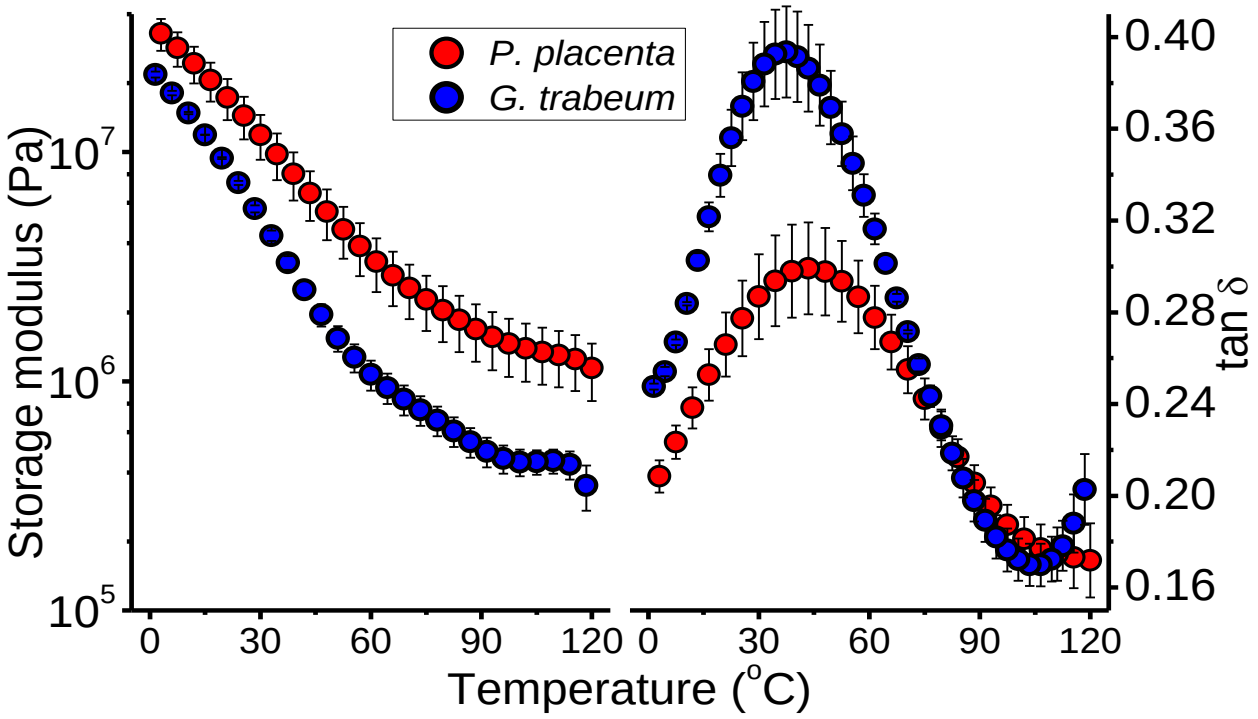
Switchgrass stem



0.6 mm thick, 8 mm dia

Chowdhury et al. ***Holzforschung***, 64, 747

…and specimens lacking mechanical integrity

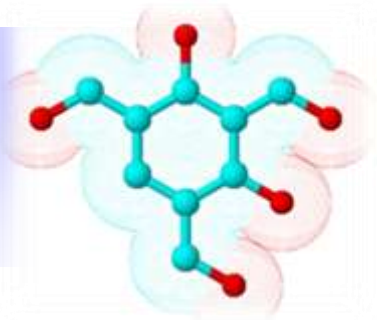


1. Fungal degradation to 50-56% mass loss.
2. Grind in liquid N_2.
3. Suspend/saturate in Et-glycol.
4. Filter; transfer filter-cake to rheometer.
5. 10 N normal force.

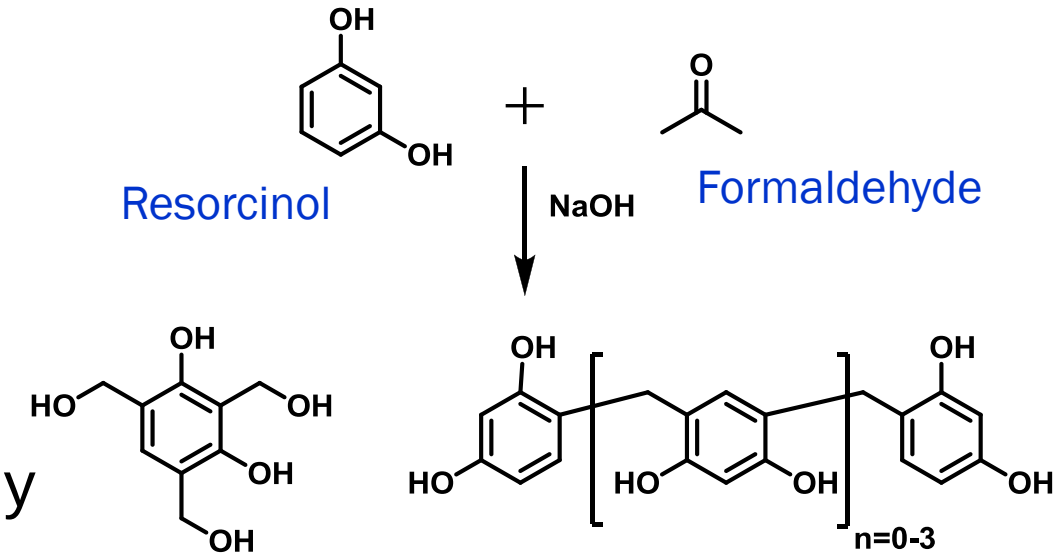
Avg. cooling scans of spruce fiber mats resulting from fungal biodegradation as indicated (In ethylene glycol, 3°C/min, 5 Hz); error bars = ± 1 standard deviation, n=3.

Chowdhury et al. ***Holzforschung***, 64, 747

Hydroxymethyl resorcinol (HMR)



- Aqueous alkaline resorcinol/ formaldehyde reacted at room temp for 4hrs.
- 5% solids; pH of 8.4
- HMR solution applied to wood; allowed to dry; apply adhesive.

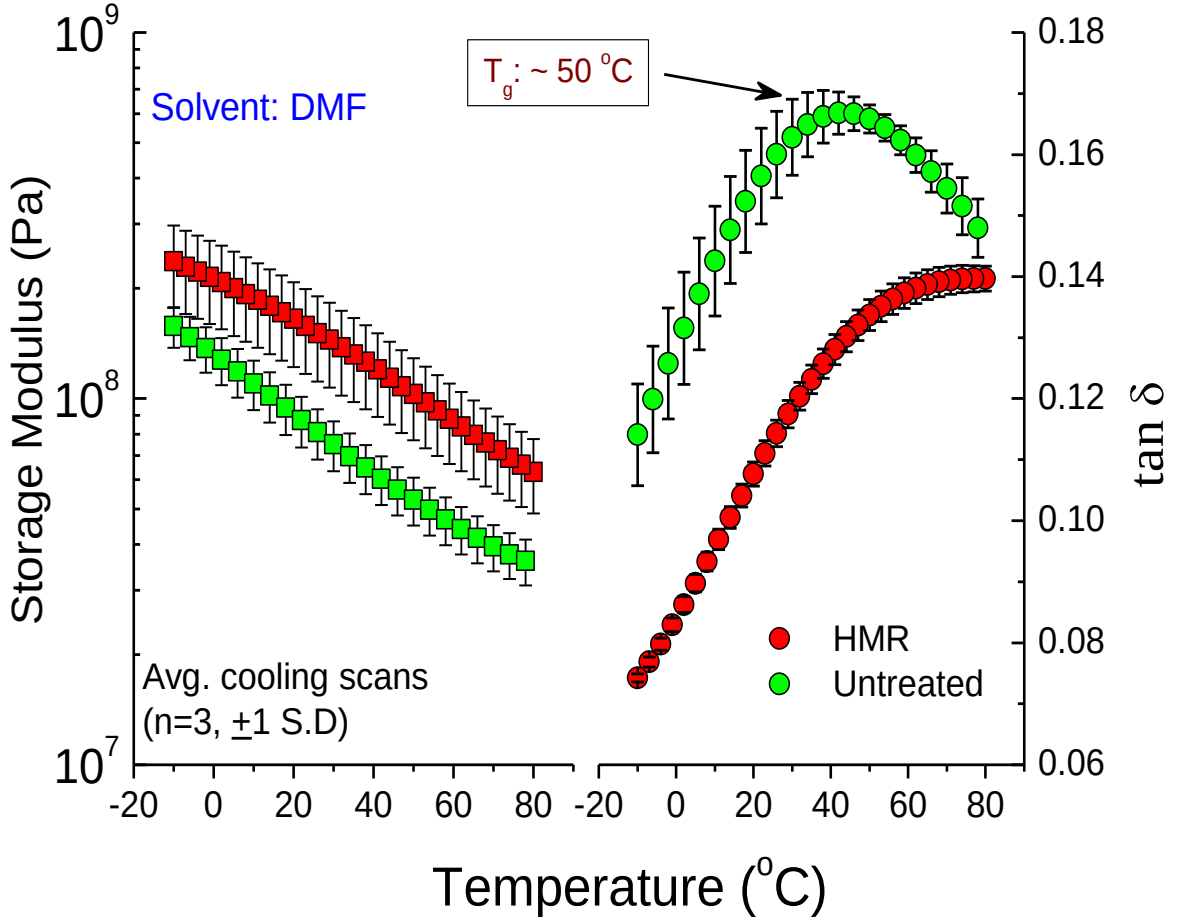


Vick et al., Wood and Fiber Sci. 27(1) 2, 1995

Dramatic improvement in wood-adhesive bond durability.

Effect of HMR on polymer mobility

- Increased rubbery plateau modulus.
- T_g significantly increased.
- Lower mobility; physical and chemical cross-linking.



HMR efficacy can be correlated with cell wall crosslinking

3°C/min, 5 Hz Freq., 35000 Pa Osc. Stress.

Submersion-Torsion Rheology- Summary

- *Extremely versatile technique to study polymeric mobility as a function of technologically relevant treatments.*
  - Extremely small specimen, no required specimen mechanical integrity.
  - Correlating fundamental polymer mobility with pretreatment efficacy.

Deuterium Nuclear Magnetic Resonance

Objectives

- Optimize for lignocellulosic biomass.

- Gain new perspectives on oriented cell wall morphology.

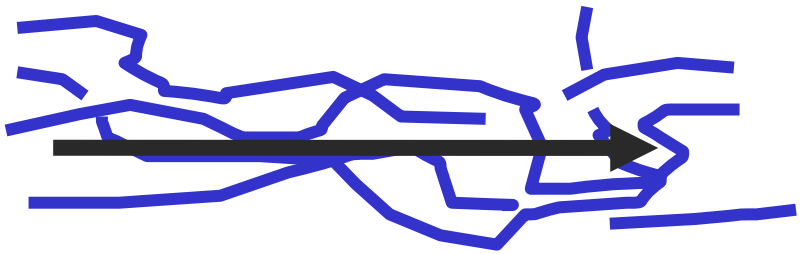
NMR – a highly specific probe

Local probe of magnetic field → spins

Orientationally and chemically specific
Dynamics (motions, kinetics)

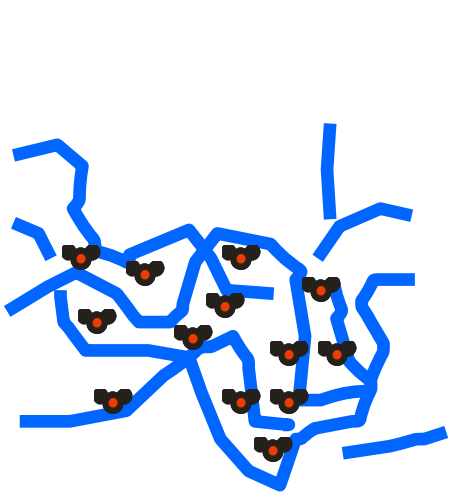
Spatial imaging (MRI)

Quantitative - highly developed theory
Non-destructive, *in-situ*

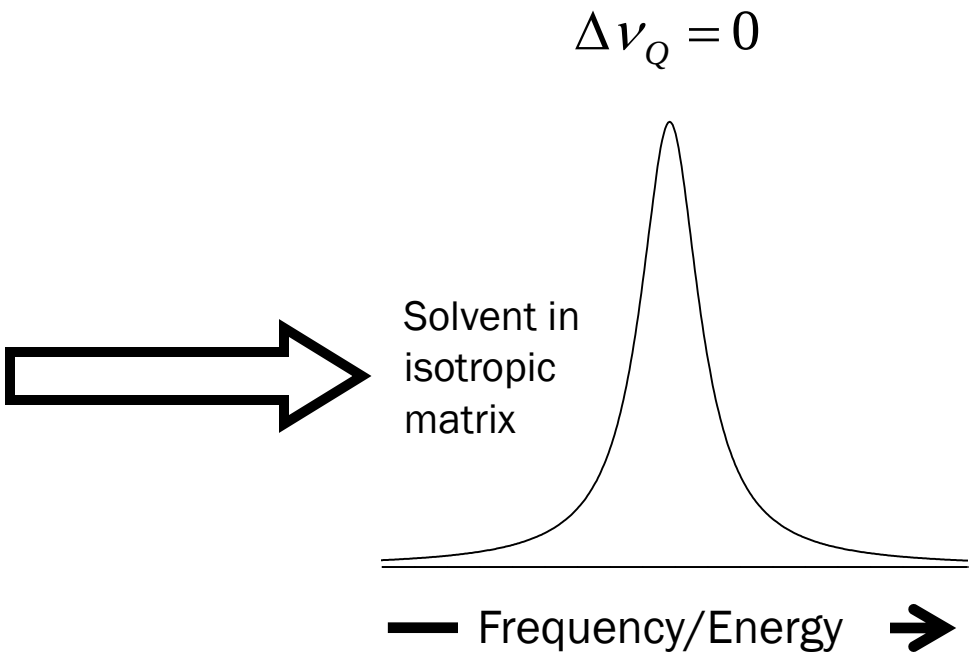


^2H NMR to study polymer morphology

- Small deuterated solvent molecules doped into bulk polymer.
- Measuring solution state signal of ^2H.

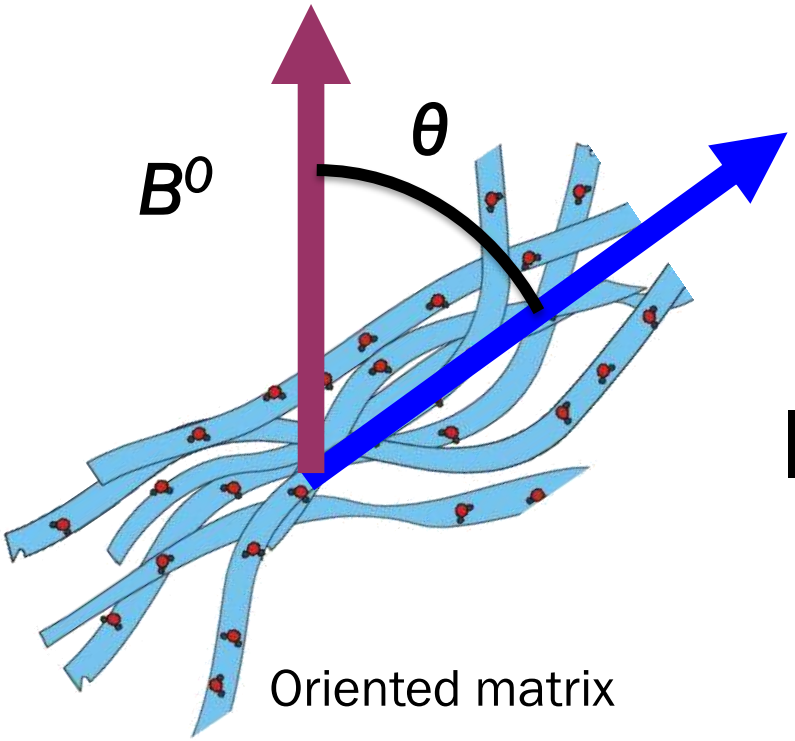


Isotropic matrix

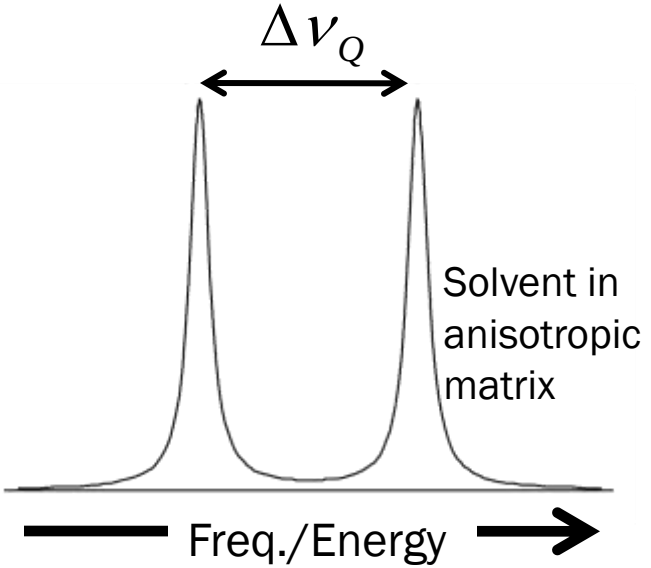


: Deuterated probe (D_2O)

^2H NMR as a local probe of order



Oriented matrix



$$\Delta\nu_Q = Q_p * S * P_2(\cos\theta)$$

Q_P = Quadrupolar coupling constant

S : Orientational order parameter

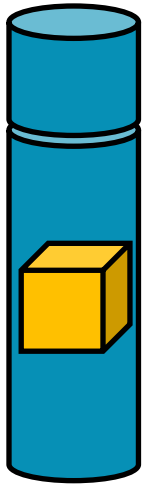
$$P_2(\cos\theta) = \left(\frac{3\cos^2\theta - 1}{2}\right)$$

Deuterated probe (D_2O):

Hydrophilic channel:

Deloche and Samulski, *Macromolecules*, **1981**, 14, 575

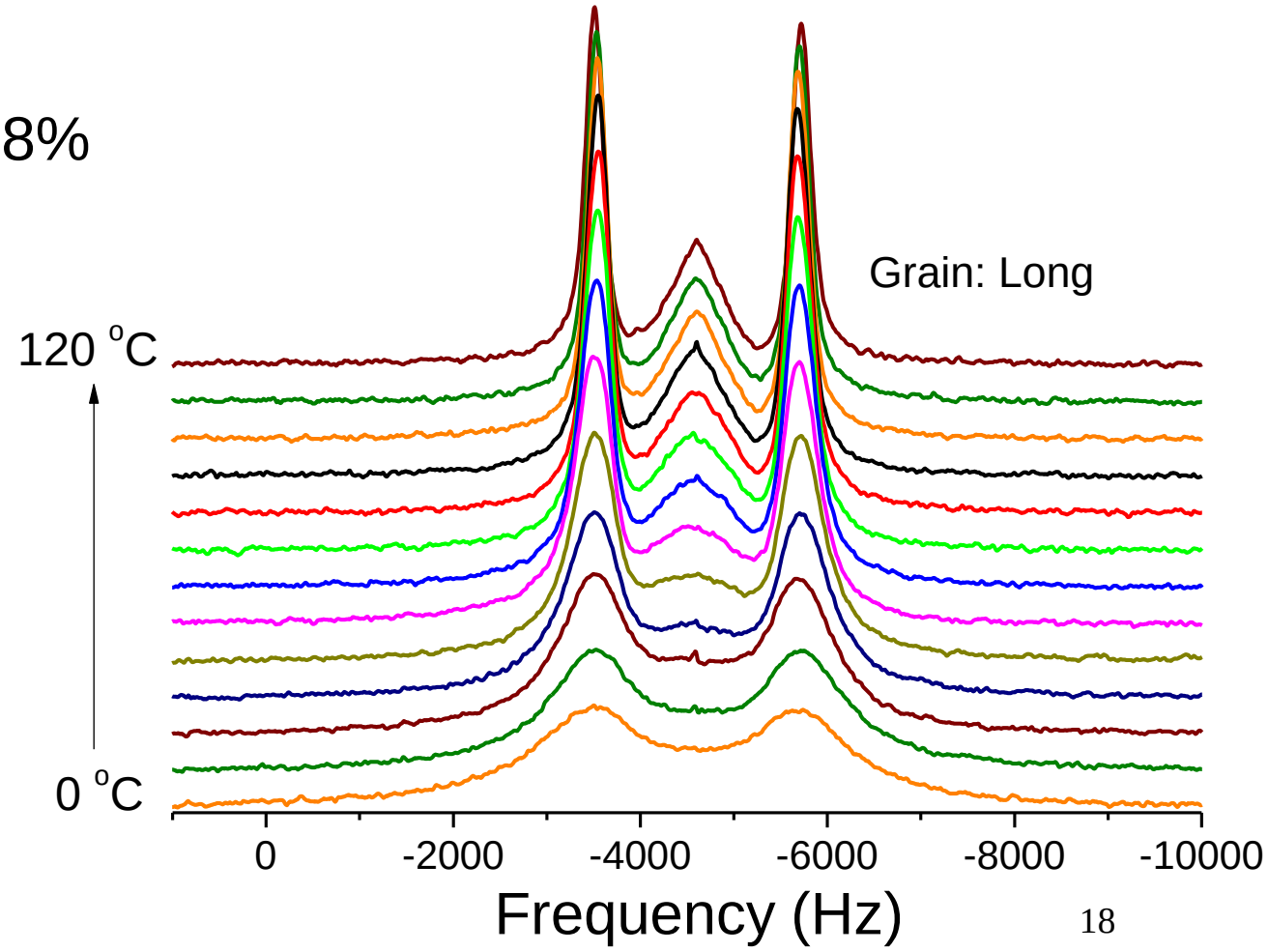
^{2}H NMR of wood – methodology



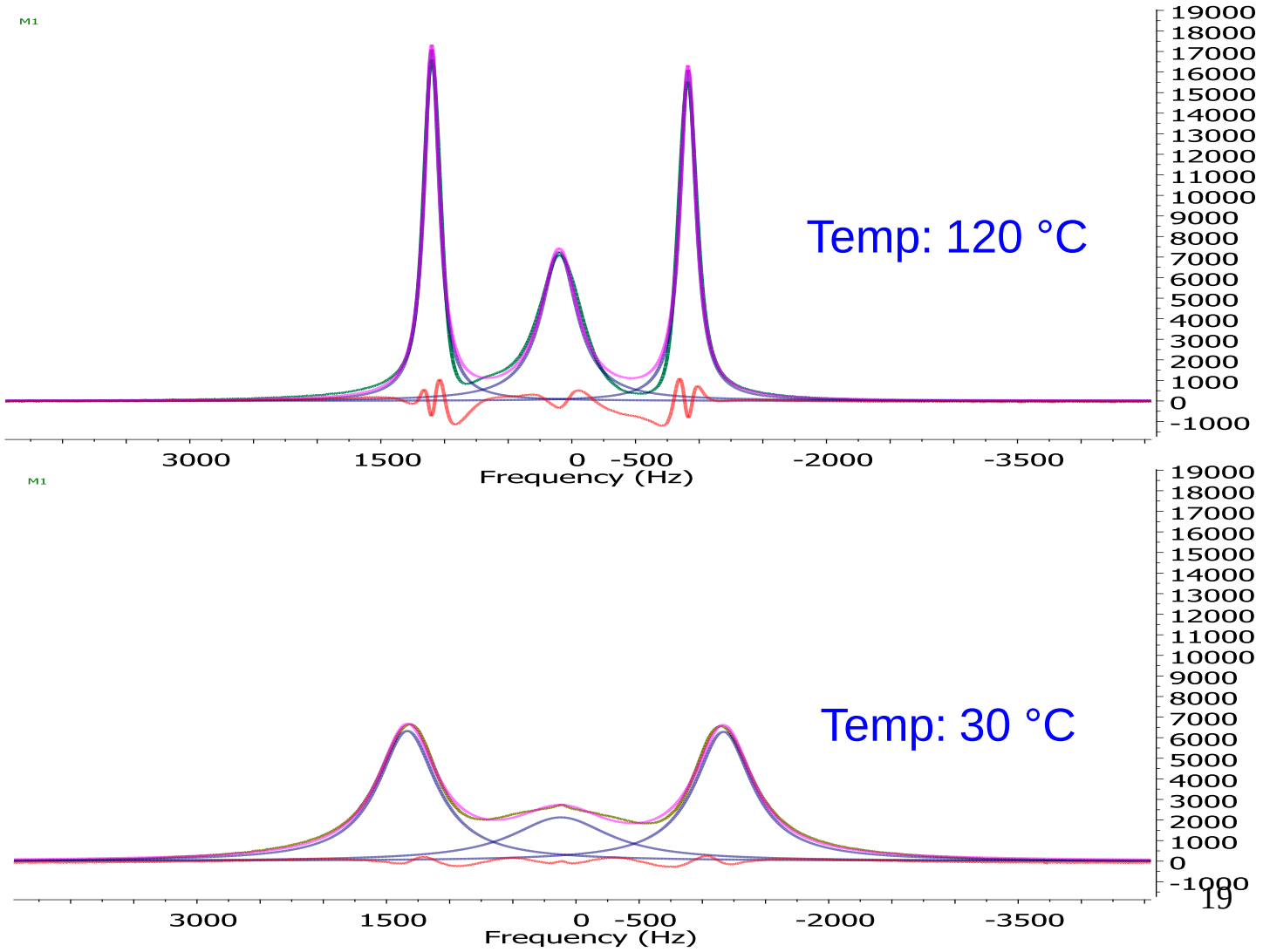
- Yellow-poplar solid wood
  - 2 mm cube
- Probe molecules:
  - Ethylene glycol (d4): $HO–(CD_2)_2–OH$
  - DMF (d1): $DCON(CH_3)_2$
- Solvent content: Close to the FSP
  - Intended for no/negligible free solvent
- Isothermal ^{2}H NMR spectra at different temp.

Et-glycol (d4) in yellow-poplar

- Solvent content: 28%
- Doublet: Aligned phase
- Singlet: Isotropic phase



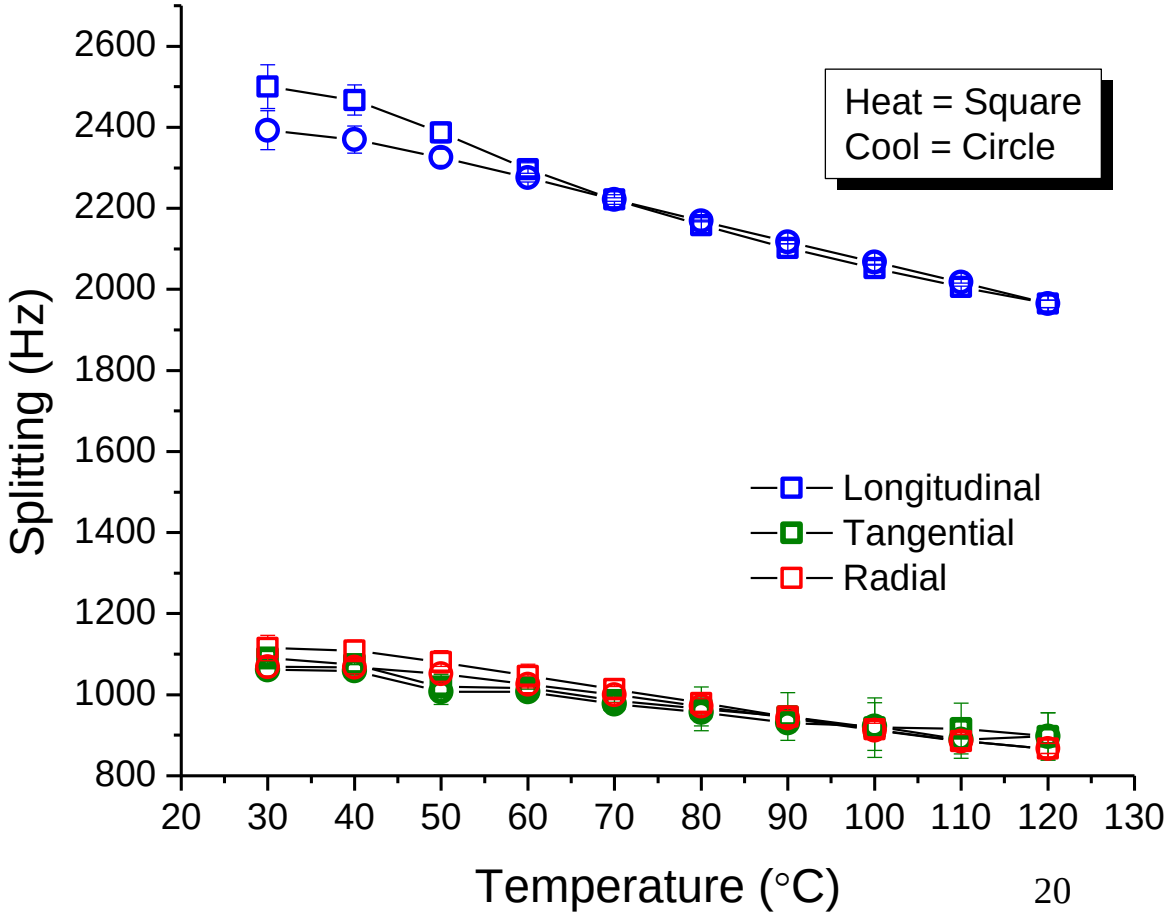
Splitting from peak deconvolution



Effect of grain direction: splitting profiles

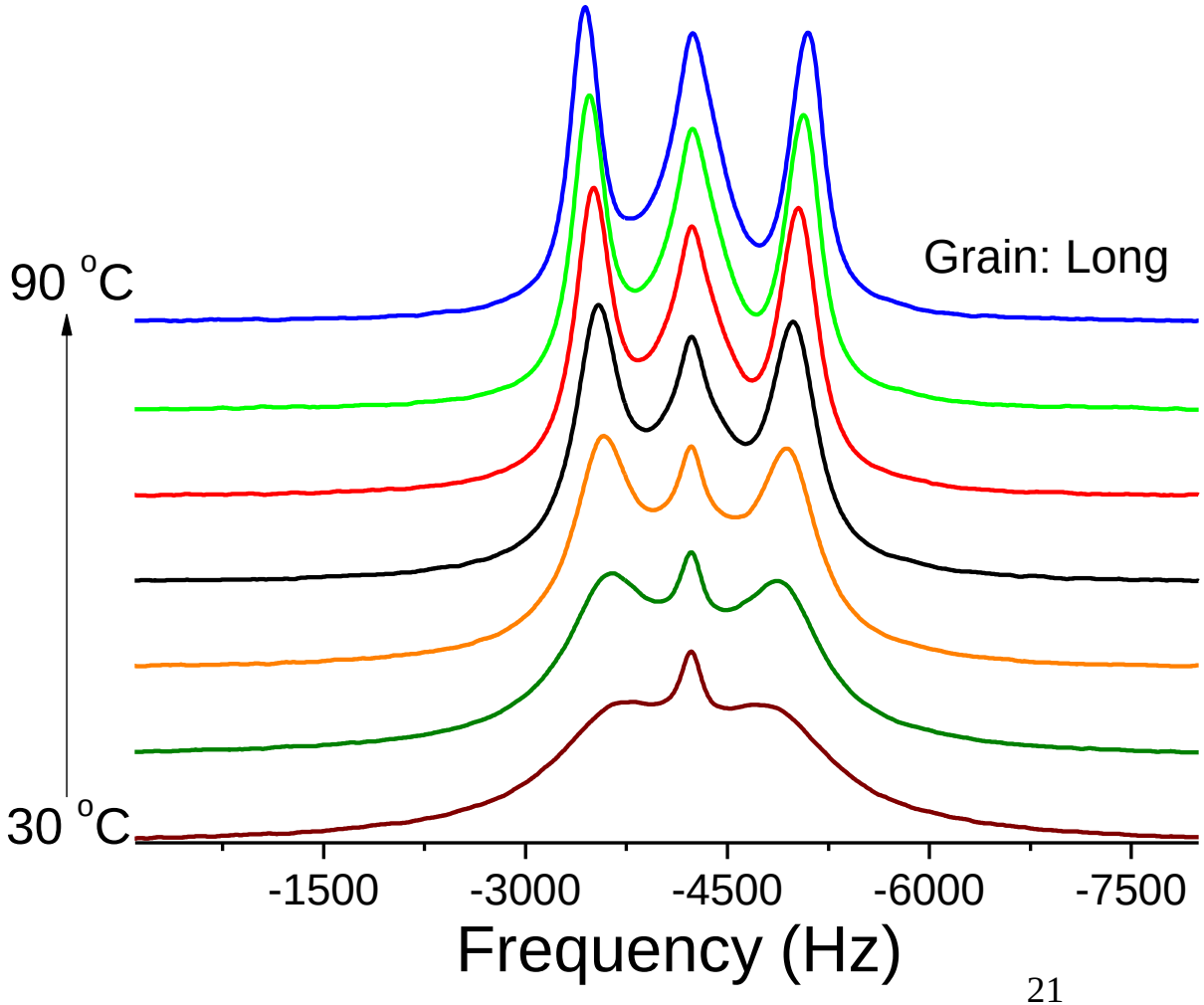
- Similar splitting for radial and tangential.
- Uniaxial orientation
- Decrease in net orientation with increasing temp.

Higher splitting → Higher anisotropy



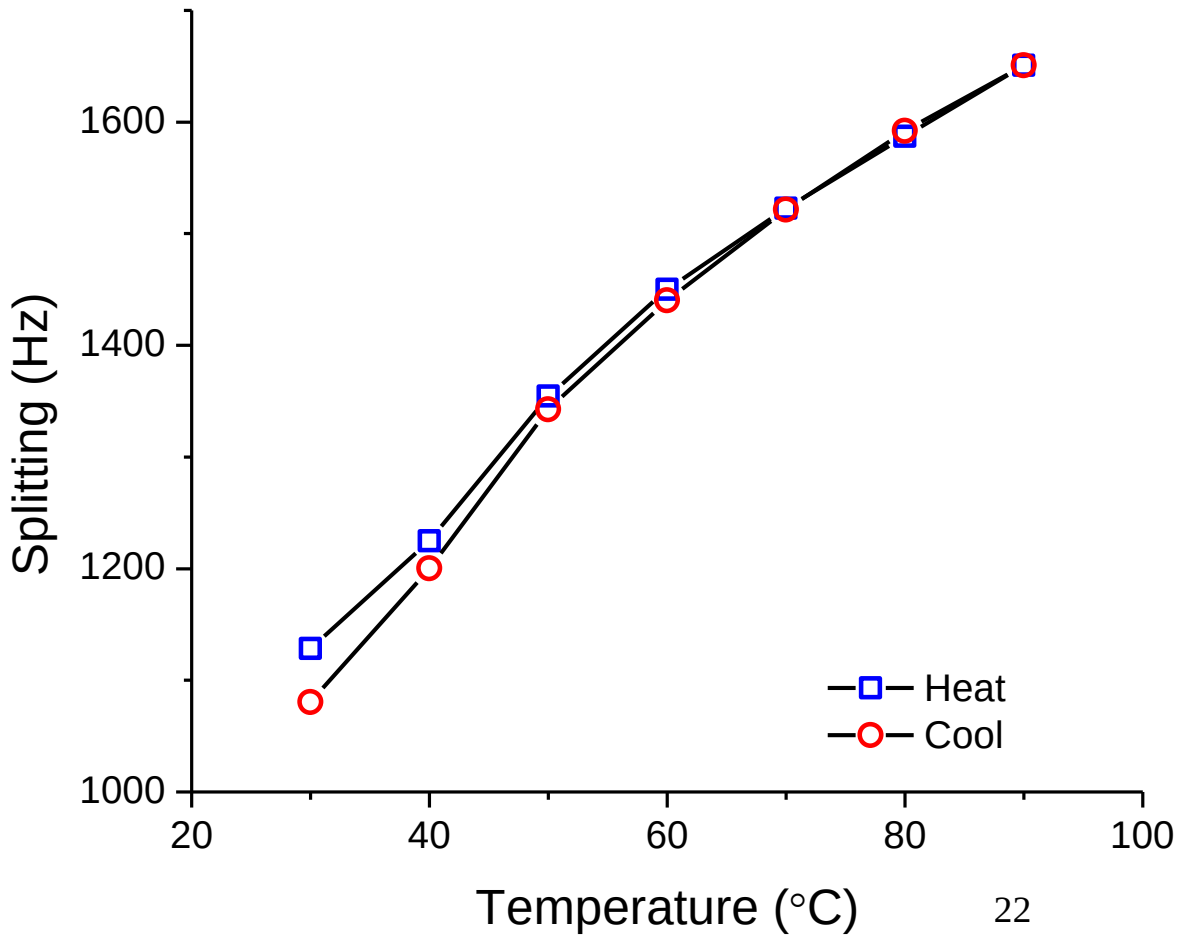
DMF-D1 in yellow-poplar

- DMF: 25%
- Two phases
  - 1 doublet
  - 1 broad singlet



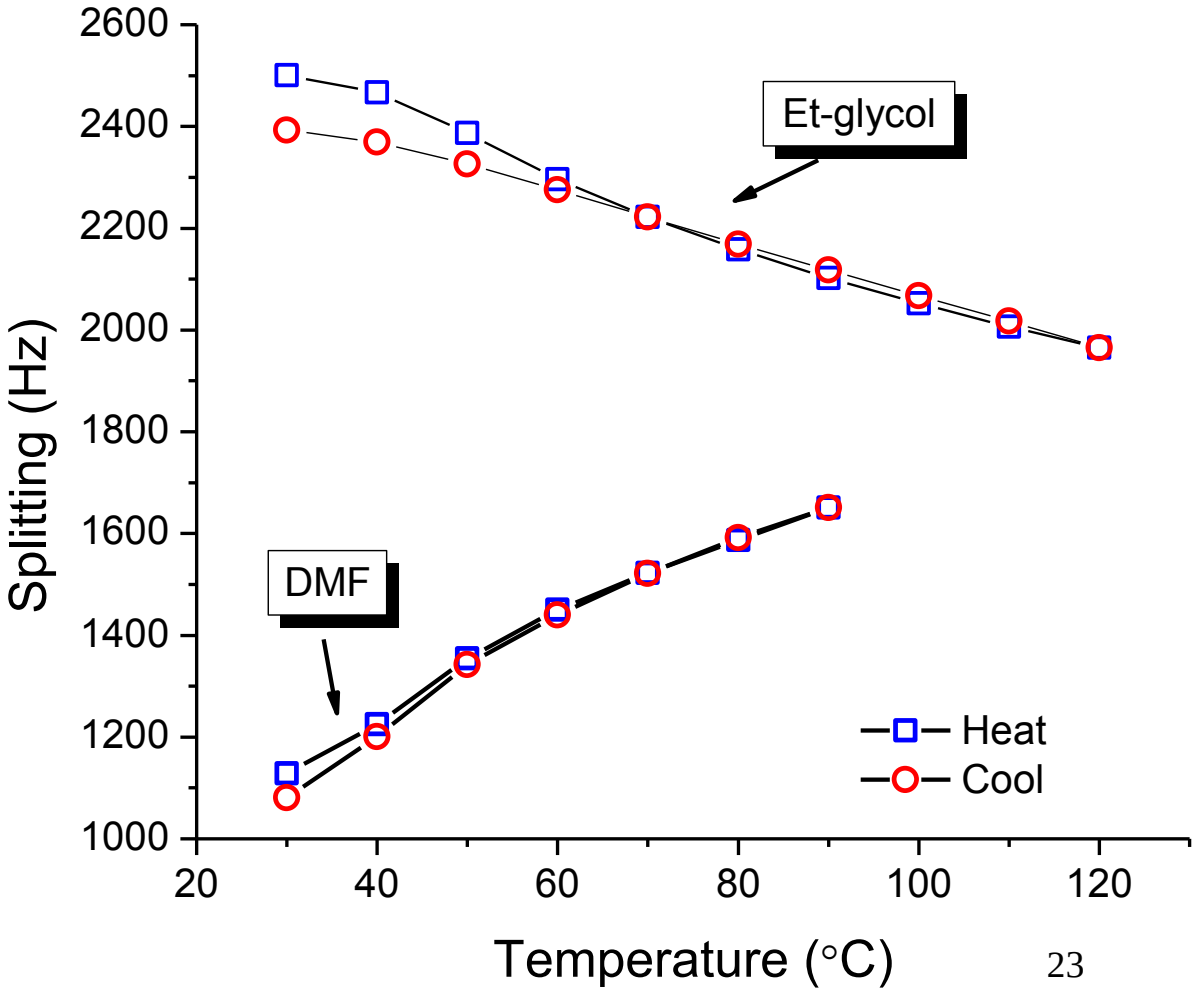
Splitting vs. Temp – DMF

- Temp ↑ Splitting↑
- Orientation increased with increasing temp.



Comparison of Et-glycol and DMF in wood

- Completely different temp dependence.
- DMF interacts with wood in a radically different way.



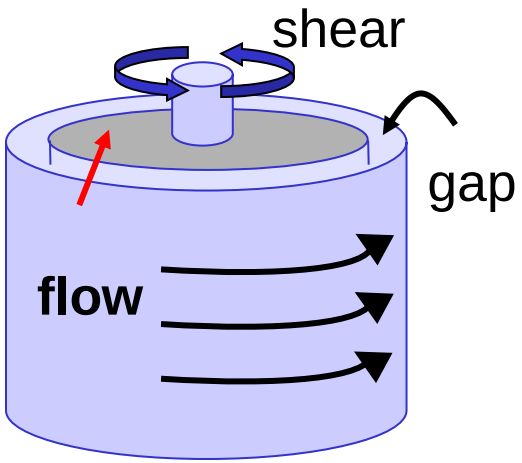
^2H NMR Summary

- ^2H NMR quadrupolar coupling is introduced in the study of lignocellulosic materials.
- An extremely powerful tool to study structure-property relationship and phase transitions in biomass with plasticizer “probe” molecules.
- Significantly different interaction of DMF and Et-glycol with wood cell wall.

Relevant Future Steps

- Morphology/organization of lignocellulosic biomass as a function of: Deconstructive treatments and Genetic modification
  - Small specimen rheology, ^{2}H NMR.
  - Rheo-IR: Micromechanical interactions between cell wall polymers.

- Rheo-NMR: Molecular interactions induced by shear, measured using NMR.
- Correlate rheology with molecular phenomena.



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