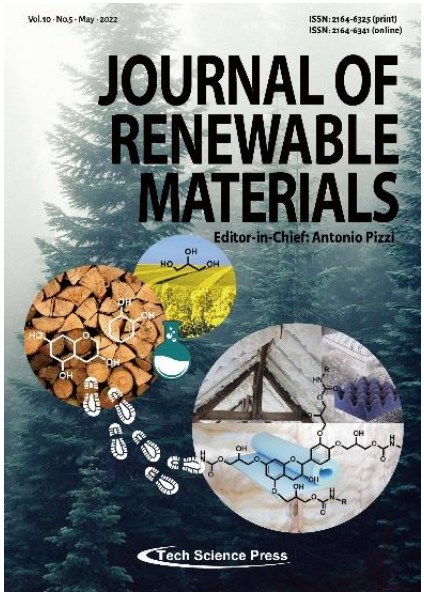
ChemXtraMat



Chemical-modified polyphenolic wood-extract for eco-friendly materials.

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Context —

The rarefaction of fossil resources easily accessible awakens from a few years back a growing interest in the use of renewable raw materials. Thus, industry is more willing to develop and use bio-sourced molecules to replace oil-derived synthetic products to give a "green "label to the products in which these molecules are included. Bio-sourced chemistry has developed mainly from annual agricultural resources and a number of reviews and reports do record the interest showed in developing such resources. At present the interest starts to focus on the use of the lignocellulosic biomass derived from wood as this constitutes a source of renewable carbon which is both abundant and not in competition with food resources.

However, the chemistry based on wood is still in its infancy, both at the national and international level, as wood has not found as yet its place among the other agricultural raw materials. Thus, the French forestry resource while being in continuous growth is also underexploited. Moreover, the wood primary transformation industry, such as sawmills, generates yearly a considerable volume of waste (slabs, sawdust, knots, bark…) which are at present either recycled to serve other industries, such as the particleboard or paper pulp industries, or used as a source of energy, hence towards uses at low added value.

Objectives —

This project is part of this context of sustainable development and the valorisation of wood industry by-products not for the use of polymers from this biomass but for the exploitation of easily extractable secondary metabolites from wood. In particular, this project complements the BARK-TAN-BIO (Labex) and Extra-For-Est (Ministry of Agriculture, Food and Forestry) projects directed by Dr Francis Colin and focused on the availability and variability of the extractives from wood resource. This project therefore focuses on the downstream part of this type of research and more specifically targets the valorisation of polyphenolic extractives such as tannins or flavonoids in order to design new environmentally friendly materials. A lot of research is currently being carried out on the design, characterisation and development of new bio-sourced materials to replace synthetic materials of fossil origin.

Condensed tannins are extractable molecules that represent up to 30% by mass of the dry matter in the bark or wood of various hardwoods (mimosa, acacia, pine, quebracho, etc.). Their chemical structure allows them to polymerise into networks of variable architecture and to be easily functionalised. Their aromatic character makes them excellent precursors of speciality carbons. Thus, tannin-furan polymers obtained by mixed polymerisation of furfuryl alcohol (obtained from the pentoses of lignocellulosic biomass) and tannins, are 90% derived from biobased materials.

Approaches —

Two approaches were considered in this project:

- The first is the continuation and further development of a previously started study on the incorporation of hydrophobic polyphenolic extractables into foams that can be used as insulating materials; this type of foam is among the most innovative foams proposed in recent years. In particular, tannin-furan foams, based on a co-condensation of tannins from bark and furfuryl alcohol, have been prepared, characterised and extensively studied in the laboratory. Both compounds are of plant origin and are relatively inexpensive. The project consists of chemically modifying these tannins or flavonoid monomers by grafting a hydrocarbon unit in variable proportions and using these hydrophobic polyphenol derivatives in the tannin-furan foam formulations developed previously. The foams obtained from native tannins are, in general, too hydrophilic and water permeable; the grafting of water-repellent fatty chains onto the polyphenol should improve the hydrophobicity of the materials and increase their water resistance and friability. For this approach, a formulation adaptation phase based on this type of chemically modified compounds was necessary and implemented.

- The second concerns the field of wood material protection.
Wood is indeed known to be a biodegradable material and sensitive to the attack of various biotic and abiotic agents. In the absence of natural durability, a preservation treatment is essential to obtain the necessary durability for use as a material. So far, most preservation treatments involve the impregnation of biocidal substances into the material. However, it should be noted that many preservatives have been banned in recent years due to their toxicity. In view of the directives in this field (Biocide Directive, Air Act in particular), it is urgent and unavoidable to find and develop alternatives for the protection of wood, especially when used in outdoor conditions, especially as the regulations are likely to restrict the spectrum of authorised molecules more and more.One of the alternative routes that we aimed at in this project was to make a hydrophobic wood-polymer composite using the same formulation as that used for foams but without the foaming effect in order to avoid the use of biocides altogether.
Another route studied for the design of wood-polymer composites is the polymerisation of a polyphenolic monomer by developing a methodology for obtaining isocyanate-free polyurethanes from glycerol using catechin as a carbon skeleton support.
In addition, we have also studied the durability conferred on less durable species by the impregnation of a hydrophobic polyphenol such as catechin (the basic motif of catechic tannins). The use of polyphenolic compounds, which are known to be involved in wood durability, may be an interesting way of conferring durability on species that are susceptible to biological attack and deterioration. Thanks to their antioxidant properties, polyphenols can interfere with the biochemical mechanisms used by fungi to degrade wood. Being hydrophobic should limit the absorption of water allowing good dimensional stability of the material and present unfavourable conditions for the development of microorganisms.

Key results — (presented as separated bullet points)
- **Hydrophobation of insulating foams**. The work carried out corresponds to the grafting of one or more hydrophobic hydrocarbon chains of different lengths (between 8 and 18 carbons) onto tannin via an ester-type bond. The chemical modification of tannins for the grafting of hydrocarbon chains is now well mastered. Characterisation of the materials obtained has shown that the incorporation of tannins modified by this type of grafting leads to less friable foams. Moreover, these grafted tannins, contrary to conventional co-monomers, do not cause foam shrinkage. Indeed, the hardening of the foam is very rapid and not staggered in time in relation to the expansion of the foam. Finally, the incorporation of these modified tannins leads to less hydrophilic, practically hydrophobic foams. This result is therefore very interesting and can be obtained by adding only 8% of grafted tannins to a standard foam formulation. (**COM 1 and COM 2**)
- **Design of an original wood-composite** from tannin-furfuryl alcohol formulations and wood-NIPU catechin composite.
One of the alternative approaches that we targeted in this project consisted of taking advantage of the co-polymerisation of tannins, grafted or not with furfuryl alcohol, to develop a hydrophobic wood-polymer composite and thus completely avoid the use of biocides. Very interesting results were obtained in terms of durability and dimensional stability. Different proportions of tannins and furfuryl alcohol were tested as well as different catalysts.
Oral and poster presentations are planned or accepted for 2 upcoming conferences in 2022 (**COM 3 and COM 4**).

In addition, we have also considered the impregnation of a hydrophobic polyphenol such as catechin (the basic unit of catechic tannins) and the polymerisation of this polyphenolic monomer by developing a methodology to obtain isocyanate-free polyurethanes by exploiting the reactivity of glycerol derivatives (a by-product of the biofuel or soap industry) using catechin as a supporting carbon skeleton. We started the study of the synthesis of these polymers (this work was published in the journal of renewable materials and on the cover page), using catechin as a model before developing the method later on from tannins. (ACL1)
- A new method for preserving wood material using hydrophobic flavonoids. We also studied the impregnation of aqueous solutions of a simple flavonoid such as catechin, also grafted with a hydrocarbon unit by esterification at the phenolic OH. (ACL 2)

Main conclusions including key points of discussion —
Tannin-furfuryl alcohol foams could be improved by inserting hydrophobic tannins in their formulation. The combination of wood with a tannin or catechin-based polymer is a promising way to obtain fully bio-based wood composites. The use of formulations based on hydrophobic polyphenols is interesting for finding alternative solutions to the use of petrochemical formulations for the preservation of wood materials.

Perspectives —
We would like to refine and complete the study concerning the design of hydrophobic foams because it would now be interesting to modify the proportion of grafted tannins in the formulation and to replace the grafted tannin by a low proportion of hydrophobic flavonoid, the synthesis of which is easier to control.
The design of wood composites based on isocyanate-free polyurethanes has yet to be finalised by carrying out the polymerisation in the wood material and extending the methodology developed from catechin to tannins. The study of the use of polyphenols for the protection of the wood material is still to be developed in order to optimise these formulations.

Valorization —
- **ACL1** : First Results for Feasibility Study of the Synthesis of Isocyanate-Free Polyurethanes from Flavan-3-ol. Sahmim Wissem, Boer Febrina Dellarose, Chapuis Hubert, Obounou-Akong Firmin, Pizzi Antonio, Gérardin Philippe, and Gérardin-Charbonnier Christine, ***Journal of Renewable Materials*** (IF = 1,341). 10(5):1175-1184, 2022 + page de couverture du journal
- **ACL2** : One step regioselective acylation of polyphenolic wood extractive and its application for wood treatment. Sahmim Wissem, Eid Georges, Boer Febrina Dellarose, Chapuis Hubert, Gérardin Philippe, Gérardin-Charbonnier Christine, **Journal of Renewable Materials** (IF = 1,341). 10(6):1491-1503, 2022
- **COM1**: Design of novel hydrophobic tannin foams, Hubert Chapuis, Maria-Cecilia Basso, Antonio Pizzi, Christine Gérardin, Exploring Lignocellulosic Biomass Conference, 26-29 Juin 2018, Reims
- **COM2** : Conception de mousses de tannins à hydrophobie modulée. Hubert Chapuis, Cécilia Basso, Antonio Pizzi, Christine Gérardin. 7èmes Journées GDR 3544 "Sciences du Bois", Cluny 20-22 novembre 2018
- **COM3** : Environmentally Friendly Wood Modification based on Tannin-Furfuryl alcohol – Effect on thermal stability and decay durability of wood, Mahdi Mubarok, Elham Azadeh, Firmin Obounou Akong, Stéphane Dumarçay, Philippe Gérardin, Christine Charbonnier-Gérardin, Communication orale, ECWM, 25-26 avril 2022.
- **COM4** : Chemical modification of polyphenolic wood-extract for an access to isocyanate-free polyurethanes-based resin-wood composites, poster, ECWM, 25-26 avril 2022.