Effective Modification and Oxidative Activation of Lignin: Towards Bio-Based Thiol-Catechol 2K Adhesives

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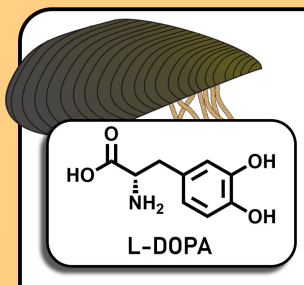
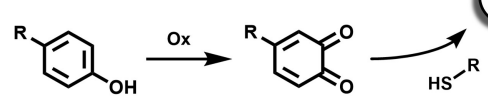
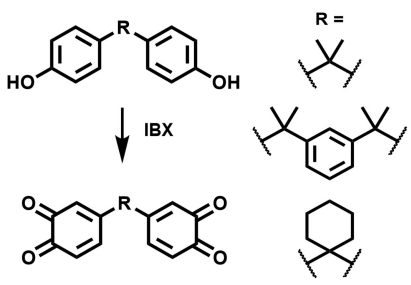
Introduction



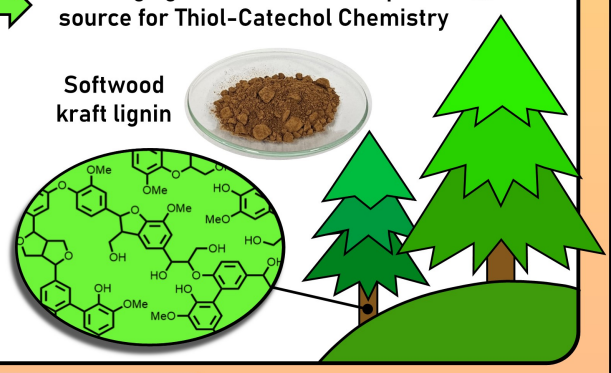
Mussel-inspired approach[1]:
chemical oxidation of phenols to *ortho*-quinones, followed by nucleophilic thiol addition to form Thiol-Catechol connectivities (TCC)



Previously established material platform[2] based on bisphenols using IBX ⚠

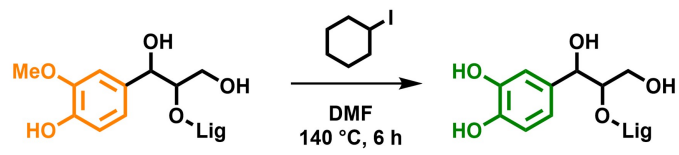


Utilizing lignin as a renewable phenol source for Thiol-Catechol Chemistry

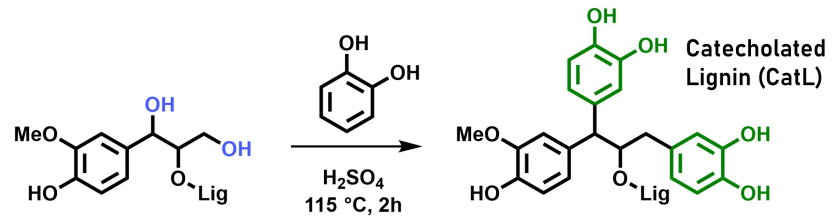


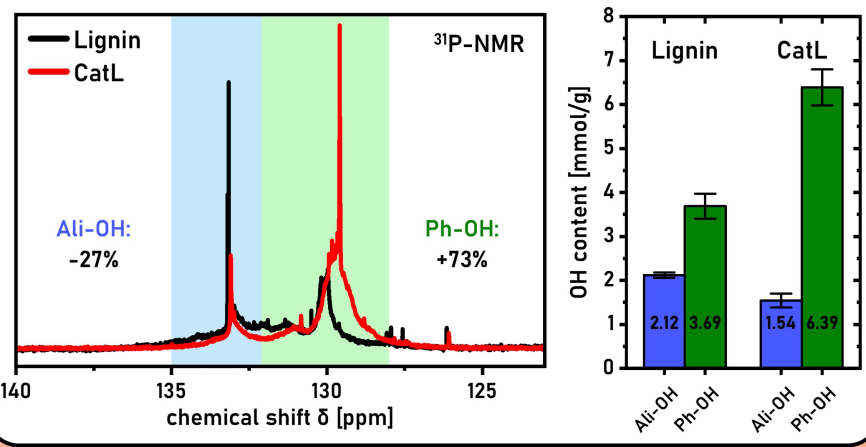
Catecholation of Lignin

Previous approach: chemical demethylation of intrinsic methoxyphenols (G-units) through *in situ* generated hydroiodic acid to obtain catechols[3]



Instead: introduction of additional catechol functionalities through electrophilic aromatic substitution of the aliphatic alcohols in the Lignin structure[4]





Oxidation of Lignin

-Highly reactive
-Oxidation of all OH-groups

Iodine (VII)
Sodium periodate

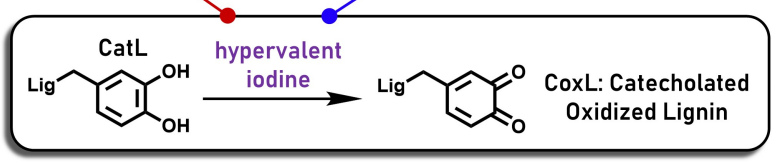
VS

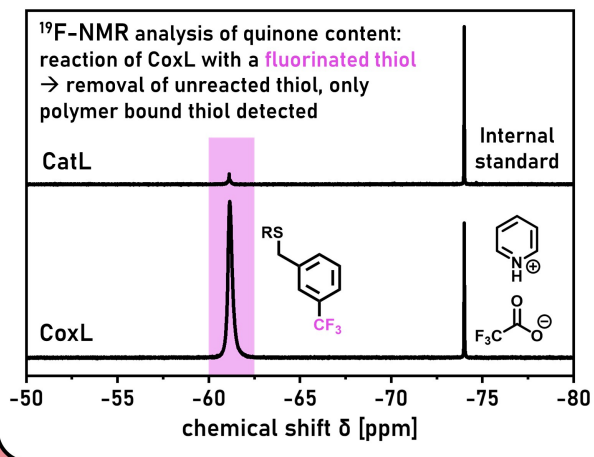
Iodine (III)
Organic hypervalent iodine

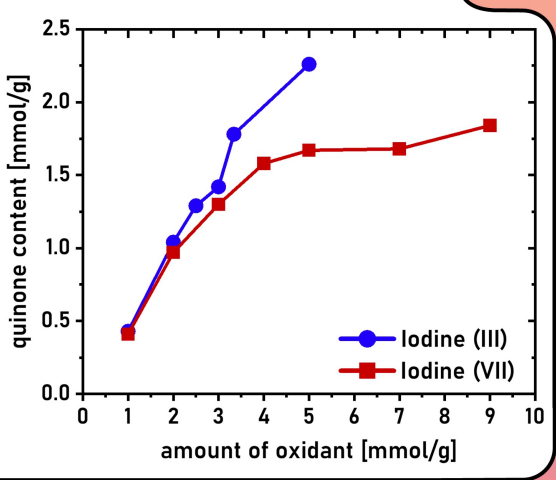
-Highly selective
-Oxidation of phenolic OH-groups

Conditions:
GVL, 10% phosphate buffer (pH=6.5)
0 °C, 1 hour

Conditions:
GVL/MeOH 2/1
RT, 15 minutes

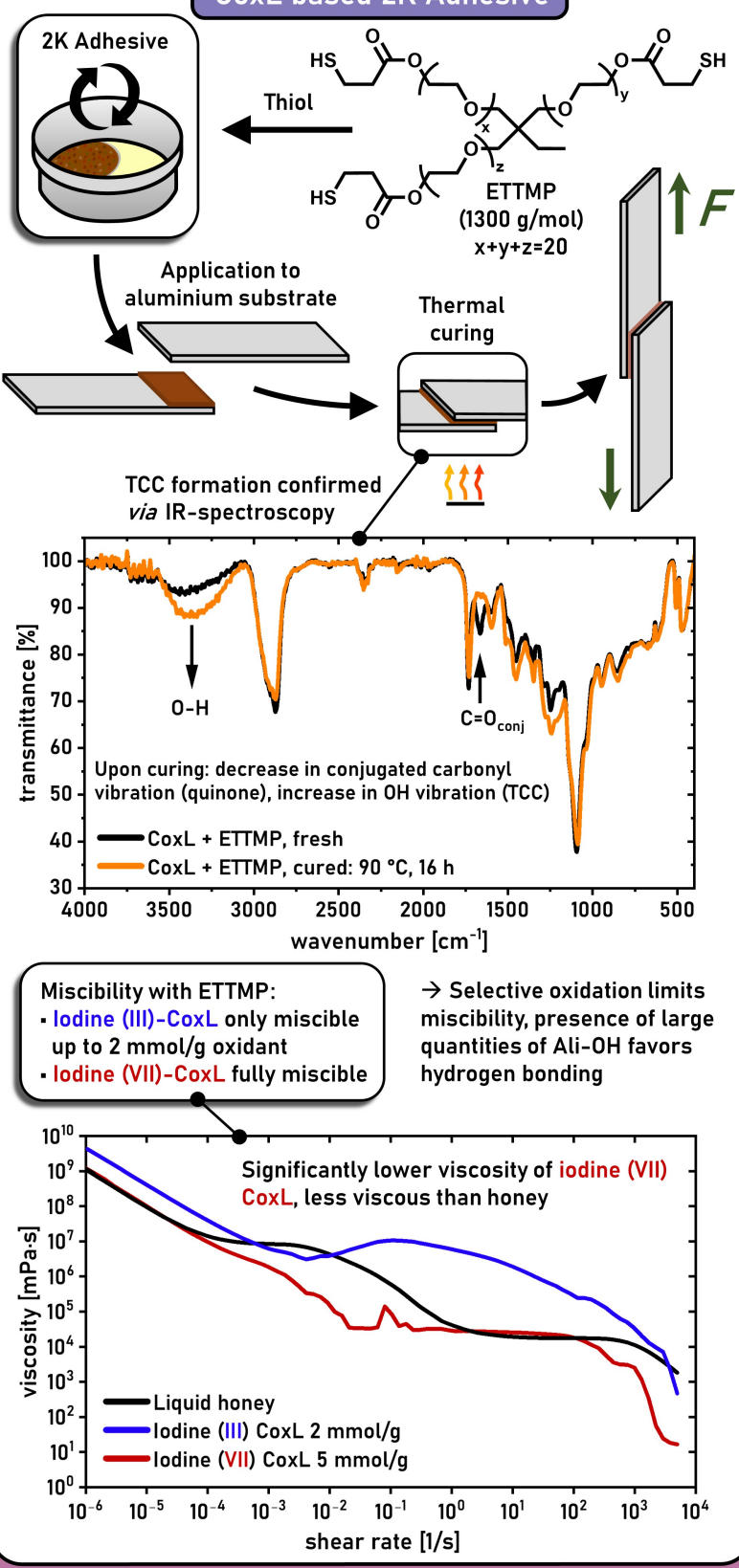






CoxL based 2K Adhesive

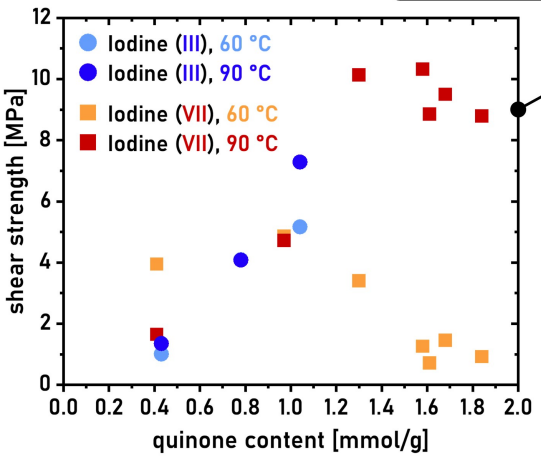
CoxL



Miscibility with ETTMP:
- Iodine (III)-CoxL only miscible up to 2 mmol/g oxidant
- Iodine (VII)-CoxL fully miscible

→ Selective oxidation limits miscibility, presence of large quantities of Ali-OH favors hydrogen bonding

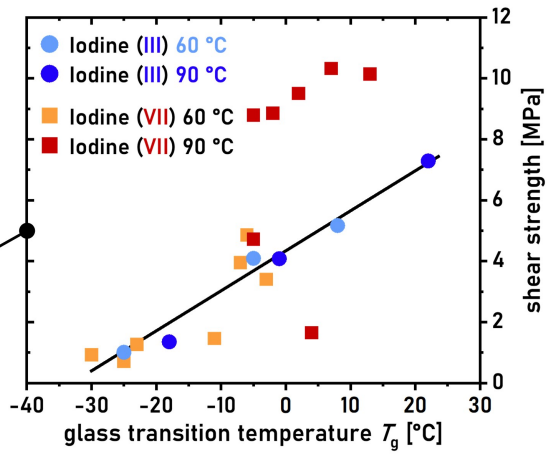
Adhesive Performance



General trend of increasing shear strength with higher quinone content

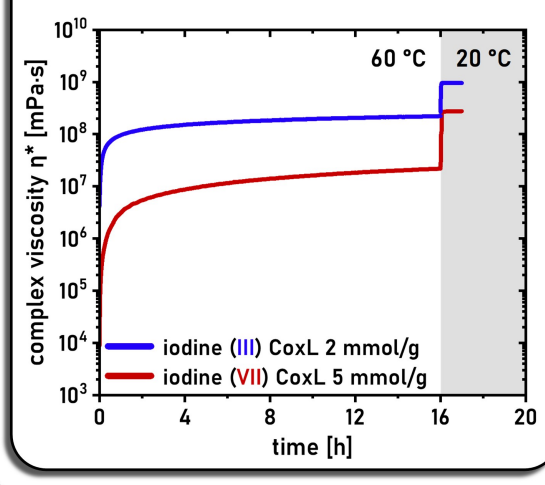
Only outlier: iodine (VII) CoxL cured at 60 °C
→ Incomplete curing and high degree of oxidation: lack of OH-groups for strong surface interaction

Correlation of shear strength with glass transition temperature T_g

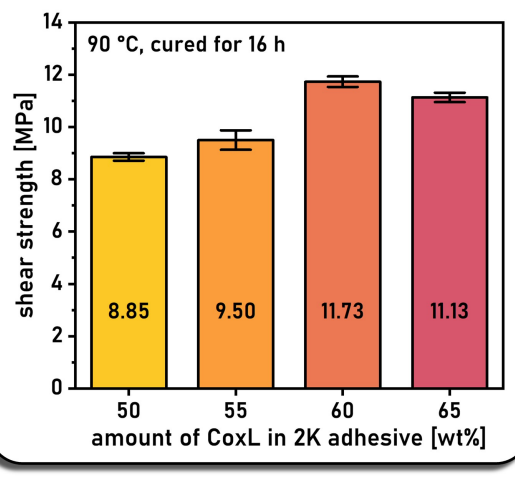


Only outlier: iodine (VII) CoxL cured at 90 °C
→ Lower T_g due to lack of OH-groups, but still high shear strength due to TCC-groups

Iodine (III)-CoxL: presence of more OH-groups
→ better curing at lower temperatures



Iodine (VII)-CoxL: low viscosity mixtures
→ up to 65 wt% Lignin content in 2K adhesive



Conclusion

Both oxidation methods have distinct advantages:

- **Iodine (III)-CoxL** offers a more selctive oxidation, retaining OH-groups and thus increasing T_g values and performance for not fully cured systems
- **Iodine (VII)-CoxL** offers great miscibility due to the non selective oxidation of all OH-groups, allowing for strong performing adhesives with the highest amount of TCC-groups

References
[1] J. Horsch, P. Wilke, M. Pretzler, M. Seuss, I. Melnyk, D. Remmler, A. Fery, A. Rompel, H. G. Börner, *Angew. Chem.* **2018**, 130, 15954-15958.
[2] J. M. Krüger, C.-Y. Choi, F. Lossada, P. Wang, O. Löschke, D. Auhl, H. G. Börner, *Macromolecules* **2022**, 55, 989-1002.
[3] C.-Y. Choi, F. Lossada, K. Walter, T. Fleck-Kunde, S. Behrens, T. Meinelt, J. Falkenhagen, M. Hiller, H. Oschkinat, A. Dallmann, A. Taden, H. G. Börner, *Green Chem.* **2024**, 26, 2044-2058.
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