Effect of lignosulfonates on the moisture resistance of phenol-formaldehyde resins

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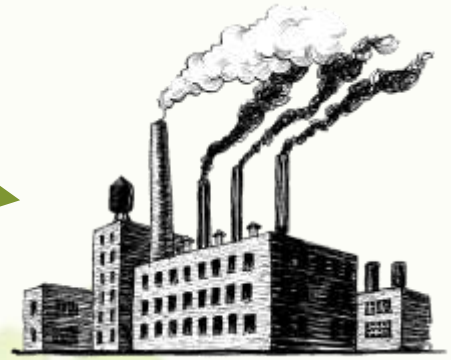
Pulp and paper industry

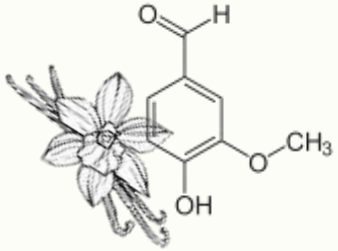


70 million tons/year

Lignin

- **Lignosulphonates**
- Kraft lignin
- Soda lignin

Value-added products



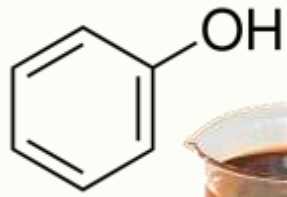
Only 2 %!

Wood-based panels

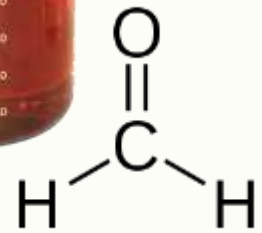
- Medium density fiberboard (MDF)
- Particleboard
- **Plywood**

Resins:

- Urea-formaldehyde (UF)
- Melamine-urea-formaldehyde (MUF)
- **Phenol-formaldehyde (PF)**

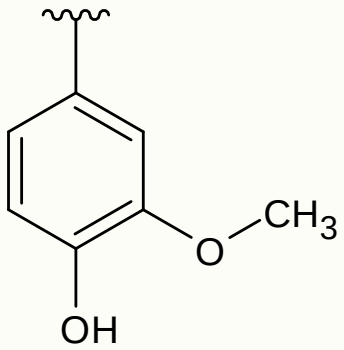


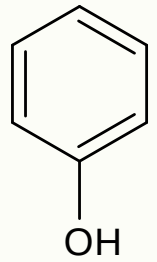
Phenol



Formaldehyde

Lignin vs Phenol





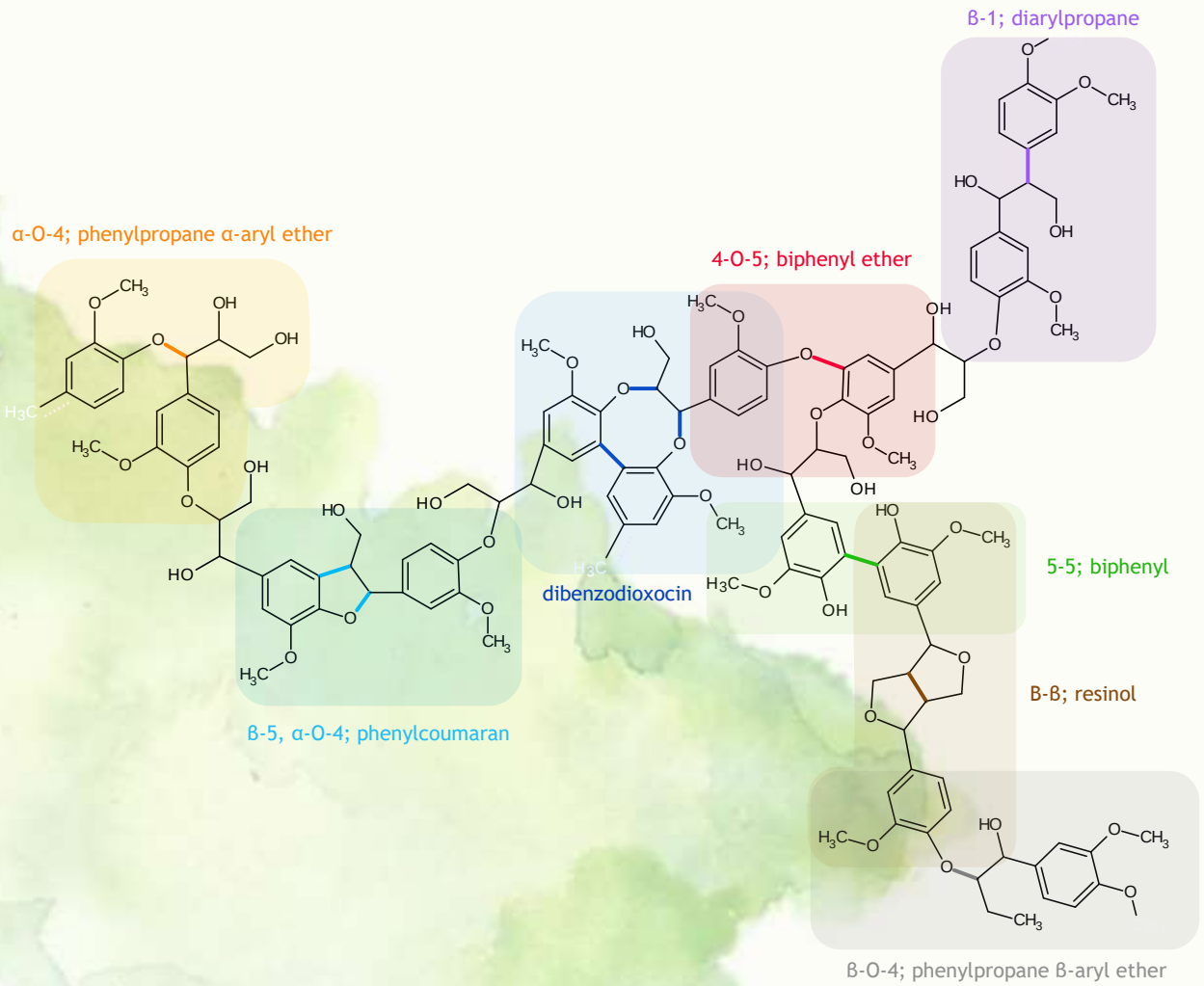
Advantages

- ✓ Most abundant natural source of phenols
- ✓ Cheap
- ✓ Nontoxic

Disadvantages

- Lower amount of reactive sites in its aromatic ring
- High polydispersity
- Complex structure

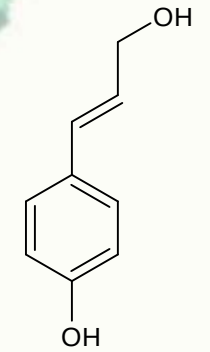
Lignin's structure



Bonds:

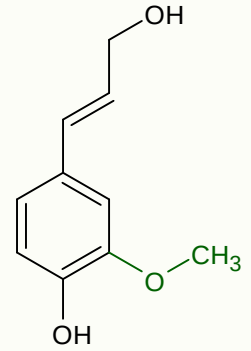
1. β-O-4
2. 5-5
3. β-5
4. α-O-4
5. 4-O-5
6. β-1
7. β-β

p-hidroxyphenyl units



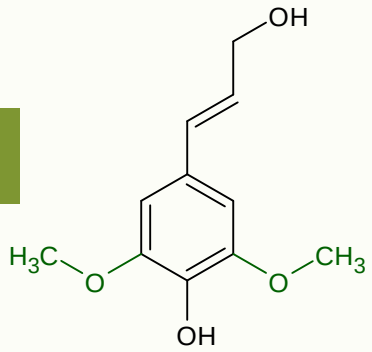
Guaiacyl units

(softwood)

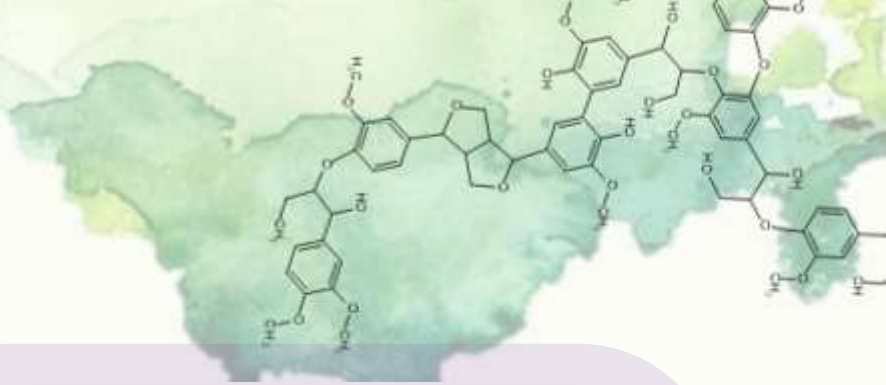


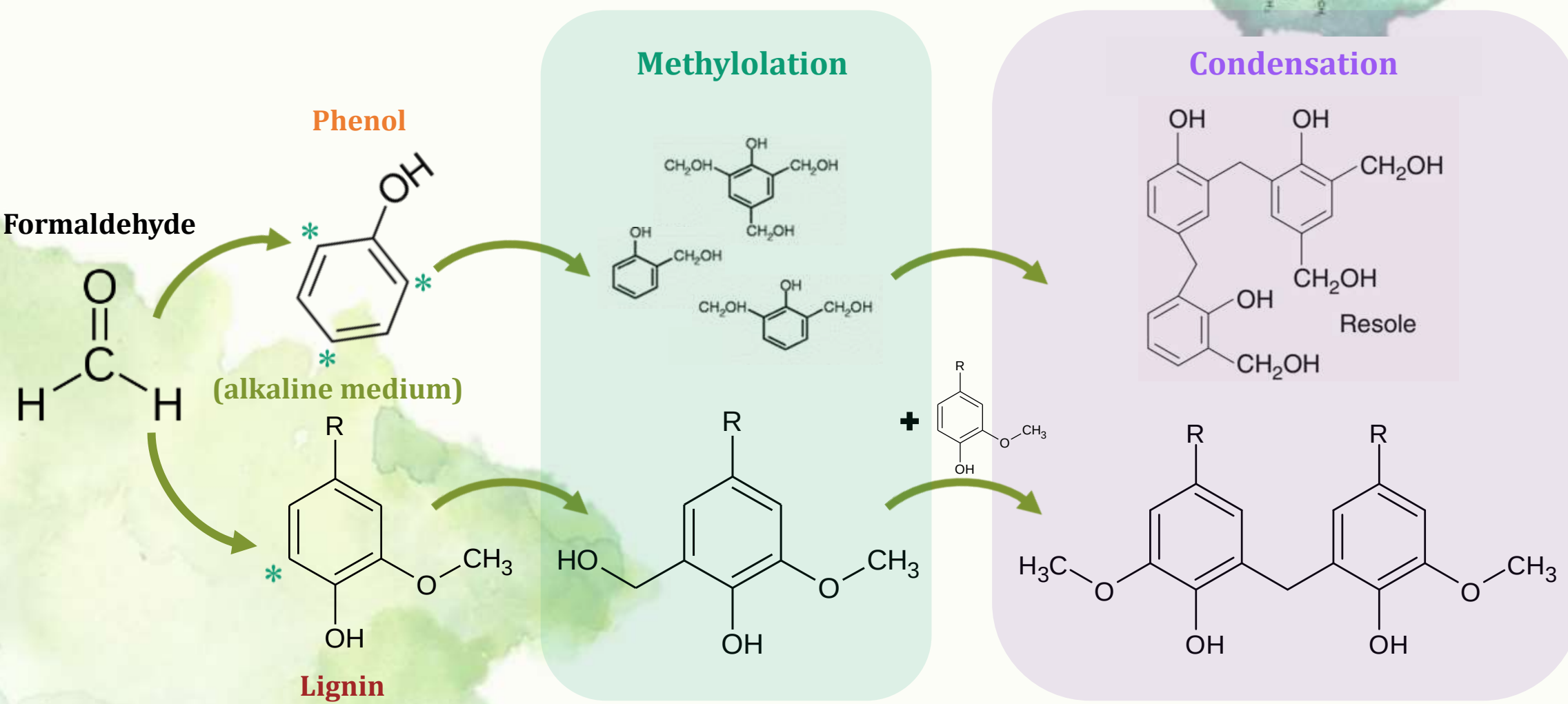
Syringyl units

(hardwood)



Phenol vs Lignin





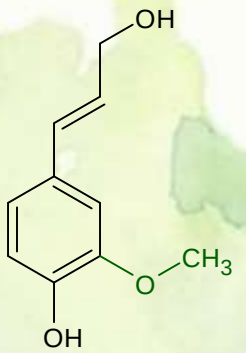
Experimental results

- **Resin synthesis**

- **Automated bonding evaluation system**

- **Plywood manufacture**

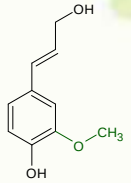
Lignin sample

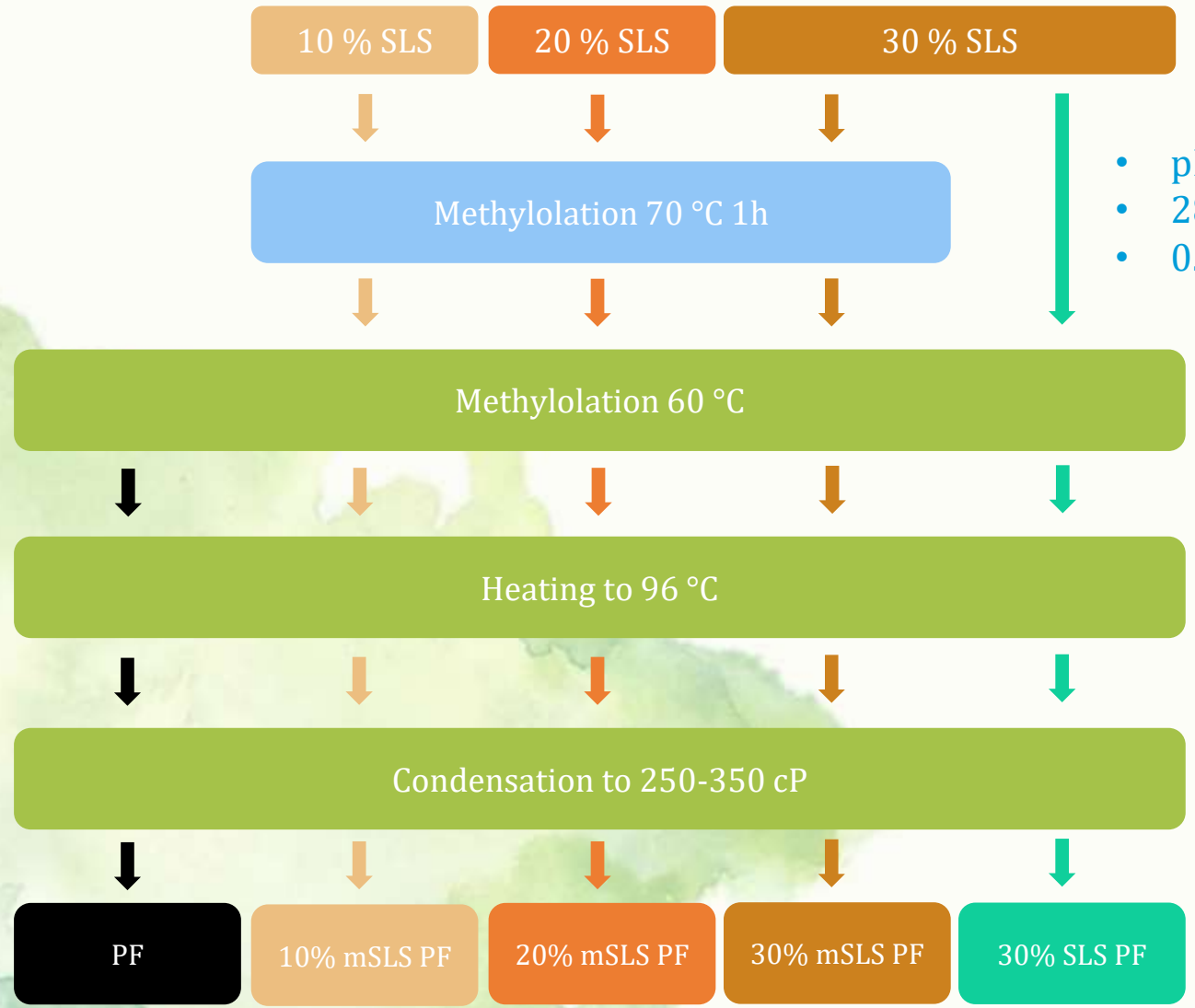


	SLS
Origin	*Picea abies* (softwood)
Form	Spray dried powder
Dry matter (%)	96
LS content (%) [a]	80

[a] on a dry matter basis

Lignin-phenol-formaldehyde resins





- pH = 9.6
- 280 g/L pure lignin
- 0.17 F/Lignin weight ratio

	PF	10 % mSLS PF	20 % mSLS PF	30% mSLS PF	30% SLS PF
pH	12,3	12,2	12,3	12,1	12,1
Viscosity (cP)	330	265	285	285	270
Solids content (%)	43,7	42,1	42,3	44,5	44,5
Density (g/cm^3)	1,190	1,192	1,201	1,218	1,217

Automated Bonding Evaluation System (ABES)

PF

30% mSLS PF

30% SLS PF

Wheat flour

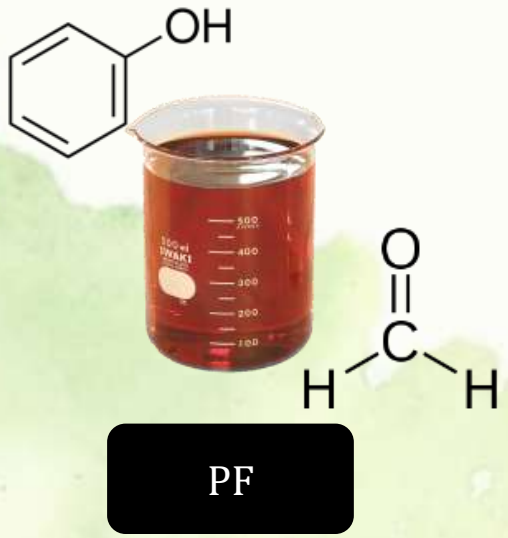
Calcium carbonate

Adhesive mixture

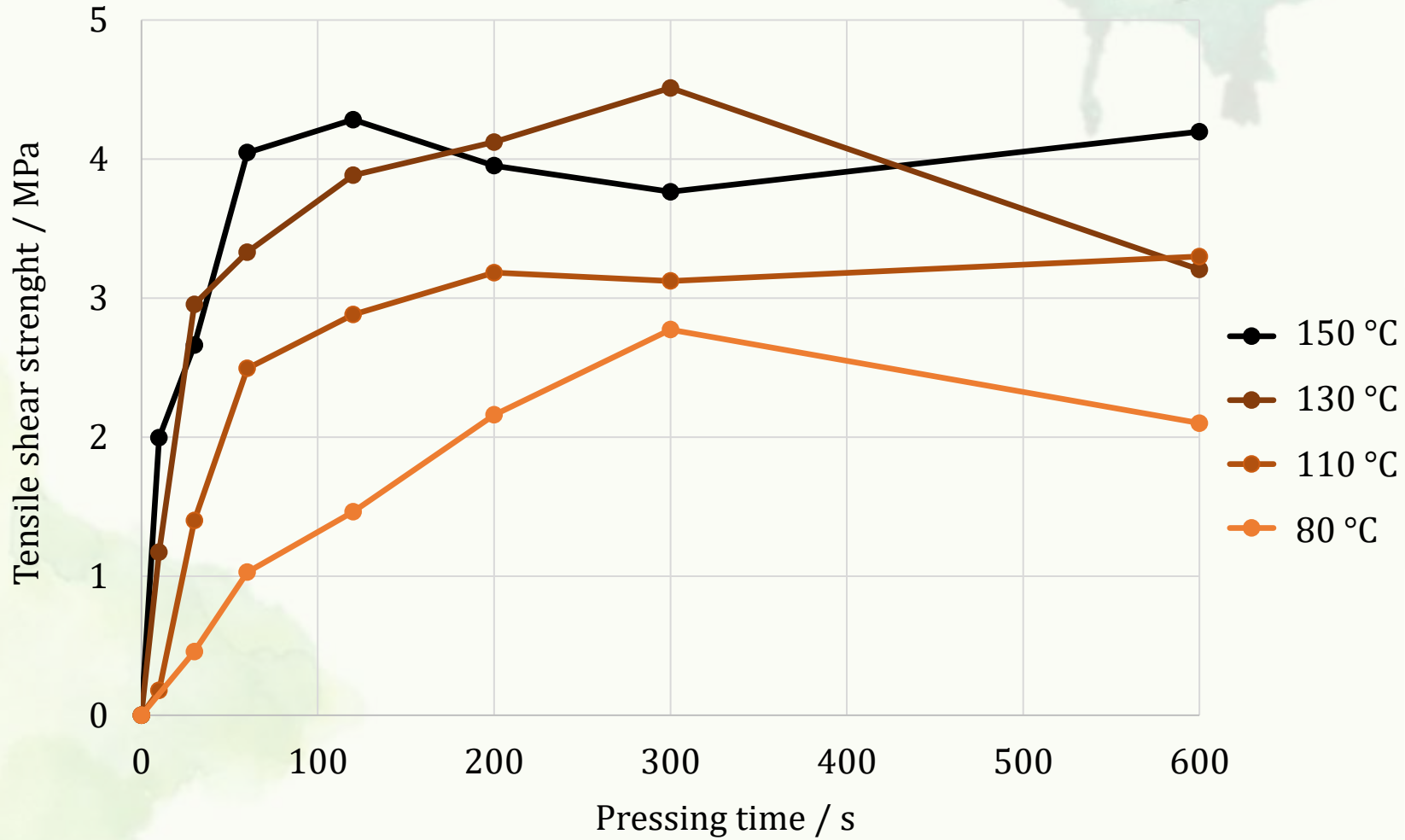
Veneer strips

- Temperatures: 80, 110, 130, 150 °C
- Pressing time: 10 to 600 s

ABES results

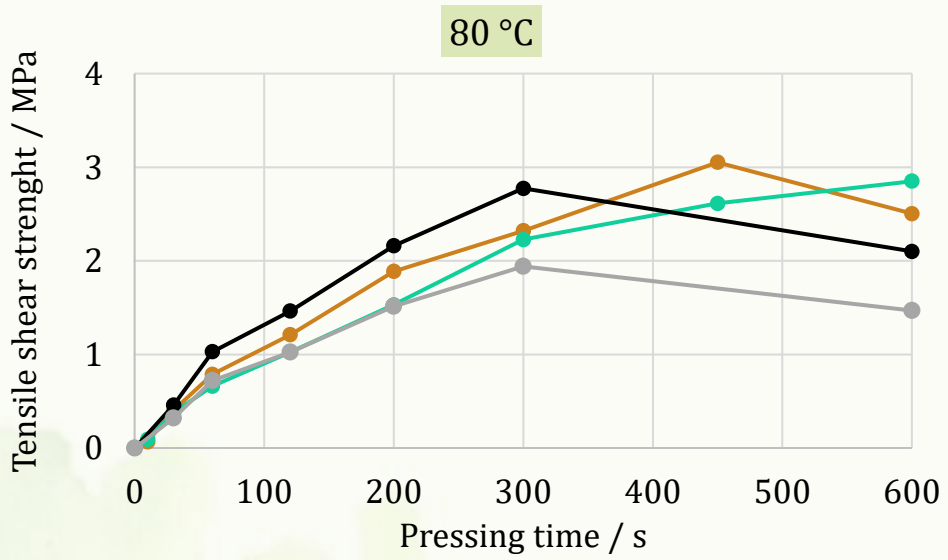


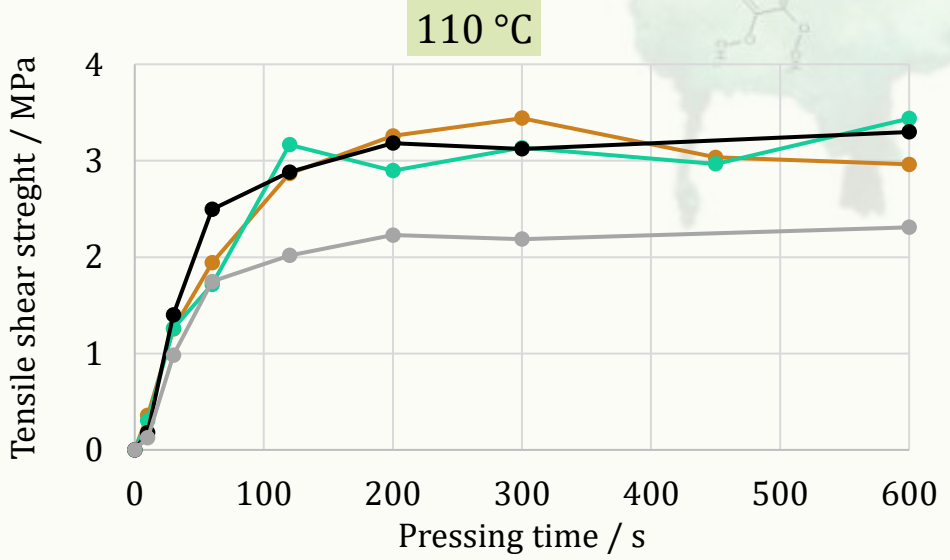
PF

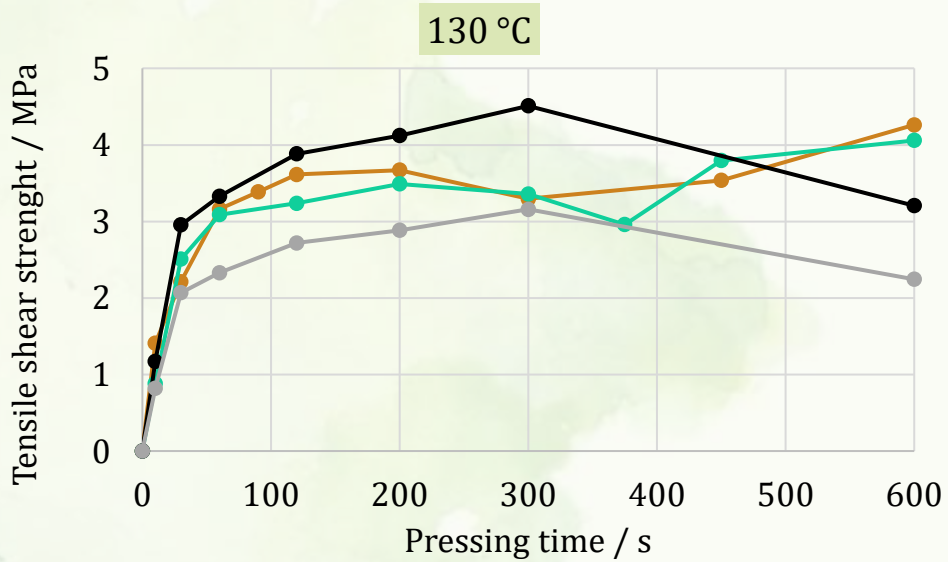


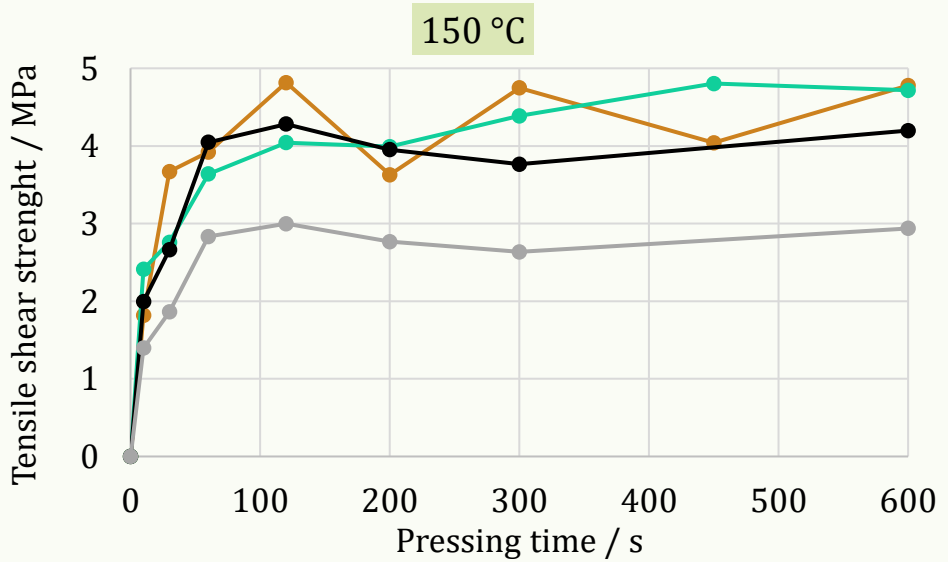
ABES results

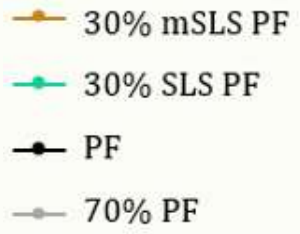
PF | 30% mSLS PF | 30% SLS PF



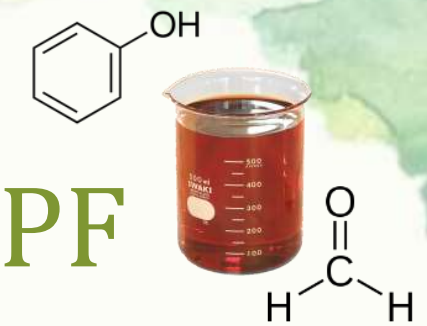








LSPF vs PF



Results:

- 30% SLS PF ≈ PF **when T>80 °C**;
- 30% mSLS PF ≈ PF;

Conclusions:

- **SLS** is a **promising** phenol substitute;
- **Methylolation** appears to be **essential** bellow 110 °C.

Plywood production

- PF
- 10% mSLS PF
- 20% mSLS PF
- 30% mSLS PF
- 30% SLS PF

Wheat flour

+

Calcium carbonate

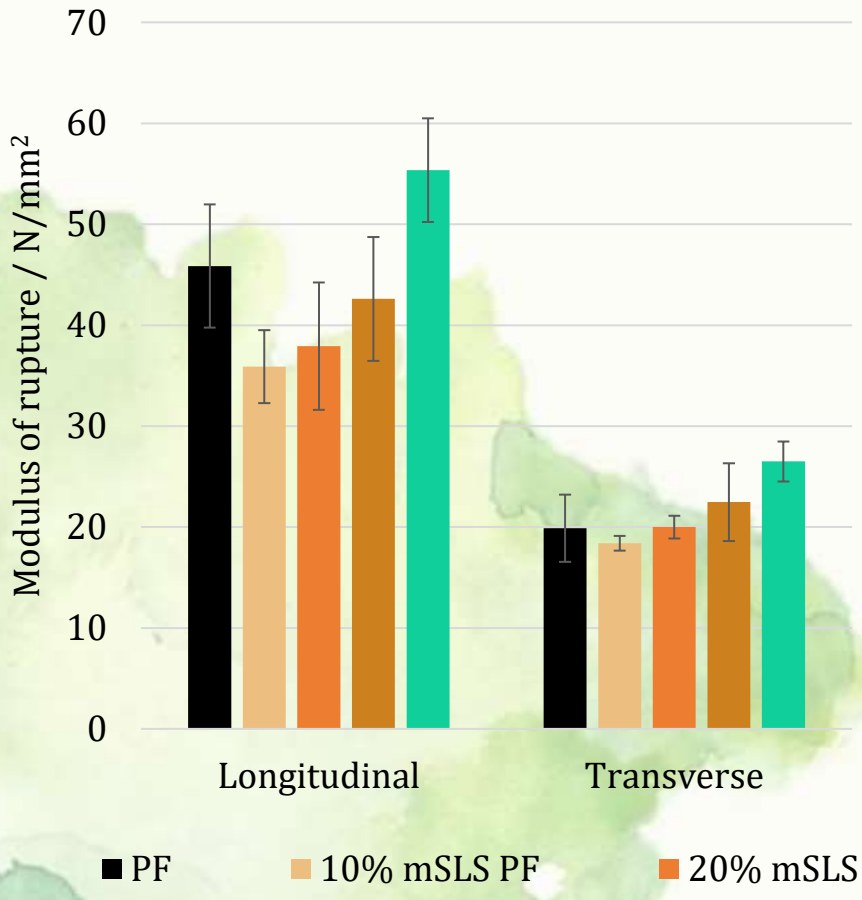
Adhesive mixture

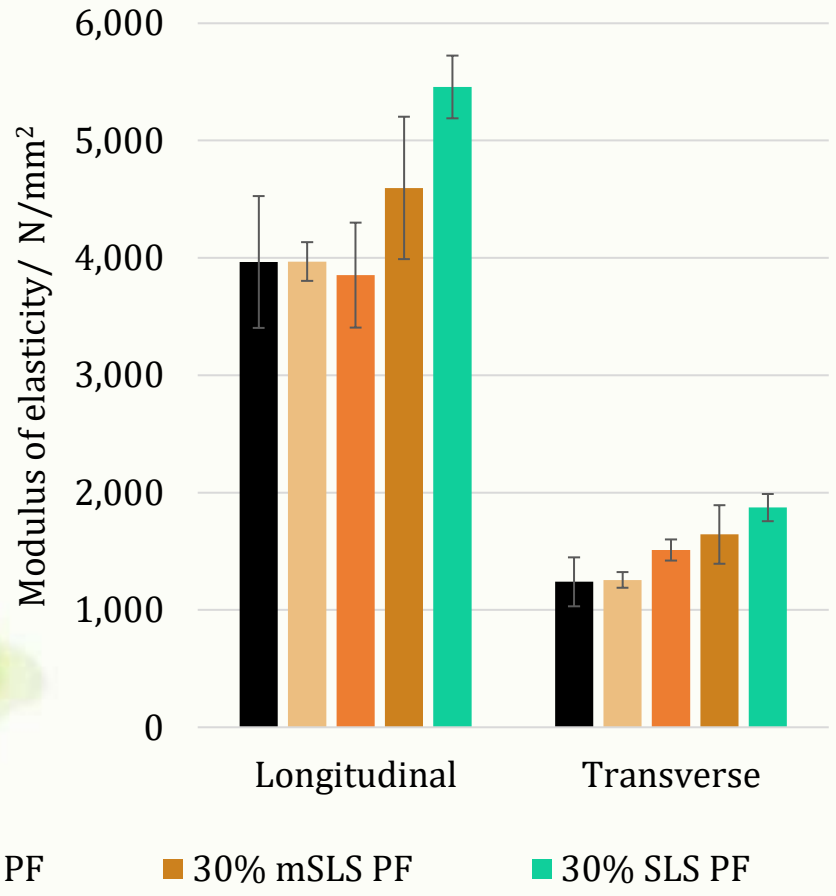
- 5-ply softwood plywood;
- Thickness: 10.5 mm;
- Temperatures: 130 °C;
- Pressing time: 10 min.

Mechanical properties

EN 310

Wood-based panels - Determination of modulus of elasticity in bending and of bending strength





PF 10% mSLS PF 20% mSLS PF 30% mSLS PF 30% SLS PF

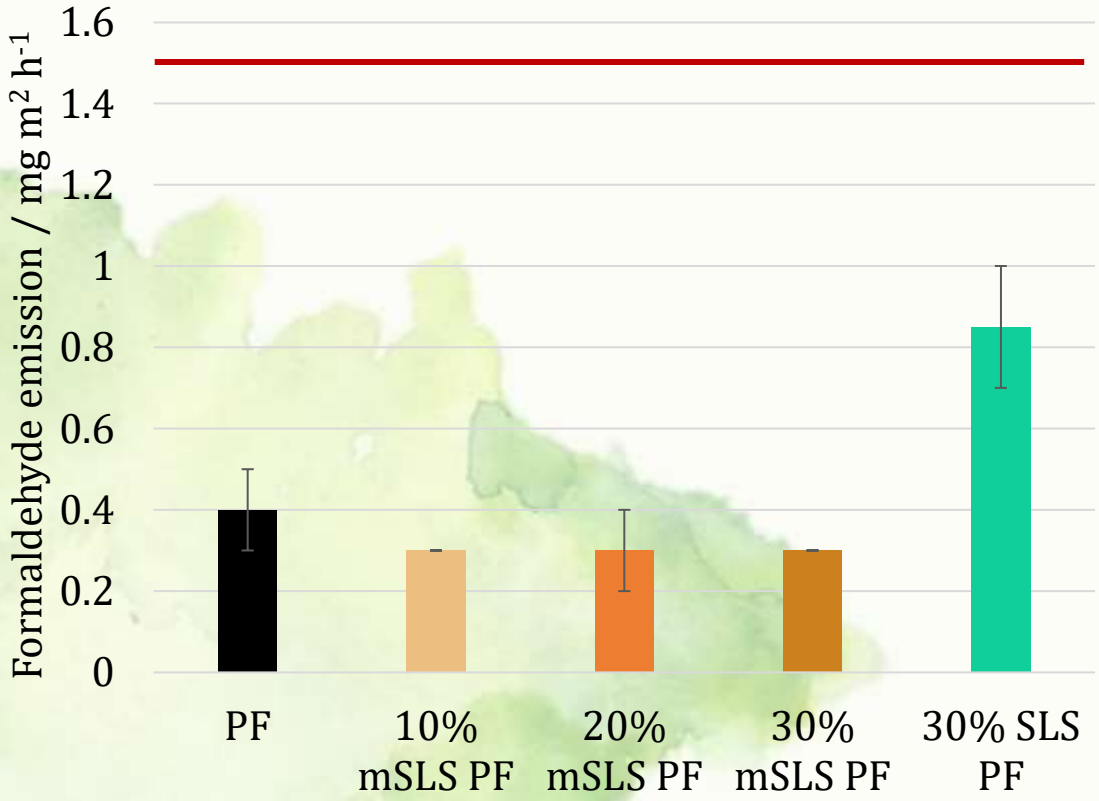
Formaldehyde emissions

EN ISO 12460-3
Determination of formaldehyde release - *Gas analysis method*

- Air flow (60 L/h) at 60 °C and <3% RH;
- Sample area 0.04 m^2;
- Formaldehyde absorbed by water in gas wash bottles;
- Sampling every hour for 4 hours.

Formaldehyde emissions

ISO 12460-3
Determination of formaldehyde release - *Gas analysis method*



Carb II

Mechanical properties

EN 314
Plywood – Bonding quality: class 3 –Exterior Conditions

24 h in water
20 °C

4 h in boiling water

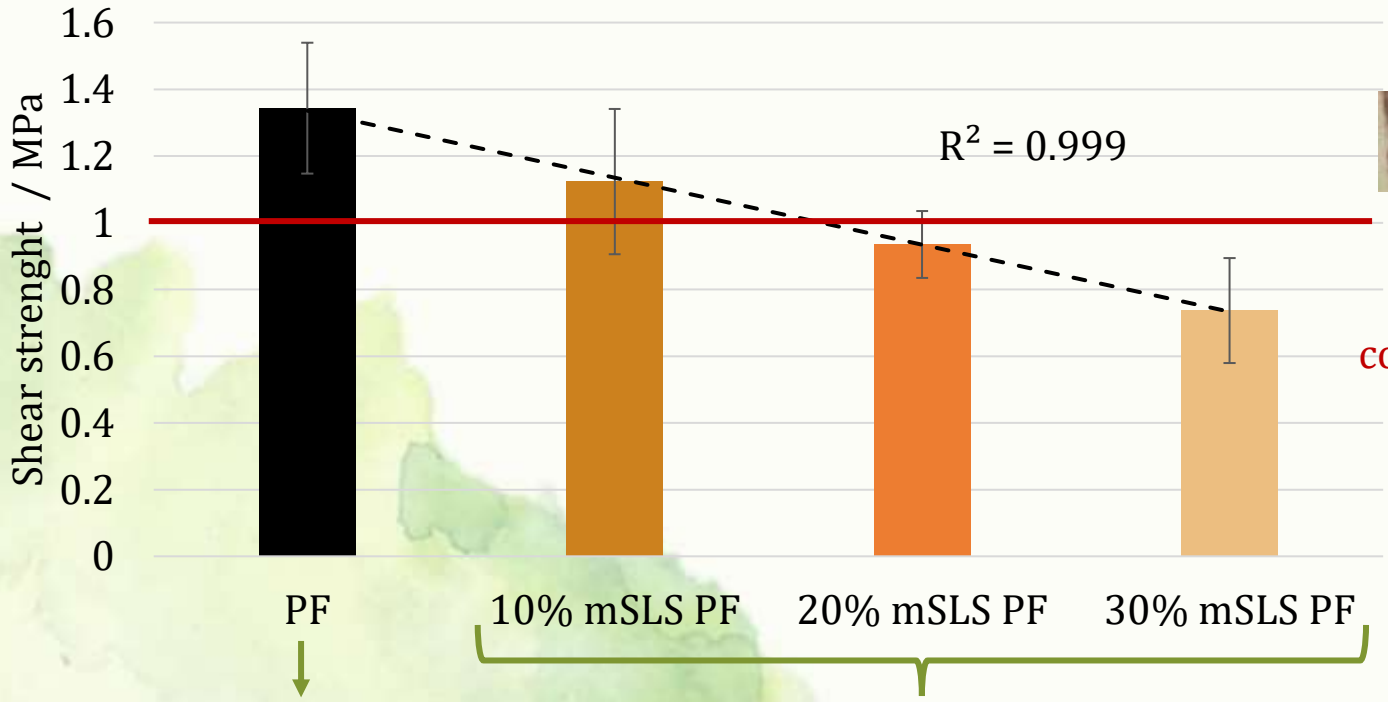
16 h at 60 °C

4 h in boiling water

Cooling in water for 1 h

Mechanical properties

EN 314
Plywood – Bonding quality : class 3 –Exterior Conditions



<40% apparent cohesive wood failure

Up to 80% a.c. wood failure

0% a.c. wood failure

Mechanical properties

EN 314
Plywood – Bonding quality : class 3 –Exterior Conditions

And the boards without methylolation?

Delamination after boiling

With methylolation

Conclusions

Lessons learned:

- LS methylolation significantly improved board performance;
- The LS boards do not obey the requirements of EN 314-2 for bonding quality – class 3.

Future work:

- LS need to be modified further – phenolation or hydrolysis;
- Additional crosslinkers need to be tested;
- Manufacturing conditions may be optimized further.

Acknowledgements

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