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Institut des sciences analytiques  
et de physico-chimie  
pour l'environnement et les matériaux



*Free formaldehyde phenolic resins for a potential use  
in adhesives formulation, wood coating  
and porous materials production*

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**iufro 2019**  
Curitiba - Brazil

Context

Objectives

Introduction

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IUFRO 2019

29 Sep. – 5 Oct., Curitiba - Brazil

# Context

## Sustainability and bio-based production

### Lignocellulosic biomass

Why ?



Renewable chemicals

Cleaner environment

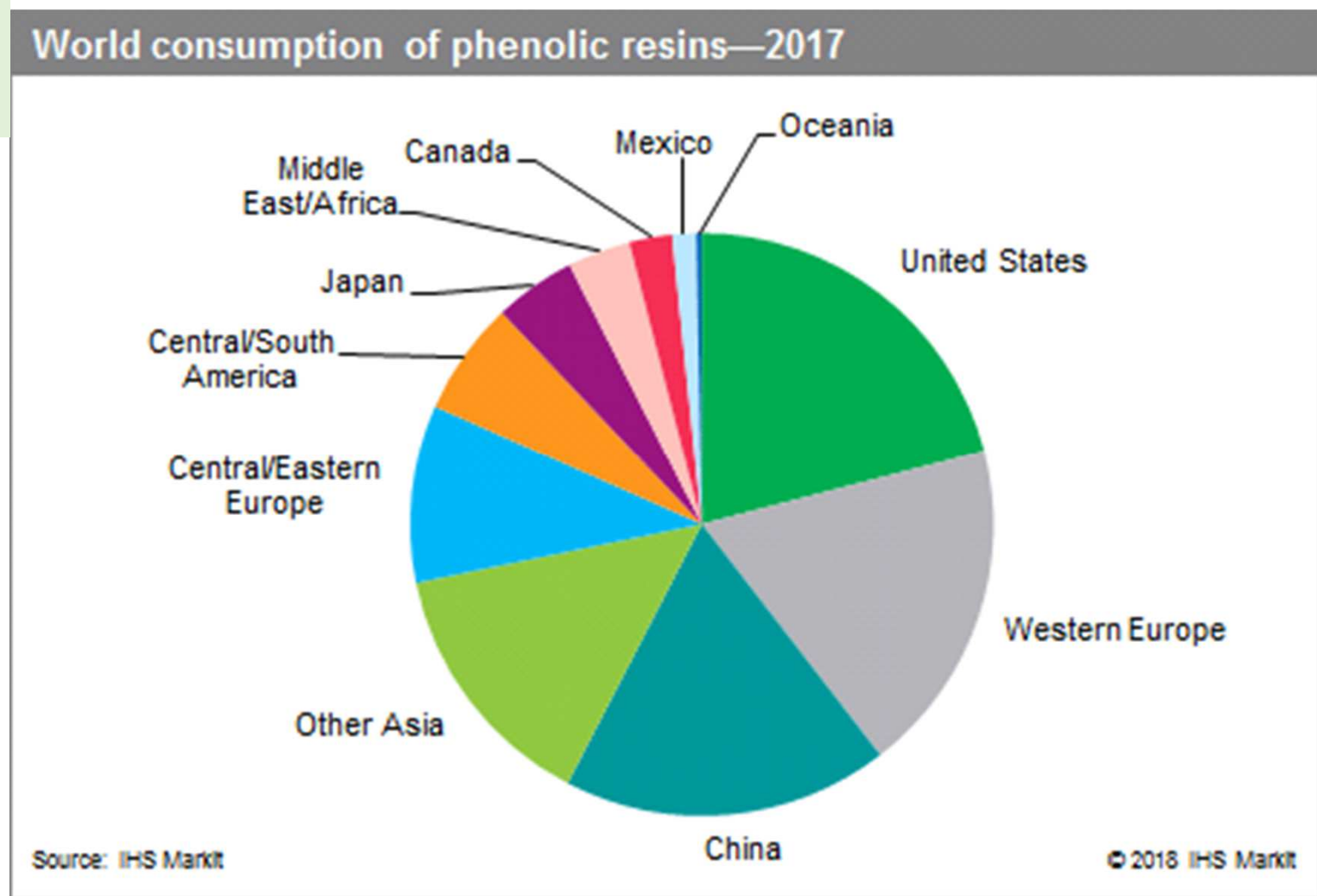
Sustainable

Depletion of fossil fuels inevitable

Cheap raw material

Bioplastics

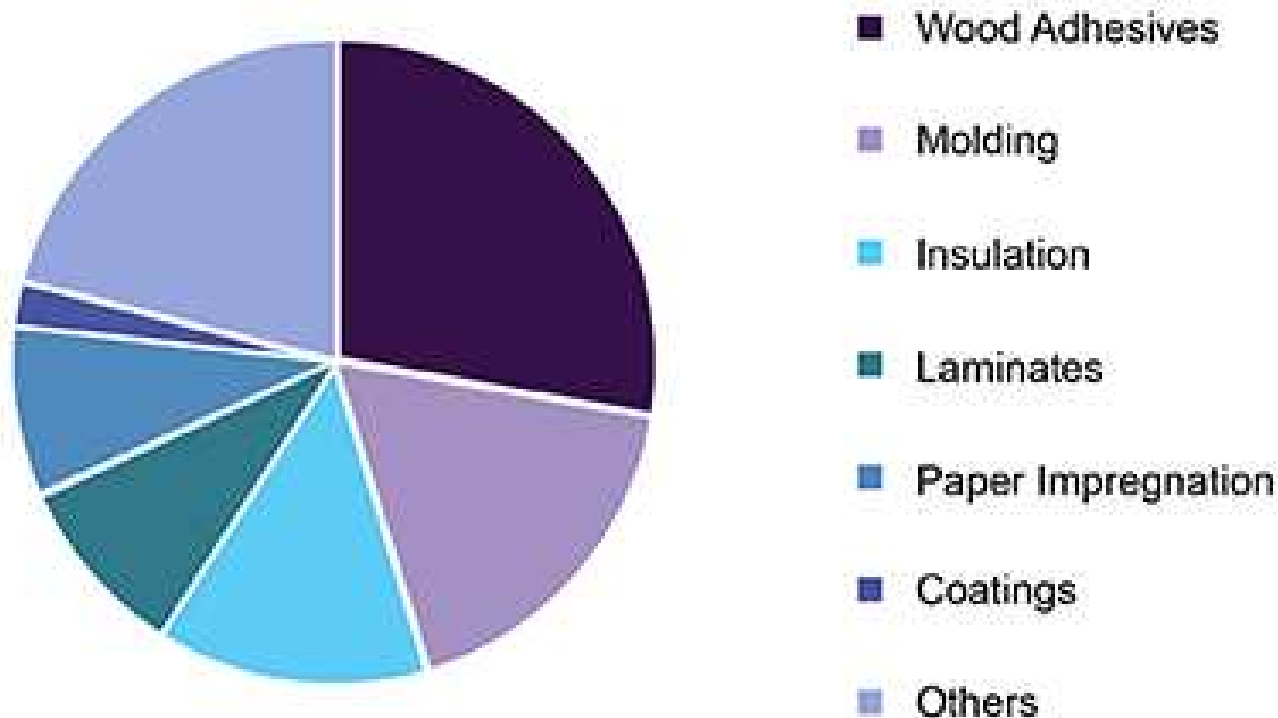
## Context



➔ Wood adhesives will continue to have the largest market share and will drive phenolic resin consumption on a global scale.

## Context

### Global phenolic resins market share, by product, 2018 (%)



Source: [www.grandviewresearch.com](http://www.grandviewresearch.com)



Global PF resin consumption is expected to grow at an average annual rate of 2.5–3% during 2017–22.

## Context

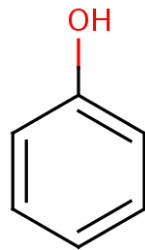
**Phenolic Resin is synthesized from the condensation reaction of phenol with formaldehyde in the presence of a catalyst.**

## Problems

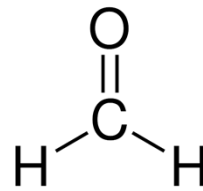
**The raw materials:**

➔ **are derived from petrochemicals, which are non-renewable and therefore ultimately limited in supply**

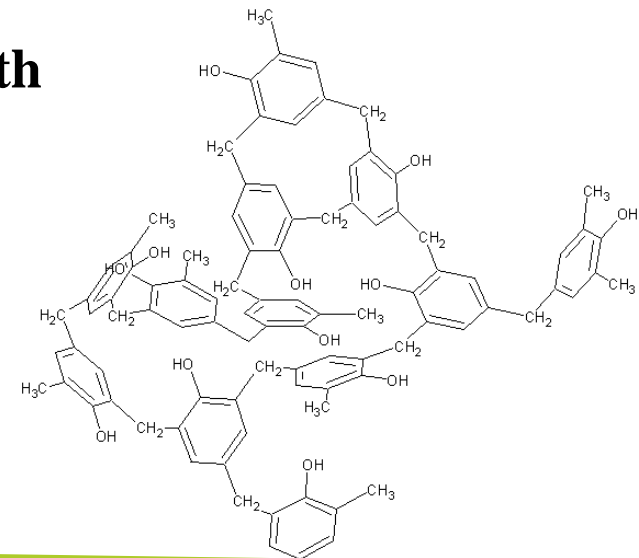
➔ **have an impact on the environment and health**



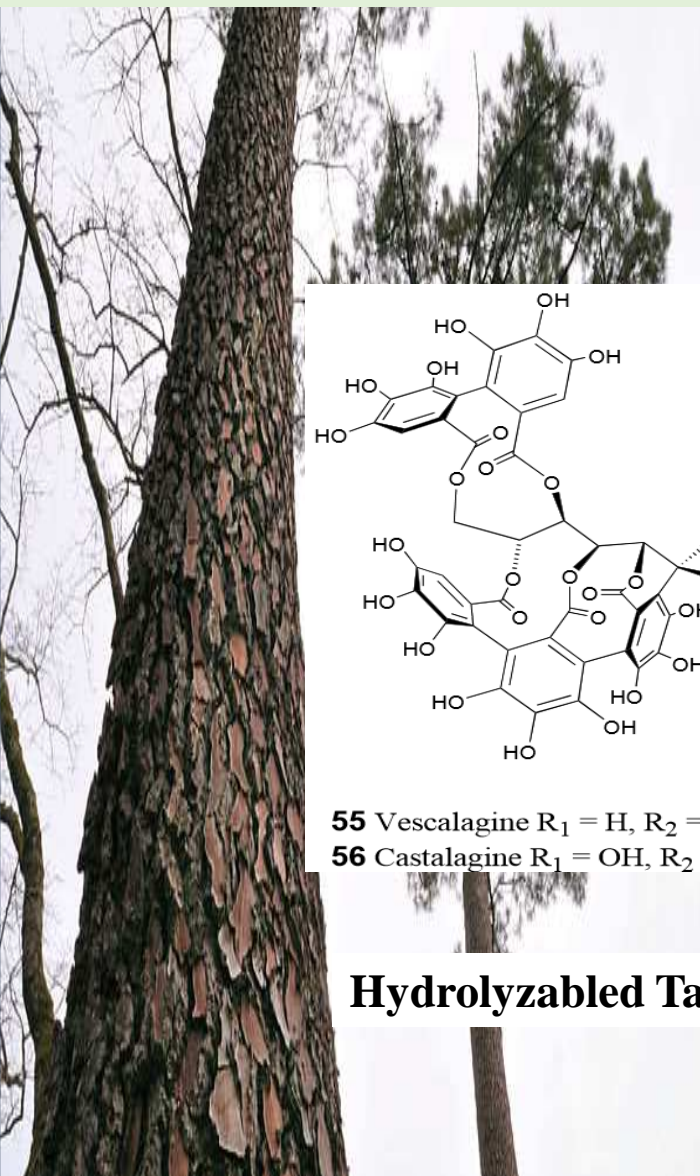
Phenol



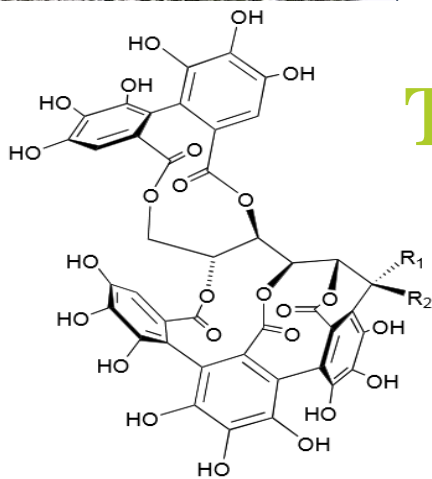
Formaldehyde



# Context



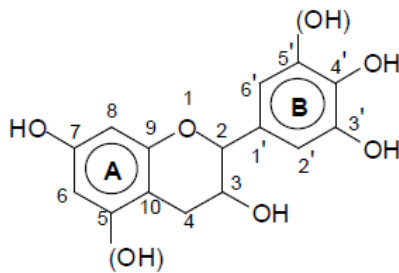
## Tannins



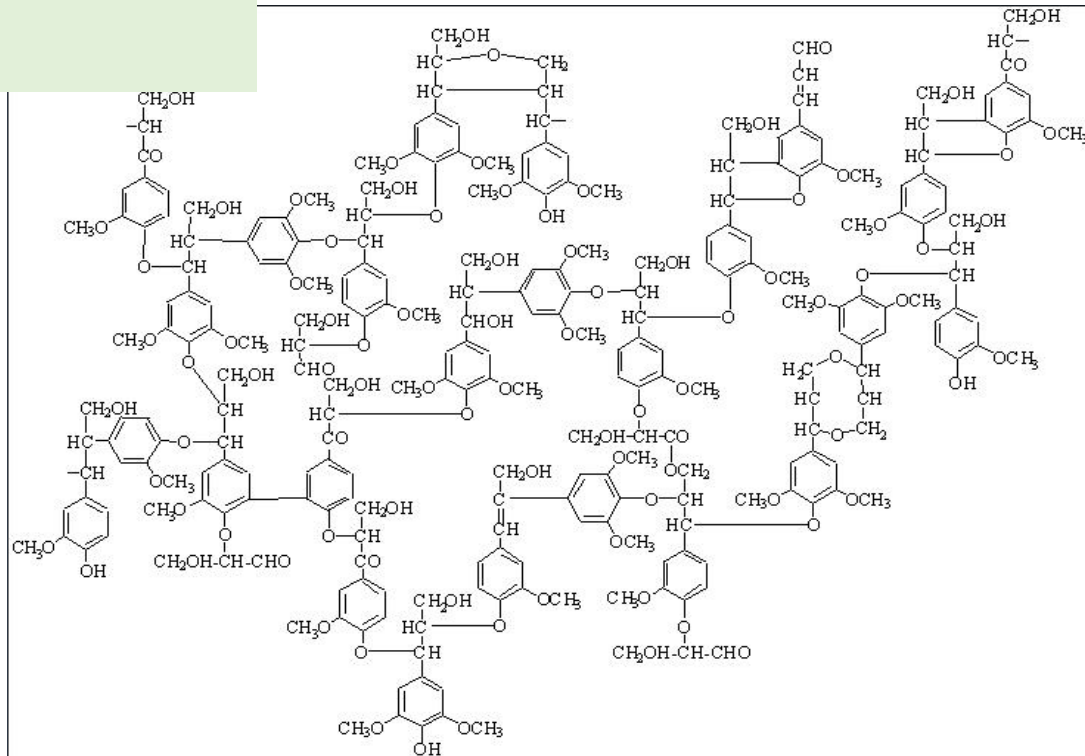
55 Vescalagine  $R_1 = H, R_2 = OH$

56 Castalagine  $R_1 = OH, R_2 = H$

### Hydrolyzabled Tannins



### Condensed Tannins



## An example of the Lignin structure



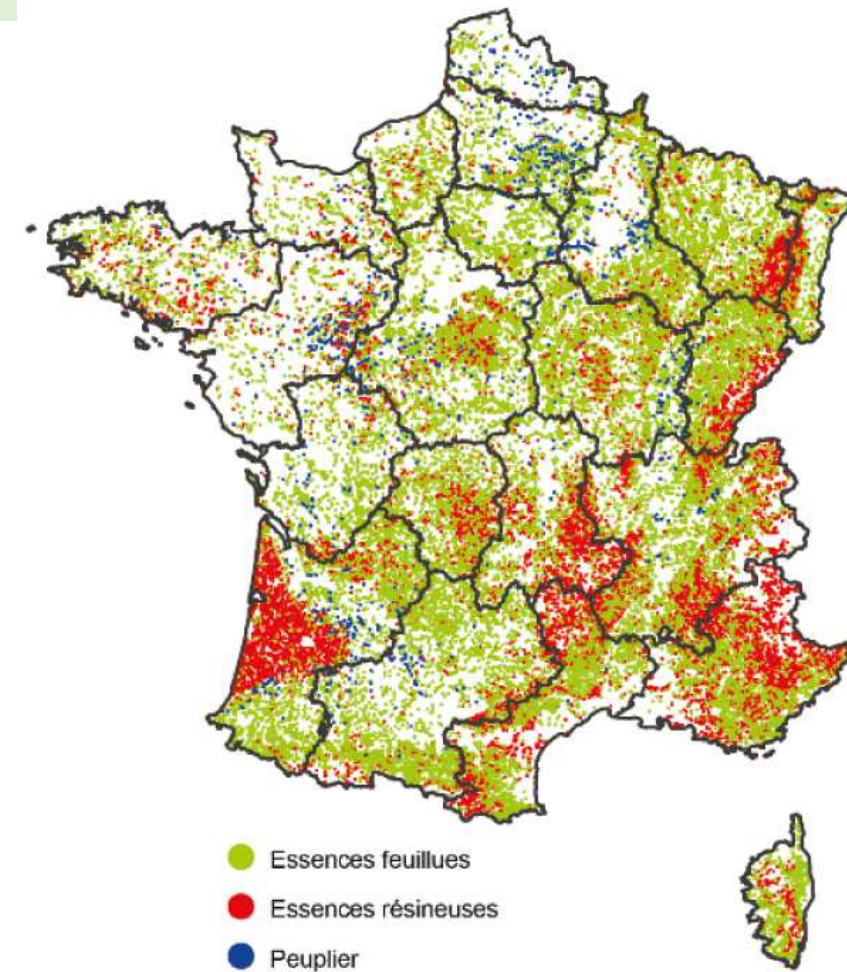
## Context

Répartition des formations boisées en France par type d'essences

### The figures in wood industry

- **16 million hectares** of forest, of which:
  - **28%** of the territory
  - **440,000 jobs** spread throughout the country
  - 190 000 upstream,
  - 250 000 downstream.
- **60 billion euros** of turnover:
  - 20 billion euros for the upstream
  - 40 billion euros for the downstream.

Source: <http://xylofutur.fr/les-filieres/la-filiere-en-chiffres/>



Source : e-IGN - 2012 ; Traitement FCBA 2012



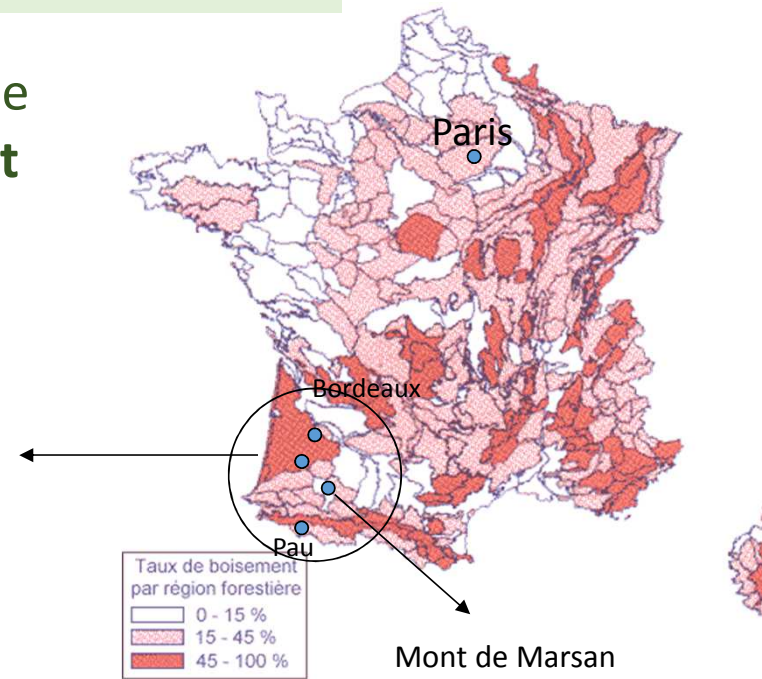
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# Context

Biggest man-made Maritime pine forest in Europe => **Landes Forest**



- Paper industry
- Wood based panels industry

Aquitaine Forest of *Pinus Pinaster*:

- 1,2 millions of ha
- Harvesting 8,5 millions of m<sup>3</sup>
- ¼ of national wood production
- First region for softwood production



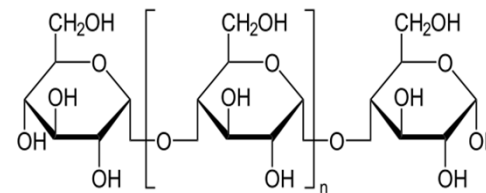
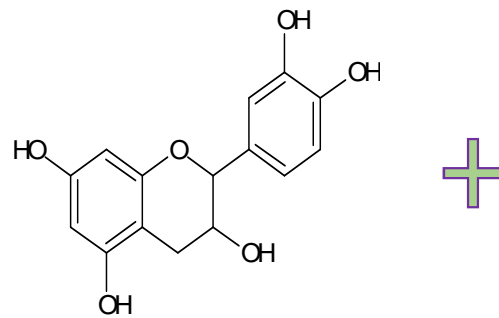
## Objetives

- **Valorization of forestry and wood industry residues.**
- **Synthesis of a biosourced and environmentally friendly phenolic resin.**
- **To replace the synthetic phenolic resin in its main applications:**
  - **Wood adhesives**
  - **Coating**
  - **Insulation**



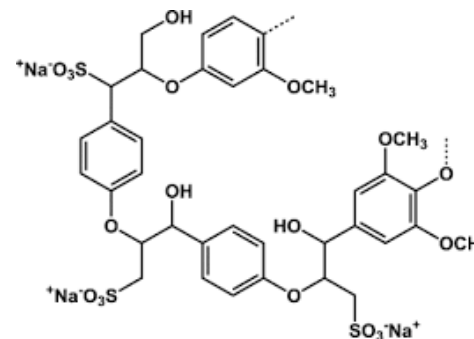
## Previous work: Wood adhesives

Formulation of free-formaldehyde resins for the particle boards industry, by including natural and renewable products such as the starch of corn and the tannins of maritime pine.



Starch

or



Lignosulfonate

*Moubarik A. et al., Eur. J. Wood Prod., 2010.*

*Chupin L. et al., Journal of Thermal Analysis and Calorimetry, 2015*

## Introduction

## Wood adhesives



Particleboard production at pilot scale (Egger-Rion-des-Landes factory)

- Particleboard bonded with formaldehyde-free corn starch-tannin adhesive showed comparable mechanical properties to the panels made with the commercial UF resin.
- Panels qualified P4 (requirements for panels used in a dry environment)

*Moubarik A. et al., J. of Adhesion Science and Technology, 2013.*

## Introduction

## Coating

wood and wood-based panels lead them to occupy an important place in buildings and interior fittings



### Vulnerability against fire

#### Traditionally

Halogen based fireproofing agents (F, Cl, Br)

#### Fireproofing treatment

#### Nowadays

State of the art fireproofing agent (halogen free)

#### Intumescent coating

*Saad H. et al., Chap. 11 in Green and Sustainable Advanced Materials: Processing and Characterization, Volume 1, Wiley, 2018. ISBN: 978-1-119-40737-9*

➔ Phenolic foam board is recognized as a kind of important building insulation material.

➔ The demand for phenolic foam board is expected to continue increasing during the remaining years of the forecast period of 2017-2023.

➔ The worldwide market for Phenolic Foam Board is expected to grow at a CAGR of roughly 2.7% over the next five years, will reach 1890 million US\$ in 2024.

<https://www.marketwatch.com/press-release/phenolic-foam-board-market-2019-global-industry-size-share-business-growth-revenue-trends-global-market-demand-penetration-and-forecast-to-2024-360-market-updates-2019-05-20>

*Charrier – El Bouhtoury F. Innovative green foams: opportunities and challenges in industrial potential applications. In Green Polymer Composites Technology: Properties and Applications. RCS Press, 2016. ISBN 9781498715461*



# Introduction

*Pinus pinaster*

Lignin isolation  
(Lab.scale)

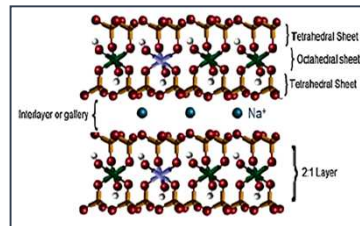
Lignin

*Acacia mearnsii*

Tannin isolation  
(Ind.scale)

Mimosa tannins

Inorganic nanoparticles



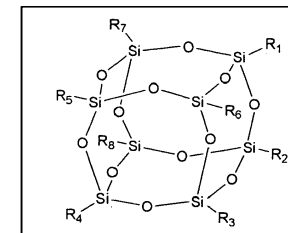
Dellite 43B  
Organically modified  
Montmorillonite  
(OMMT)

LAVIOSA

# Coating

|                           |       |
|---------------------------|-------|
| Acid Insoluble lignin (%) | 90.69 |
| Acid Soluble lignin (%)   | 1.97  |
| Ashes (%)                 | 4.80  |
| Sugars                    | 0.98  |
| Molecular weight(g/mol)   | 4782  |

SILVATEAM



POSS1458  
Polyoligomeric  
silsesquioxane  
(POSS)

HYBRID  
PLASTICS®

Polyoligomeric  
silsesquioxane  
(POSS)

*de Hoyos-Martínez et al., Waste Management, 2018*

*de Hoyos-Martínez et al., Polymer science, 2019*

- **Chemical parameters of the resins**

| RESIN   | LIGNIN | TANNIN | OMMT | POSS |
|---------|--------|--------|------|------|
| Control | x      | x      | -    | -    |
| R1      | x      | x      | x    | -    |
| R2      | x      | x      | -    | x    |

| RESIN   | pH    | Density (g/cm <sup>3</sup> ) | Non-volatile content (NVC) (w/w) |
|---------|-------|------------------------------|----------------------------------|
| Control | 8.920 | 1.169                        | 36.811                           |
| R1      | 9.015 | 1.173                        | 37.416                           |
| R2      | 8.990 | 1.177                        | 37.412                           |

➤ Different resins were synthesized to evaluate the influence of their composition over the resins properties and coatings performance.

➤ pH values around the same range ( $\approx 9$ ).

➤ The density followed a slightly increasing tendency.

➤ The NVC increased slightly after the addition of the nanoparticles.

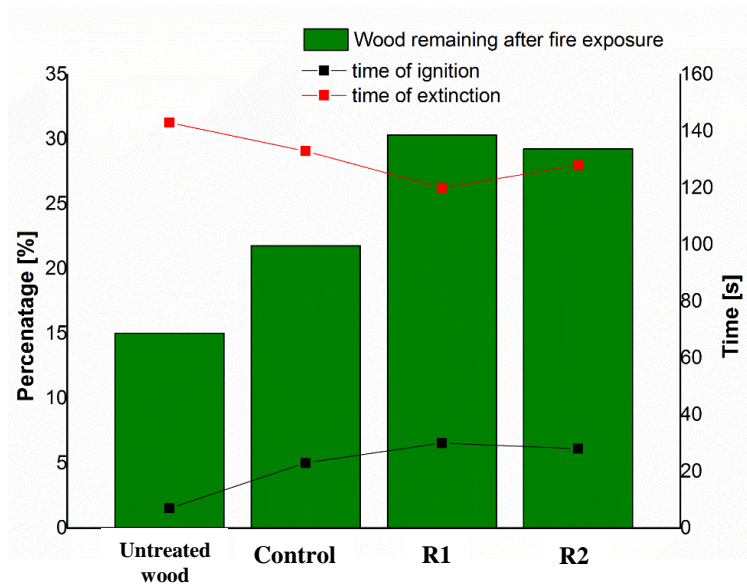


## Main results and discussion

## Coating

### • Fireresistance of the wood coatings

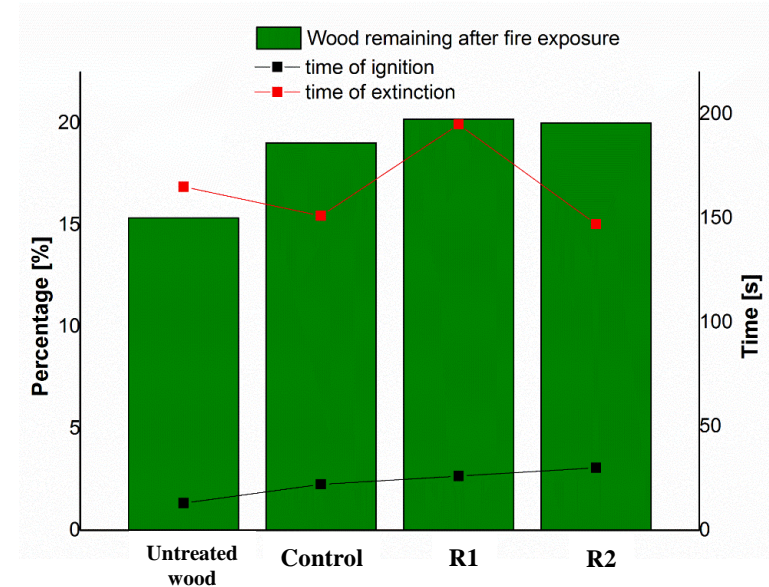
#### *Pinus pinaster*



#### Intumescent effect

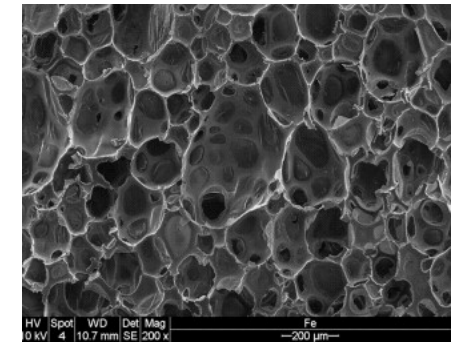
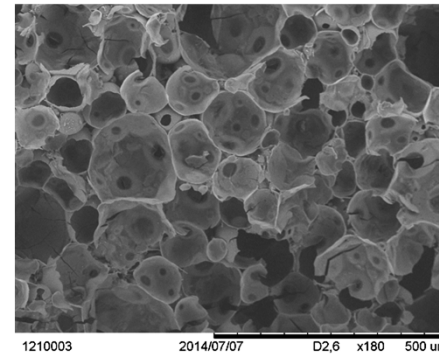


#### *Fagus silvatica*



- The amount of wood remaining after combustion increased in the samples with coating.
- The time of ignition of the wood samples was delayed after the coating application.
- The time of extinction generally decreased in the wood coated samples.

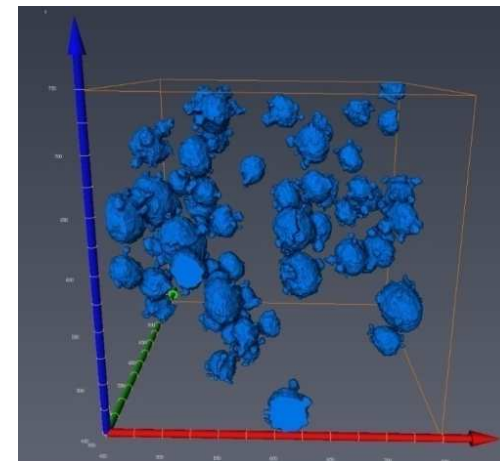
*de Hoyos-Martínez, et al., IRG/WP 19-30745*



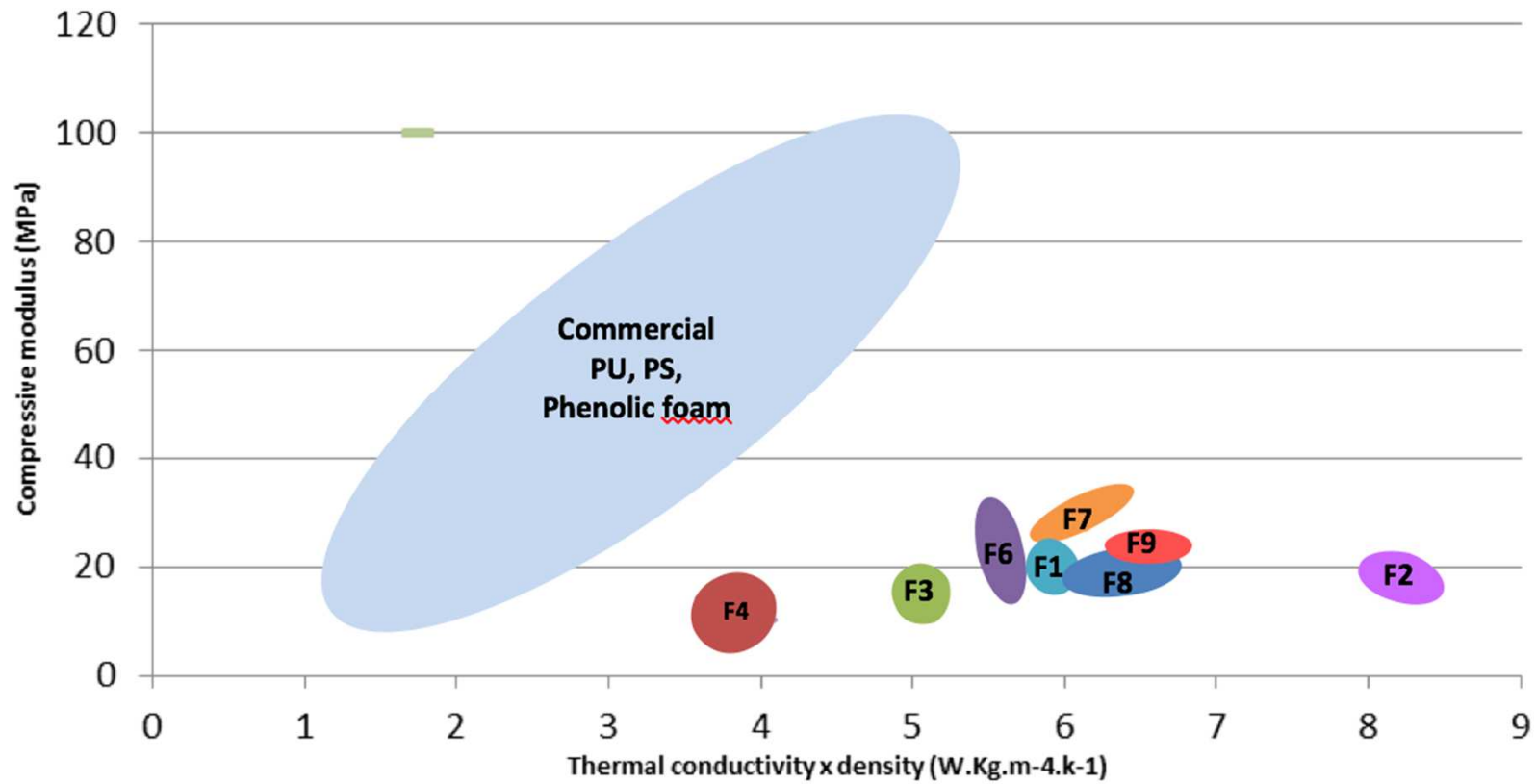
Structural characterisation: SEM comparison between biobased foams (left) and PU foam (right)

Different phenolic resins formulations were elaborated using lignin and tannins and glyoxal as phenol and formaldehyde substitutes. Mechanical foaming

*Application N° FR 1551638; filed on February 26, 2015 (UPPA / CNRS)*



Tomography



|   | Conductivité thermique (mW.K <sup>-1</sup> .m <sup>-1</sup> ) |
|---|---|
| Phenolic foams                            | 18-24   |
| Polyurethane                              | 22-40   |
| Extruded polystyrene                      | 32-37   |
| Expanded polystyrene                      | 31-38   |
| Cellulose                                 | 37-42   |
| <b>Tannin- Lignosulfonate based foams</b> | <b>35-44</b>  |
| Cork                                      | 37-50   |
| <b>Tannin- black lignin Kraft foams</b>   | <b>40-42</b>  |
| Mineralized wood fibers                   | 60-107  |

*Merle J. et al., Arabian Journal of Chemistry, 2016*

*Merle J. et al., Materials & Design, 2016*



## Conclusions

- ✓ Formaldehyde-free Phenolic Resins were synthesized from natural and environmentally friendly compounds.
- ✓ Wood residues from Maritim Pine (*Pinus pinaster*) were successfully valorized to be used as raw materials.
- ✓ Valorisation of industrial waste.
- ✓ Elaboration of adapted resin formulations targeting applications.
- ✓ The tests conducted, including fireproofing for coating and foam's thermal properties, show that the biobased resins can fulfill the requirement of applications fields such as intumescent coatings for the wood protection as well as insulating materials for buildings.



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# Thank you for your attention

*And thanks to:*



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