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Softwood bark polyphenols – extraction and applications

Petri Widsten[1,*], Satu Salo[1], Marc Borrega[1], Anna Kalliola[1], Lauri Tuominen[1], Melissa Agustin[1], Jenni Rahikainen[1], Elisa Spönla[1], Andreas Treu[2]
[1] VTT Technical Research Centre of Finland Ltd, Finland
[2] Norwegian Institute of Bioeconomy Research (NIBIO)
* Corresponding author email address: petri.widsten@vtt.fi

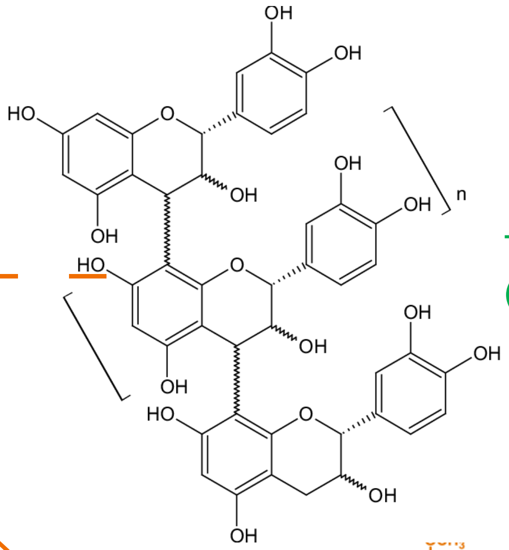
Content

- Spruce bark tannin (ST)
  - Extraction
  - Characterisation

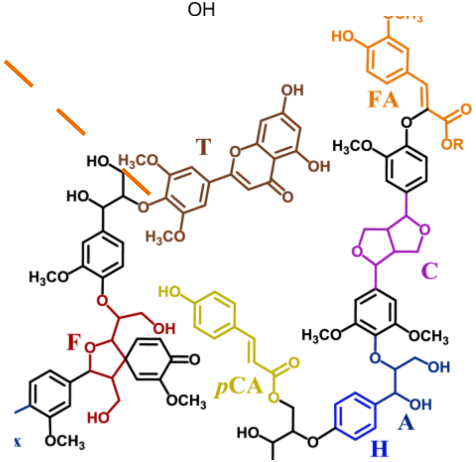
- Applications of ST currently investigated at VTT
  - Tannin nanoparticles (TNPs) for antibacterial coatings (Miria EU project, RIA)
  - Formaldehyde-free plywood/particleboard/MDF adhesives (SuperBark EU project, RIA)
  - Nitrogen-based flame retardants (Biophenom EU project, RIA; Biosafire EU project, IA)
  - Wood preservative (BarkBuild ERA-NET project)

ERA-NET Cofund Action "ForestValue — Innovating forest-based bioeconomy"

Spruce tannin (ST)



Tannin (procyanidin)

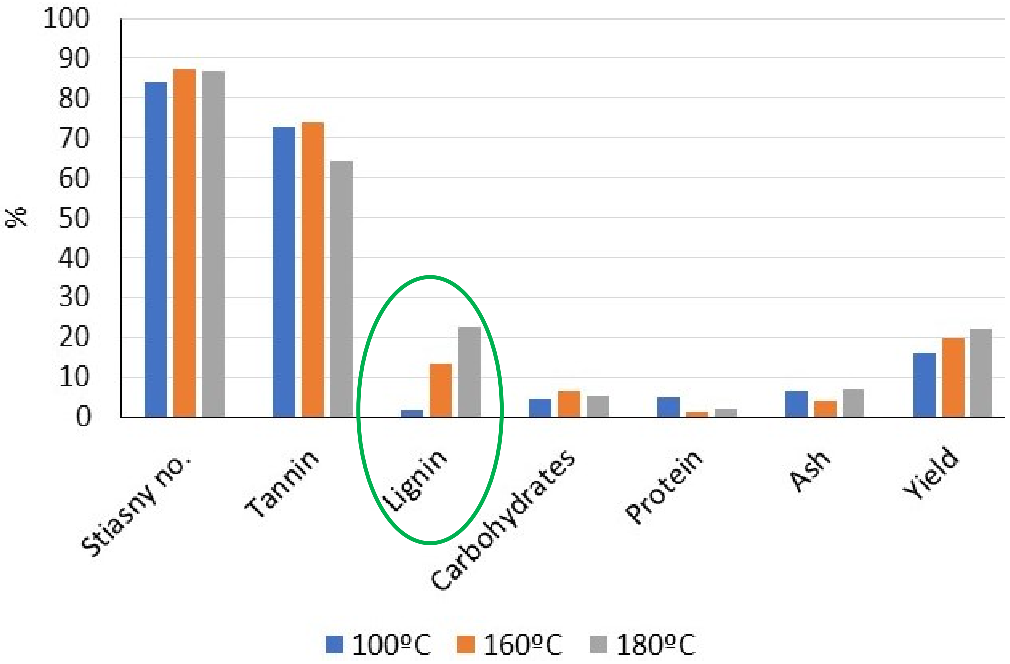


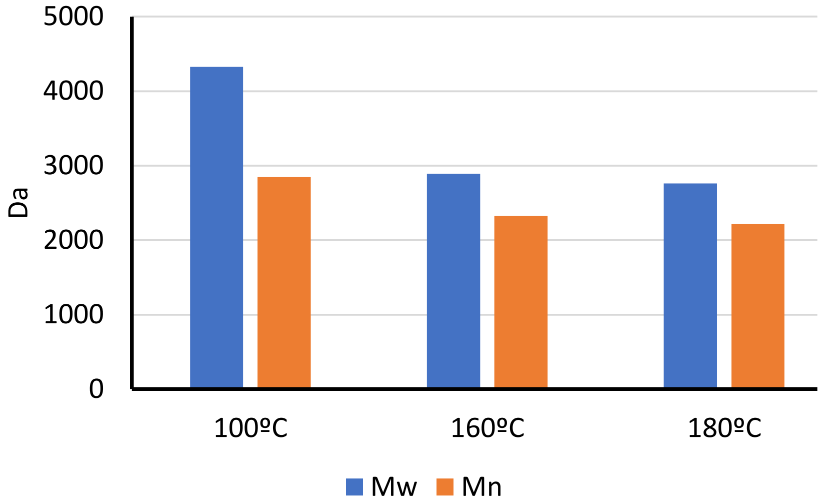
Lignin

Hot-water extraction of bark: low yield, low polyphenol (tannin) content
Alkali extraction of bark: high yield and polyphenol (tannin + lignin) content

Alkali-extracted ST

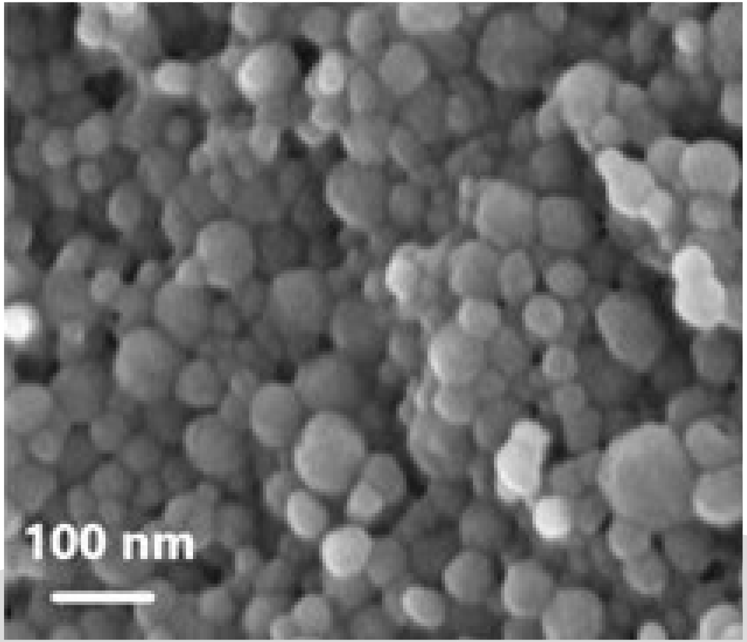
- Bark extraction temperatures: 100-180ºC
- Typical pilot-scale extraction: 160ºC, 90 min, 25% NaOH, 5:1
- Tannin recovered from black liquor by acid precipitation, washing and drying





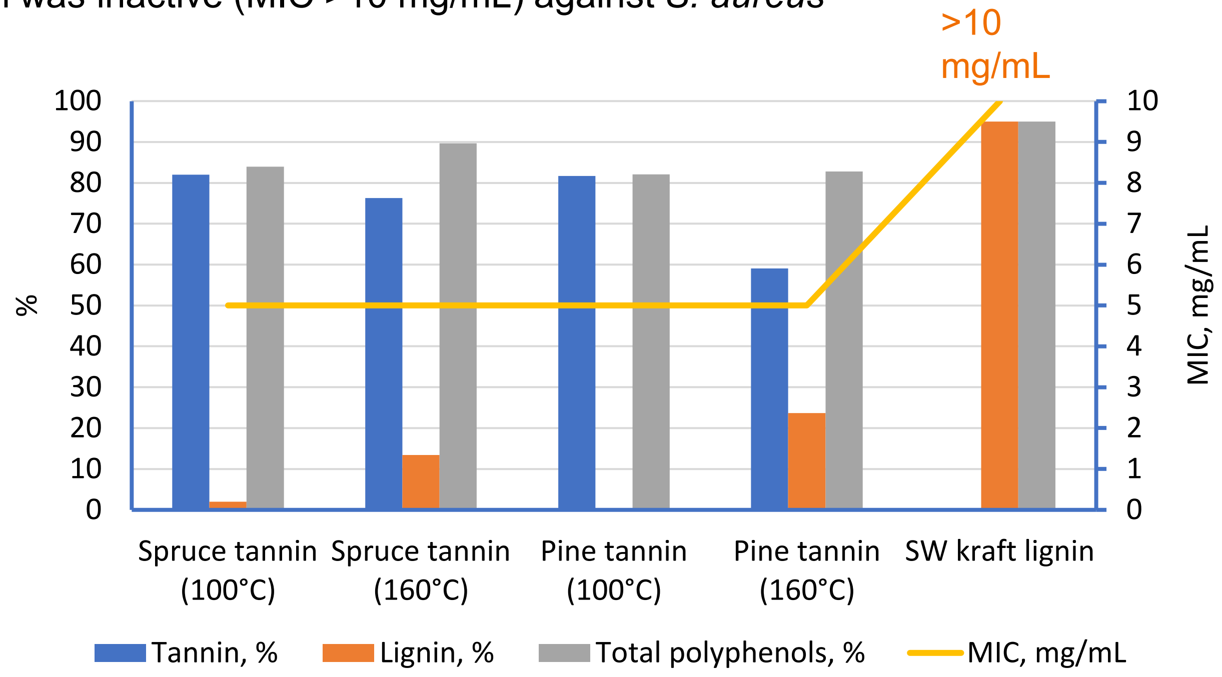
Tannin nanoparticles (TNPs) – EU Miria

- Unlike commercial tannins, ST has low to zero solubility in water at low pH levels
- Nanoprecipitation (solvent-exchange) can be applied to make TNPs in the same way as lignin nanoparticles (LNPs) are made
- Tannin is dissolved in 70% acetone and the solution is added to water, the antisolvent. The acetone is then removed
- Sizes of water-dispersed TNPs typically 50-200 nm
- TNP dispersions can be applied as foam, spray or dip coatings on textiles or other substrates to impart antimicrobial properties



Antibacterial efficacy of TNPs vs LNPs

- TNP dispersions made from tannins obtained from soda cooks of SW bark at two different temperatures were compared. LNPs from SW kraft lignin served as a reference
- All TNP dispersions had an MIC (minimum inhibitory concentration) value of 5 mg/mL against *S. aureus* bacteria despite different polyphenol profiles and contents
- The LNP dispersion was inactive (MIC >10 mg/mL) against *S. aureus*



Antibacterial efficacy of TNP spray coatings

- TNP coatings have far better water resistance than coatings of water-soluble tannins which dissolve in contact with water

- TNP coating (5 mg/mL) applied by spraying inhibited 99.999% MRSA (log 5) (> Log 3 inhibition defined as bacteriocidal)

Antibacterial efficacy of TNP foam coatings

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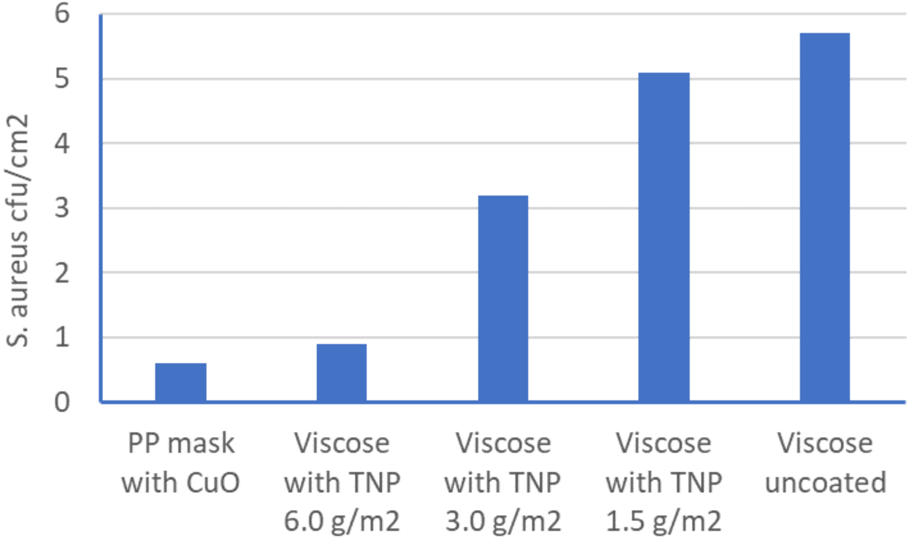
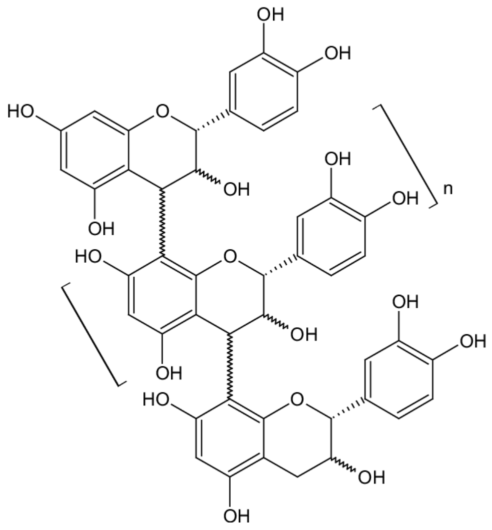
TNP-foam coated viscose

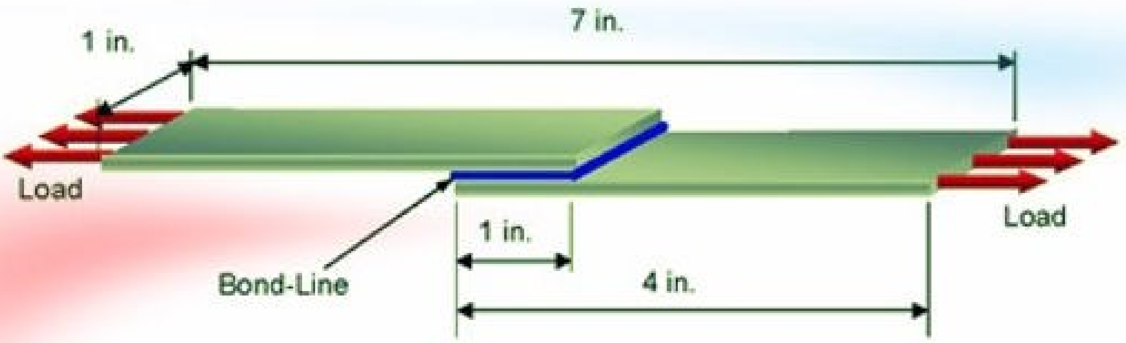


Antibacterial effect of TNP foam coats on viscose fabric increases with an increase in coating coverage

Tannin-based plywood adhesives – EU SuperBark

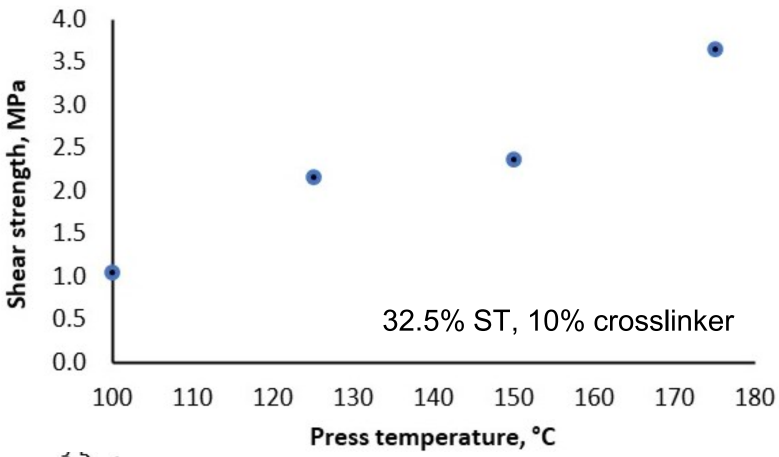
- Tannin-biocrosslinker adhesives were formulated with STs extracted at different soda cooking temperatures (100°C, 160°C, 180°C) of bark, and then dissolved in alkali
- The main challenge was the high viscosity that negated solids contents higher than 35%
- The lowest viscosity and highest solids content were obtained with ST 160°C
- Birch veneer lap joints were prepared by hot pressing and tested for dry shear strength (goal is high wet strength after boiling to comply with the EU standards for class 3 plywood)

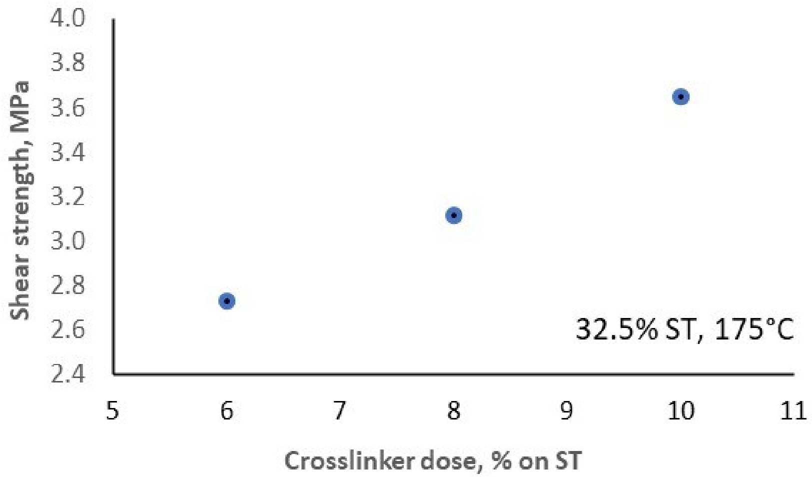


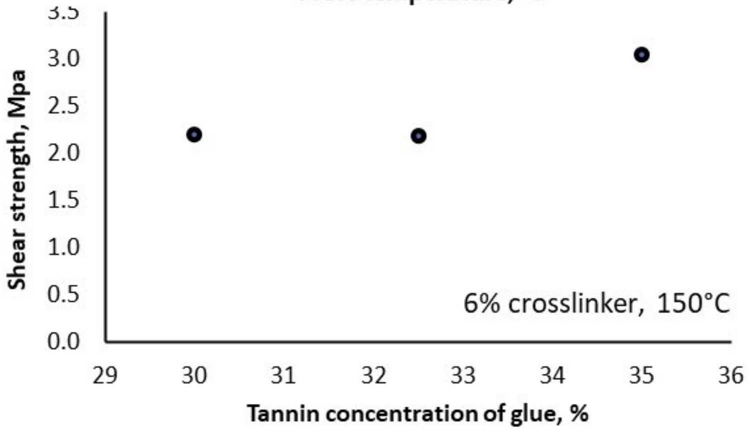


Shear strength testing of veneer lap joint

Shear strength of veneer lap joints bonded with ST-Biocrosslinker (EU SuperBark)







Dry shear strength increases with an increase in:

- Press temperature
- Biocrosslinker dose
- Tannin concentration

Effects of press time and pressure to be investigated

Tannin-based flame retardants – EU BioPhenom

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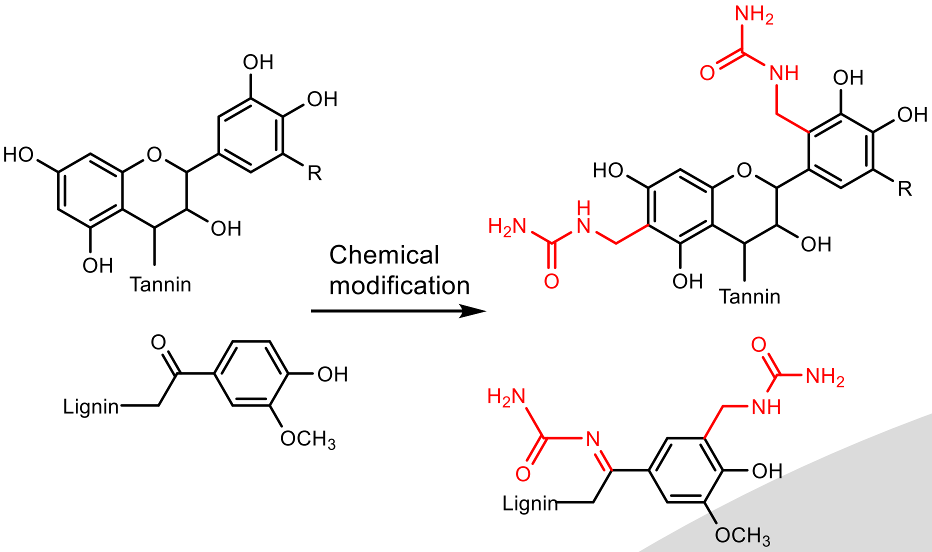
BioPhenom

- ST was reacted with urea and formaldehyde to make intumescent nitrogen-modified tannin flame retardants (FRs)
- The polyphenols provide char and the gases produced by the nitrogen functionalities impart intumescence to the char. The expanded char layer insulates the underlying material



Both tannin and lignin will react whereby they will contain >10% nitrogen

Amino groups of urea react with formaldehyde and the product adds to the aromatic units (Mannich reaction). The amino groups may also add to existing carbonyl groups (Schiff base reaction)

Tannin-impregnated wood blocks: mass change after impregnation and water leaching – BarkBuild ERA-NET

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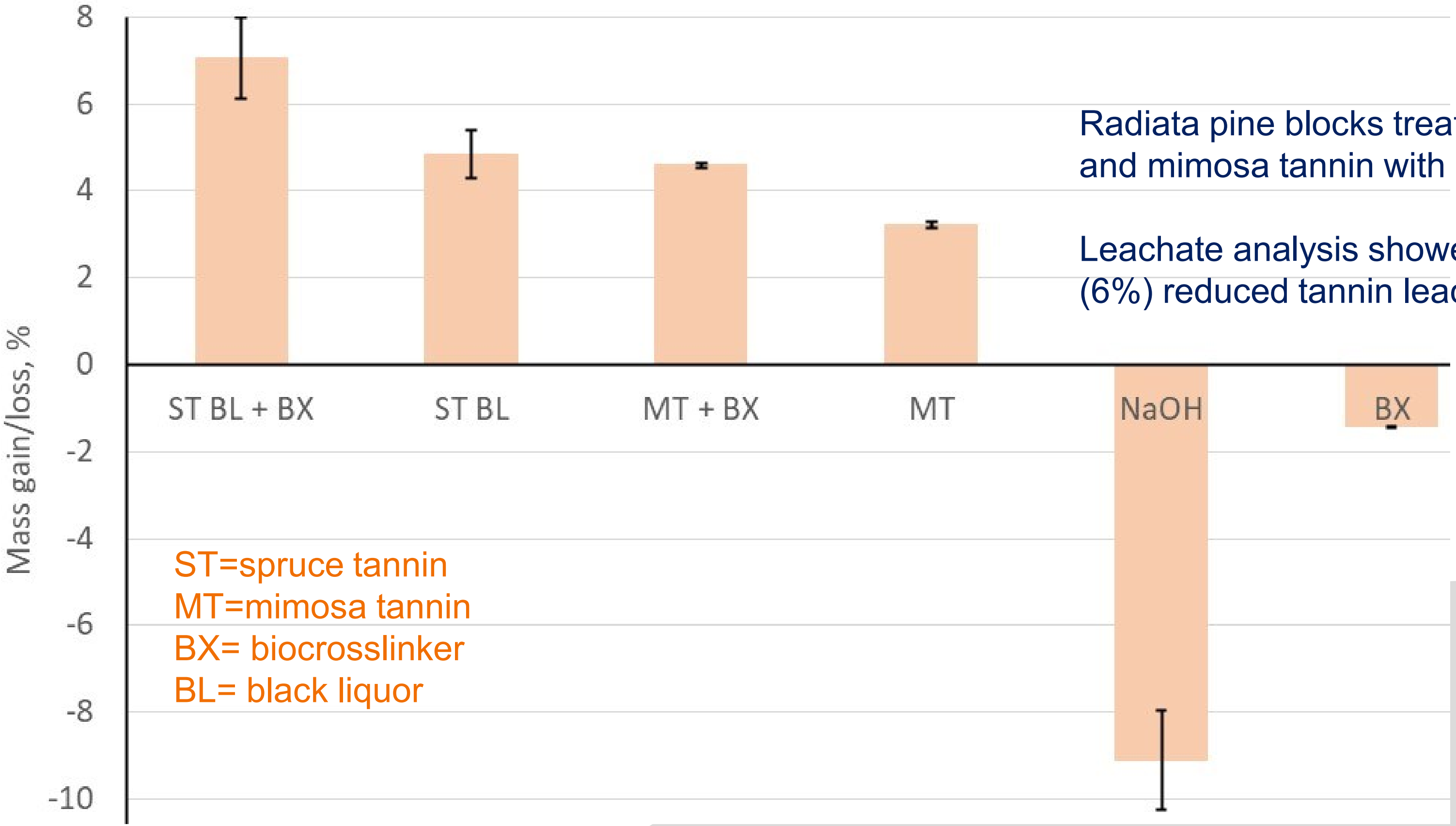

ST=spruce tannin
MT=mimosa tannin
BX= biocrosslinker
BL= black liquor

Radiata pine blocks treated with ST black liquor and mimosa tannin with and without crosslinker

Leachate analysis showed that biocrosslinker (6%) reduced tannin leaching by up to 60%

Antifungal efficacy of SW tannins in radial growth test (BarkBuild ERA-NET project)

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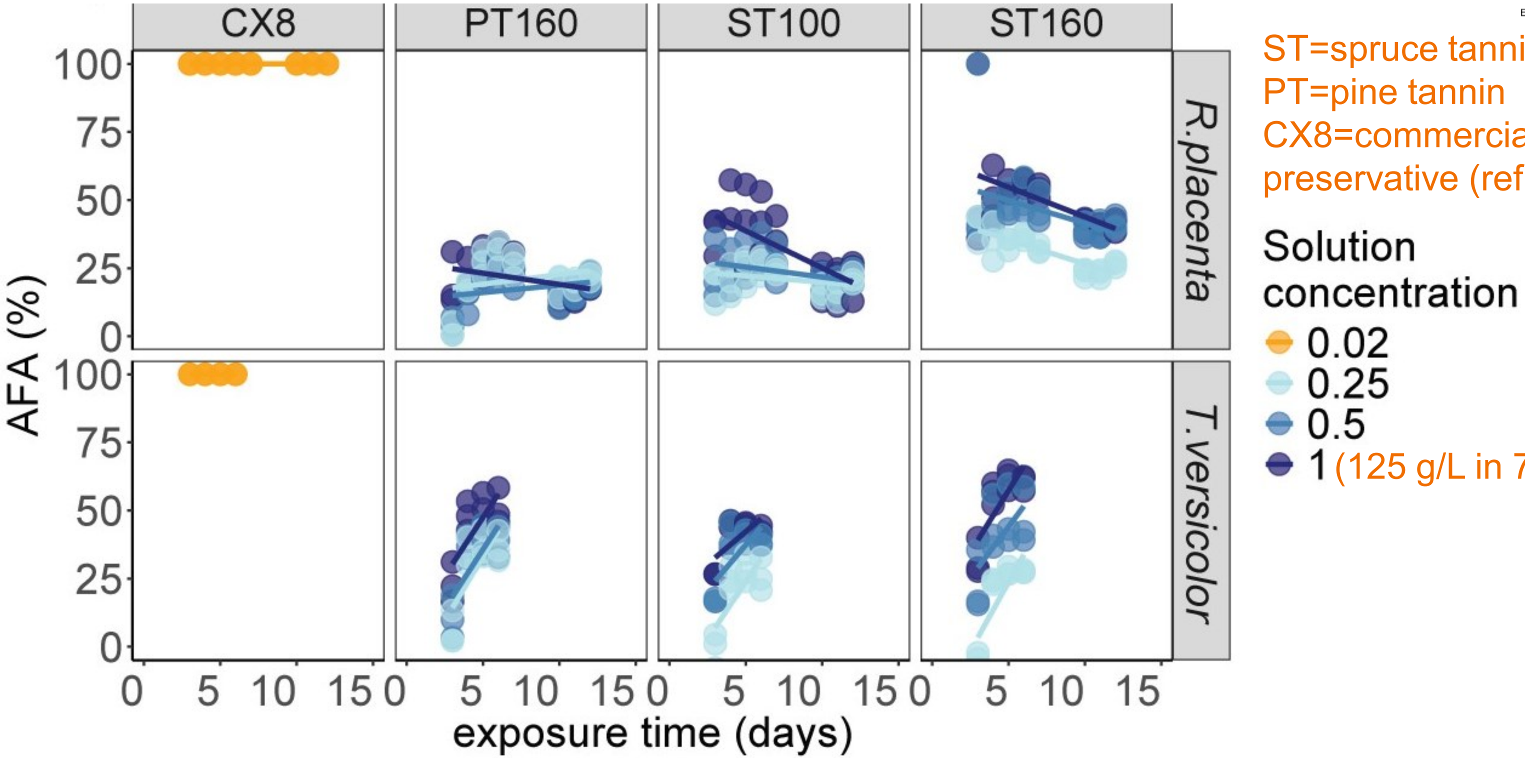

ST=spruce tannin
PT=pine tannin
CX8=commercial preservative (ref)

(125 g/L in 70% acetone)

AFA increases with tannin dose and content

Summary

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Tannin extraction from wood bark

- Tannin and some lignin can be alkali-extracted from softwood bark at a yield of ca. 20% and a polyphenol content (Stiasny number) of 82-90, comparable to commercial tannins from other tree species

Production of antibacterial nanoparticles and nanocoatings

- Softwood tannin can be converted into nanoparticles (TNPs) showing greater antibacterial efficacy that softwood lignin nanoparticles (LNPs)
- TNP spray and foam coatings on cellulose-based materials show good antibacterial efficacy against *S. aureus*

Tannin-based bioadhesives

- Spruce tannin can be combined with a bio-based crosslinker to make a thermosetting wood adhesive. Initial testing of bonded lap joints in dry conditions show promising shear strength

Tannin-based flame retardants

- Spruce tannin can be modified with nitrogen-based chemicals to make intumescent flame retardants

Tannin wood preservatives

- Spruce tannin can be combined with a bio-based crosslinker to enhance the retention of tannin in impregnated wood upon water leaching. The tannin reduces the wood mass loss by wood-decaying fungi

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MIRIA: DEVELOPMENT OF ANTIMICROBIAL, ANTIVIRAL, AND ANTIFUNGAL NANOCOATINGS FOR EVERYDAY SURFACES (HORIZON-CL4-2021-RESILIENCE-01-20, PROJECT 101058751)

SUPERBARK: SAFE, SUSTAINABLE AND HIGH-PERFORMANCE ADHESIVES AND COATINGS FROM INDUSTRIAL SOFTWOOD BARK (HORIZON-JU-CBE-2022-R-02, PROJECT 101112447)

BIOPHENOM: MULTIFUNCTIONAL BIOPHENOLS FOR SAFE AND RECYCLABLE MATERIALS (HORIZON-CL6-2023-ZEROPOLLUTION-02-2-TWO-STAGE, PROJECT 101135107)

BARKBUILD: TREE BARK AS A RENEWABLE SOURCE OF WOOD PROTECTION MATERIALS FOR BUILDING APPLICATIONS (ERA-NET COFUND ACTION "FORESTVALUE – INNOVATING THE FOREST-BASED BIOECONOMY")

ERA-NET Cofund Action "ForestValue — Innovating forest-based bioeconomy"

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