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Eco-friendly adhesives from pine bark extracts

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Pinus radiata

1,4 Million
hectares plantations

Round wood:
26 Million m³/year

Pulp:
3,2 Million ton/year

Wood-based panels:
1,8 Million m³/year

Lumber:
8,3 Million m³/year

Bark > 1 Million
ton/year

Mainly used as fuel

Calorific value: 8 – 13 MJ/kg

Water content : 30 – 60%

Pinus radiata

Some bark extractives of commercial interest

1. Hydrolysable tannins (e.g. gallic acid)
2. Flavonols/flavones/flavanones (e.g. catechin)
3. Flavonoids and bioflavonoids
4. Lignans
5. Stilbenes and stilbene glucosides
6. Condensed tannins (proanthocyanidin polymers)

Possible products:

- "Natural adhesive resins" (without phenol)
- Phenol-formaldehyde additive (speed reinforcement, formaldehyde catcher)

Wood adhesives in Chile

Chilean wood-adhesive industry

- The national wood-adhesive industry uses products based on fossil-fuels/petroleum-derivatives and formaldehyde, e.g., phenol-formaldehyde (PF), urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF), etc.

- According to resin producers, approximately 70.000 ton of phenol per year are required to produce PF resins used as adhesives for plywood and OSB boards.

- While bio-based adhesives were commercially produced during the last decade, their industrial production was abruptly ended due to uncompetitive costs.

- Increasing environmental concerns encourage a reconsideration of their value, but production costs are still considered a major hurdle for their resurgence.

Bark extraction methods

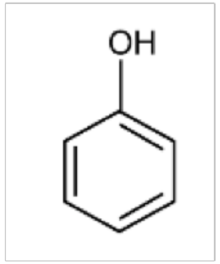
Industrial tannin extraction

- Currently, industrial production of condensed tannins is based on Quebracho wood in Argentina and Mimosa bark in Brazil and South Africa.
- The industrial extraction processes are done with aqueous sulfite solutions under alkaline conditions.
- The processes are operated in discontinuous extractors.

Tannin reactivity: A major challenge

Types of tannins

Phenol



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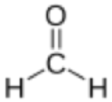
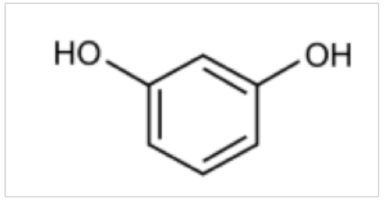


slow

Resorcinol



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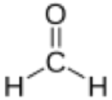
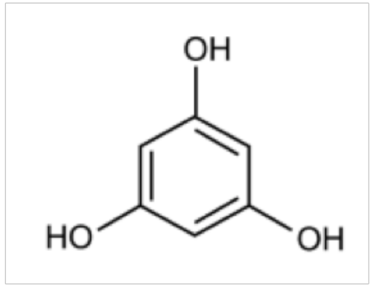


fast

Phloroglucinol



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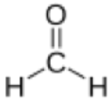
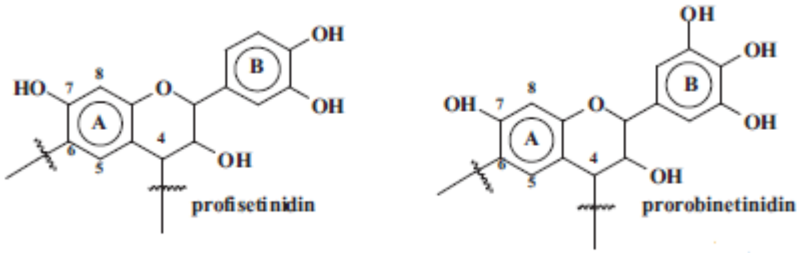
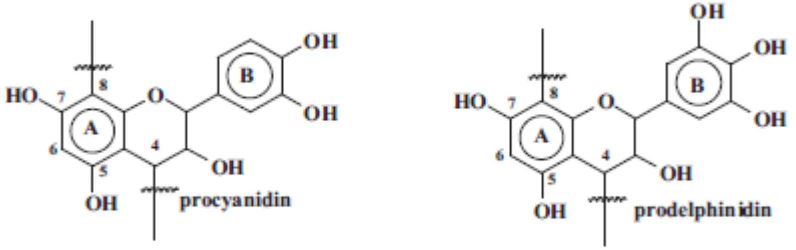


very fast



Resorcinolic tannins



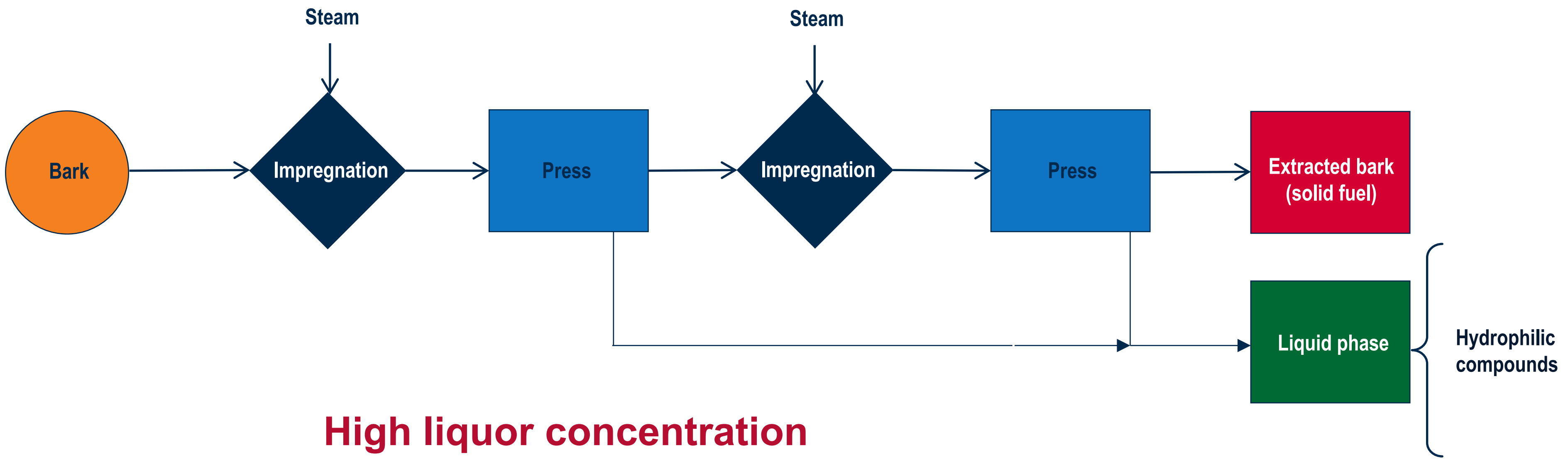
Phloroglucinic tannins

Ciencia, Tecnología e Innovación en Bioeconomía

Source: Tannin molecule from Schofield, Mbugua, and Pell (2001).

Bark extraction process

Continuous pilot-scale process for extraction of *Pinus radiata* bark



High liquor concentration

Low residence time

Bark extraction process

Pilot-scale processes for extraction of *Pinus radiata* bark

1. This continuous plant has a processing capacity of 150 kg biomass / day, using water as solvent. This operation affords yields of 14-16%.

2. We have also develop a discontinuous process, which has been evaluated using the following solvents:
   - Water: Yield of 13-15% wt. with respect to dry bark.
   - Methanol: Yield of 12-15% wt. with respect to dry bark.
   - Ethanol: Yield of 9-11% wt. with respect to dry bark.

Developing adhesives from pine bark extracts

Required properties

To compete with commercial phenol-based adhesives, bio-based wood adhesives formulations must satisfy several requirements:

- Viscosities: 400-500 cP for particleboards and 1000-1200 cP for plywood boards.
- Minimize water content to avoid issues during panel manufacture.
- Adhesive strength comparable to that of their commercial counterparts (this varies according to panel type).

Developing adhesives from pine bark extracts

Chemical modifications

- Three different samples were tested:
  1. The soluble fraction of the aqueous extracts without modifications.
  2. The soluble fraction obtained after sulfitation (5% w/r to solid wt.) of the whole aqueous extract.
  3. The soluble fraction of the aqueous extracts acetylated with an acetic anhydride / acetic acid (1:1) solution at 50° C during 1 h.
- Solutions of 35% wt. were prepared with each of these samples.
- Prepare additional solutions, adjusting pH to 8 and 10.
- The viscosity of all the samples was measured.
- Samples within acceptable ranges of viscosity were used to prepare adhesive formulations with different crosslinkers (hexamine, glyoxal, TRIS and UFC). Their adhesive performance was evaluated using ABES.

Developing adhesives from pine bark extracts

Viscosity of the extracts

Sample	pH	Viscosity (cP)
Soluble fraction of aqueous extract	4.2 (natural)	1200
	8	**> 9000**
	10	**> 12000**
Soluble fraction of sulfited extract	3.1 (natural)	270
	8	340
	10	380
Acetylated soluble fraction of aqueous extract	5.3 (natural)	540
	8	650
	10	1120

Solutions based on aqueous extracts were prepared with a 30% of solid content.
Higher concentrations result in excesive viscosities.

Developing adhesives from pine bark extracts

Adhesive formulations

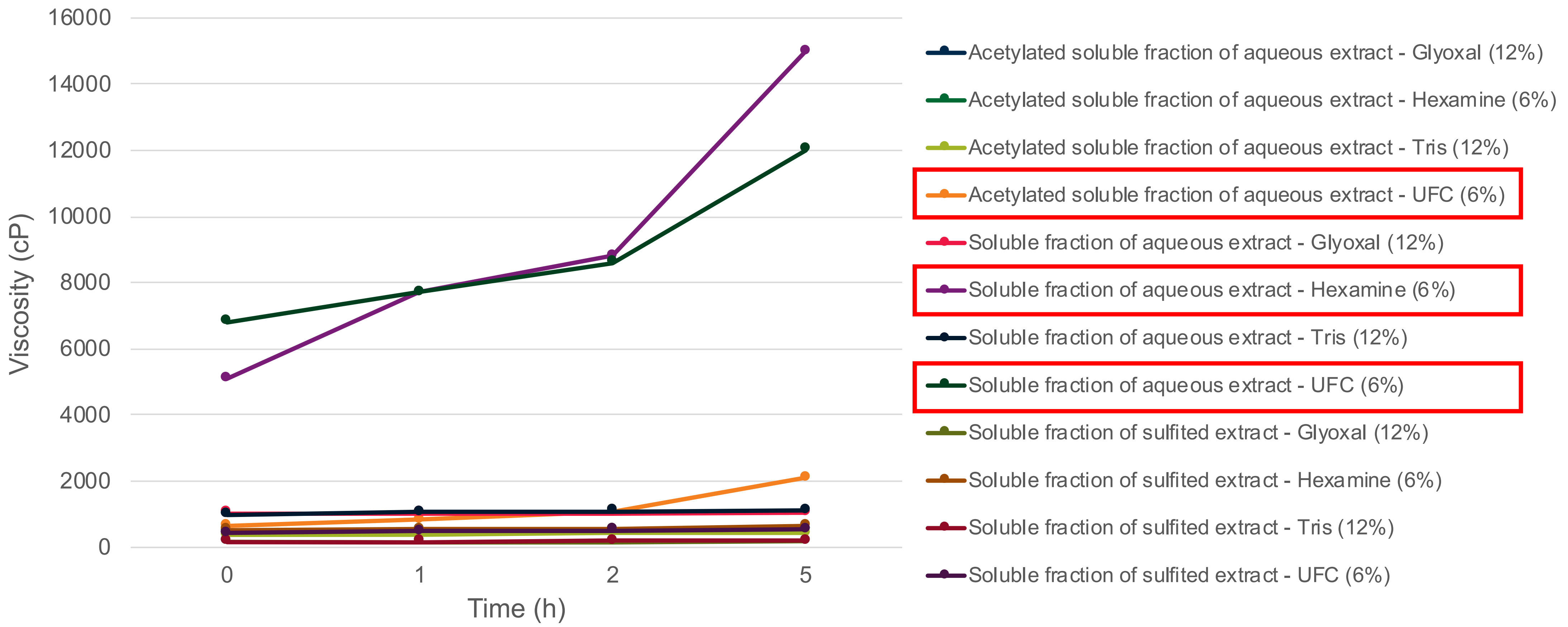
- **Adhesive formulations were prepared using ideal pH ranges for the chosen crosslinkers:**

Crosslinker	Stable pH range
Glyoxal	< 7.5
Hexamine	> 6.0
Tris	< 5.0
UFC	7.0 – 8.0

- **Ideal crosslinker concentration was determined by trial-and-error, considering optimal pH ranges and viscosity requirements.**
- **Formulations with viscosities over 1200 cP were discarded, thus their adhesive performance was not evaluated.**

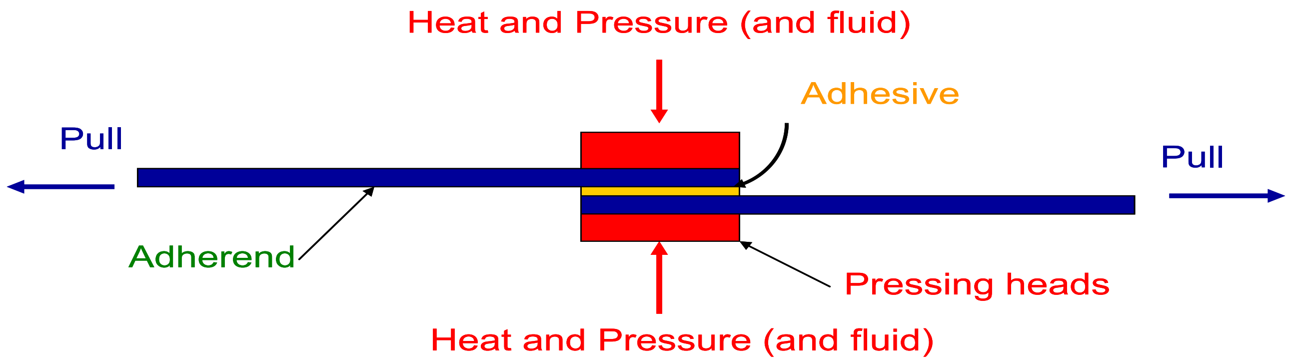
Developing adhesives from pine bark extracts

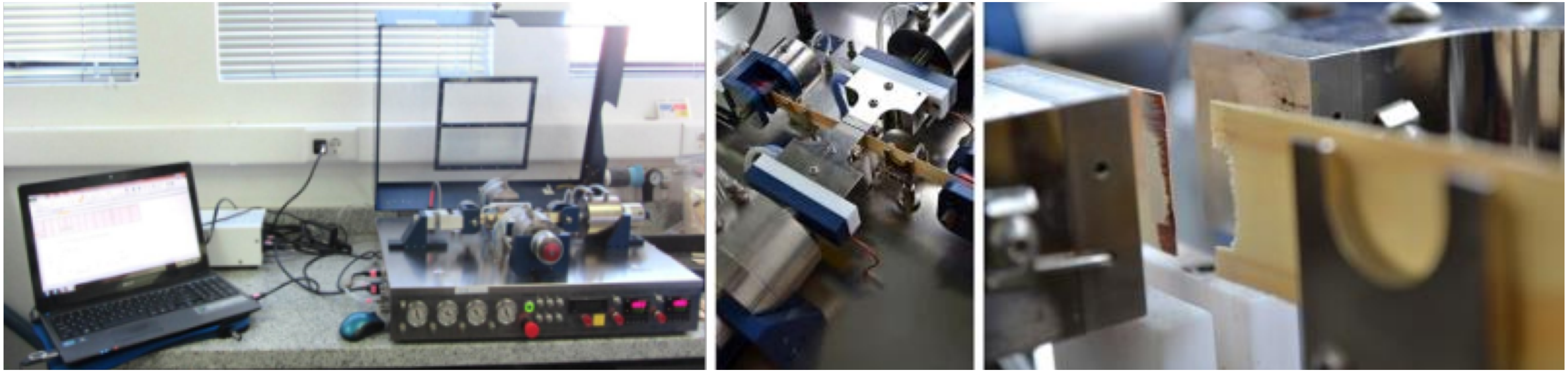
Viscosity of main adhesive formulations



Developing adhesives from pine bark extracts

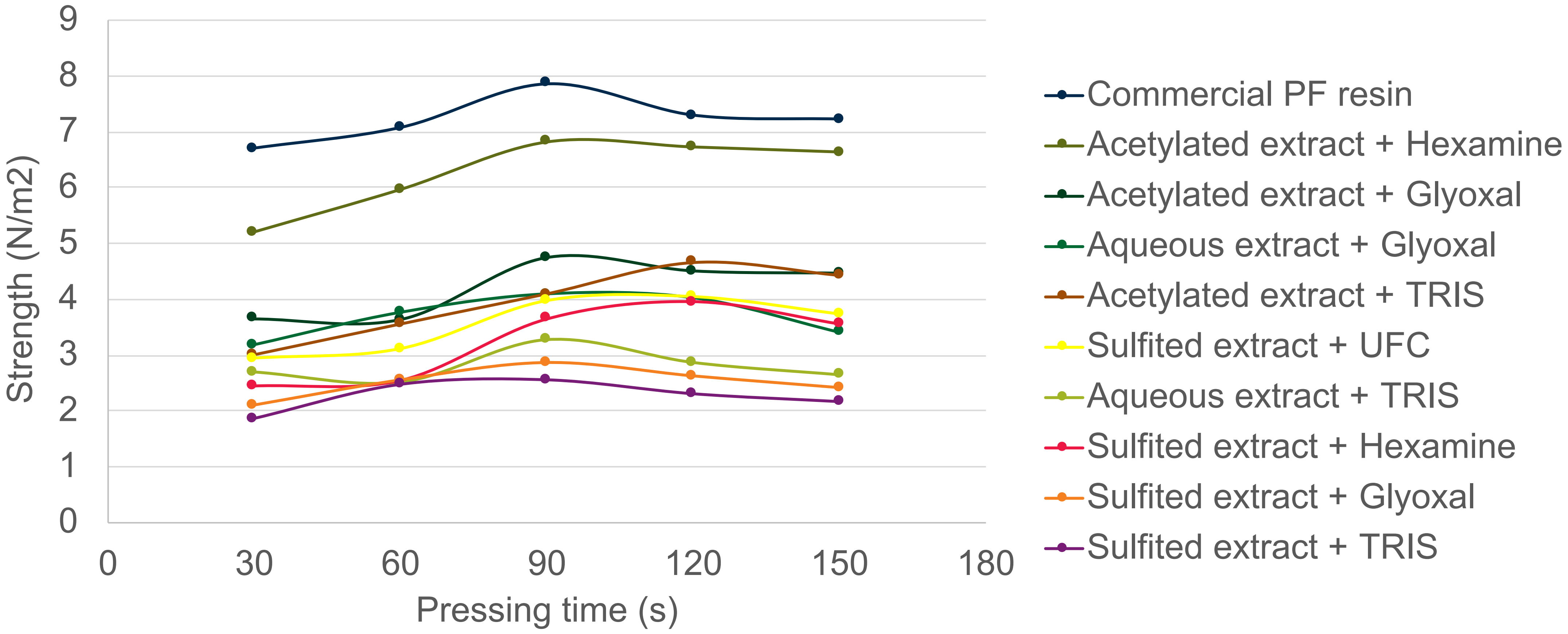
ABES adhesive evaluation





Developing adhesives from pine bark extracts

ABES evaluation of selected formulations



Developing adhesives from pine bark extracts

ABES results

- TRIS and glyoxal show low performance with extract.
- Sulfitation has a negative influence on adhesive strength of the resin formulations.
- Acetylated extracts have a good compatibility with hexamine.
- Further improvements are required.

Developing adhesives from pine bark extracts

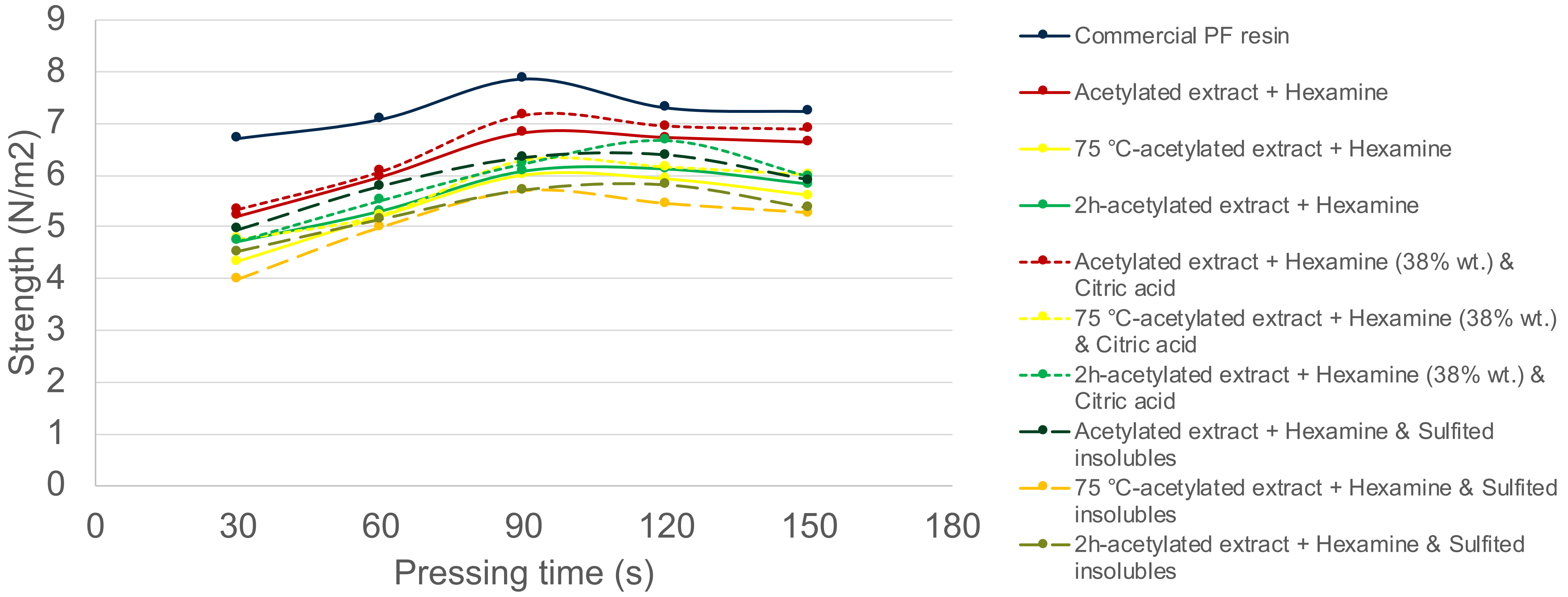
Further improvements

In order to make better use of the extracted material, and at the same time, enhance the adhesive performance of the resin formulations, additional changes were evaluated:

- To **take advantage of the insoluble fraction** of the extracts, this fraction was sulfited and added to the acetylated extract. Viscosity and adhesion were tested.
- To **increase solid content of the tannic solutions**, new formulations with addition of 50% wt. citric acid (to reduce viscosity) were tested.
- To **improve the adhesive performance of the acetylated extract formulation**, harsher acetylation conditions were evaluated.

Developing adhesives from pine bark extracts

ABES evaluation of the proposed modifications



Conclusions

General observations

- The wide availability of tannins, coupled with the moderate costs required for their recovery, makes them a very interesting raw material for adhesive resins.

- The use of a natural product, such as bark extracts, at industrial scale is very challenging, not only because of its chemical structure, but also due to their variable behavior, depending on its origin and processing method.

- Acetylation seems to be a promising approach to modify the properties of pine bark extracts for wood adhesive applications, but the current processing conditions must be improved.

Conclusions

Improvement proposals

- The effect of extracting lipophilic compounds before the aqueous extraction may benefit the soluble/insoluble fraction ratio.

- Acetylation conditions must be improved. Performing the extraction in an acetic medium should be evaluated.

- The other modifications for insoluble fraction should be tested. Assuming an important presence of high-molecular-weight carbohydrates, an acid or alkaline hydrolysis may help to lower their viscosity without decreasing their compatibility with the soluble fraction.

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