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Characterization of mechanical properties from technical lignins by microscopy-aided nanoindentation

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Motivation

Lignin, a main component of plants, is extracted as a by-product of the pulp and papermaking industry in large quantities [1], making it a major renewable chemical [2]. Knowing the mechanical properties of hot-pressed lignins is essential to develop renewable materials, like lignin-based composites. However, only Cousins [3,4,5] studied the elastic properties of hot-pressed lignins. In addition, lignin's macromolecule composition varies depending on the feedstock and extraction process [1], which raises the question of whether this affects the mechanical properties. Therefore, we study five lignins, which differ in their feedstock and extraction process with light microscopy-aided nanoindentation.

Material

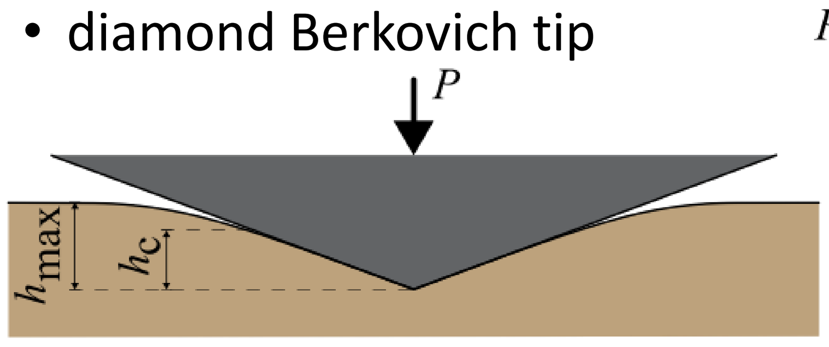
Lignin	Process	Feedstock
Alkali	Kraft pulping	Softwood
ChemicalPoint	Organosolv	Grass
Leuna	Organosolv	Hardwood
Spruce	Organosolv	Softwood
UPM	Enz. Hydrolysis	Hardwood

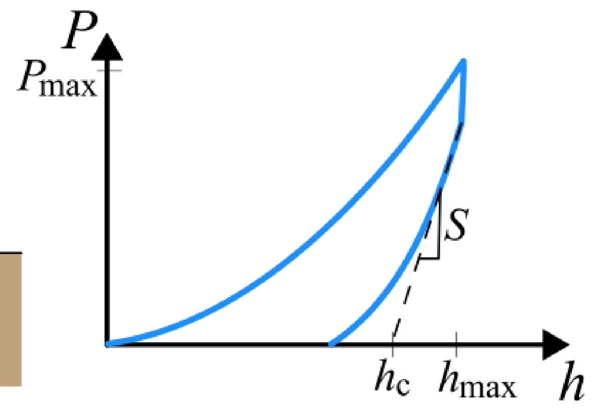
The lignin powders were hot-pressed into disc-shaped samples under 108 MPa for 2 min at 90 °C.

Methods

Grid nanoindentation

- **20,650 indents**
- displacement controlled
- Oliver-Pharr [6] method
- diamond Berkovich tip
- h_{max}={150, 300, 600, 900, 1000, 1200} nm

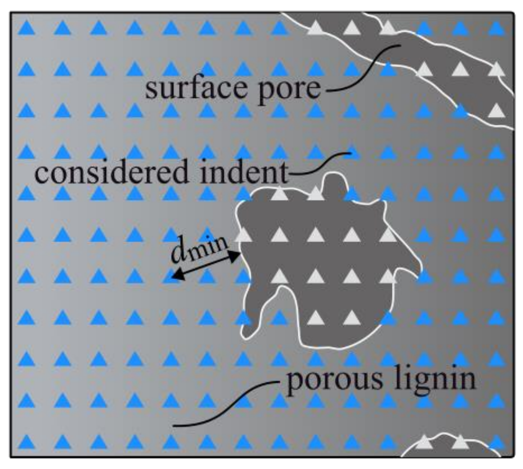




- indentation modulus E^r
- indentation hardness H

Image-guided evaluation

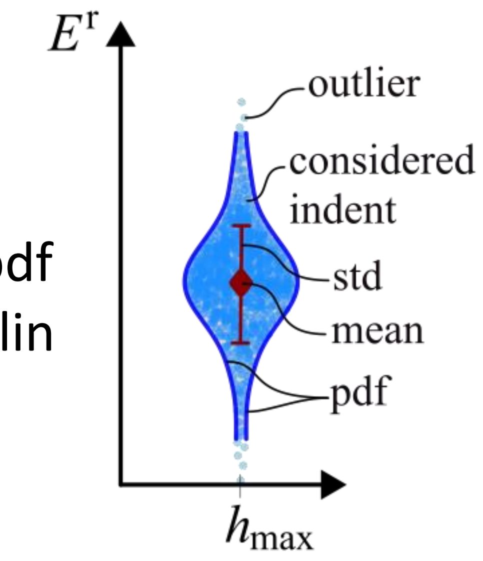
- **58 grids (5x5 to 40x40)**
- identify surface pores
- calculate distance d_{min} between indent and closest pore



- porosity φ
- distance plots
- exclude indents in pores

Statistical evaluation

- **6 indentation depths**
- kernel density estimation for pdf displayed as violin plots
- exclude outliers

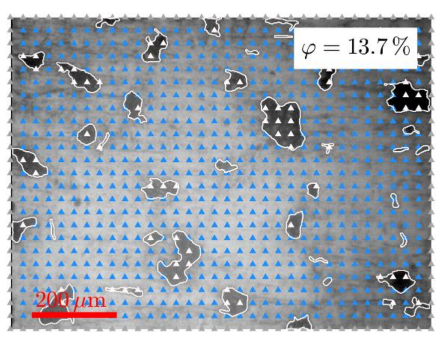


- mean
- study size effect
- std

Results and Discussion

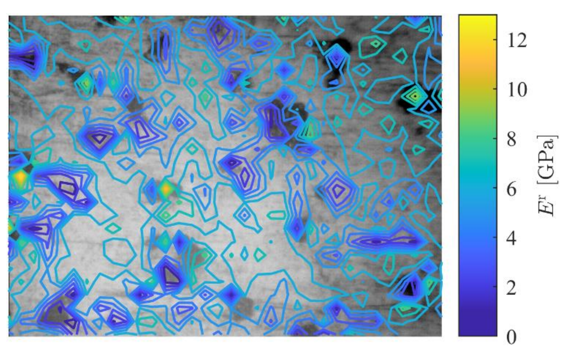
Porosity, mapping and distance plots

Microscopy image of probed area



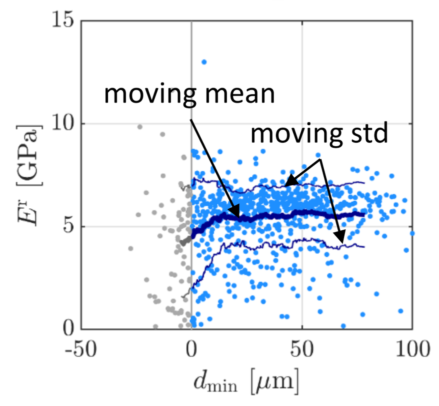
The pressing process introduced a porous microstructure with a different porosity for each lignin.

Indentation modulus map



Stiffness gradients correlate with surface pores. Similar gradients in the lignin reveal pores below the surface.

Boundary distance plot

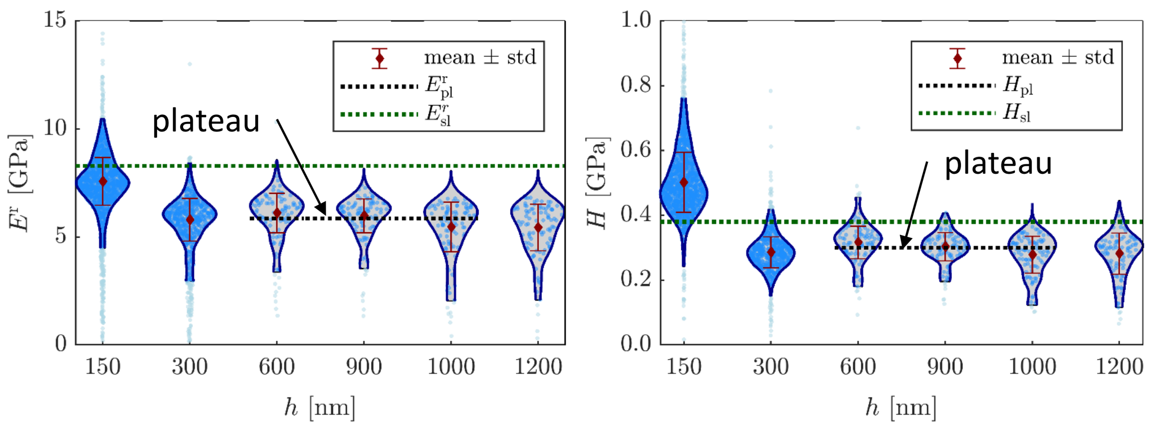


The surface pores influence only indents close to the surface pore boundary.

Images are from UPM lignin at an indentation depth of 300nm.

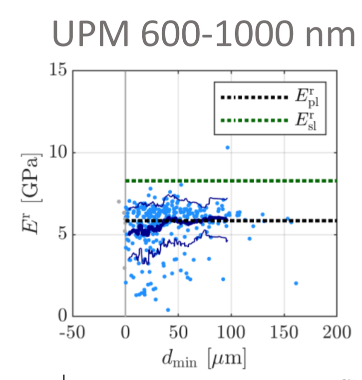
Emerging plateaus

The indentation modulus and hardness decrease with increasing indentation depth. Similar indentation size effects are also observed in other polymers [7]. However, in our case, $E^r$and H only decrease until 300 nm for UPM and Spruce and 600 nm for Alkali, ChemicalPoint, and Leuna, respectively. This emerging plateau at indentation depths from 600 nm to 1000 nm allows us to retrieve reliable size independent mechanical properties.

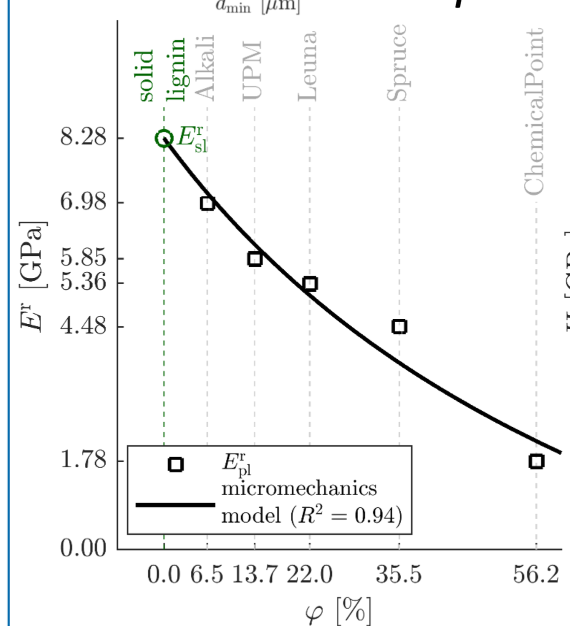


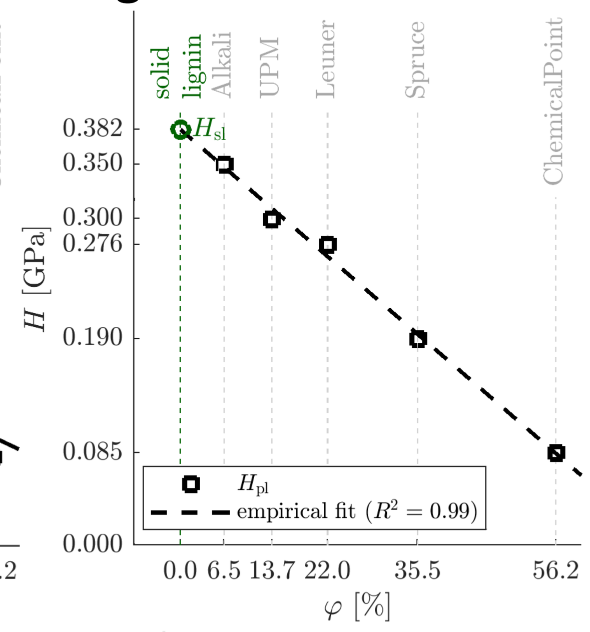
Images are from UPM lignin at an indentation depth of 300nm.

From porous to solid lignin



plateau corresponds to moving mean → plateau characterizes the (macroscopic) properties of *porous* lignin





Plateau values decrease with increasing porosity φ along virtually unique curves.

- micromechanics model fit → indentation modulus of *solid* lignin E^r_{sl}
- empirical fit→ hardness of *solid* lignin H_{sl}

Conclusion

1. Reliable mechanical properties of *porous* lignin can be retrieved with the described method.
2. *Solid* lignin's indentation modulus and hardness can be back-identified, resulting in 8.28 GPa and 0.382 GPa, respectively.
3. The herein studied lignins, although differing in their production process and feedstock, are mechanically rather similar.

References

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