Bio-based adhesives from lignin and tannin

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Innovations & potential new technologies - the uncharted possibilities of utilizing the European LKWS in the bio-based products

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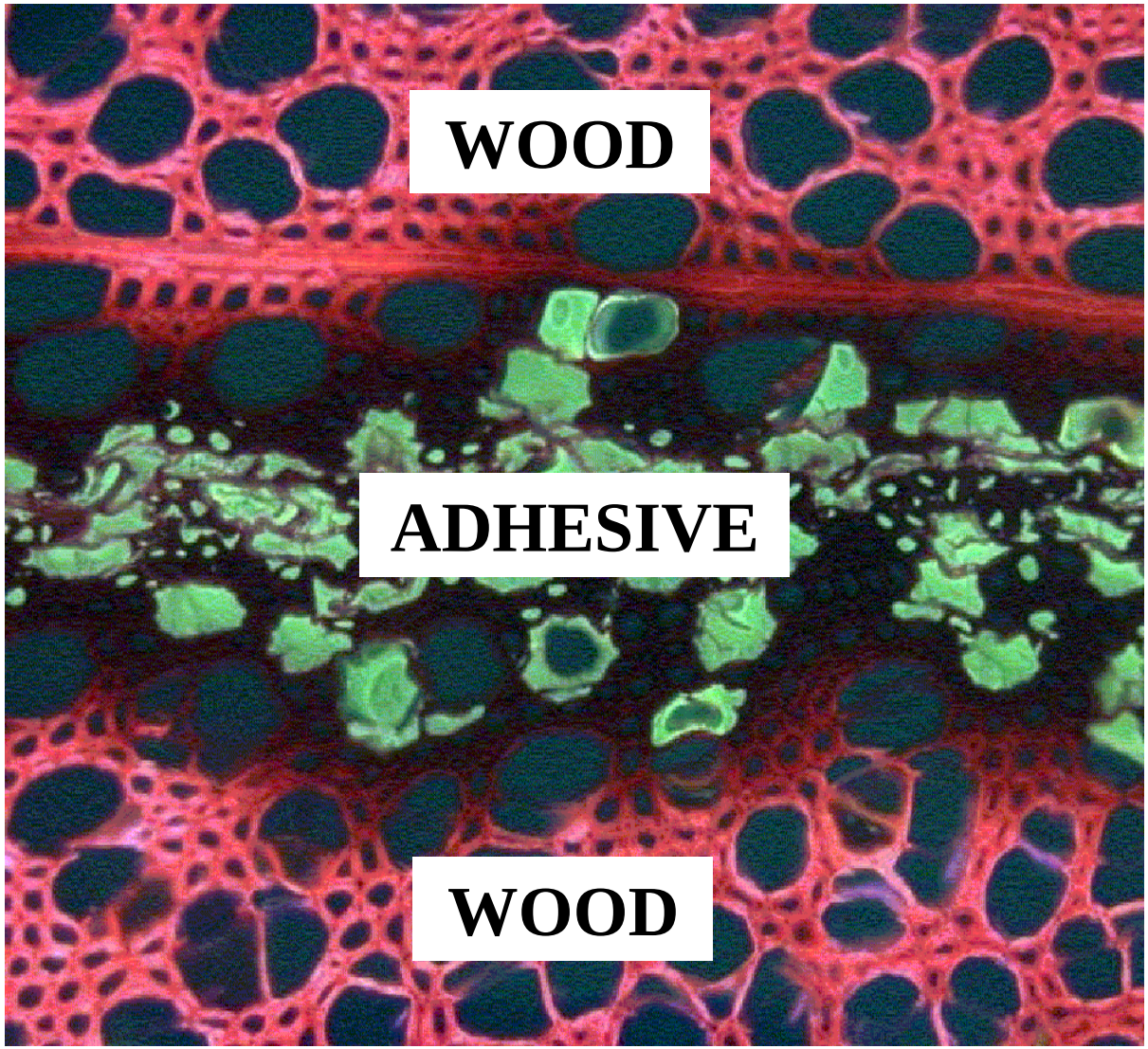
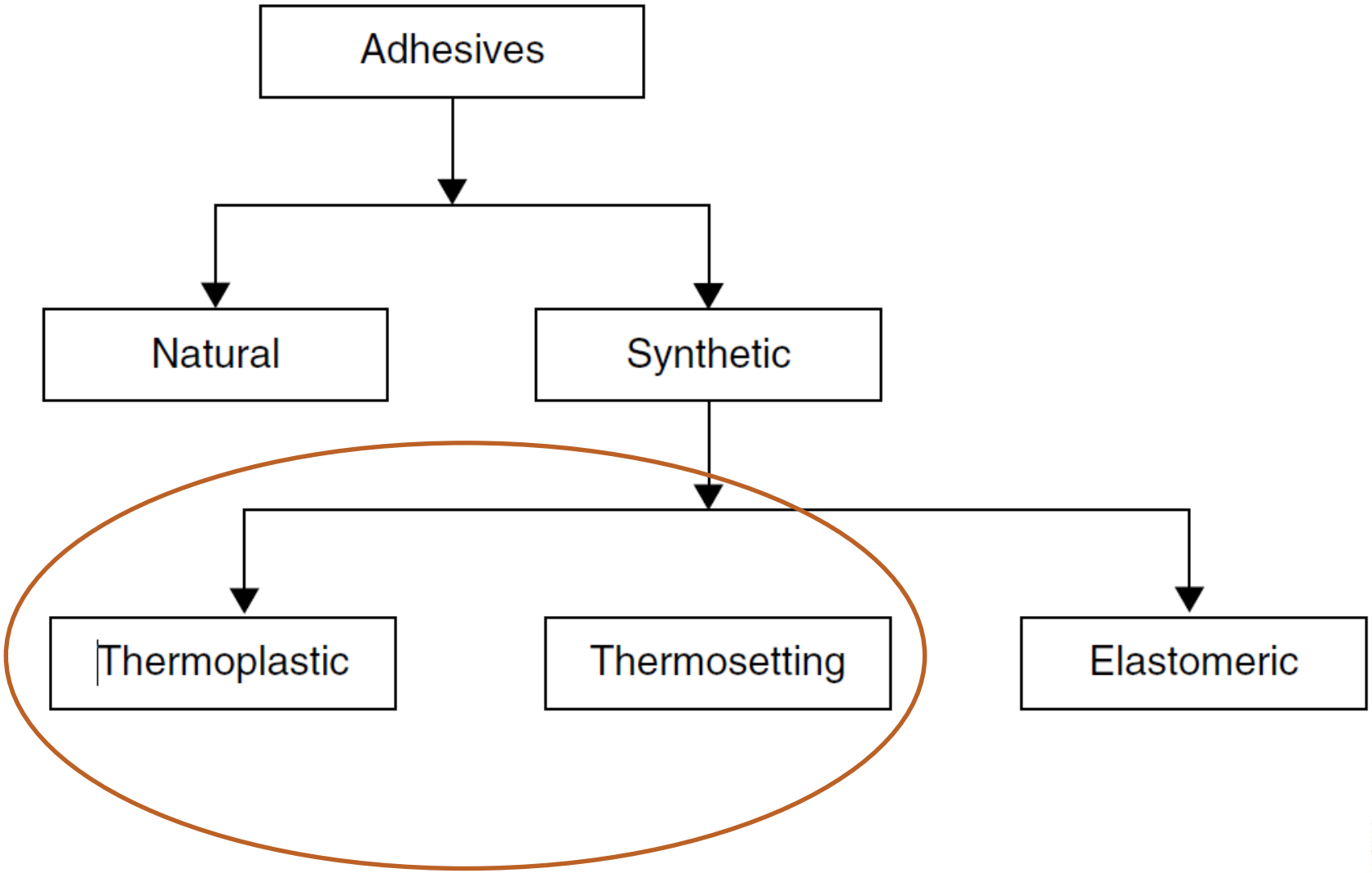
Outline of the presentation

1. **Introduction**
2. **Bonding of wood with bio-based adhesives**
   - Bonding with tannin-based adhesives
   - Bonding with lignin-based adhesives
   - Bonding with liquefied wood
     - Pure LW
     - Combination of LW and MUF
3. **Conclusions**

Wood-adhesive bond

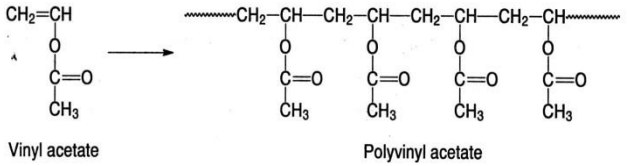


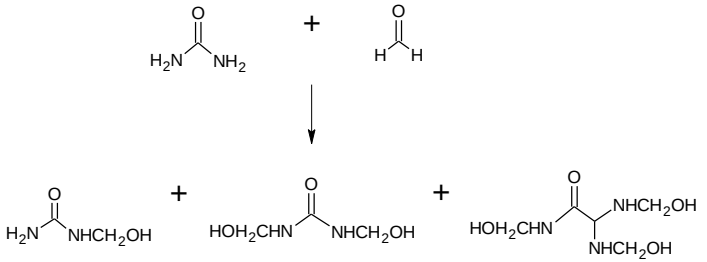
Adhesives - classification

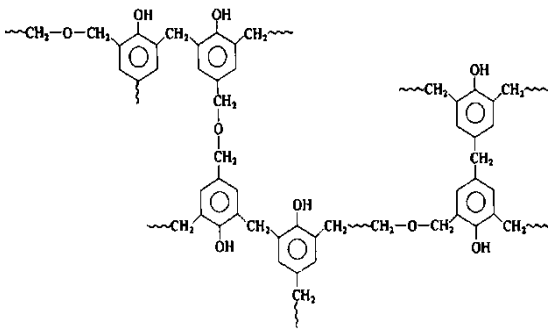


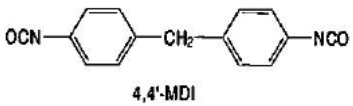
Typical adhesives in wood industry

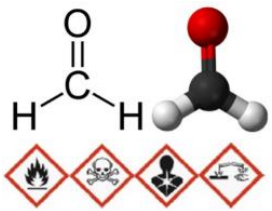
- Polyvinyl acetate (PVAc)
- Urea-formaldehyde (UF)
- Melamine-formaldehyde (MF)
- Melamine-urea-formaldehyde (MUF)
- Phenol-formaldehyde (PF)
- Resorcinol-formaldehyde (RF)
- Phenol-resorcinol-formaldehyde (PRF)
- Isocyanate (pMDI)
- Polyurethane (PUR)
- Hot-melt
- …





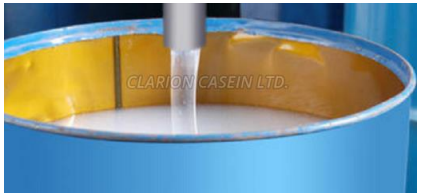


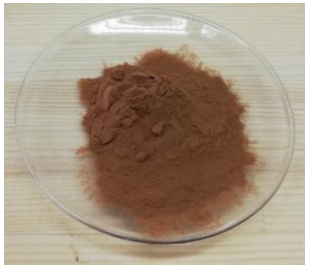




Natural adhesives

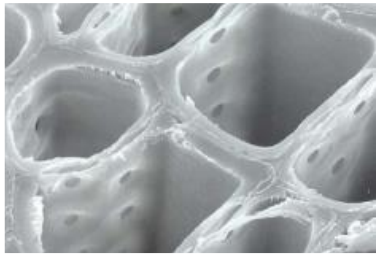
- Protein
  - Plant-based
    - Soybeans
  - Animal-based
    - Glutin
    - Blood
    - Casein
- Carbohydrate
  - Starch
  - Cellulose
- **Lignocellulosic**
  - **Tannin**
  - **Lignin**
  - **Liquefied wood**



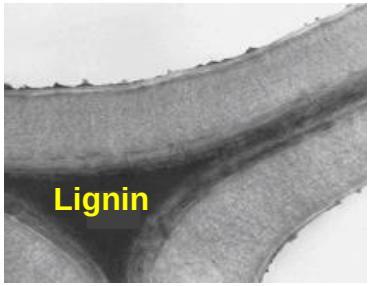


Wood, lignin and tannin

Wood



Lignin



Tannin

Furniture

Construction

Timber

GLULAM

CLT

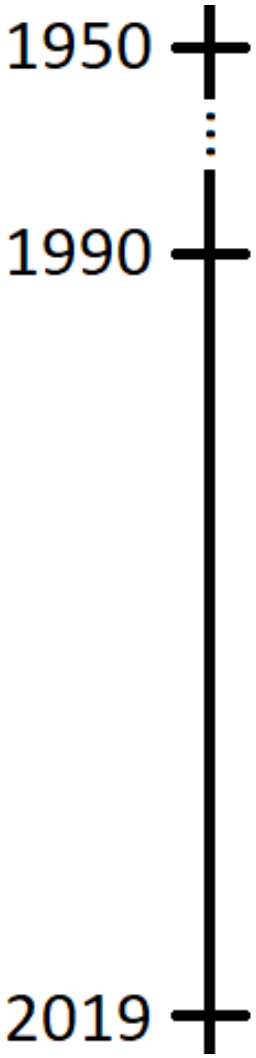
Composites

Extractives

…

Adhesives

Tannin and lignin adhesives



- Replacing up to ⅓ phenol or resorcinol in FF and RF adhesives with lignin / tannin (quebracho, mimosa, chestnut, …)
- Use of VOC-free hardeners (hexamine, glyoxal, furfuryl alcohol,…)
- Modification of lignin
- Tannins from European conifers
- The most commercially interesting tannin-hexamine

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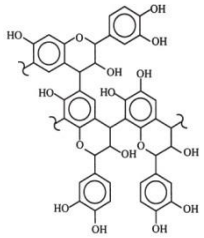
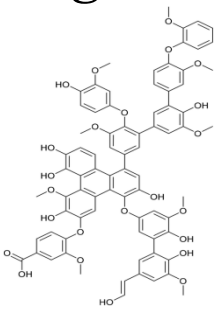
Adhesive formulations

- Tannin

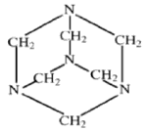


50%

- Lignin



- Hexamine 6%



- Water 44 %

Different formulations:

- Pure tannin adhesive +
- Pure lignin adhesive -
- Tannin / Lignin adhesives:

100/0

80/20

60/40

40/60

20/80

0/100

Curing characterization of the bio-adhesives

- **DSC:**
  - HP DSC1 (isothermal or dynamic conditions)
  - Heat flow => degree of cure

- **DMA:**
  - oscillatory tests (rheometer ARES G2)
  - G‘, G“ => gel / vitrification time

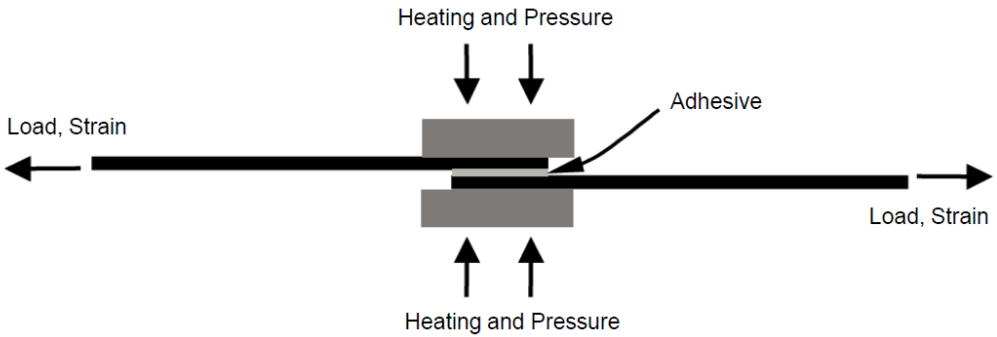
- **DEA:**
  - LCR meter and IDEX sensor
  - electrical conductivity => degree of cure

- **Cure kinetics:**
  - model-based kinetics (such as the nth-order model)
  - model-free kinetics (MFK)

Strength and durability testing

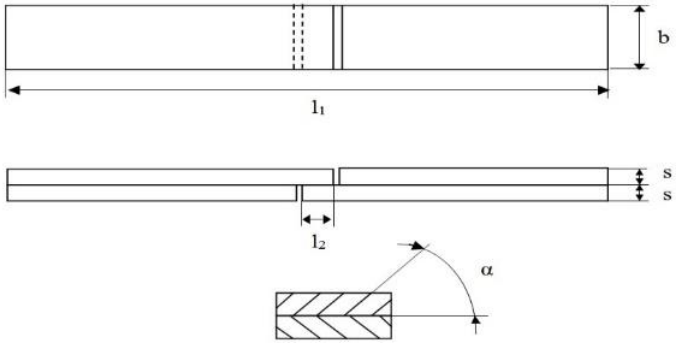
- **Testing machine- Zwick:**
  - EN standard – shear test
  - Exposure to different conditions

- **ABES:**
  - Optimisation of pressing parameters
    - Press temperature
    - Cooling effect
  - Bond strength development



Adhesive bonding

- Beech lamellas according EN 205
  - 5 mm
  - 10 %
- 200 g/m^2

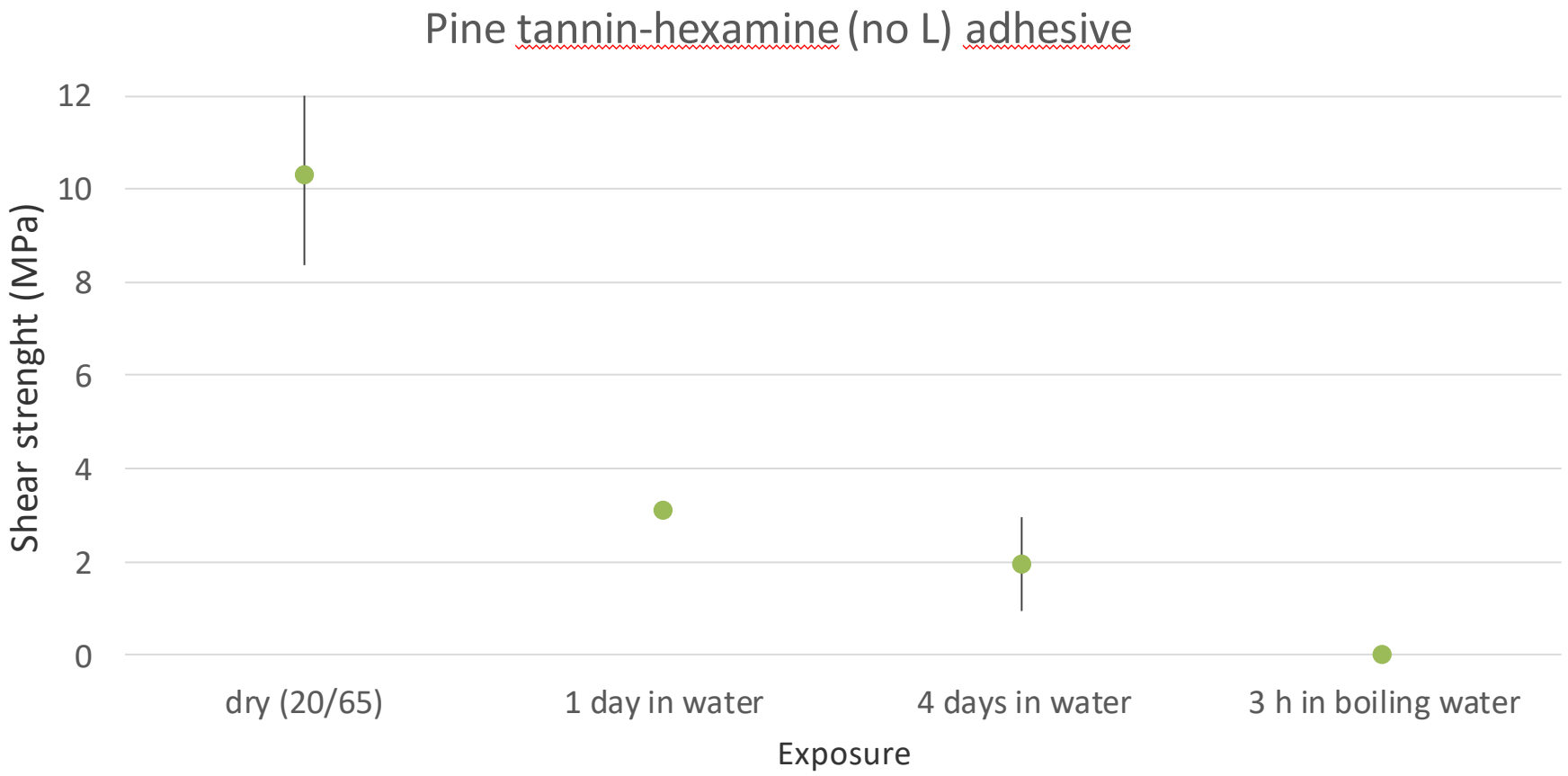


- Hot press:
  - 150 - 170 °C
- 15 bars
- 10 min

Adhesive bond performance

- Shear strength test of lap joints
- % of wood failure
- Pre-treatment:
  - Dry
  - Wet
    - Cold water
    - Boiling

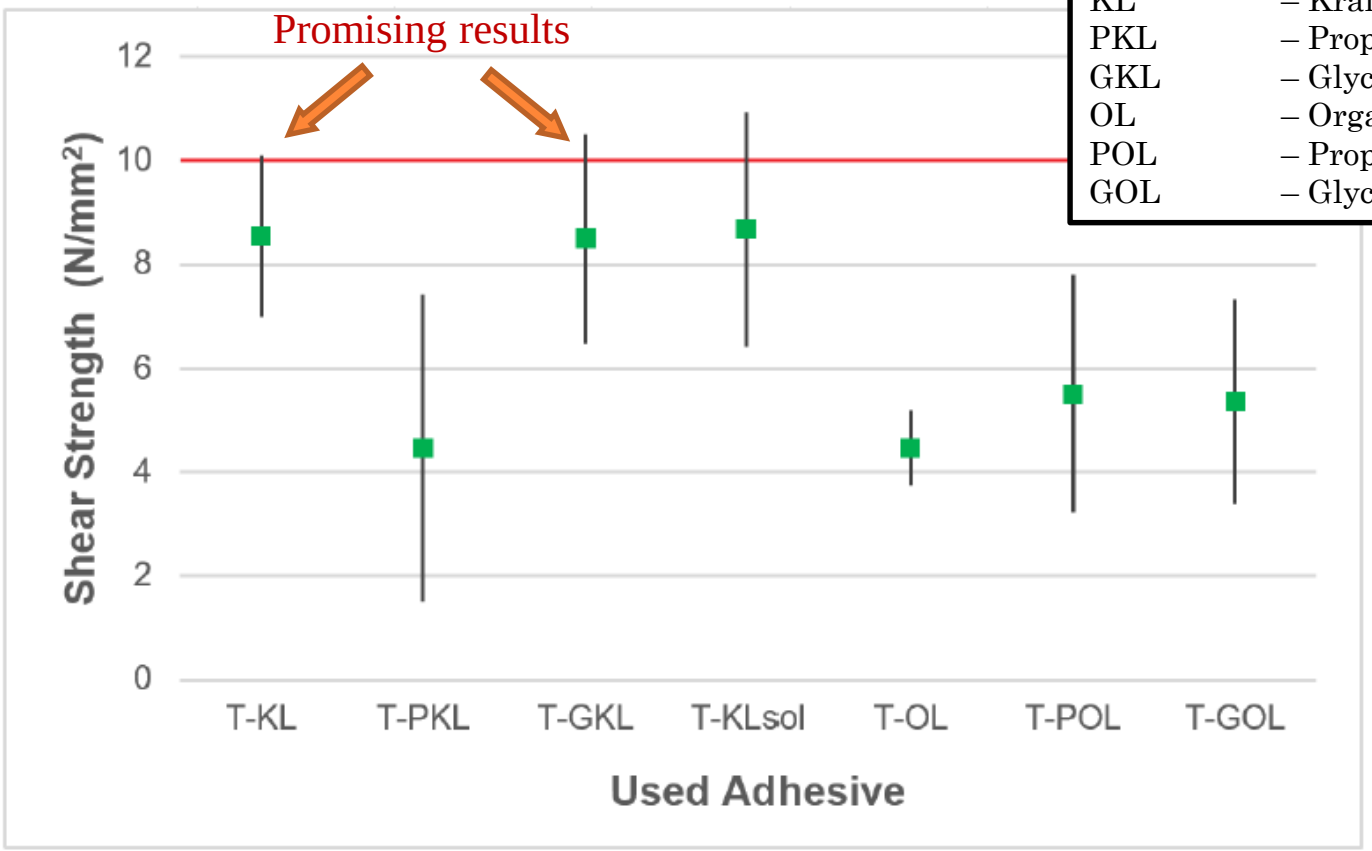
Shear strength of tannin adhesive



Pine tannin = Maritime pine (*Pinus pinaster*) containing 92-94 % of polyphenols

Tannin-lignin-hexamine adhesives

Pine tanin : lignin : hexamine = 50 : 50 : 6



*** Pine tannin + hexamine +**

No L	– without lignin
KL	– Kraft lignin
PKL	– Propoxylated Kraft
GKL	– Glycidolated Kraft
OL	– Organosolv lignin
POL	– Propoxylated Organosolv
GOL	– Glycidolated Organosolv

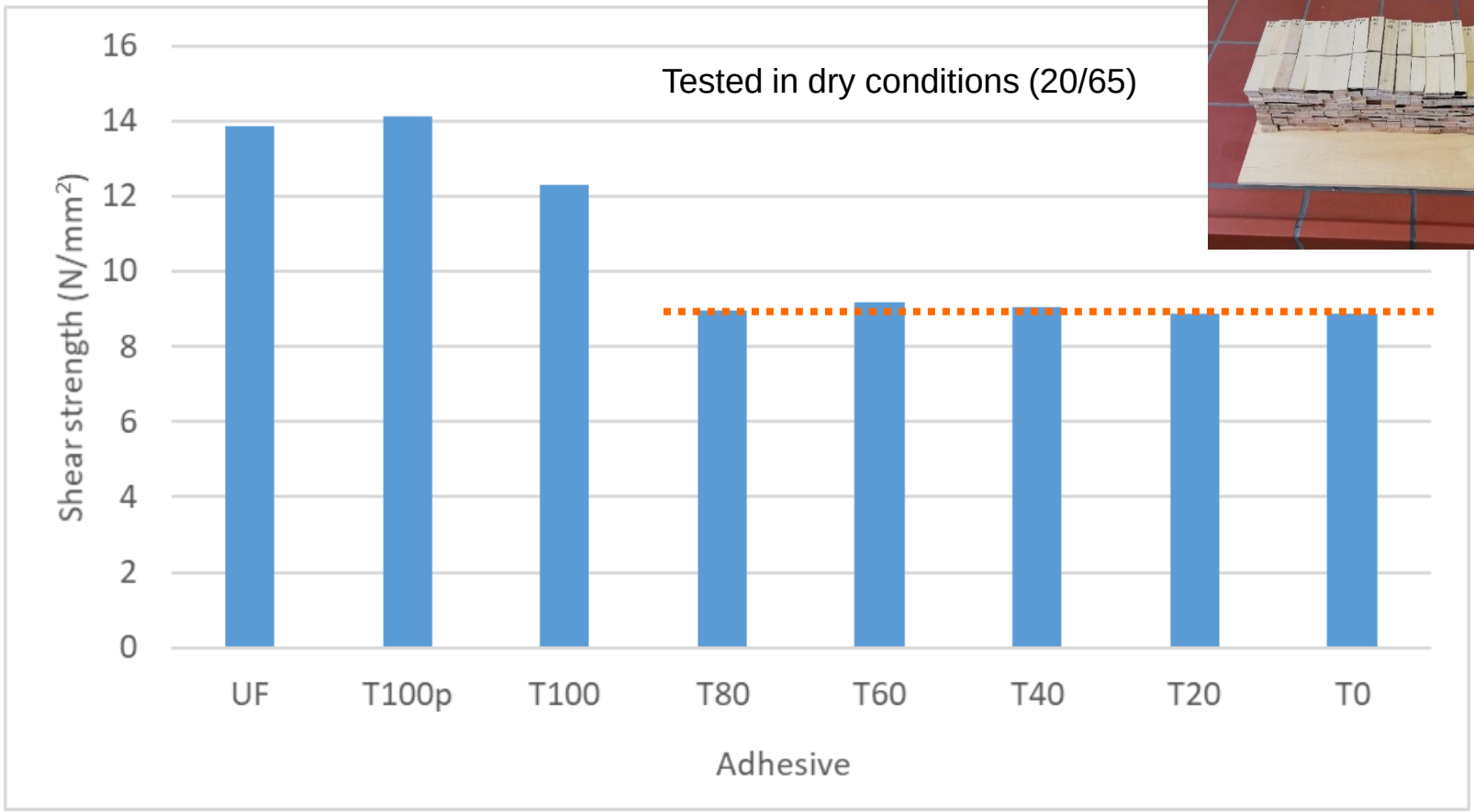
Shear strength of the biobased adhesive bonds synthesized from tannins and different types of lignins

Classification according to EN 12765

Conditioning sequences		Adhesive strength in N/mm² **Durability classes**			
Sequence number	Duration and condition	**C1**	**C2**	**C3**	**C4**
1	7 days in standard atmosphere 20 °C / 65 % RH	≥10	≥10	≥10	≥10
2	7 days in standard atmosphere 1 day in water at 20±5 °C		≥7	≥7	≥7
3	7 days in standard atmosphere 3 h in water at 67±2 °C 2 h in water at 20±5 °C			≥4	
4	7 days in standard atmosphere 3 h in boiling water 2 h in water at 20±5 °C				≥4

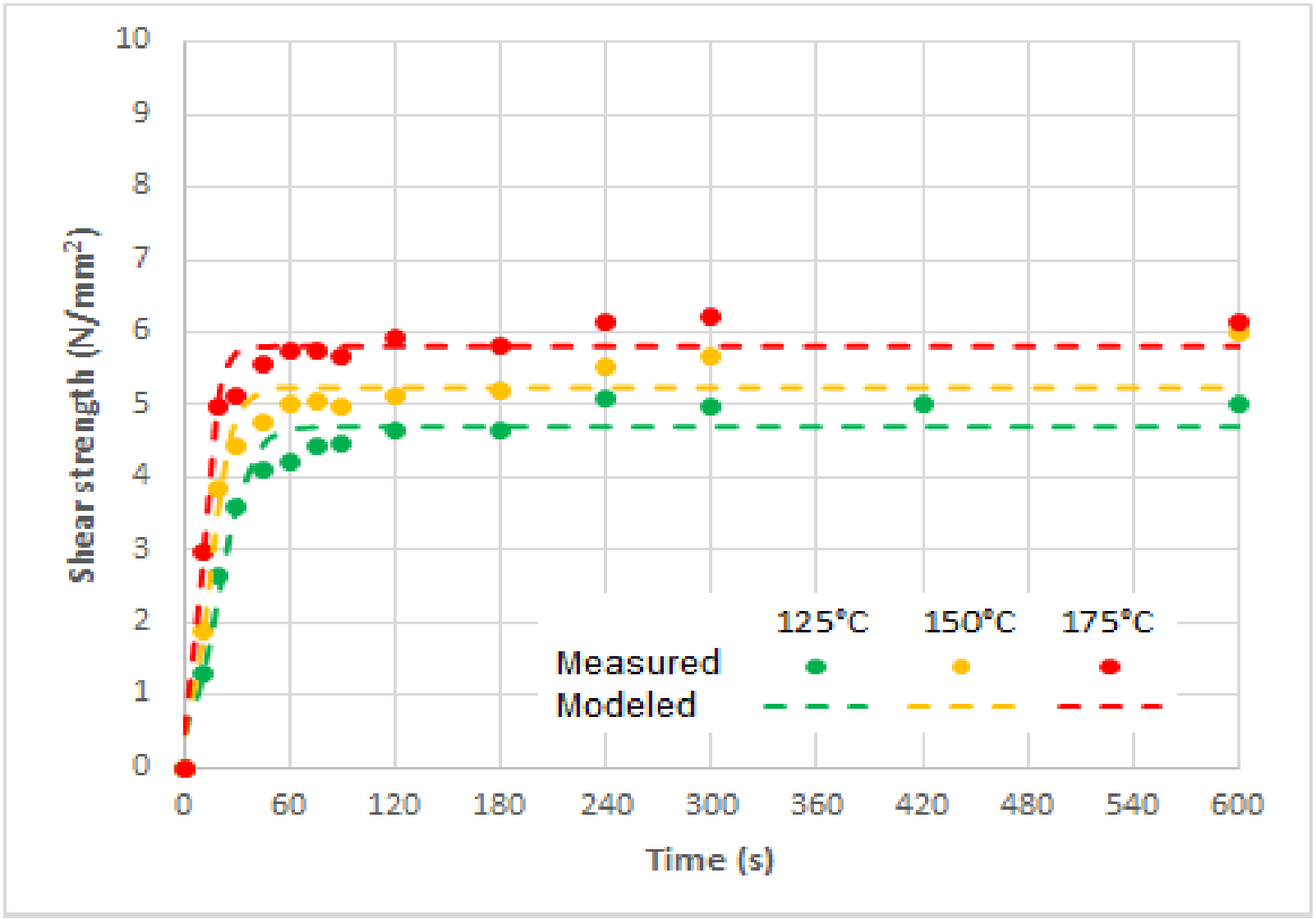
C1 = Interior application, EMC < 15%

Tannin / Kraft lignin adhesive



- UF = urea-formaldehyde as reference adhesive
- T100p = reference tannin adhesive (pH=6,5)
- T100, … T0 => T = tannin, # = % of tannin, rest is % of lignin (pH=11)

ABES of tannin adhesive



Liquefied Wood as an Adhesive

- Synthesis of adhesives based on liquefied wood
  - PF, epoxy, PUR
- **Combination with commercial synthetic adhesives**
  - UF, MF, MUF
  - up to 50 % of liquefied wood, mostly 25 - 30 %
- **<u>As an independent component</u>**

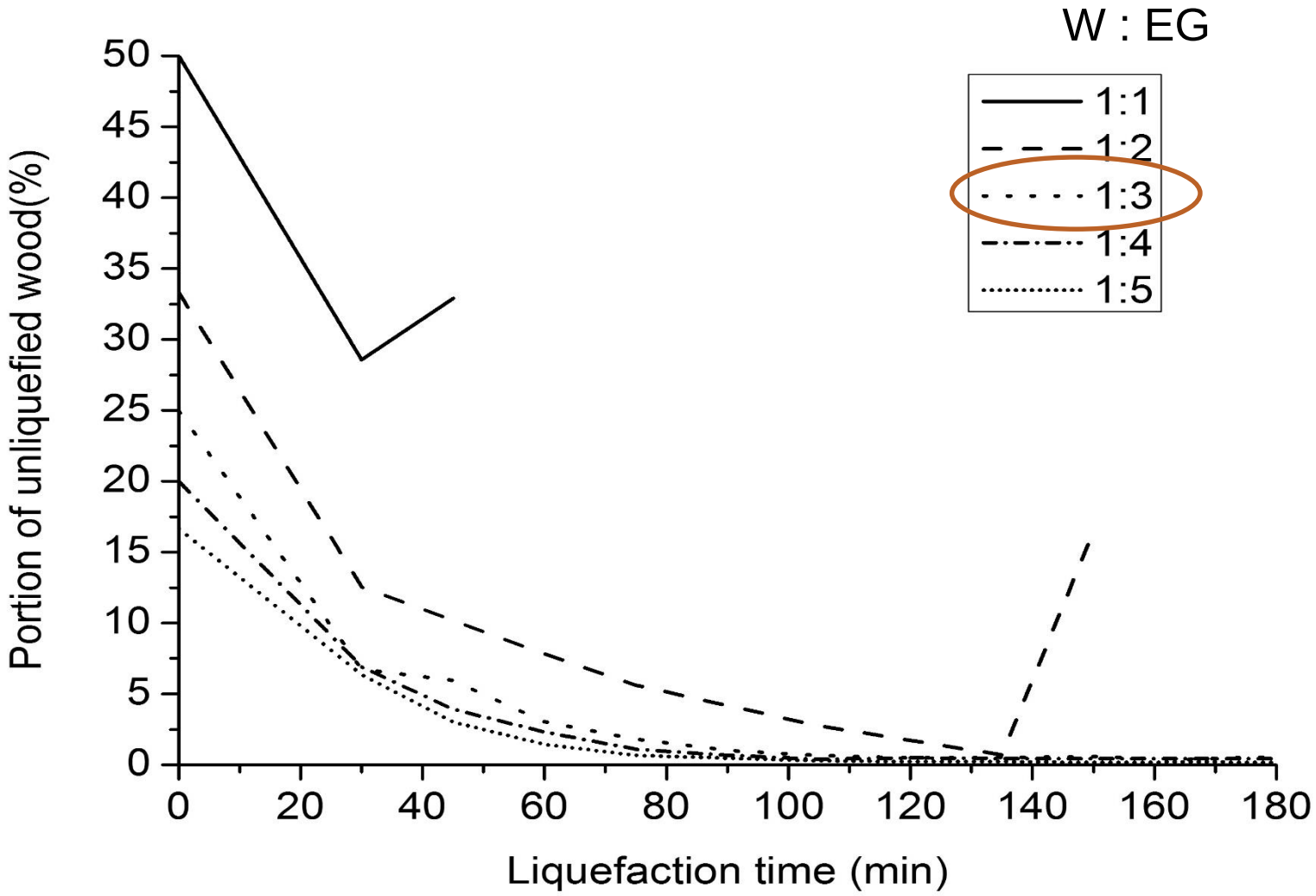
Materials for Liquefied Wood

WOOD: black poplar (*Populus nigra* L.)

SOLVENT: ethylene glycol (EG)

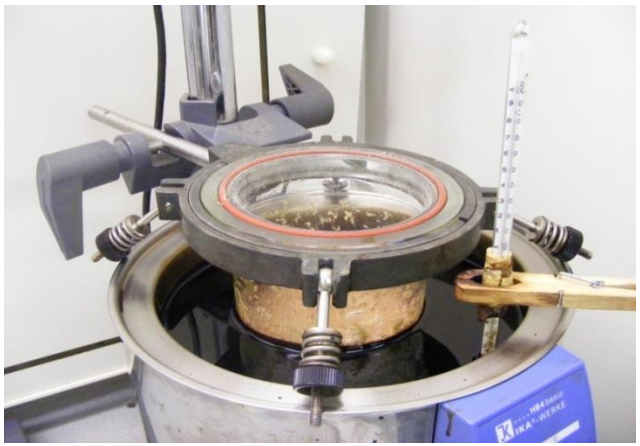
CATALYST: sulphuric acid

Optimization of wood liquefaction



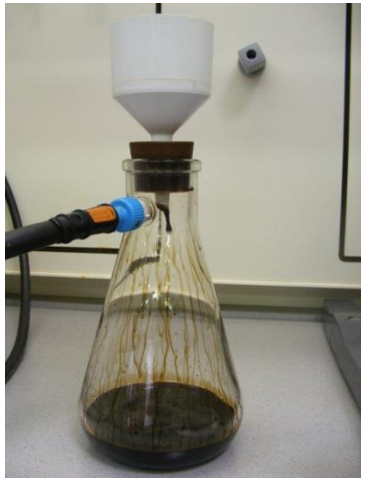
Methods: Liquefaction

Poplar:EG = 1:3
3 % sulphuric acid



180 °C

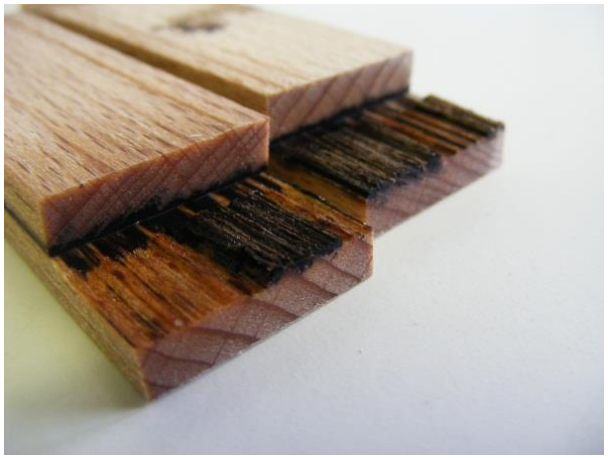
120 min



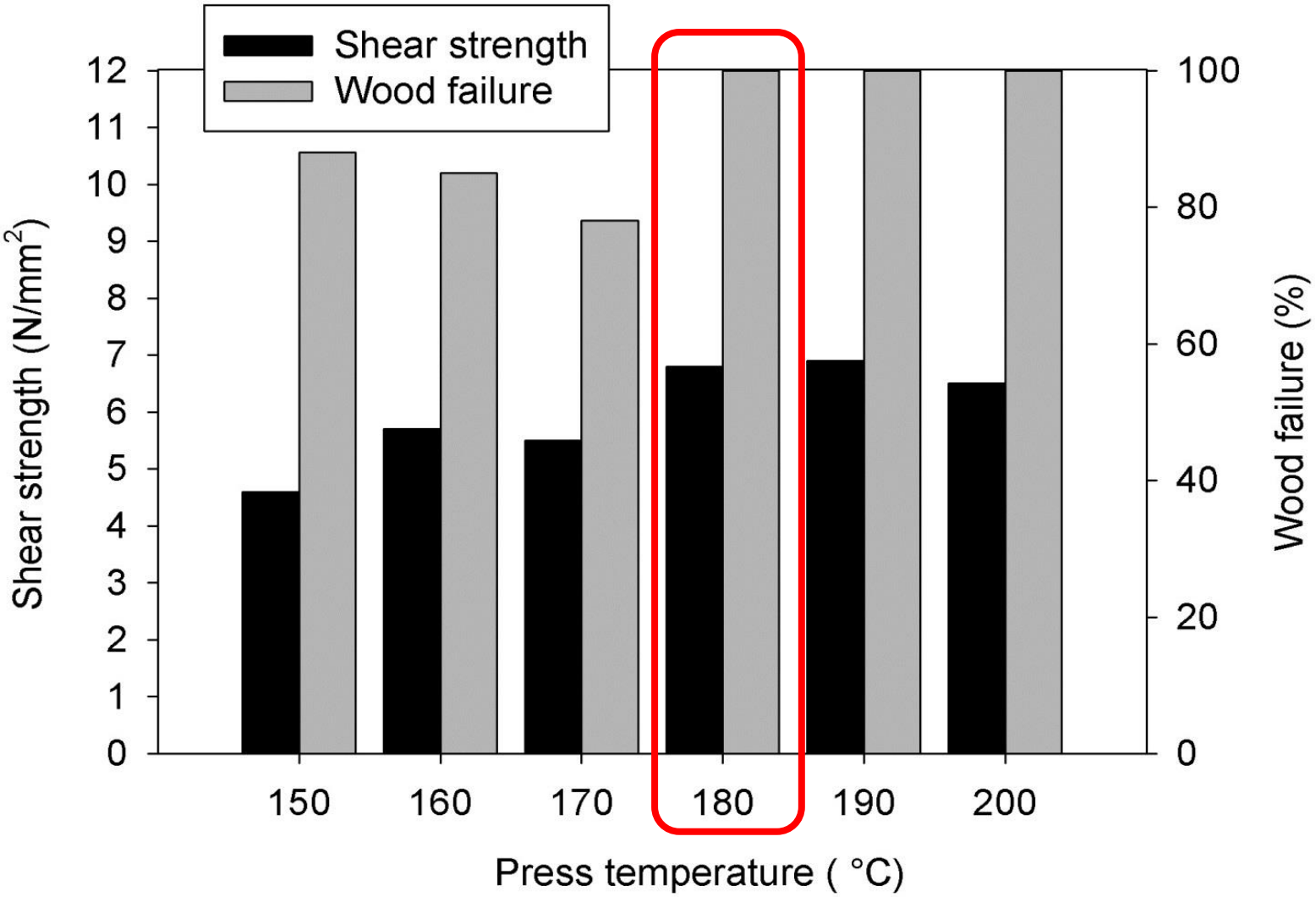
Filtration

Rotary evaporation

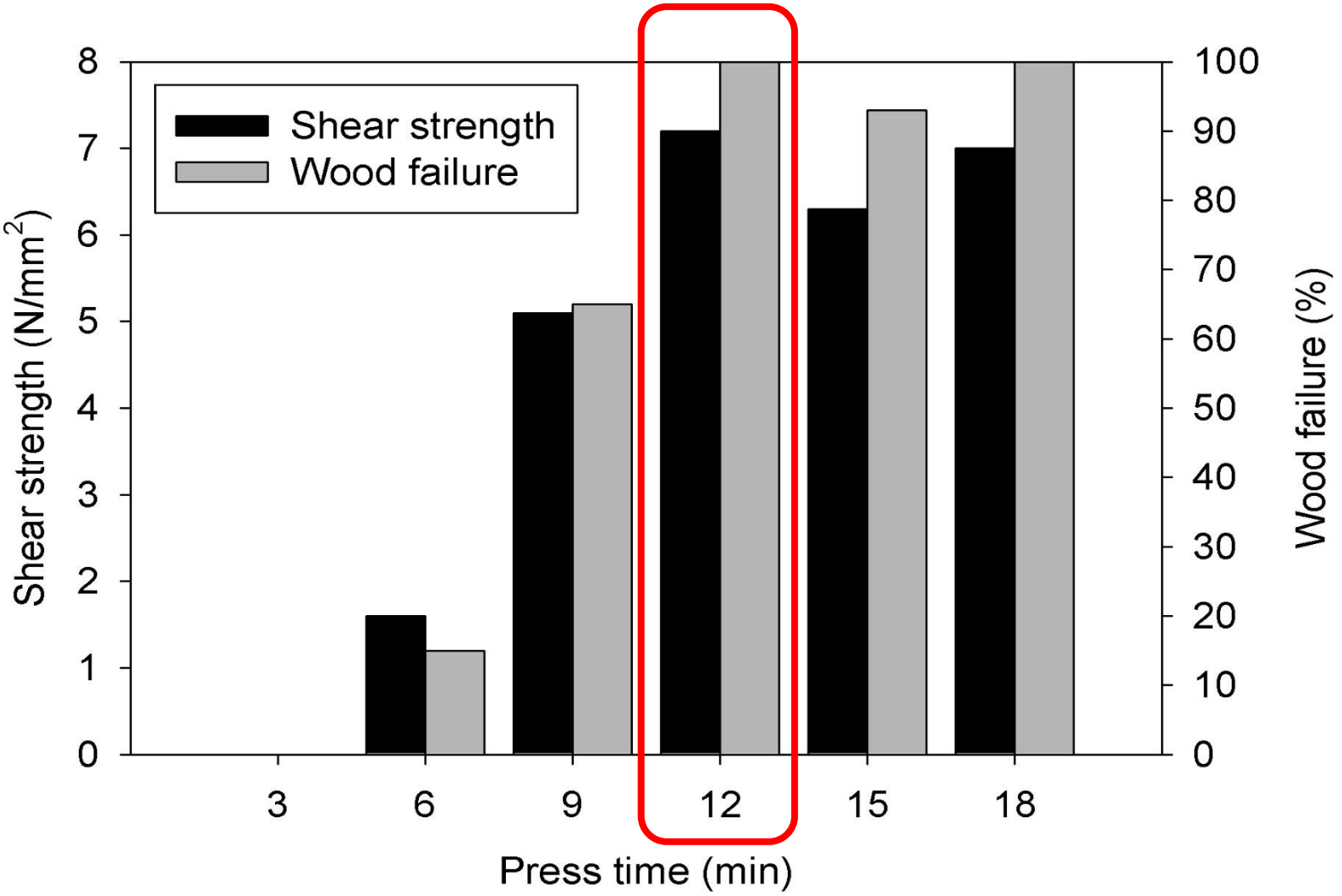
Bonding and Testing



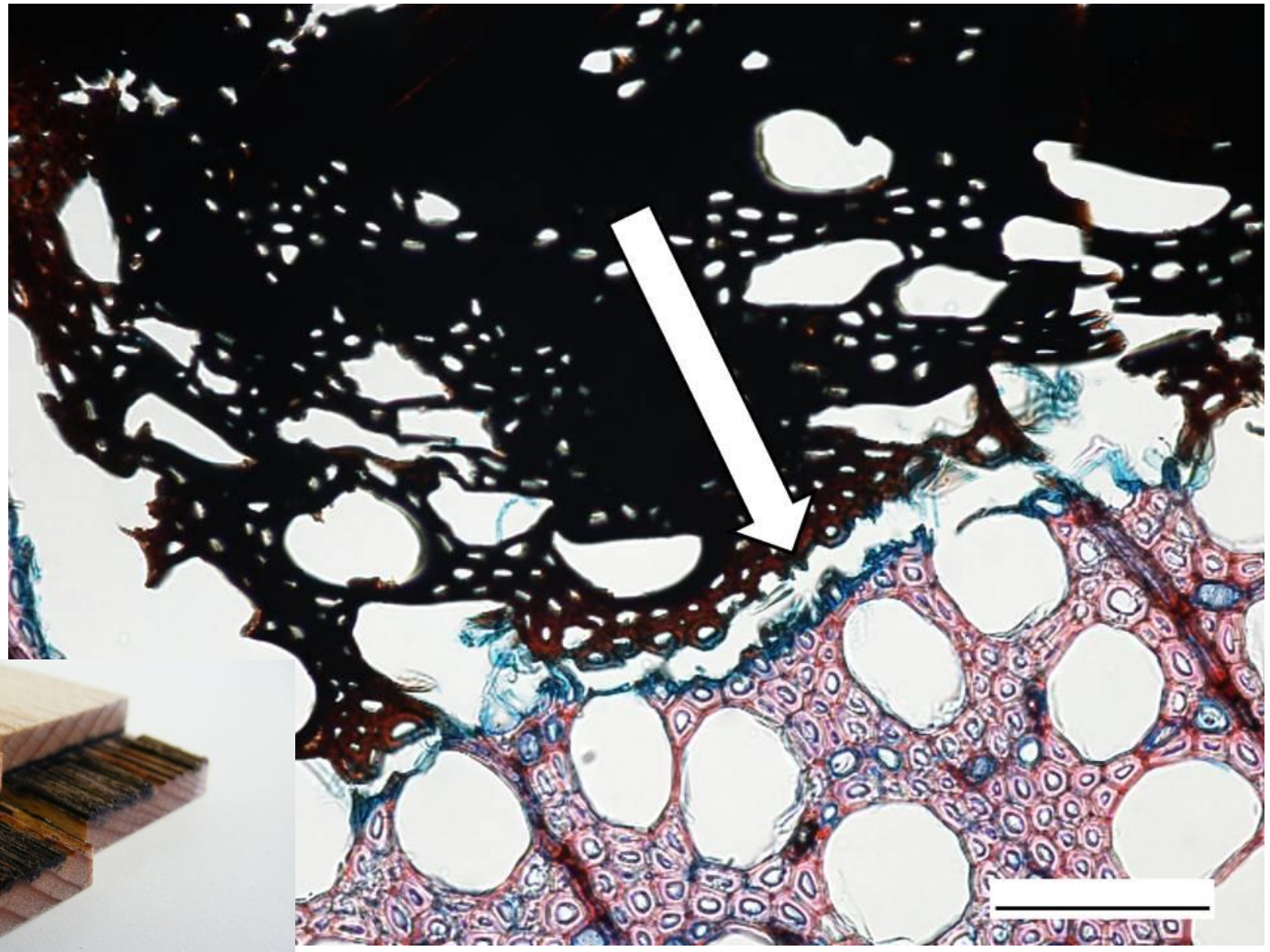
Influence of press temperature

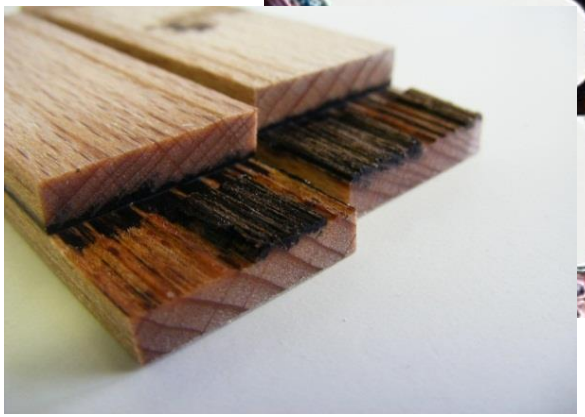


Influence of pressing time



Bond line of liquefied wood

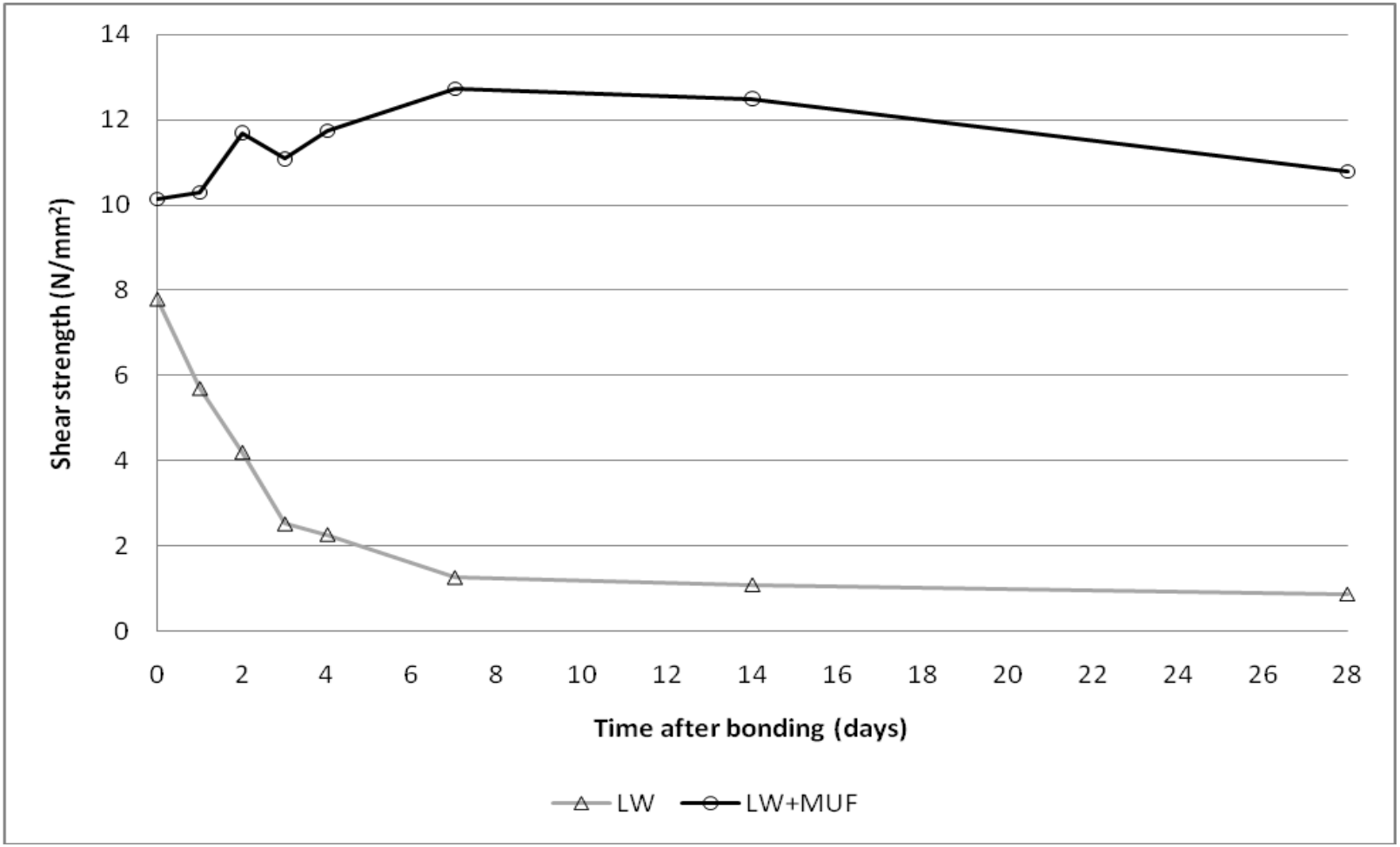




Liquefied wood and MUF

- To combine pure LW with melamine-urea-formaldehyde MUF) resin to improve the adhesive properties:
  - 25/75 (LW+MUF)
  - 100/0 (LW)
- High frequency technology
  - 200 °C
  - 600 seconds
  - 10 bar
- Shear test EN 205

Liquefied wood and MUF



Conclusions

- **Tannin:**
  - Two tannin adhesives passed the threshold value for C1.
- **Lignin:**
  - All the specimens bonded with the adhesive mixture containing lignin did not achieve requirement for C1.
- **Liquefied wood:**
  - All the specimens bonded with the liquefied wood did not achieve requirement for C1.
- **General:**
  - With further optimization of the mixtures and pressing at higher temperatures, bio-based adhesives have a potential for development and application.
  - Non-structural applications in dry conditions.