DENISSE CONCEPCIÓN VEGA VILLARRUEL

TANNIN-BASED PHENOLIC FOAMS OF *Anadenanthera peregrina*: SYNTHESIS AND CHARACTERIZATION

LAVRAS – MG

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Dissertação apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduaçãoem Engenharia de Biomateriais, área de concentração Engenharia de Biomateriais, para obtenção do título de Mestre.

Prof. Dr. Fábio Akira Mori

Orientador

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TANNIN-BASED PHENOLIC FOAMS OF A*nadenanthera peregrina*: SYNTHESIS AND CHARACTERIZATION

BIOESPUMAS FENÓLICAS À BASE DE TANINO DE *Anadenanthera peregrina*: SÍNTESE E CARACTERIZAÇÃO

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2023

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Muito obrigada!

RESUMO

As espumas à base de taninos são materiais porosos leves de origem natural, obtiDAS pela policondensação de taninos e álcool furfurílico. Apresentam excelentes propriedades de resistência ao fogo e isolamento térmico comparáveis às espumas de fenol-formaldeído inflamáveis e não ecológicas; no entanto, sua fragilidade e resistência mecânica relativamente baixa desafiam ainda mais essas características. Neste estudo, quatro tipos de espumas à base de taninos (ST, TT, TB e TTB) foram preparados sem formaldeído, usando taninos de Anadenanthera peregrina (ST) e a incorporação de polissorbato80 como surfactante (TT), fibras de bambu como reforço (TB) e a combinação de ambos (TTB). Os valores médios dos taninos extraídos do índice de Stiasny e do teor de taninos condensados foram 72,41 % e 12,81 %, respectivamente. Além disso, a morfologia e as propriedades físico-mecânicas DAS espumas resultantes foram avaliaDAS por densidade, porosidade, compressão mecânica, absorção de água, resistência ao fogo, microscopia eletrônica de varredura (MEV), espectroscopia de infravermelho (FTIR) e Termogravimetria (TGA). De essa forma, a adição de fibras de bambu e polissorbato80 nas formulações teve um impacto mínimo na densidade da espuma em torno de 1,383 ± 0,05 $g \cdot cm^{-3}$, e uma porosidade média de 87 %; enquanto isso, sua resistência à compressão melhorou ligeiramente (0,12 - 0,19 Mpa). Por fim, as espumas produziDAS apresentaram comportamento autoextinguível, e os resultados de TGA mostraram estabilidade térmica semelhante às espumas, aumentando a temperatura de início da degradação e ainda apresentando matéria residual em torno 800°C.

Palavras-chaves: Tanino. *Anadenanthera peregrina*. Espumas biofenólicas. Ignífugos. Materiais de isolamento.

ABSTRACT

Tannin-based foams are lightweight porous materials of natural origin, obtained by polycondensation of tannins and furfuryl alcohol. They have excellent fire-resistant and thermal insulation properties comparable with phenol-formaldehyde flammable non-environmental friendly foams; however, their brittleness and relatively low mechanical resistance challenge further improve these characteristics. In this study, four types of tannin-based foams (ST, TT, TB, and TTB) were prepared without formaldehyde, by using *Anadenanthera peregrina* tannins (ST) and the incorporation of polysorbate 80 as a surfactant (TT), bamboo fibers as filler reinforcement (TB), and the combination of both (TTB). The extracted tannins' average values of Stiasny's index and condensed tannin content were 72,41 %, and 12,81 % respectively. Besides, the resulting foams' morphology and physical-mechanical properties were evaluated by density, porosity, mechanical compression, water absorption, fire resistance, scanning electron microscopy (SEM), Infrared Spectroscopy (FTIR) and Thermogravimetry (TGA). Thus, the addition of bamboo fibers and polysorbate 80 to the formulations had a minimal impact on the foam density around 1,383 ± 0,05 $g \cdot cm^{-3}$, and an average porosity of 87 %; meanwhile, their compressive strength slightly improved (0,12 - 0,19 MPa). Finally, the foams produced showed self-extinguishing behavior, and TGA results showed similar thermal stability of the foams, increasing the degradation onset temperature and still presenting residual matter around 800 °C.

Keywords: Tannin. *Anadenanthera peregrina*. Bio-phenolic foams. Fireproofing. Insulation materials.

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SUMMARY

1. INTRODUCTION

In recent decades, there has been a continuous move towards the substitution of synthetic materials in the industry by natural products obtained from vegetal sources. After cellulose, hemicellulose, and lignin, tannins are the most abundant compounds found in nature, and recently they have attracted significant attention as a green feedstock for new materials due to their biological activity and technological uses in several fields (BORRERO-LÓPEZ et al., 2022).

Tannins are secondary polymeric compounds produced by plants; they are found distributed, in stems, seeds, roots, buds, leaves and mainly in the bark of plant logs. The bark constitutes the external tissues surrounding trees, mainly treated as a disposable sub-product from wood processing. Currently, the majority of the bark generated in the industry represents a cheap energy source used for incineration and landfill purposes. On the other hand, recent research on their structural and chemical characterization has proven to contain high fractions of extractives, that can be employed as a renewable source of compounds, like tannins, that stand out due to their presence in greater quantities and biological activity as a potential substitute of synthetic phenols in a variety of applications (FENGet al., 2013; CHEN et al., 2021).

In this context, Brazil as a strong wood producer possesses 12 % of the world's total forest cover, corresponding to 58.5 % of the territory, that is distributed in native forests around 487.4 million ha (98 %) and 9.9 million ha (2 %) of commercial plantations. The last, intended for the pulp and paper industry, and processed wood products, from these activities it is estimated that 10 to 20 % of the total volume used is disposable bark, not fully employed, that can have long-lasting effects on the environment and actually be a potential source of natural compounds and reduce the dependence on petroleum products, valorizing the waste generated in the industry (IBA, 2022; SNIF, 2022; HILLING et al., 2009).

Among the forest species explored in the country for tannin exploitation, black wattle (*Acacia mearnsii*), and pine (*Pinus pinaster*) have been widely studied and commercially produced. Thus, it is important to look for supplementary forest species that can provide good quality tannins, along with, high reactivity and sustainability. As it is known, the tree of *Adenanthera peregrina* possesses a large amount of tannins, typically used in the leather and dyeing industries, as well as, in popular medicine (MARTINs, et al., 2020) Red angico as commonly known in the country, belongs to the Leguminosae family, and is found in the

Cerrado territory; has high-density, resistant wood used for flooring and building construction, besides the bark, is considered a natural source of phenolic compounds, especially for tannins extraction which further promotes the use of non-wood products (MOTA et al., 2017).

From the numerous applications of tannins, in the last few years, tannin-based phenolic foams have been intensively investigated as an alternative to synthetic foams used as insulating materials in the construction, transportation, and packaging industry. Phenolic foams are often produced with formaldehyde that has been classified as non-environmentally friendly and carcinogenic to humans (VARILA et al., 2019; SARIKA et al., 2021; LIU et al., 2022). Despite their good thermal insulation properties, low density and low thermal conductivity, these fossil-based foams are highly flammable and can release toxic gases during combustion which negatively associate them to fire hazards and the need to switch toward bio-based products (CHEN et al., 2021; SARIKA et al., 2021).

In this context, looking to produce environmental friendly insulating materials, formaldehyde-free tannin foams are being considered due to their similar phenolic structure to replace synthetic phenols and excellent characteristics such as lightweight, high fire resistance, and self-extinguishing character (DELGADO-SANCHEZ et al., 2018). Recent bio-based phenolic foams research has focused on improving the mechanical properties of the foams while simultaneously preserving or boosting their thermal performance and fire resistance (MOUGEL et al., 2019).

Given the above, the present work aims to verify the quality and behavior of the *Adenanthera peregrina* tannins in the production of phenolic foams without formaldehyde. As well as, to evaluate the influence of incorporating an additive, and a reinforcement, on the physical, mechanical, and thermal properties of different foam formulations.

2. LITERATURE REVIEW

2.1 Tannins

Tannins are natural bioactive compounds ample found in nature, lately researches on tannin's biological activity and industrial uses have revealed their potential as green raw material for several fields, gaping in recent decades continuous move towards the replacement of synthetic materials used in the industry by natural products (BACELO et al., 2016; DE HOYOS-MARTÍNEZ ET AL., 2019). Defined as polyphenolic secondary metabolites of plants, tannins are distributed almost in all parts of the plant mainly in bark, stems, seeds, roots, buds, leaves, and fruits (ARBENZ & AVÉROUS, 2015; DAS et al., 2020; SHIRMOHAMMADLI et al., 2018). Generally, tannins possess high molecular weights between 500 and 20,000 Da, and a heterogeneous chemical structure, about 12 to 16 phenolic groups and 5 to 7 aromatic rings. They also present hydroxyl groups, with hydrophilic and aqueous solubility properties that represent them; due to their phenolic nature they are able to bind and form complexes with proteins, carbohydrates, or alkaloids and act as trap of ions and radicals scavengers (ARBENZ & AVÉROUS, 2015; FRAGA-CORRAL et al., 2021).

Produced as a result of stress, this metabolites perform as defensive agents of plants, protecting them from organisms such as fungi, pathogens, insects and herbivorous animals, moreover, they confer photoprotection against UV rays, free radicals and protection from severe environmental conditions, as dryness (DAS et al., 2020; FRAGA-CORRAL et al., 2021). Tannin's abundance and occurrence depend on several aspects such as the plant species and parts considered. Its content varies even within the same species between different parts of the plant, for instance, their content might vary with seasonal and environmental factors like water availability, temperature, light intensity, and soil quality (FRAGA-CORRAL et al., 2021; SHIRMOHAMMADLI et al., 2018).

Typical botanicals sources of tannins (Table 1.) are black mimosa bark (*Acacia mearnsii*), quebracho wood (*Schinopsis batansae*), oak bark (*Quercus spp*.), sweet chestnut (*Castanea sativa*), Pine (*Pinus radiata*) trees, among others, they are also available in foodstuffs, biomass, like, tea, grape, pomegranate, pecans, or tara (PALAGRIO et al, 2021; BACELO et al., 2016).

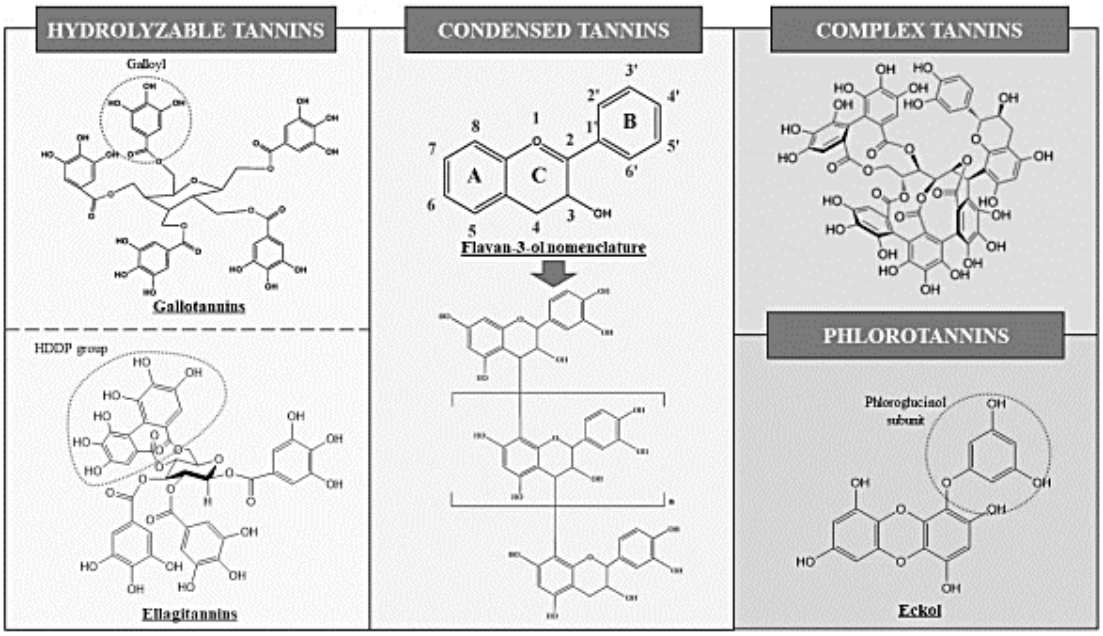
Table 1. Tannin content of some vegetable materials.

Plant Material	%
Quebracho wood	20 – 30
Wattle (acacia bark)	15 – 50
Black oak	8 – 12
Pinus pinaster bark	22.5
Eucalyptus bark	16 – 40
Mangrove bark	15 – 42

Note: Adapted from Bacelo et al. (2016).

Broadly, tannins are categorized into two main groups, hydrolysable and condensed tannins, according to their chemical characteristic and structural properties as presented in the figure; the classification incudes complex tannins, of high molecular weight, created as a result of the bonding between flavan-3-ols units with gallotannins, or ellagitannins and phlorotannins, an exclusive class of tannins found in the brown marine algae species of the Phaeophycean class (ARBENZ & AVÉROUS, 2015; SHIRMOHAMMADLI et al., 2018). Tannin structural classification is presented in Figure 1.

Figure 1. Tannins structural classification.

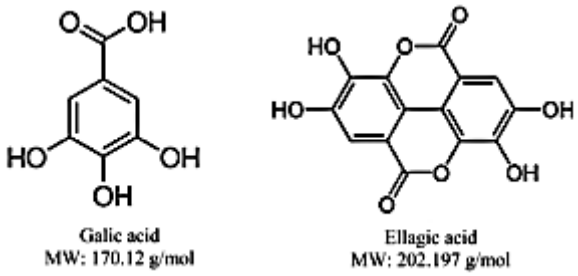


Note: Adapted from Fraga-Corral et al. (2021).

2.1.1. Hydrolysable tannins

Hydrolysable tannins (HTs), are mixtures of simple phenols that can be hydrolyzed by weak acids or bases, they are formed by esters of phenolic acids (Figure 2.), either ellagic acid (EA) or gallic acid (GA), and a polyol mainly glucose (FRAGA-CORRAL et al., 2021; BULE et al., 2020). HTs can be largely found in fruits, berries, legumes, and different tree species, like chestnut, red oak, and others. (ARBENZ & AVÉROUS, 2015). They present antimicrobial, antiviral, anti-inflammatory and antioxidant properties, commonly used as food additives and preservatives, moreover their astringency characteristic has increased their importance in the production of drugs (BULE et al., 2020).

Figure 2. Hydrolysable tannins molecules.



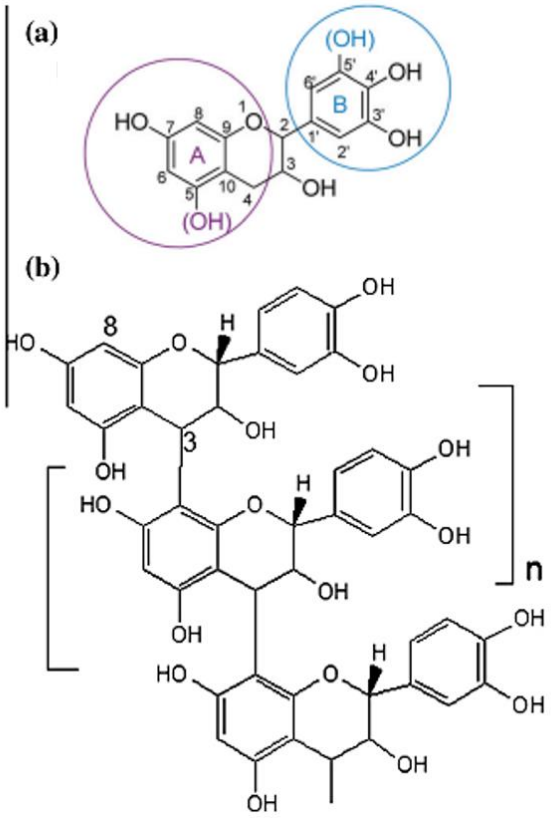
Note: Adapted from Shirmohammadli et al. (2018).

2.1.2. Condensed tannins

Condensed tannins (CTs) are polymeric flavonoids (flavan 3-ol or flavan 3, 4-diol), composed of two phenolic rings (A and B) having different reactivities, the A ring is formed by phloroglucinol or resorcinol, and the B ring from catechol or pyrogallol, without a sugar core (FRAGA-CORRAL et al., 2021; SHIRMOHAMMADLI et al., 2018) illustrated in Figure 3.

The flavonoids from condensed tannins are mostly derived from flavan-3-ol and flavan-3,4-diol and the type of bonding between the units depends on the nucleophilic nature of the rings (Figure3.). A-rings are known to be more reactive than the B-rings due to the position of the OH group on the rings, which difference their reactivity, the type A-ring present high nucleophilicity on C6 and C8 positions characteristic of the resorcinol and C4–C8 positions are relevant in the B-ring (ARBENZ & AVÉROUS, 2015).

Figure 3. Schematic representation of a) a catechin unit and b) a condensed tannin.



Note: Adapted from Arbenz & Avérous, (2015) and Bacelo et al. (2016).

CTs present high reactivity towards aldehydes and their complex interaction with proteins, makes them more interesting in terms of economy and chemical usage for various purposes. Mainly produced in Europe, America, Africa and Asia, condensed tannins constitute more than 90 % of the total world production of commercial tannins from plant species like wattle, quebracho, mangrove hemlock, and pine (ARBENZ & AVÉROUS, 2015; FENG et al., 2013). According to market intelligence database, in 2020 the global tannin market size was estimated at 2.2 billion with a production is expanding rate of 6.7 %, basically focused in four main applications: leather tanning, wood adhesives, wine manufacture, and in anticorrosive coatings (DAS et al., 2020; PAGLIARO et al., 2021; GVR, 2023). In Brazil there are two major companies, SETA and TANAC that produce tannins from Acacia species and some tannin derivates, according to COMTRADE database for example, United States imports from Brazil of tannin and derivatives, was around US$1,7 million during 20211, and China imported around 11 million in the same year as well, with an expected growth tendency in demand (COMTRADE, 2022).

2.2. Extraction of Tannins

In general, tannins are extracted either by hot water or by using aqueous solvent solutions from plant materials (DAS et al., 2020). Due to tannins heterogeneous nature, the extraction process remnants as a main challenge for their valorization. The extraction is not done by single practice, there are various methodologies and new technology available widely variable, the most important factor to be considered in the method selection is the final use of the tannins as well as, other parameters which influence on both quality and quantity of the extracted materials like solvent type, time and temperature of extraction, solvent to solid ratio and particle size of the sample (SHIRMOHAMMADLI et al., 2018).

Besides water there is a wide range of polar solvents used for the extraction like, methanol, ethanol, acetone, aqueous solutions and newel ionic liquids (Table 2.). In terms of the extraction time, an increment can provide a higher content of tannins, as the contact with the sample increase however, longer times can lead to a compound degradation with low extraction yields. As well as an elevate temperatures can increase the tannins yield despite too high temperatures are not desirable for a possible denaturalization of tannins and solvent evaporation. Considering the solid-liquid ratio, a decrease of this parameter provides higher extraction yields, and a reduced particle size its preferred as it represents a greater contact area between the solvent and the sample (BELLO et al., 2020; DAS et al., 2020; SHIRMOHAMMADLI et al., 2018).

Table 2. The yield of tannin extraction from different species by various solvents.

Extraction method	Plant species	Yield (%)
Hot water	*Pinus pinaster* (bark)	6
Alkaline solution		
Water at 60 °C	European larch (bark)	20.1
	Norway spruce (bark)	18.2
Water + salt addition	*Pinus oocarpa* (bark)	~39
Sulphite-water (12-15)	Pine (bark)	12–25
Commercial tannin		
Hot Water	Minmosa bark	30-33
	Quebracho (wood)	26-29
	Pine (bark)	13-15

Note: Adapted form Shirmohammadli et al. (2018).

In the last years, new extraction methods have been developed and laboratory proven for the development of the process from microwave, ultrasound, infrared assisted to novel enzymes extraction, which can be translated into elevated tannin yield and reduced extraction

times (BOURAS et al., 2015; CHEMAT et al., 2017; PATIL et al., 2021; WANG et al., 2017; XUAN CUONG et al., 2020). In spite of the different methods available, hot water extraction is still the most commonly used technique for the industrial tannin extraction, as well as in the laboratory due to its simplicity and low cost (DAS et al., 2020; FRAGA-CORRAL et al., 2021; KEMPPAINEN et al., 2014).

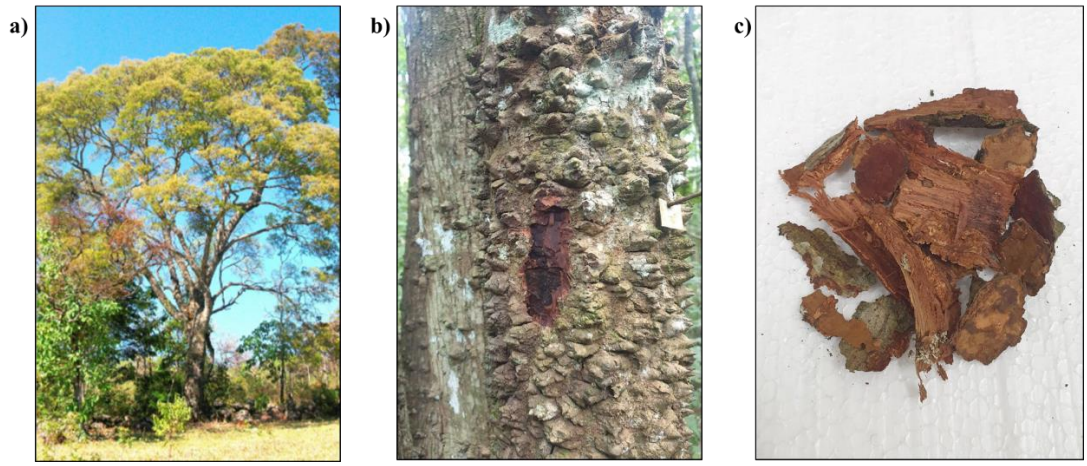
2.3. Plant Species

2.3.1. *Anandenanthera peregrina* (Red Angico)

A. peregrina plant belongs to the family Leguminosae and subfamily Mimosaceae. Is a fast-growing species commonly named angico or red angico in Brazil, mainly found throughout the Cerrado territory and in in the south region of the country practically in Tocantins, Goiás, Bahia, Minas Gerais, Rio de Janeiro, São Paulo, Mato Grosso and Mato Grosso do Sul (CARVALHO, 2003).

They are trees from 20 to 30 m in height, the stem from 60 to 110 cm in diameter, covered by a dark bark with axillary spines or thorns, and its inner bark is reddish, possibly associated with its high tannin content (IBF, 2020). It has bipinnate leaves, white flowers and the fruit looks like a flattened follicle where the seeds of the tree are found.

Figure 4. a) *Anadenanthera peregrina* tree species, b) appearance of the trunk of the *A. peregrina*, c) bark extracted from the *A. peregrina* tree.



Note: Author, (2022).

The *A. peregrina* wood is dense (0,85 to 1,10 g/cm^3), inelastic, and has great mechanical strength as well as rotting, although its cuttings have been shown to be highly resistant to xylophagous agents (CARVALHO, 2011). It is suitable for civil and naval construction, for example in beams, doors, and window frames, furniture manufacturing up to turned parts. Its

high lignin content makes it an important option in the production of energy in the form of firewood as well as alcohol and coke (OLIVEIRA, et al., 2007; CARVALHO, 2011). Another use of the species is for leather tanning, as it has tannins in the fruits and especially in the bark (13% to 20%), and angico bark is one of the main non-wood products occurring in the Cerrado (OLIVEIRA, et al., 2007; SARTORI, 2012; AFONSO, 2008).

Still, the bark is also used in home medicine for its hemostatic, astringent and pectoral properties. And for forest recovery and environmental preservation projects because of its rapid growth and easy adaptation, as a pioneer species (SEMIL, 2016; CARVALHO, 2011).

2.4. Tannins applications

Thus, the phenolic structure of tannins and versatile chemistry, they are suitable for many different applications in numerous fields, largely used in the tanning industry, transforming hides into leather with thermal stability and antimicrobial properties (PAGLIARO et al, 2021). Followed by wood adhesives, that present comparable reactivity and crosslinking to the phenol in formaldehyde systems; wine production, and anticorrosive primers (ZOU et al., 2019). Tannins have also proven to be adequate to be used in several other advanced applications (Table 3.), like for environmental purposes in water treatment plants, insulating foams, mineral industry as adsorbents, wood composites and improvers as biocide and fungicide, animal nutrition, food supplements, and in the pharmaceutical and medical industry (DAS et al., 2020; ZOU et al., 2019)

Table 3. Condensed tannins sources and applications.

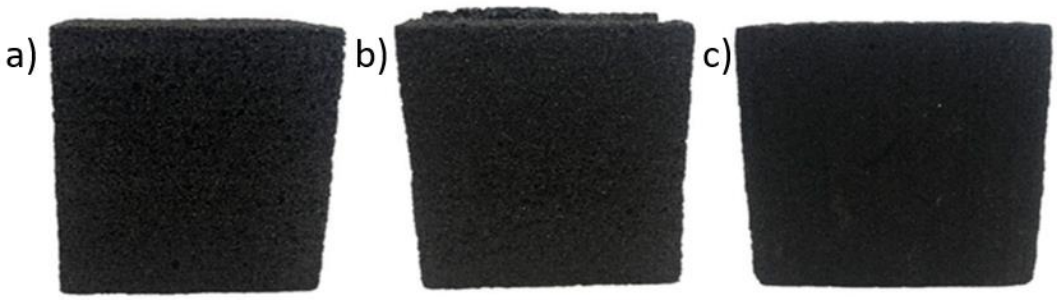
Application	Properties	Sources
Leather processing	Higher shrinkage temperature, resistance to damage in leather industry	Quebracho, Acacia, Wattle, Angico tree
Wood adhesive	Better strength and adhesive properties of wood composites, superior water resistance properties	Acacia, Pinus, Myrcia eximia bark, Angico tree
Anticorrosive for metal	Protection against corrosion	Quebracho, black wattle, mangrove
Water and wastewater treatment	High coagulation efficiency, methylene blue and heavy metals absorbents	Spruce, wattle
Packaging	Anti-oxidant, UV shielding	Quebracho
Animal food	Nutritional	Red quebracho, black wattle, chestnut

Note: Adaptated from Das et al., (2020).

2.5. Tannin-based phenolic foam

Among the mentioned industrial utilizations of tannins, bio-based foams (Figure 5.), have attracted significant attention on recent years, as an alternative to petroleum-based insulation foams used in the industry. These lightweight porous materials are based on natural origin compounds, and have proven to present excellent fire resistance and thermal insulation properties (SEPPERER et al., 2021). The first record of a tannin-based foam formulation appeared in 1994 from a work published by Meikleham and Pizzi, with comparable characteristics to phenolic synthetic foams dominating the construction and transportation industry (PIZZI, 2019; LACOSTE et al., 2015).

Figure 5. Tannin-based foams from different extracts: a) mimosa, b) quebracho and c) chesnut.



Note: Adapted from Eckardt et al., (2023).

Bio-foams created from tannin bark extracts and furfuryl alcohol, allows the complete or partial substitution of synthetic phenol, commonly resol-type phenolformaldehyde, with condensed tannins due to their similar phenolic structure. These foams are obtained by the incorporation of four main components, a catalyst, crosslinker, surfactant, and a foaming agent, that leads to the evaporation of a low boiling point solvent and simultaneous hardening of the polymer (SEPPERER et al., 2021). A typical tannin foam formulation is presented in Table 4., together with the components role in the preparation (FENG et al., 2013; MARIE et al., 2019).

Table 4. Standard formulation of tannin-based foams.

Ingredients and roles in the formulation	Mass (g)
Mimosa tannin extract; base of the resin	30
Para-toluene sulphonic acid (pTSA, 65%); catalyst	11
Furfuryl alcohol; co-reagent	10,5
Formaldehyde (37%); crosslinker	7,4
Water; solvent	6
Diethyl ether (DEE); blowing agent	3

Note: Adapted from Marie et al. (2019).

In general, the foam formation process includes three steps the mixing of the reagents, the expansion stage and the aging. Varying the concentration and type of its components, as well as, using biomass resources and other modifiers, reinforcements would determine the properties of the resulting foam (LI et al., 2019; SEPPERER et al., 2021).

2.5.1 Type of components in foams

There are different types of components that takes part in the foam's formulation, being one of the principals the phenol. main component for the preparation of foams are phenols, these aromatic compounds constitute the structural chain of the polymer, formed by hydroxyl groups bonded to benzene ring possess three reactive sites. The similar structure of tannins with the synthetic phenols make them suitable to replace the latter from the foam's formulation. As a result, tannins can share three bonds for the polarization reaction, with aldehydes, especially through the nucleophilic sites of their A ring, which produce the crosslinking and form rigid foams (LACOSTE et al., 2014; TONDI et al., 2009).

Several studies have been carried out exploring different kinds of tannins for the preparation of foams with comparable properties to the industrial ones, such as mimosa (*Acacia mernsii*) (TONDI, 2017; ECKARDT et al., 2023), quebracho (*Schinopsis lorentzii*) (BASSO et al., 2015; SANTIAGO-MEDINA et al., 2018) and pine (*Pinus pinaster*) (LACOSTE et al., 2014; COP et al., 2015). Martinez de Yuso et al., (2014), studied quebracho foams and compare their thermal and mechanical properties with those of mimosa and pine, showing very similar behavior with mimosa foams, due to the identical structure and A-ring reactivity, therefore they can be prepared following same formulations. In contrast, pine tannins possess different flavonoid nature with higher reactivity resulting on different foams performance (LACOSTE et al., 2014).

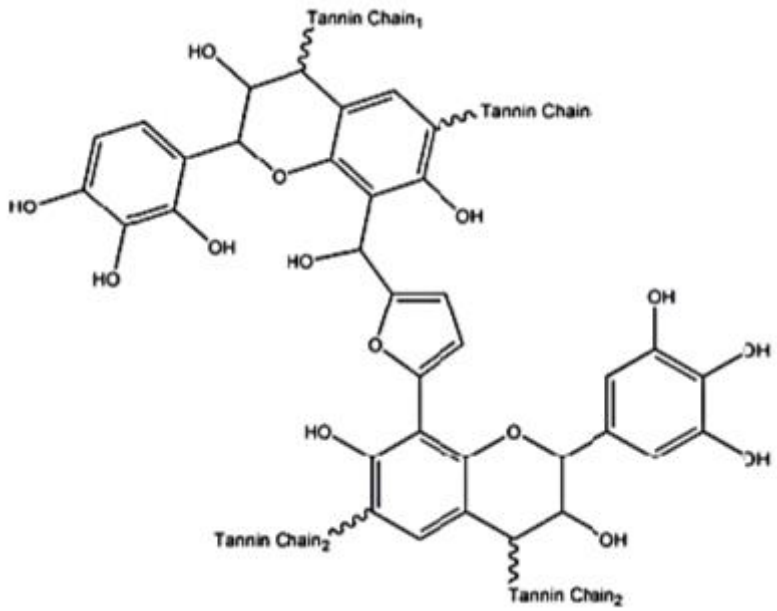
According to Lacoste et al., (2014) pine bark tannins correspond to procyanidin type structure, more reactive towards formaldehyde, than resorcinol A-ring type from mimosa and quebracho, having a significant effect on the tannin reactivity and behavior. On the other hand, Eckardt et al., (2023) found mimosa tannin foams to have slightly higher compression strength and thermal conductivity compared to quebracho foams; besides stated that other properties like density and foamability depended on the surfactant concentration and tannin type. Thus, it is important to base on the requirement and application for the foam product in order to determine the tannin type to be used.

Another common type of component is the crosslinker. Phenolic foams are typically produced from petroleum-based materials, formaldehyde is the most common used crosslinker in the foam's formulations, due to its low price and availability, this chemical reacts with the linear chain of tannin polymers and bond with several of its reactive sites forming a polymer network (BORRERO-LÓPEZ et al., 2022). Properties like density and dimensional stability depends on the amount of the crosslinker used. Other types of aldehydes have also been considered for the formaldehyde substitution due to its toxic and carcinogenic character (VARILA et al., 2019; SARIKA et al., 2021; LIU et al., 2022). Thus hexamine, glyoxal, maleic anhydride, and glutaraldehyde were analyzed by Tondi, (2017), showing promising polymerization possibilities, especially hexamine as an efficient hardener for mimosa tannin foams. Likewise, Lacoste et al. (2013), has used glyoxal and glutaraldehyde, in the formulation of pine tannin foams with prominent results. And in recent years, some formulations without using formaldehyde have been carried out following more environmental trends (BASSO et al., 2011; LI et al., 2015). Liu et al., (2022) developed a bayberry tannin foam through the polycondensation of glyoxal and furfuryl alcohol and lignin, with efficiently mechanical strength and a lower pulverization degree showing a possible complete substitution of formaldehyde in the formulation.

The second main component to produce tannin foams, is furfuryl alcohol can be obtained from the acidic hydrolysis of corn and wheat residues (hemi-cellulose) into furfural and catalytic reduction into furfuryl alcohol (SEPPERER et al., 2021; LIU et al., 2022). This bio-sourced compound represents the "engine" of the foam polymerization, that leads to a highly exothermic reaction due to its self-condensation and reaction with the tannin under acidic conditions (Figure 6.), where the heat generated allows the foam expansion and cure, while evaporating the blowing agent; furthermore, its incorporation will increase the mechanical strength of the tannin foams (TONDI & PETUTSCHNIGG, 2016; VARILA et al., 2019;

SARIKA et al., 2021).

Figure 6. Suggested reaction mechanism between condensed tannin and furfural alcohol.



Note: Adapted from Link et al., (2011).

Following with the foaming agent or blowing agent that cause the expansion of the matrix during the foaming process, by the production of gas bubbles that increase in quantity and pressure forming the foam (SARIKA et al., 2021). There are two types of blowing agents, physical and chemical. Physical expansion agents produce the phase change of a liquid with a low boiling point solvent, caused by the exothermal self-condensation of the furfuryl alcohol in the mixture and the solvent evaporation. They are divided into inorganic like air, nitrogen, carbon dioxide and organic such as diethyl ether, 4,4′-methylene diphenyl diisocyanate, pentane or hexane (BORRERO-LÓPEZ et al., 2022; ISSAOUI et al., 2021). On the other hand, chemical expansion, refers to the formation of internal gases, like CO_2, during the reaction between isocyanates and water (BORRERO-LÓPEZ et al., 2022).

Another principal compound in the foaming reaction is the catalyst. it starts the polymerization reaction between the phenolic compounds and the cross-linking agents, where the gelation of the tannin initiates to form the resin and extra heat is produced for the evaporation of the blowing agent (ISSAOUI et al., 2021; SARIKA et al., 2021). The most commonly used catalysts are organic or inorganic acids and alkaline agents, the p-toluene sulfonic acid (p-TSA) and phenol sulfonic acid are organic acids used in the synthesis of

phenolic foams. Between the inorganic acids sulfuric and chlorohydric acid have been tested, as well as phosphoric and boric acid that can improve the fire resistance characteristics (TONDI & PETUTSCHNIGG, 2016). Moreover, a combination of different catalyst might allow to control the expansion/hardening ratio during foaming (BASSO et al.,2015). Tondi et al., 2009, also prepared a foam combining both organic and inorganic acids, with ortho-phosphoric acid and p-TSA solution that allowed an increase of fire resistance as well as, good resistance to strong acid and bases.

Other type of components that can enhance the formulation of the foams are additives. Chemical additives like oils, surfactants, adhesives and plasticizers have been used to enhance properties such as elasticity, flexibility, or mechanical strength on the foaming mixture. Form the before mentioned, surfactants have been widely studied and presented best foaming results; these copolymers are used to improve the homogenization of the mixing, they modify the surface tension at the interface of the hydrophilic resin with the hydrophobic blowing agent forming a stable emulsion (ECKART et al., 2023). In general, these compounds help to solubilize or disperse a compound, increase the wetting of the mixture in the mold, plasticize the polymer, and facilitate the nucleation of gas bubbles increasing the matrix porosity (BORRERO-LÓPEZ et al., 2022; SARIKA et al., 2021).

A variety of ionic and non-ionic surfactants, have been tested in the foam production such as Tween-80 (non-ionic), ethoxylated castor oil (non-ionic), sodium dodecyl sulfate (anionic), tritonX-100 (non-ionic), Brij 35 (non-ionic), and Pluronic F127 (non-ionic) showing good foaming behavior, good mechanical properties and homogeneous cell wall (SARIKA et al., 2021; SEPPERER et al., 2021). According to Sepperer et al., (2021) the best results in terms of foam stability, homogeneity, and mechanical behavior were observed using Tween 80 for mimosa tannin-furanic foams. Santiago-Medina et al., 2018, used non-ionic ethoxylated amine surfactant in the formulation of quebracho tannin foams, resulting on reduced cell size and improved uniformity of the foam. Same was reported by Basso et al., 2015, non-ionic silicone surfactant leaded to smaller cell size and homogeneous distribution in tannin-furanic foams.

Another type of additives used for reinforcement are fillers. Phenolic foams can be reinforced by adding different type of fillers, including minerals, ceramics, or metals in order to enhance their mechanical properties. The incorporation of fiberglass, calcium carbonate, carbon nanotube or tire rubber on the foaming mixture have shown to increase the compressive strength and dimensional stability of the foams (ZHOU et al., 2013; SONG et al., 2017).

Recently, several studies have reported to use more environmentally thought materials due to their abundance, low cost, low density, and good thermal insulating properties (WU et al., 2020; LI et al., 2019). Natural resources such as wood particles (LI et al., 2019), lignin (LIU et al., 2022; ISSAOUI et al., 2021) or lignocelluosic fibers (WU et al., 2020) incorporation can improve the foams mechanical performance. Li et al., (2019), reported that using cork powder on tannin foams formulation improved the mechanical properties and reduced the friability.

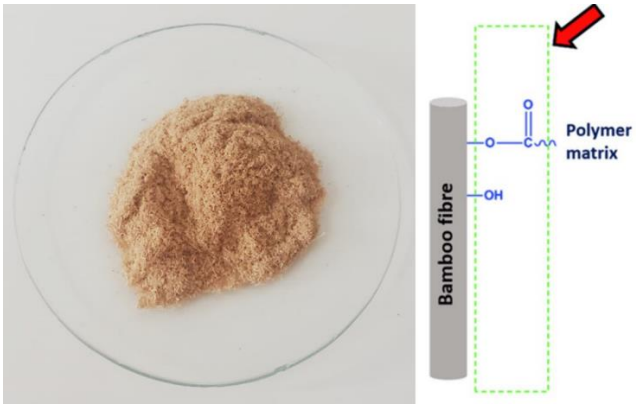
Similar results were found by Liu et al., (2022), incorporating lignin with larch condensed tannins resulted in lower pulverization degree, improved heat resistance and compression strength. According to Saz-Orozco et al., (2015) phenolic foams reinforced with 2% cellulose fibers showed a 18% improvement in their compressive strength. As well as Wu et al., (2020) found that 2% wood fibers addition provided the best mechanical and thermal properties for quebracho tannin foams.

2.5.2 Natural fibers as reinforcement

Following this trend, natural fibers, including bamboo, jute, flax and hemp have been studied as conventional reinforcement materials and are gaining attention because of their sustainability, full biodegradability and high mechanical strength. Among them, bamboo fibers are very promising reinforcement, due to their low density, high stiffness, high strength and rapid growth rate (QIU et al., 2021; NURAZZI et al., 2022).

Bamboo is a perennial plant, occurring in tropical and subtropical regions, the most common species in Brazil is *Bambusa vulgaris* featuring fast growth, high biomass productivity and small production cycles (MUHAMMAD at el., 2019; SANTANA et al., 2019). The primary chemical constituent of bamboo fibers is cellulose, around 26 – 60 % of its composition, presenting with high tensile strength, in addition, possess hemicellulose responsible for humidity absorption, lignin for the hardness and rigidity and abundant hydroxyl groups that can react with polyols and isocyanates (Figure 7.) (QIU et al., 2021; MOUSAVI et al; 2022).

Figure 7. Schematic compatibilization between the bamboo fiber with a polymer matrix.



Note: Adapted from Nurazzi et al., (2022).

They have been utilized to reinforce thermoplastic and thermosetting matrices, showing high mechanical properties (YUSUF et al., 2018; MUHAMMAD et al., 2019). According to Qiu et al., 2021, polyurethane foams reinforced with 5 % bamboo fiber showed the best physico-mechanical performance than other analyzed foams, suggesting a strong reinforcement effect; moreover, the thermal stability of the foam increased. Recent researches have revealed that the presence of bamboo fibers in polymers composites, leads to improved mechanical properties, especially tensile and flexural strength, attributed to the high strength and modulus of the bamboo fibers (MOUSAVI et al., 2022).

2.5.3 Tannin foams synthesis and characterization

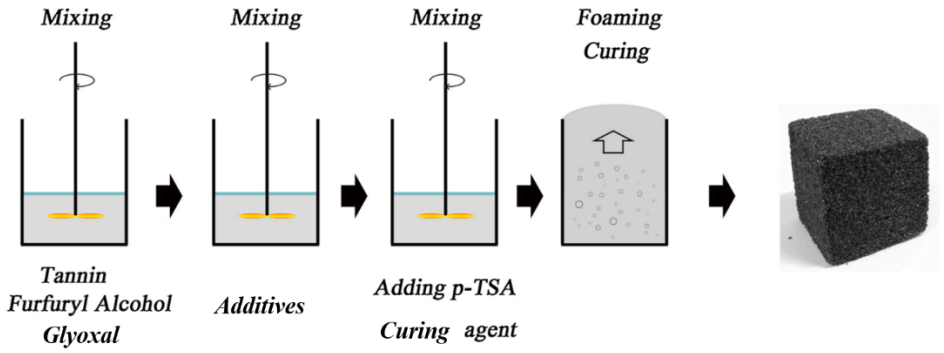
The foaming process to obtain tannin-based rigid foam consists of three phases: mixing, expansion and curing. The most common studied foaming processes for rigid foams are, chemical and physical. Chemical foaming consists on the polymerization reaction, between a solvent and blowing agent that expands producing a gas, commonly carbon dioxide CO_2, and forming the lightweight porous skeleton of the foam (CHEN et al., 2020; MARIE et al., 2020). And, physical foaming that occurs, by a sudden evaporation of a low boiling point-liquid added to the formulation producing vapor (MARIE et al., 2020).

The most used method for phenolic foams production, is by physical foaming, volatilizing a solvent with a low boiling point temperature. Considered as phenolic-type foams, the tannin, furfuryl alcohol, blowing agents, and additives are initially mixed followed by the curing agents until complete homogenization (Figure 8). The synthesis of the foams occurs by tannin gelification, where condensed tannins are used as a substitute of the phenol, that in

contact with a crosslinker substance, induce polymerization through methylene bridge linkages on the nucleophilic sites of the A ring of tannin flavonoid molecules, initiating the gelatinization process (LACOSTE et al., 2015; LI et al., 2021).

This phenomenon is carried out along with the volatilization of the blowing agent, that starts when the curing agent is added leading to the exothermic reaction, resulting in foam expansion. During the foaming process, the curing agent and external heating cause the resin mixture to cure and harden at the same time into a solid foam. This is a very subtle process, where slightly modifications on the amount of the solvent or crosslinking product added may result into non-effective foams (DELGADO-SANCHEZ et al., 2018; SÁNCHEZ-MARTÍN et al., 2013).

Figure 8. Schematic illustration of the fabrication of tannin-based foams.



Note: Adapted from Chen et al., (2021).

There has been outlined some parameters to be considered when formulating the tannin-based foams that can affect the, apparent density, homogeneity, cell morphology and surface area of the bio-foams. According to Zhao et al., (2010), the amount of blowing agent is related with the pore structure of the foam, having a major effect on its apparent density; the incorporation of additives, can improve some of the foam properties, like easier the production of bubbles in the process, increase the liquid viscosity, thus, influence the pore structure. Besides, regarding to the geometry of the molds used in the foaming process, a deeper and narrower mold lead to elongate the cells while a broad one is expected to form an isotropic pore structure and limiting the expansion of the material during foaming could modify the pore structure as well.

Tannin- phenolic foams typically have shown many favorable properties like a low density, low thermal conductivity, high fire and chemical retardancy to organic solvents and

acids, self-extinguishing nature and absence of harmful smokes when exposed to flame (SARIKA et al., 2021; WU et al., 2021).

Furthermore, they are water-resistant, thermal insulation, sound resistance and has cushioning properties, all these advantageous characteristics have converted tannin foams into promising competitive materials for packaging, transportation, flower preservation, and building applications for roofing, flooring as insulation materials (TONDI et al., 2016; SANTIAGO-MEDINA et al., 2018). Recently there have been increasingly works on condensed tannins foams used in metal ion adsorption, for water treatment, and sandwich core composite materials applications (CHEN et al., 2020; LACOSTE et al., 2015; WU et al., 2020; LIU et al., 2022).

The fire resistance and self-extinguishing flame behavior make tannin phenolic foams an outstanding insulation material. The thermal insulation depends on its thermal conductivity and the benzene rings present on their phenolic structure that are responsible for the flame-retardant properties of the foam (SEPPERER et al., 2021; SARIKA et al., 2021).

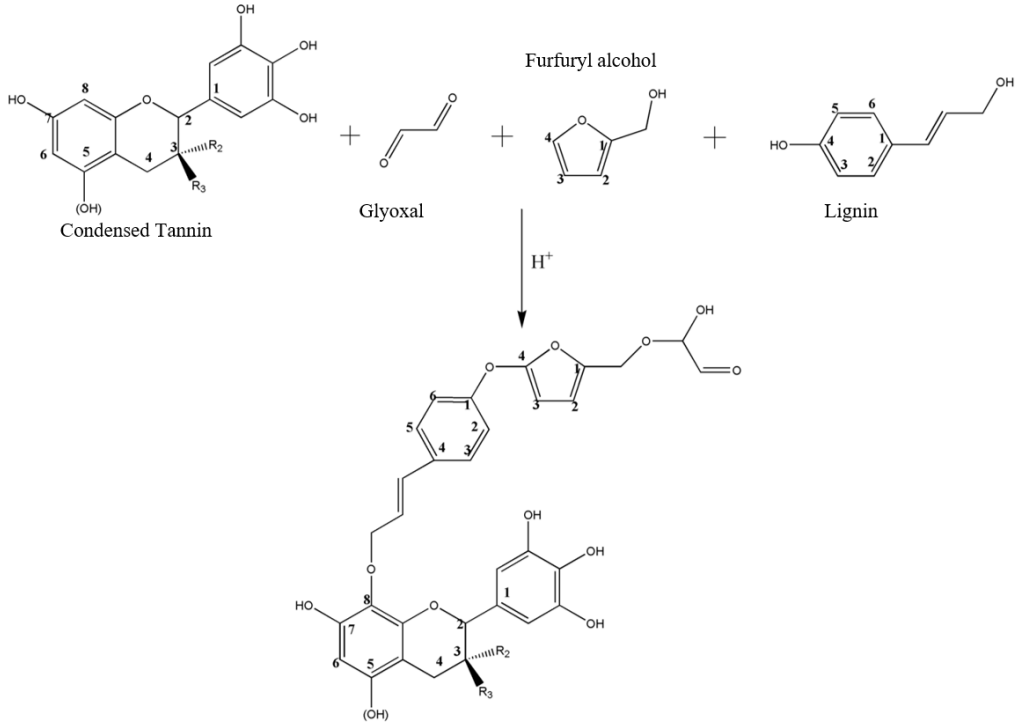
There are many factors that affect the thermal conductivity like density, foaming temperature, cell size and moisture content, these parameters can be regulated depending on the application needed like building materials, aircrafts, chemical pipelines, or naval structures in which fire resistance is crucial (SARIKA et al., 2021). Besides, density directly affects the mechanical resistance of the foams, this parameter can be controlled by the amount of blowing agent as above mentioned an elevated amount of blowing agent results in a lower density foam with larger pores (FENG et al., 2013; LINK et al., 2011).

Despite those promising characteristics, the major drawback in the production of sustainable phenolic foams is their relatively low mechanical stability and brittleness (CELZARD et al., 2010; LI et al., 2019; WU et al., 2020). Poor mechanical performance, low compressive and flexural strength compare to other foams have made it important to improve the mechanical properties while maintaining their excellent insulation and fire-retardant behavior. Several chemical modifications on the phenolic mixture adding plasticizers, glycerol, isocyanates, and by the introduction of fibers and nanoparticles into the resin matrix (MOUGEL et al., 2018; WU, et al., 2020).

2.5.4 Tannin Formaldehyde-free Foams

Environmental concerns have led to the search for alternatives to improve the tannin foams properties and thereby broaden their range of applications, foams have been produced with or without blowing agents, formaldehyde and from different tannins (BASSO et al., 2013; LACOSTE et al., 2015; PIZZI, 2019).

Figure 9. Suggested condensation reactions proceeding among tannin, furfuryl alcohol, glyoxal and lignin.



Note: Adapted from Liu et al., (2022).

In the case of formaldehyde-free foams, the crosslinking occurs between the tannin oligomers and furfuryl alcohol through the nucleophilic sites C6 and C8 of the A ring as illustrated in the figure 9., which results in a longer time requirement for the foam to harden, lower mechanical resistance structure and more easy water catchability (LINK et al., 2011).

Merle et al., (2016) prepared tannin-based phenolic foams without formaldehyde, using both hydrolyzable and condensed tannins and lignin from black liquor by the mechanical foaming process. Obtaining, low thermal conductivity and high mechanical strength, open-celled foams, potential for insulation applications. Formaldehyde-free tannin foams have also demonstrated that could be polymerized in acid environments with temperature (120 - 160 °C) resulting in high homogeneity foams. Moreover, their density (50 - 180 kg/m^3) can be controlled

by changing the components proportion, resulting in light-weighted foams with low mechanical strengths but higher water affinity (FENG et al., 2013).

More recently, Issaoui et al., (2021) also developed a tannin foam without using formaldehyde, isocyanate or blowing agents. The tannin-based foams, used a combination of lignin alkaline liquor with hexamine and glyoxal as blowing agents resulting on a lower thermal conductivity and good mechanical properties foams acceptably to be used for acoustic and thermal insulation. The foaming preparation included a mixture of two types of tannins, mimosa and hydrolysable tannins, the lignin alkaline liquor, obtained from a pulping process, glyoxal and hexamine, that were mixed in deionized water, and maintained under mechanical stirring at 50 °C.

The foaming preparation included a mixture of two types of tannins, mimosa (condensed) and hydrolysable tannins, a lignin alkaline liquor, obtained from pulping processes, glyoxal and hexamine, with deionized water, and was maintained under mechanical stirring at 50 °C. Then the foaming process started with the addition of a surfactant, Tween 80, that aided the air bubbles formation to obtain a liquid foam solution, heated at 85 °C for 24 h and cooled at room temperature resulting in a rigid foam (ISSAOUI et al., 2021).

Lastly, numerous foams formulations can be prepared according to the desired application hence, attention must be paid to the impact of each component on the final characteristics of the bio-based foams, that represent an innovative product for the new generation of green insulation materials.

3. CONCLUDING REMARKS

In general, tannins have proven to be adequate as insulation materials used in the construction industry; however, these still need further investigation which could open new scopes for the usage of more natural insulation materials replacing the synthetic derived from fossil sources.

Tannin-based foams have demonstrated to have comparable properties with commercial phenolic foams as they present high fire resistance, self-extinguish behavior and good chemical resistance. Besides, present a competitive low thermal conductivity thus excellent thermal insulating and acoustic resistance desirable for building construction materials.

Tannin-based foams naturally tend to exhibit low mechanic performance ang high friability, hence, to improve these properties, there has been proposed variants on the foam

formulation, controlling the type and amount of its components, as well as, the incorporation of fillers like natural fibers to strengthen the mechanical performance of the foams.

Further studies regarding to the development of these product are needed, with diverse natural additives, as low-cost, non-toxic substituents to improve their mechanical, density, and porosity which makes them suitable to replace non-environmental friendly petroleum based insulating materials.

REFERENCES

AFONSO, S.R. Análise sócio-econômica da produção de nãomadeireiros no Cerrado brasileiro e o caso da cooperativa de pequi em Japonvar, MG. Dissertação. Brasília: Departamento de Engenharia Florestal, Universidade de Brasília; 2008.

ARBENZ, A.; AVÉROUS, L. Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures. 2015. **Green Chemistry**, *17*(5), 2626–2646. https://doi.org/10.1039/c5gc00282f

BACELO, H. A. M.; SANTOS, S. C. R.; BOTELHO, C. M. S. Tannin-based biosorbents for environmental applications - A review. 2016. **Chemical Engineering Journal**, *303*, 575–587. https://doi.org/10.1016/j.cej.2016.06.044

BASSO, M. C.; GIOVANDO, S.; PIZZI, A.; LAGEL, M. C.; CELZARD, A. Alkaline tannin rigid foams. 2014. **Journal of Renewable Materials,** *2*(3), 182–185. https://doi.org/10.7569/JRM.2013.634137

BASSO, M. C.; PIZZI, A., CELZARD, A.; FIERRO, V.; SÁNCHEZ, M. C.; FRANCO, J. M. Industrial Crops & Products Projectable tannin foams by mechanical and chemical expansion. 2018. **Industrial Crops & Products,** *120*(March), 90–96. https://doi.org/10.1016/j.indcrop.2018.04.048

BELLO, A.; VIRTANEN, V.; SALMINEN, J.; LEIVISKÄ, T. Separation and Puri fi cation Technology Aminomethylation of spruce tannins and their application as coagulants for water clari fi cation. 2020. **Separation and Purification Technology,** *242*(December 2019), 116765. https://doi.org/10.1016/j.seppur.2020.116765

BORRERO-LÓPEZ, A.; NICOLAS, V.; MARIE, Z.; CELZARD, A.; FIERRO, V. A Review of Rigid Polymeric Cellular Foams and Their Greener Tannin-Based Alternatives. 2022. **Polymers**, 14, 3974. https:// doi.org/10.3390/polym14193974

BOURAS, M.; CHADNI, M.; BARBA, F. J.; GRIMI, N.; BALS, O.;VOROBIEV, E.. Optimization of microwave-assisted extraction of polyphenols from Quercus bark. 2015 **Industrial Crops and Products**, *77*, 590–601. https://doi.org/10.1016/j.indcrop.2015.09.018

BULE, M.; KHANB, F.; NISARD, M.; NIAZ, K. Tannins (hydrolysable tannins, condensed tannins, phlorotannins, flavono-ellagitannins. 2020. **Recent Advances in Natural Products Analysis**. pp.132-146. ISBN: 9780128175194

CARVALHO, P. Espécies Arbóreas Brasileiras: Angico Vermelho. 2011. **EMBRAPA**. Recuperado de: https://www.alice.cnptia.embrapa.br/bitstream/doc/1137299/1/Especies-Arboreas-Brasileiras-vol-1-Angico-Vermelho.pdf

CELZARRD, A.; ZHAO, W.; PIZZI, A.; FIERRO, V. Mechanical properties of tannin-based rigid foams undergoing compression. 2010. **Materials Science and Engineering**, A 527 4438–4446. doi:10.1016/j.msea.2010.03.091

CELZARD, A., SZCZUREK, A., JANA, P., FIERRO, V., BASSO, M., BOURBIGOT, S., STAUBER, M., & PIZZI, A. *Latest progresses in the preparation of tannin-based cellular solids*. 2014. **Materials Science and Engineering** *7198*. https://doi.org/10.1177/0021955X14538273

CHEMAT, F., ROMBAUT, N., SICAIRE, A. G., MEULLEMIESTRE, A., FABIANO-TIXIER, A. S., & ABERT-VIAN, M. Ultrasound assisted extraction of food and natural products.

Mechanisms, techniques, combinations, protocols and applications. A review. 2017. **Ultrasonics Sonochemistry**, *34*, 540–560. https://doi.org/10.1016/j.ultsonch.2016.06.035

CHEN, X., Xi, X., PIZZI, A., FREDON, E., ZHOU, X., LI, J., GERARDIN, C., & DU, G. Preparation and characterization of condensed tannin non-isocyanate polyurethane (NIPU) rigid foams by ambient temperature blowing. 2020. **Polymers**, *12*(4). https://doi.org/10.3390/POLYM12040750

CHEN, X., Li, J., PIZZI, A., FREDON, E., GERARDIN, C., ZHOU, X., & DU, G. Tannin-furanic foams modified by soybean protein isolate (SPI) and industrial lignin substituting formaldehyde addition. 2021. **Industrial Crops and Products**, vol. 168, 113607. https://doi.org/10.1016/j.indcrop.2021.113607

COMTRADE. Trading Economics. United States Imports of Tanning, dyeing extracts, tannins, derivatives, pigments. 2022. Disponível em: https://tradingeconomics.com/united-states/imports/tanning-dyeing-extracts-tannins-pigments

ČOP, M., LACOSTE, C., CONRADI, M., LABORIE, M., PIZZI, A., & SERNEK, M. The effect of the composition of spruce and pine tannin-based foams on their physical, morphological and compression properties. 2015. **Industrial Crops and Products**, vol 74, pages 158-164.https://doi.org/10.1016/j.indcrop.2015.04.009

DAS, A. K., ISLAM, M. N., FARUK, M. O., ASHADUZZAMAN, M., & DUNGANI, R. Review on tannins: Extraction processes, applications and possibilities. 2020. **South African Journal of Botany**, *135*, 58–70. https://doi.org/10.1016/j.sajb.2020.08.008

DE HOYOS-MARTÍNEZ, P. L., MERLE, J., LABIDI, J., & CHARRIER – EL BOUHTOURY, F. Tannins extraction: A key point for their valorization and cleaner production. 2019. **Journal of Cleaner Production**, *206*, 1138–1155. https://doi.org/10.1016/j.jclepro.2018.09.243

DELGADO-SANCHEZ, C., SANTIAGO-MEDINA, F., FIERRO, V., PIZZI, A., & CELZARD, A. Optimisation of " green " tannin-furanic foams for thermal insulation by experimental design. 2018. **Materials & Design**, *139*, 7–15. https://doi.org/10.1016/j.matdes.2017.10.064

ECKARDT, J., SEPPERER, T., CESPRINI, E., ŠKET, P., & TONDI, G. Comparing Condensed and Hydrolysable Tannins for Mechanical Foaming of Furanic Foams: Synthesis and Characterization. 2023. **Molecules**, 28, 2799. https://doi.org/10.3390/molecules28062799

FENG, S., CHENG, S., YUAN, Z., LEITCH, M., & CHARLES, C. Valorization of bark for chemicals and materials : A review. 2013. **Renewable and Sustainable Energy Reviews** *26*, 560–578. https://doi.org/10.1016/j.rser.2013.06.024

FRAGA-CORRAL, M., OTERO, P., ECHAVE, J., GARCIA-OLIVEIRA, P., CARPENA, M., JARBOUI, A., NUÑEZ-ESTEVEZ, B., SIMAL-GANDARA, J., & PRIETO, M. A. By-products of agri-food industry as tannin-rich sources: A review of tannins' biological activities and their potential for valorization. 2021. **Foods**, *10*(1). https://doi.org/10.3390/foods10010137

GVR. Grand view research. Tannin Market Size, Share & Trends Analysis Report By Sources (Plants, Brown Algae), By Product (Hydrolysable, Non-hydrolysable, Phlorotannins), By Application (Leather Tanning, Wine Production, Wood Adhesives), & Segment Forecasts, 2020 - 2025. Available in: https://www.grandviewresearch.com/industry-analysis/tannin-market

HILLIG, É., SCHNEIDER, V. & PAVONI, E. Geração de resíduos de madeira e derivados da indústria moveleira em função DAS variáveis de produção. 2009. **Produção**, v. 19, n. 2, p. 292-303.

IBA. **Indústria brasileira de árvores**. 2022. Relatório Anual 2022. Available in: https://www.iba.org/datafiles/publicacoes/relatorios/relatorio-anual-iba2022-compactado.pdf

IBF, **Instituto Brasileiro de Florestas**. 2020. Angico Vermelho. Available in: https://www.ibflorestas.org.br/lista-de-especies-nativas/angico-vermelho

ISSAOUI, H., SALLEM, F., LAFAILLE, J., GRASSL, B., & CHARRIER–EL BOUHTOURY, F. Biosorption of Heavy Metals from Water onto Phenolic Foams Based on Tannins and Lignin Alkaline Liquor. 2021. **International Journal of Environmental Research**, *15*(2), 369–381. https://doi.org/10.1007/s41742-021-00313-5

KEMPPAINEN, K., SIIKA-AHO, M., PATTATHIL, S., GIOVANDO, S., & KRUUS, K. Spruce bark as an industrial source of condensed tannins and non-cellulosic sugars. 2014. **Industrial Crops & Products**, *52*, 158–168. https://doi.org/10.1016/j.indcrop.2013.10.009

LACOSTE, C., BASSO, M. C., PIZZI, A., LABORIE, M., CELZARD, A., & FIERRO, V. Pine tannin-based rigid foams : Mechanical and thermal properties. 2014. **Industrial Crops & Products**, *43*, 245–250. https://doi.org/10.1016/j.indcrop.2012.07.039

LACOSTE, C., BASSO, M., PIZZI, A., CELZARD, A., EBANG, E. E., GALLON, N., & CHARRIER, B. Pine (P . pinaster) and quebracho (S . lorentzii) tannin-based foams as green acoustic absorbers. 2015. **Industrial Crops & Products**, *67*, 70–73. https://doi.org/10.1016/j.indcrop.2014.12.018

LI, J., LIAO, J., ESSAWY, H., ZHANG, J., LI, T., WU, Z., DU, G., & ZHOU, X. Industrial Crops & Products Preparation and characterization of novel cellular / nonporous foam structures derived from tannin furanic resin. 2021. **Industrial Crops & Products**, *162*, 113264. https://doi.org/10.1016/j.indcrop.2021.113264

LI, X., SRIVASTAVA, V. K., PIZZI, A., CELZARD, A., & LEBAN, J. Nanotube-reinforced tannin / furanic rigid foams. 2013. **Industrial Crops & Products** *43*, 636–639. https://doi.org/10.1016/j.indcrop.2012.08.008

LI, J., ZHANG, A., ZHANG, S., GAO, Q., ZHANG, W., & LI, J. Larch tannin-based rigid phenolic foam with high compressive strength, low friability, and low thermal conductivity reinforced by cork powder. 2018. **Composites Part B: Engineering**, vol. 156, Pages 368-377, ISSN 1359-8368.https://doi.org/10.1016/j.compositesb.2018.09.005.

LINK, M., KOLBITSCH, C., coometrade, G., EBNER, M., WIELAND, S., & PETUTSCHNIGG, A. Formaldehyde-Free Tannin-Based Foams And Their Use As Lightweight Panels. 2011. **BioResources** 6(4), 4218-4228. DOI: 10.15376/biores.6.4.4218-4228

LIU, B., ZHOU, Y., ESSAWY, H., FENG, S., LI, X., LIAO, J., ZHOU, X., ZHANG, J. & XIE, S. Formaldehyde Free Renewable Thermosetting Foam Based on Biomass Tannin with a Lignin Additive. 2022. **Journal of Renewable Materials**, 10 (11), 3009-3024. https://doi.org/10.32604/jrm.2022.019848

MARIE, Z., NICOLAS, V., CELZARD, A., & FIERRO, V. Industrial Crops & Products Experimental investigation of the physical foaming of tannin-based thermoset foams. 2019. **Industrial Crops & Products**, *138*(May), 111424. https://doi.org/10.1016/j.indcrop.2019.05.073

MARIE, Z., NICOLAS, V., CELZARD, A., & FIERRO, V. International Journal of Thermal Sciences First approach for modelling the physical foaming of tannin-based thermoset foams. 2020. **International Journal of Thermal Sciences**, *149*, 106212. https://doi.org/10.1016/j.ijthermalsci.2019.106212

MARTINS, R., GOMES, I., MENDONÇA TELLES, A., KATO, L., SOUZA, P., & RODRIGUES CHAVES, A. Molecularly imprinted polymer as solid phase extraction phase for condensed tannin determination from Brazilian natural sources. 2020. **Journal of Chromatography** A 1620 460977. https://doi.org/10.1016/j.chroma.2020.460977

MARTINEZ DE YUSO, A., LAGEL, M., PIZZI, A., FIERRO, V., & CELZARD, A. Structure and properties of rigid foams derived from quebracho tannin. (2014). **Materials & Design**. vol. 23, pages 208-212. https://doi.org/10.1016/j.matdes.2014.05.072

MERLE, J., BIROT, M., DELEUZE, H., MITTERER, C., CARR´E, H., & CHARRIER-EL BOUHTOURY, F. New biobased foams from wood byproducts. 2015. **Materials and Design**. doi: 10.1016/j.matdes.2015.11.07

MOTA, G., SARTORI, C., MIRANDA, I., QUILHÓ, T., MORI, F., & PEREIRA, H. Bark anatomy, chemical composition and ethanol-water extract composition of *Anadenanthera peregrina* and *Anadenanthera colubrina*. 2017. **PLoS ONE** 12(12): e0189263. https://doi.org/10.1371/journal. pone.0189263

MOUGEL, C., GARNIER, T., CASSAGNAU, P., & SINTES-ZYDOWICZ, N. Phenolic foams: A review of mechanical properties, fire resistance and new trends in phenol substitution. 2019. **Polymer**, vol. 164, Pages 86-117, ISSN 0032-3861. https://doi.org/10.1016/j.polymer.2018.12.050.

MOUSAVI, S., ZAMANI, M., ESTAJI, S., TAYOURI, M., ARJMAND, M., JAFARI, S., NOURANIAN, S., & KHONAKDAR, H. Mechanical properties of bamboo fiber-reinforced polymer composites: a review of recent case studies. 2022. **J Mater Sci** (2022) 57:3143–3167. https://doi.org/10.1007/s10853-021-06854-6

MUHAMMAD, A., RAHMAN, M., HAMDAN, S., & SANAULLAH, K. Recent developments in bamboo fiber-based composites: a review. 2019. **Polymer Bulletin**. **76**, 2655–2682. https://doi.org/10.1007/s00289-018-2493-9

NURAZZI, N., NORRRAHIM, M., SABARUDDIN, F., SHAZLEEN, S., ILYAS, R., LEE, S., PADZIL, F., AIZAT, G., AISYAH, H., MOHIDEM, N., ASYRAF, N., ABDULLAH, N., SAPUAN, S., ABDAN, K., & NOR, N. Mechanical performance evaluation of bamboo fibre reinforced polymer composites and its applications: a review. 2022. **Funct. Compos. Struct**. 4, 015009. https://doi.org/10.1088/2631-6331/ac5b1a

OLIVEIRA MORI, C., MORI, F., MENDES, L., SILVA, J. Potencial da madeira de angico-vermelho para móveis. 2007. **Revista da Madeira**. N°108

PAGLIARO, M., ALBANESE, L., SCURRIA, A., ZABINI, F., MENEGUZZO, F., & CIRIMINNA, R. Tannin: a new insight into a key product for the bioeconomy in forest regions. 2021. **Biofuels, Bioproducts and Biorefining**, 1–7. https://doi.org/10.1002/bbb.2217

PATIL, P. D., PATIL, S. P., KELKAR, R. K., PATIL, N. P., PISE, P. V., & NADAR, S. S. Enzyme-assisted supercritical fluid extraction: An integral approach to extract bioactive compounds. 2021. **Trends in Food Science and Technology**, *116*(July), 357–369. https://doi.org/10.1016/j.tifs.2021.07.032

PIZZI, A. Tannin-based biofoams-A review. 2019. **Journal of Renewable Materials**, *7*(5), 477–492. https://doi.org/10.32604/jrm.2019.06511

QIU, C., LI, F., WANG, L., ZHANG, X., ZHANG, Y., TANG, Q., ZHAO, X., DE HOOP, C., PENG, X., YU, X. & HUANG, X. The preparation and properties of polyurethane foams reinforced with bamboo fiber sources in China. 2021. **Materials Research Express**, vol 8, 45501. DOI 10.1088/2053-1591/abf1cd

SÁNCHEZ-MARTÍN, J., BELTRÁN-HEREDIA, J., DELGADO-REGAÑA, A., & RODRÍGUEZ-GONZÁLEZ, M. A. Adsorbent tannin foams : New and complementary applications in wastewater treatment. 2013. **Chemical Engineering Journal** *228*, 575–582. https://doi.org/10.1016/j.cej.2013.05.009

SANTANA, G., TRUGILHO, P., BORGES, W., BIANCHI, M., PAES, J., NOBRE, J., & MORAIS, R. Activated carbon from bamboo (*Bambusa vulgaris*) waste using CO_2 as activating agent for adsorption of methylene blue and phenol. 2019. **Ciênc. Florest**. 29 (2). https://doi.org/10.5902/1980509828648

SARIKA, P., NANCARROW, P., KHANSAHEB, A., IBRAHIM, T. Progress in Bio-Based Phenolic Foams: Synthesis, Properties, and Applications. 2021. **ChemBioEng Rev** 2021, 8, No. 6, 612–632. DOI: 10.1002/cben.202100017

SARTORI, C. (2012). Avaliação dos teores de compostos fenólicos nas cascas de *Anadenanthera peregrina* (angico-vermelho). Dissertação (mestrado)-Universidade Federal de Lavras, Programa de Pós-graduação em Ciência e Tecnologia da Madeira. p. 94.

SAZ-OROZCO, B., ALONSO, M., OLIET, M., DOMÍNGUEZ, J., & RODRIGUEZ, F. Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. 2015. **Composites Part B: Engineering**, vol. 75, Pages 367-372, ISSN 1359-8368. https://doi.org/10.1016/j.compositesb.2015.01.049.

SEMIL. **Secretaria Infraestrutura e Meio Ambiente Governo do Estado de São Paulo**. (2016). Angico, um Forte da Flora Brasileira. Disponível em: https://www.infraestruturameioambiente.sp.gov.br/2016/03/angico-um-forte-da-flora-brasileira/

SEPPERER, T., ŠKET, P., PETUTSCHNIGG, A., & HÜSING, N. Tannin-Furanic Foams Formed by Mechanical Agitation: Influence of Surfactant and Ingredient Ratios. 2021. **Polymers**, 13, 3058. https:// doi.org/10.3390/polym13183058

SHIRMOHAMMADLI, Y., EFHAMISISI, D., & PIZZI, A. Tannins as a sustainable raw material for green chemistry: A review. 2018. **Industrial Crops and Products**, *126*(June), 316–332. https://doi.org/10.1016/j.indcrop.2018.10.034

SNIF, **Serviço Florestal Brasileiro**. Concessões Florestais: Um Panorama das Flonas Concedidas ao Longo dos Anos. 2022. Ed.1. Disponóvel em: https://www.gov.br/agricultura/pt-br/assuntos/servico-florestal-brasileiro/snif-sistema-nacional-de-informacoes-florestais/boletim_snif_30-12-2022.pdf/view

SONG, E., JEONG, S., PARK, J., KIM, S., KIM, H., & SONG, J. Polyurethane-Silica Hybrid Foams from a One-Step Foaming Reaction, Coupled with a Sol-Gel Process, for Enhanced Wound Healing. 2017. **Mater. Sci. Eng**. *C, 79*, 866–874. https://doi.org/10.1016/j.msec.2017.05.041Get rights and content

TONDI, G., ZHAO, W., PIZZI, A., DU, G., FIERRO, V., & CELZARD, A. Tannin-based rigid foams: A survey of chemical and physical properties. 2009. **Bioresource Technology**, vol. 100, Issue 21, pages 5162-5169. https://doi.org/10.1016/j.biortech.2009.05.055

TONDI, G., FIERRO, V., PIZZI, A. CELZARD, A. Tannin-based carbon foams. 2009. **CARBON** 47,1480 – 1492. doi:10.1016/j.carbon.2009.01.041.

TONDI, G., & PETUTSCHNIGG, A. Middle infrared (ATR FT-MIR) characterization of industrial tannin extracts. 2016. **Ind. Crop. Prod.** 422e428 https://doi.org/10.1016/ j.indcrop.2014.11.005.

VARILA, T., ROMAR, H., LUUKKONEN, T., & LASSI, U. Physical activation and characterization of tannin-based foams enforced with boric acid and zinc chloride. 2019. **AIMS Materials Science**, 6(2): 301–314. DOI: 10.3934/matersci.2019.2.301

WANG, L., DUAN, H., JIANG, J., LONG, J., & YU, Y. RESEARCH PAPER A simple and rapid infrared-assisted self enzymolysis extraction method for total flavonoid aglycones extraction from Scutellariae Radix and mechanism exploration. 2017. **Analytical and Bioanalytical Chemistry**. 5593–5602. https://doi.org/10.1007/s00216-017-0497-1

WU, X., YAN, W., ZHOU, Y., LUO, L., YU, X., LUO, L., FAN, M., DU, G., & ZHAO, W. Thermal , morphological , and mechanical characteristics of sustainable tannin bio-based foams reinforced with wood cellulosic fibers. 2020. **Industrial Crops & Products** *158*(May). https://doi.org/10.1016/j.indcrop.2020.113029

XUAN CUONG, D., HOAN, N., DONG, D., MINH THUY, L., VAN THANH, N., THAI HA, H., TUYEN, D., & CHINH. Tannins: Extraction from Plants. 2020. **IntechOpen**. DOI: http://dx.doi.org/10.5772/intechopen.86040

YUSUF1, S., SYAMANI, F., FATRIASARI, W., & SUBYAKTO. Review on Bamboo Utilization as Biocomposites, Pulp and Bioenergy. 2018. **IOP Conf. Series: Earth and Environmental Science**, 141, 012039. doi :10.1088/1755-1315/141/1/012039

ZHAO, W., PIZZI, A., FIERRO, V., DU, G., & CELZARD, A. Effect of composition and processing parameters on the characteristics of tannin-based rigid foams . Part I : Cell structure. 2010. **Materials Chemistry and Physics**, *122*(1), 175–182. https://doi.org/10.1016/j.matchemphys.2010.02.062

ZOU, L., SHAO, P., ZHANG, K., YANG, L., YOU, D., SHI, H., PAVLOSTATHIS, S. G., LAI, W., LIANG, D., & LUO, X. Tannic acid-based adsorbent with superior selectivity for lead(II) capture: Adsorption site and selective mechanism. 2019. **Chemical Engineering Journal**, *364*(January), 160–166. https://doi.org/10.1016/j.cej.2019.01.160

4. **ARTICLE 1:** TANNIN-BASED PHENOLIC FOAMS OF *Anadenanthera peregrina*: SYNTHESIS AND CHARACTERIZATION

Tannin-based phenolic foams of *anadenanthera peregrina*: synthesis and characterization

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ABSTRACT

Tannin-based foams are natural origin porous materials with excellent fire-resistant and thermal insulation properties comparable with flammable non-environmental friendly synthetic foams; however, their brittleness and relatively low mechanical resistance challenge further improve these characteristics. This work aimed to investigate four types of tannin-based foams (ST, TT, TB, and TTB) prepared without formaldehyde, by using *Anadenanthera peregrina* tannins (ST) and the incorporation of polysorbate 80 as a surfactant (TT), bamboo fibers as filler reinforcement (TB), and the combination of both (TTB). In order to evaluate the effectiveness of the treatments on the foams properties, mechanical and chemical characterization was performed as well as, SEM microscopy. Thus, the addition of bamboo fibers and polysorbate 80 to the formulations had a minimal impact on the foam density around 1,383 ± 0,05 $g \cdot cm^{-3}$, and an average porosity of 87 %; meanwhile, their compressive strength slightly improved (0,12 - 0,19 MPa) and all the foams produced showed fireproofing and self-extinguishing behavior.

1. Introduction

In recent decades, there has been a continuous move towards the substitution of synthetic materials in the industry by natural products obtained from vegetal sources. After cellulose, hemicellulose, and lignin, tannins are the most abundant compounds found in nature, and recently they have attracted significant attention as a green feedstock for new materials due to their biological activity and technological uses in several fields (Borrero-López et al., 2022).

Tannins are polymeric compounds produced by plants and mainly found in the bark of plant logs. Currently, the bark is treated as a disposable sub-product from wood processing and used as a cheap energy source, that can actually be a potential source of natural compounds as a substitute for synthetic phenols in a variety of applications (Feng et al., 2013; Chen et al., 2021). and reduce the dependence on petroleum products, valorizing the waste generated in the industry (IBA 2022; SNIF, 2022; Hilling et al., 2009).

Brazil is a strong wood producer and possesses 12 % of the world's total forest cover, tannin exploration in the country has been focused on the forest species of black wattle (*Acacia mearnsii*), and pine (*Pinus pinaster*). Thus, looking for further species that can provide good-quality tannins, high reactivity, and sustainability is important. This is the case of the *Adenanthera peregrina* species possessing a large amount of tannins, typically used in the leather and dyeing industries, as well as, in popular medicine (Martins, et al., 2020)

In recent years, tannin-based phenolic foams have been intensively investigated as an alternative to synthetic foams used as insulating materials in the construction, transportation, and packaging industries. Phenolic foams are often produced with formaldehyde that has been classified as non-environmentally friendly and carcinogenic to humans (Varila et al., 2019; Sarika et al., 2021; Liu et al., 2022). Despite their good thermal insulation properties, low density, and low thermal conductivity, these fossil-based foams are highly flammable and can release toxic gases during combustion which negatively associate them with fire hazards and the need to switch toward bio-based products (Chen et al., 2021; Sarika et al., 2021).

In this context, looking to produce environmentally friendly insulating materials, formaldehyde-free tannin foams are being considered due to their similar phenolic structure to replace synthetic phenols and excellent characteristics such as lightweight, high fire resistance, and self-extinguishing character (Delgado-Sanchez et al., 2018). Recent bio-based phenolic foams research has focused on improving the mechanical properties of the foams while simultaneously preserving or boosting their thermal performance and fire resistance (Mougel et al., 2019).

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Given the above, the present work aims to verify the quality and behavior of the *Adenanthera peregrina* tannins in the production of phenolic foams without formaldehyde. As well as, to evaluate the influence of incorporating an additive, and a reinforcement, on the physical, mechanical, and thermal properties of different foam formulations.

2. Materials and Methods

2.1. Materials

The external bark of the *A. peregrina* specie was collected from native forest trees in the experimental plantation of the Federal University of Lavras (UFLA). The collection was made using a knife, carefully removing the wood bark, from about 60 trees, between 10 and 15 cm in diameter. The wood chips obtained were dried at open air and then grounded in a Lucano hammer mill, the material passed through a set of 40 and 60-mesh particle classification sieves; where the particles retained on the 60-mesh sieve were stored and dried for later moisture determination.

2.2. Methods

2.2.1. Extraction and obtention of tannins from A. peregrina

Extraction of *A. peregrina* wood tannins were carried out following the methodology of Sartori et al., (2014) and Mori, (2003), with sodium sulfite (Na_2SO_3), using 1500 ml of distilled water, 100 g of bark (liquor/bark ratio of 15: 1 v/p), and 3% sodium sulfite (Na_2SO_3) (w/w) based on the dry mass of the bark; the beaker was placed in a water bath at 70 °C for 3 hours. Then the extract was filtered using a fine cloth funnel and sieved through 200 mesh, finally it was vacuum pump filtered with a number 2 porosity crucible. After filtration, the extract was placed in glass refractories, and taken to an oven with air circulation at 40 ± 3 ºC, until the complete evaporation of the liquid to get the dry material. The remaining tannins were macerated in a porcelain mortar and pestle up to a 200 mesh granulometry (Mori, 2003).

2.2.2. Characterization of tannins from A. peregrina

For the tannin characterization, moisture, Stiasny Index, and condensed tannin content of the extracts were determined. Moisture was obtained by weighing 0,5 g of tannins extract under ambient conditions and taken to a drying oven at 45 ± 3 ºC for 48 hours. Subsequently, they were removed from the oven to cool, placed in a desiccator, and weighed again.

Moisture was determined according to Equation1:

$$\mathrm{MC} = \frac{(\mathrm{Mi} - \mathrm{Mf})}{\mathrm{Mf}} * 100 \qquad (1)$$

where, MC (%), is the moisture content expressed as a percentage, Mi (g) is the initial weight and Mf (g) the weight after drying.

Stiasny Index (SI) was obtained from a concentrated tannin extract, where 20 g of extract was weighed in a 250 ml flat-bottom flask, then 10 ml of deionized water, 2 ml of HCl 10N, and 4 ml of formaldehyde (37 %) were added. The samples were heated on a thermal plate under reflux for 30 minutes, counted from the moment it boiled. After this period, the samples were filtered in Nº 2 crucibles under vacuum and taken to dry in an air circulation oven at 105 °C ± 3 °C for 24 hours, later they were removed and left to cool in a desiccator for 30 minutes. Finally, the crucibles were weighed and the dry mass of the precipitate was obtained. Simultaneously, the mass of solids in 20 g of concentrated extract was determined, by letting the sample dry in an oven with air circulation at 105 ºC ± 3 ºC for 24 hours.

The Stiasny Index (SI) was calculated according to Equation 2:

$$\mathrm{SI}\ (\%) = \frac{Dry\ mass\ of\ precipitate}{Total\ mass\ of\ solids\ in\ 20\ g\ of\ extracts} \times 100 \qquad (2)$$

Finally, condensed tannins (TC) percentage in the extracts was calculated according to Equation 3:

$$\mathrm{TC}\ (\%) = \ \mathrm{SI}\ \times \mathrm{humid\ mass\ of\ tannin} \qquad (3)$$

Moreover, the tannin was characterized by Infrared Spectroscopy using Fourier Transform (FTIR) and Thermogravimetric analysis (TGA). These analyses will be held in the Chemical Analysis and Prospecting Center (CAPQ), in the Federal University of Lavras (UFLA).

The FTIR analysis was performed using the Varian 600-IR Series Spectrometer equipment, with Attenuated Total Reflectance (ATR). The samples were scanned from 4000 to 700 cm-1 with 32 scans for each spectrum with a 4 cm^{-1} resolution (LI et al., 2018). And the thermogravimetric measurements were obtained in a Shimadzu DTG-60AH simultaneous TG/DTA thermogravimetric module. The samples were submitted to a heating ramp from 25 to 900 ºC with a rate of 10 ºC/min. The equipment atmosphere was saturated with nitrogen at a constant flow rate of 50 ml/min (Tondi & Petutschnigg, 2016; Li et al., 2018).

2.2.3. Formulation and synthesis of tannin foams

Four formulations were studied in the synthesis of the bio-foams, each formulation represents a treatment as described in Table 1. The foam formulations were composed of water, furfuryl alcohol (exothermic agent), glyoxal 40 % (curing agent), pentane (blowing agent), p-toluene sulfonic acid (p-TSA 65 %) (catalyst), tannins from *A. peregrina* (aromatic blocks), polysorbate Tween 80 (additive), and bamboo fibers (filler reinforcement).

Table 1
Formulation of A. peregrina tannin foams.

Formulation	ST	TT	TB	TTB
Tannin (g)	37	37	37	37
Furfuryl alcohol (g)	26	26	26	26
pTSA 65 % (g)	18	18	18	18
Water (g)	6	4	6	4
Glioxal 45% (g)	8	8	8	8
Pentane (g)	5	5	5	5
Tween 80 (g)	-	2	-	2
Bamboo fibers 2% (g)	-	-	0,74	0,74

Tannin phenolic foams were prepared in two stages as follows. First water, furfuryl alcohol, glyoxal 40 %, and pentane were mixed in a beaker. Then the tannin was progressively incorporated with vigorous stirring for 15 s until homogenization. For the treatments (TT; TTB) with the presence of an additive, Tween 80; and the filler, Bamboo fibers (TB; TTB) it was added in the first step before combining the tannin with the reagents. In the second stage, the pTSA 65% catalyst was added and the mixture was stirred for 20 s. Later the mixture was placed in a water bath at 70 ^{o}C for several minutes until the foam was fully expanded, and then taken out to rest for 48 hours and cure. Once hardened, the top of the foam was cut off and removed to evaporate the remaining blowing agent. After the resting and curing time was completed, the foams were extracted from their molds and subsequently cut into parallelepipeds for characterization purposes (Martinez, et al., 2014).

2.2.4. Characterization of the tannin foams

2.2.4.1 Apparent density, real density, and porosity

The apparent density was determined according to the ASTM D1622-03 standard, by the ratio between the mass of the material and the total volume occupied. Foam samples of 3 x 3 x 3 cm dimensions were prepared for the test, and 3 repetitions were performed for each treatment (Li et al., 2018). Before weighing, the foams were kept in an oven at 60 °C for 24 hours to eliminate any residual gases.

The pycnometer method carried out in the Laboratory of Wood Anatomy (UFLA) measured the skeletal density or real density. The test was performed in triplicate for each treatment with 1 g of foam macerated in a mortar and pestle. Then the density was calculated according to Equation 4:

$$d_s = \frac{d_w \times (m_{p+s} - m_p)}{(m_{p+s} - m_p) - (m_{p+s+w} - m_{p+w})} \quad (4)$$

where:

d_s = skeletal density kg/m^3

d_w = density of the water used in the test (kg/m^3);

m_{p+s} = mass of pycnometer + specimen (kg);

m_p = mass of pycnometer (kg);

m_{p+w} = mass of pycnometer + deionized water (kg)

m_{p+s+w} = mass of pycnometer + specimen + deionized water (kg)

The foam porosity (Φ) was determined from bulk and skeletal densities following Equation 5:

$$\Phi = 1 - \frac{d_a}{d_s} \quad (5)$$

where d_a is the bulk density and d_s refers to the skeletal density.

2.2.4.2. Mechanical resistance

The compression strength of the foam was measured using an Arotec universal testing machine, in the Experimental Unit of Wood Panel (UFLA) equipped with a 5 kN head and a 2 mm min^{-1} load rate (Tondi, et al., 2009; Martinez, et al., 2014). Samples of 3 x 3 x 3 cm dimensions were tested following the ASTM D162-10 standard with some adaptations (Li et al., 2018).

2.2.4.3. Friability

Friability describes the tendency of a solid to break into smaller pieces. The friability test was assessed following the ASTM C421 standard. Foam samples of 2.5 x 2.5 x 2.5 cm dimensions were placed in a 40 cm diameter metal drum, together with twelve wood cubes of 2 x 2 x 2 cm per side; then the drum was rotated at 60 ± 2 rpm for 1 min (Li et al., 2018; Mougel et al., 2019). Finally, the samples were weighed before and after the test to determine the mass loss according with the next Equation 6:

$$Mass\ loss\ (\%) = \frac{Initial\ mass - final\ mass}{initial\ mass} \times 100 \qquad (6)$$

2.2.4.4. Direct flame exposition

The resistance to direct flame exposure was tested with foam samples of 2 x 2 x 2 cm dimensions exposed directly to oxidizing flame, around 1400 °C using a Bunsen burner, for 20 s. The samples were weighted before and after the test, considering that the flame was extinguished when the foam reacquires its original black color (Tondi et al., 2009; Chen et al., 2020).

2.2.4.5. Scanning electron microscopy images (SEM)

The foam morphology was observed using scanning electron microscopy (SEM) to determine the influence of the different formulations on the size, distribution and frequency of cells in the material. The samples were left overnight in silica gel for drying, and fractured in liquid nitrogen. The fractured surfaces were subjected to gold sputtering to make them conductive, and were analyzed under SEM microscopy operating conditions of 10 KV, 90 pA (Wu et al., 2020; Li et al., 2019).

2.2.4.6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis shows the foams thermal stability, and were carried out over the temperature range from 20 to 900°C at a heating rate of 10°C/min; the TG and DTG curves rate of each formulation were determined (Konai et al., 2016; Li et al., 2018).

2.2.4.7. Infrared Spectroscopy analysis (FTIR)

The FTIR analysis was performed in order to evaluate and confirm that the additive and bamboo fiber were involved in the foaming reaction (Qiu et al., 2021). The foam samples were scanned from 4000 to 700 cm^{-1} with 32 scans for each spectrum with a 4 cm^{-1} resolution (Li et al., 2018; Tondi & Petutschnigg, 2016).

3. Results

3.1. Characterization of the *A. peregrina* tannins

Tannins from *A. peregrina* were characterized by the Stiasny index, total solid content, and condensed tannins, Table 6., presents the results of these parameters. The Stiasny index allows the evaluation of the purity of tannic extracts and the amount of substances that reacted with an aldehyde in an acid medium, for red angico the value was 72.41 % on average. Comparing with the values reported in the literature Sartori et al., (2014b), that studied the chemical and anatomical composition of tannins in barks of *A. peregrina* found a 75,79 % stiasny index. Similar values were found by Carneiro et al., (2006), 75,27 %, on tannins extracted with different solvents as sodium sulfite. In this context, higher Stiasny indices are desirable since a higher index means greater amount of phenolic compounds in the tannic extract, on the other hand, the lower the Stiasny Index, the lower the purity of the tannic extract, indicating the possible presence of non-tannic compounds, such as sugars and gums, which can affect the reactivity and future usage of the tannins (Sartori et al., 2014b; Mota et al., 2017).

Table 2
Average values of humidity, Stiasny index and condensed tannins content of the A. *peregrina* tannins.

Material	UBS (%)	Extractives (%)	Stiasny Index (%)	Condensed Tannin (%)
Anadenanthera peregrina	16,41±0,07	11,69±1,49	72,41±0,99	12,81±0,78

The total solids content, expressing the total amount of extractives present in the analyzed samples, averaged 11,69 %. This value was similar (11,34 %) with the obtained by Saroti et al., (2014b) in the study of A. peregrina bark in different diameter classes and relatively lower than the content registered by Carneiro et al., (2006),19,96 % of total solids, of *A. peregrina* bark. According to different authors, these differences can be attributed in general, to the extraction method, genetic variability, age, as well as the soil quality (Mota et al., 2017; Sartori et al., 2014b; Paes et al., 2010).

Finally, the content of condensed tannins found in this search was on average 12,81 %, this value was in concordance with the study of Saroti et al., (2014b) that found an average value of 12,76 % condensed tannin in *A. peregrina* bark. Other studies also presented similar values around 11,98 % (Paes et al., 2006), 14,58 % (Carneiro et al, 2006) and 13,93 % (Paes et al., 2010); representing a desirable concentration of the phenolic compound that will be used in the foam's formulation.

3.2. Infrared spectroscopy (FTIR) of *A. peregrina tannin*

Influence Figure 1., shows the Fourier Transform Infrared Spectroscopy (FTIR) spectrum of the *A. peregrina* tannins sample that allowed the identification of the hydroxyl-aromatic bonds characteristic of condensed tannins molecules (Tondi & Petutschnigg, 2016).

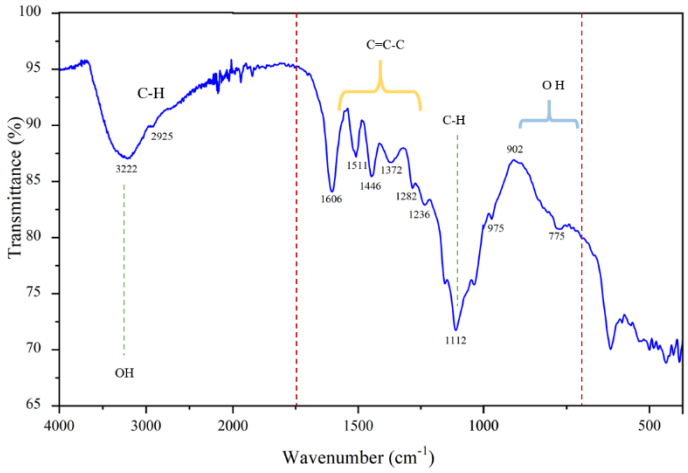


Figure 1: Infrared spectra of A. peregrina tannin.

A pronounced band was observed between 3 500 and 3 000 cm-1 attributed to the stretching vibration of hydroxyl group – OH from the aromatic ring present in phenolic structures (D'Alessandro et al., 2018). Minor peaks were identified in the region from 2 925 to 2780 cm^{-1} corresponding to the C-H bonds stretching from methyl groups, according to Ricci et al., 2015, this type of stretching is related to the methylation of aliphatic groups in condensed tannins. The spectral region between 1 750 and 700 cm^{-1} represent the fingerprint of these molecules, with five common distinguished peaks at 1 606 cm^{-1} (C=C), 1 511 cm^{-1} (C=C), 1 446 cm^{-1}(C=C), 1 372 cm^{-1} (C-H), and 1 112 cm^{-1} (C-H).

Where the area between 1 620 and 1 400 cm^{-1} is related to vibrational movements of C=C bonds characteristic of aromatic rings from phenolic compounds and the peaks located around 1372 cm^{-1} are related to the C-H bond deformation (Marques et al., 2021). Then the region between 1 300 and 1 200cm^{-1} correspond to the vibrations of the tannin B ring, while, the presence of catechin and proanthocyanidins can be identify by the peaks occurring between 1 282 and 1 236 cm^{-1} respectively (Marques et al., 2021). Finally, the range from 1 200 to 1 100 cm^{-1} is related to the tannin A ring vibrations (Tondi & Petutschnigg, 2016) and according to Konai et al, 2017 peaks located from 900 to 740 cm^{-1} are attributed to OH bonds movements from aromatic alcohols.

3.3. Thermogravimetry (TG)

Figure 2., shows the thermal degradation of the *A. peregrina* tannins. The tannin had three distinct degradation processes, the first peak observed around 30 and 150 ℃ corresponded to the vaporization of any residual water present in the sample that can be absorbed due to its hygroscopicity (Pantoja-Castroa & González-Rodríguez, 2012; Araujo et al., 2021; Zidanes et al., 2021). The second region with an initial weight loss at 200 °C where the degradation of the phenolic rings from the tannin molecules begin. In fact, according to Konai et al., 2016 between 135 °C and 255 °C, tannin starts to decompose and releases CO_2 and CO. And then a gradual decrease in the sample weight was observed over the 375 °C, which still led to a final residue tannin mass ratio of 24 % around 800 °C which demonstrates a high thermal resistance of the A. peregrina tannins (Zidanes et al., 2021).

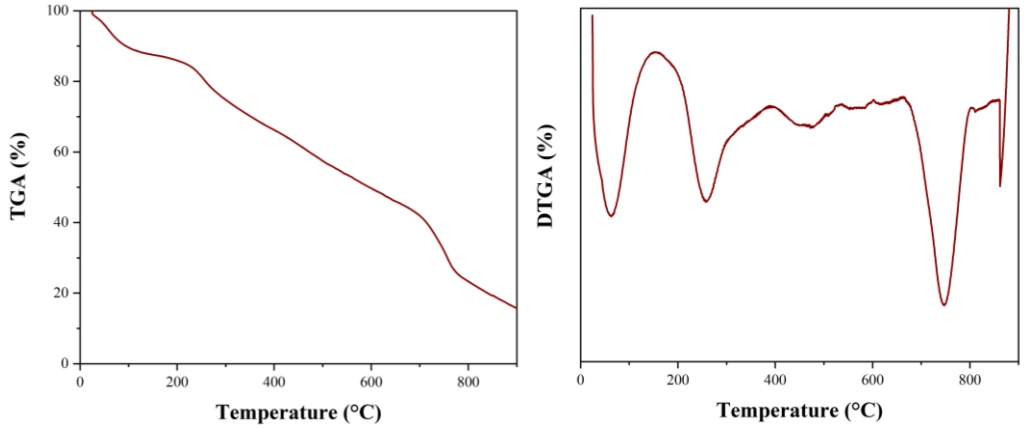


Figure 2: TG curves of A. peregrina tannin.

A comparison of the weight curves with other tannin species, for example, from Pine bark (Gauler & Grigsby, 2009) were relatively similar, however, presented a different initial temperature for the sample degradation that ranged between 160 to 200 °C and a total weight loss of 40 % at 800°C. Tannins from the *Myrcia eximia* bark (Araujo et al., 2021) also showed a high thermal resistance, starting the thermal degradation at 270 °C, and a residual tannin mass of approximately 25 % at a temperature of 900 °C. Finally, according to the thermogram the mass loss of these tannins (*A. peregrina)* occurs at high temperatures which indicates that the tannin foams to be produced will present a high thermal stability as well (Araujo et al., 2021).

3.4. Characterization of the tannin foams

3.4.1 Apparent density, real density, and porosity

Density is a fundamental parameter, that directly influences the final characteristics of the tannin foams like their thermal and mechanical properties. The average values of relative and skeletal density are shown in Table 2., as well as, the porosity values of the different treatments. The foam's apparent densities decreased slightly with the incorporation of the polisorbate80 and the bamboo fibers from 0,199 to 0,17 and 0,12 $g.cm^{-3}$ respectively. This is possibly attributed to the reactivity of the aldehyde with the tannin and the amount of blowing agent which leads to rapid foaming during the exothermic reaction, accelerating the growth of the bubbles in the foams and leading to the formation of a low-density foam (Issaoui et al., 2021; Tondi & Pizzi, 2009). In general, apparent density values were close to those reported in the literature, Issaoui et al., (2021) biobased phenolic foams showed density values in the range 0.02−0.20 $g.cm^{-3}$. And Chen et al., (2020), presented a similar behavior of decreasing foam apparent density from 0,15 $g{\cdot}cm^{-3}$ to 0,12 $g{\cdot}cm^{-3}$ with the increasing amount of citric acid as an additive.

The obtained tannin phenolic foams presented an average skeletal density of 1,34 $g{\cdot}cm^{-3}$, after pycnometer measurements whose value was similar for all the formulations showing a slight increase with the addition of the bamboo fibers and the surfactant. Eckardt et al., (2020) found a comparable trend for skeletal density (1,38 $g.cm^{-3}$) using Tween 80 and different types of blowing agents. Equally, Issaoui et al., (2021) obtained foams with an average skeletal density of about 1.495 ± 0.008 $g{\cdot}cm^{-3}$ which is typical for tannin-based phenolic foam (Merle et al., 2016). The use of additives and the proportion of furfuryl alcohol can also influence the yield of heavier foams because the greater generation of heat induces quicker curing, throughout the material hardening the matrix before foaming occurs, thus stabilizing the structure and inhibiting its expansion (Tondi & Pizzi, 2009; Borrero-López et al., 2022).

Table 3
Average values of apparent, real density, and porosity of tannin-based foams.

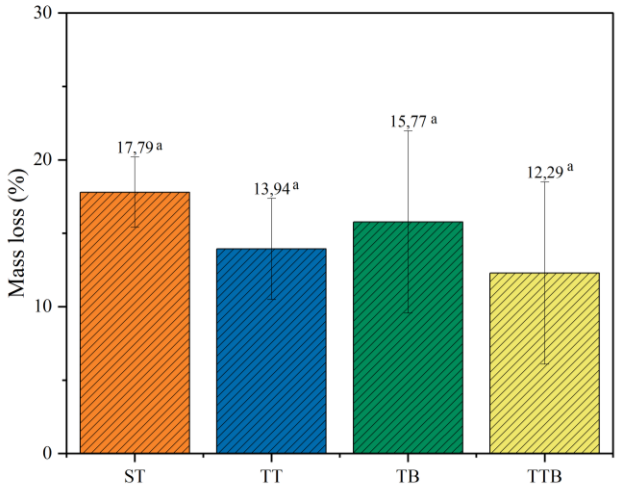
Treatments	Apparent Density ($g.cm^{-3}$)	Real Density ($g.cm^{-3}$)	Porosity (%)
ST	0,1999 ± 0,007 [a]	1,3721 ± 0,31 [a]	84,12 [a]
TT	0,1715 ± 0,007 [ab]	1,2643 ± 0,44 [a]	85,23 [a]
TB	0,1261± 0,020 [bc]	1,3295 ± 0,36 [a]	90,17 [a]
TTB	0,1235 ± 0,026 [c]	1,3831 ± 0,05 [a]	91,01 [a]

Same letters in a column suggest no significant difference at 5 % probability by the Tukey test.

Finally, the total porosities of the foams ranged from 84,12 to 91,01 %, showing that the porosity increased as the bulk density decreased, this behavior can be attributed to faster growth of bubbles in the foam, leading to an increased expanding ability and resulting in lower density foams (Chen et al., 2020; Issaoui et al., 2021). In concordance, Merle et al., (2016) obtained higher values of bulk density (0,18 $g \cdot cm^{-3}$), higher cell diameter, and less porosity (88,23 %). As well as, Sepperer et al., (2021) found porosity values between 88 to 85 % compared to bulk density values of 0,14 to 0,17 $g \cdot cm^{-3}$ following a similar trend of higher porosity lower density foams.

3.4.2 Friability

The evaluation of friability in the foams showed that the treatment with the addition of bamboo fibers and polysorbate 80 (TTB) had the lowest value compared to the other treatments. The figure 4, shows that the foam formulations were, in general, less friable than the standard foam, from more friable to less friable, Standardt > TB > TT > TTB. Demonstrating that the friability improved with the incorporation of the polysorbate 80 used as an additive (TT) and the bamboo fibers used as reinforcement (TB) from 17,8 % of the standard foam to 13,9 and 15,7 % respectively.



Same letters in a column suggest no significant difference at 5% probability by the Tukey test.

Figure 4: Friability test for ST, TT, TB, and TTB foams.

The sudden increase of mass loss observed with the addition of bamboo fibers in the foam formulation can be attributed to a non-uniform homogenization of the fibers in the matrix, leading to the formation of cracks in the material, which might promote the friability (Mougel et al., 2019). As mentioned by Li et al., (2019), using cork powder can improve the abrasive resistance of the foams, since it provides additional force to the structure; however, the different cell morphology could lead to defects in the final material, which can favor the mass loss during the friability process. Friability can also be enhanced by chemical modification, in that way the use of a surfactant provides flexible chains that react with the phenolic resin, reducing the crosslinking density and the brittleness of the foams (Mougel et al., 2019). The incorporation of tensoactives improves the foam stabilization and increases the viscosity that can limit the thickness of the cell walls obtaining a more homogeneous material and leading to the reduction of the friability.

3.4.3 Water Absorption

Water absorption of the foams was evaluated over 6 hours of immersion, the first three hours at atmospheric conditions and then under vacuum. Figure 5, describes the water absorption rate as a function of time. All foams showed hydrophilic character, the greatest water uptake occurred in the first immersion hour, then the water absorption levels tended to stabilize or increase at a slower rate. After 1h of vacuum application, it was possible to observe a marked increase, possibly due to the storage of water in the cell cavities and again it continued to increase slowly (Xi et al., 2019). The same trend was exhibited by Xi et al. (2020), foams prepared with glutaraldehyde and furfuryl alcohol were tested at 5 h water immersion, and Xi et al., (2019) 24 h water absorption of furfuryl alcohol-glyoxal foams, also presented absorption levels tending to stabilize or continue to increase at a slower rate after 5 h test.

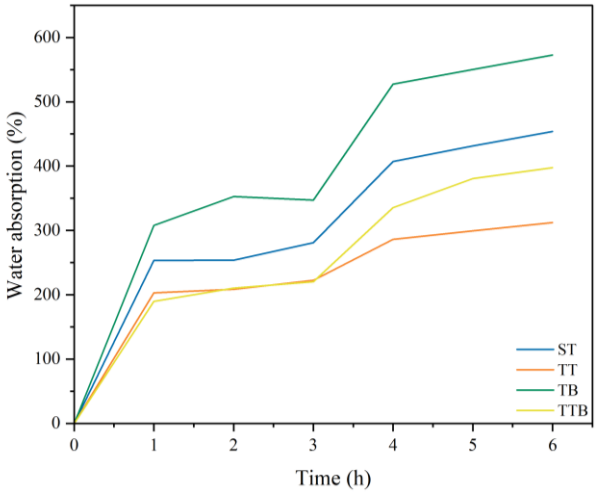


Figure 5: Water absorption curves of ST, TT, TB, and TTB foams as a function of time.

Foam TT had the smallest water absorption followed by the foam TTB, although it presented higher porosity, the slight increase in the TTB treatment was due to the presence of bamboo fibers in the formulation. Therefore, foam TB had the greatest water absorption from all the treatments, as the bamboo fibers addition appears to induce higher water absorption as they have abundant hydroxyl groups which can generate active sites for water absorption allowing water catchability on the cell walls (Qiu et al., 2021).

In general, water absorption is directly related to their density, lower-density foams absorption rates tend to be faster than higher-density ones (Tondi & Pizzi, 2009). However, foam ST showed a quick water absorption considering that it presented the highest apparent density of the treatments; this increased water absorption might be explained due to the larger cell size of the interconnecting holes of the foam; in accordance to Tondi & Pizzi, (2009) and Xi et al., (2020), that water absorption is related to the different cell morphology of the foam; meaning that more empty spaces represent lower density and greater porosity a greater number of pores in the matrix.

3.4.4 Mechanical Resistance

All foams were tested in compression to evaluate their mechanical properties through strength and stiffness values. Figure 6, shows the stress-strain curves for all treatments that follow the typical stages of rigid cellular solids compression behavior. The initial portion of the curves showed a linear elastic region, up to 25 % strain, followed by a stress-plateau zone ranging from 25 % to 70 % strain, and then the stress sharply increases again (Tondi et al., 2009b; Mougel et al., 2019; Borrero-Lopez et al., 2022). The maximum stress point in the treatments was reached at the end of the elastic region followed by a slight decrease before reaching the unstable plateau, as mentioned by Tondi et al., (2009b) and Delgado-Sanchez et al., (2018). This serrated plateau is characterized by successive cell wall fractures or cracks, typical of brittle foams (Basso et al., 2013; Tondi et al., 2009b; Borrero-Lopez et al., 2022).

The mechanical resistance of TTB foam was higher than the other evaluated treatments, TB and TT foams, stress-strain curves possess a comparable trend, due to the fact that both present modifiers in their formulation, and were better than ST foam control treatment. TB foam exhibits slightly better mechanical resistance than TT as it contains 2 wt.% bamboo fibers as reinforcement. Indeed, the presence of fillers as fibers or particles usually increases the mechanical strength, due to their high stiffness; however, compatibility with the phenolic matrix is important as the mixture viscosity can increase affecting the mixing and expansion of the foams (Mougel et al., 2019).

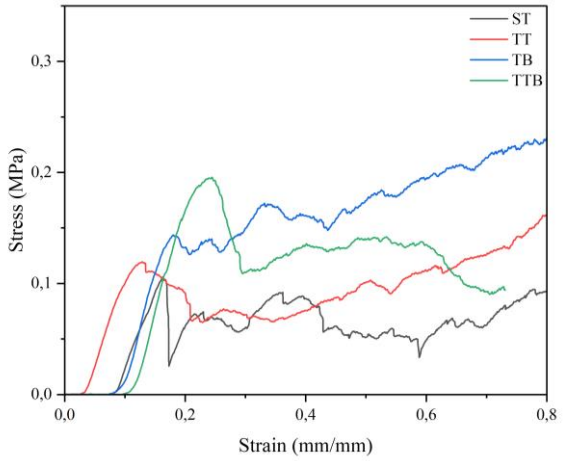


Figure 6: Compressive stress-strain curves of ST, TT, TB and TTB foams.

In concordance, Sas-Orozco et al., (2015), found that the incorporation of 2 wt.% of cellulose fibers increased the compressive strength, whereas the addition of a higher amount of fibers resulted in the reduction of this parameter. Similarly, according to Li et al., (2018) the addition of 1 wt.% of cork powder, showed to enhance the compressive properties of larch tannin foams and further incorporation weakened the strength. Likewise, the chemical modification of the mixture improves the compressive strength by adding flexible chains to the phenolic resin, thus, modifying the crosslinking density and cell structure of the foams. Surfactants like Tween 80, used in the formulation of TT foam provide compatibility to the reagents in the mixture and modify the cell wall of the foams showing an enhanced compression behavior compared to the standard tannin-based foam formulation. Sepperer et al., (2021) tween-based foams obtained high compression resistance foams explained by the formation of thick cell walls with stable microstructure and high density exhibited.

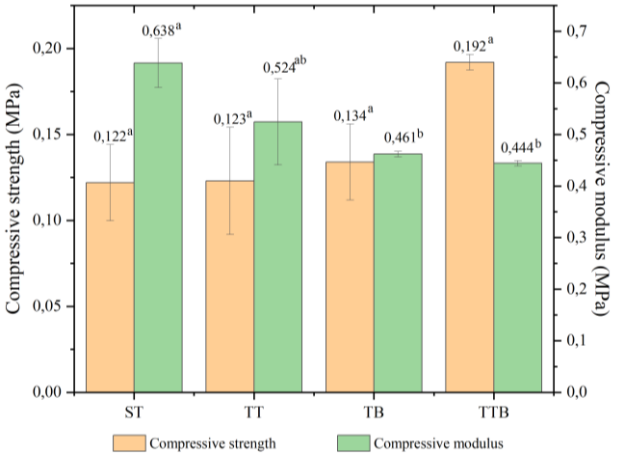


Figure 7: Compressive strength and modulus of ST, TT, TB and TTB foams.

In general, it has been reported that mechanical strength is directly dependent on the foam's density (Varila et al., 2019; Xi et al., 2019). Nevertheless, in the present study (Figure 16), the highest compressive strength (0,19 MPa) was obtained by the less dense foam (0.12 g/cm^3), besides, all tannin foams were higher than 0,08 MPa, which value is characteristic of rigid materials (Borrero-Lopez et al., 2022). This, possibly attributed to the compatibility of the reagents, especially the modifiers incorporated, thus the combination of the surfactant and the fibers in the mixture might have led to the better compression strength exhibited in this study. Like Eckard et al., (2020) formaldehyde-free tannin foams (0.07 g/cm^3) showed approximately three times higher strength (0.15 MPa) compared to a standard foam (0.05 MPa) evaluated with the same density. The same trend was observed by Varila et al., (2019) in tannin foams activated with zinc chloride ($ZnCl_2$) and boric acid (H_3BO_3) the activated samples presented lower densities than the other treatments, but the mechanical strength increased.

Hence, the addition of a surfactant in the mixture allows the modification of the cell size separately from the density, forming a more homogeneous foam with finer and smaller cells improving the compression resistance (Xi et al., 2019). And the addition of bamboo fibers might alter the bonding with the polymer matrix, whereas the insufficient interfacial adhesion between the fibers and the polymer matrix reduces the strength (Nurazzi et al., 2022; Yusuf et al, 2018). These results indicate that the strength is not fully influenced by the density and also, this property is in close relation to the cell wall perforations number and dimensions, as smaller and more uniform pores have been demonstrated to have higher compression resistance (Chen et al., 2020; Xi et al., 2019).

3.4.5 Direct flame exposition

The fire behavior of the tannin-based foams formulations is presented in Figure 8. The foams weight loss rate was recorded, following a similar trend and showing no statistically difference between the treatments, after being exposed to direct flame of a Bunsen burner. TB and TTB foam showed a slight increase of weight loss in the initial phase, and after 1 minute all foams tend to stabilize their weight loss rate, due to the release of water, solvents, and the burning of the external surface of the foams (Eckardt et al., 2020).

All formulations were flame resistant and self-extinguished instantaneously after being removed from the fire; no ignition was observed and the foams did not burn completely, as the flame only perforate the surface of the samples. For instance, Borrero-Lopez et al., (2022) observed no ignition for the tannin-based foams when compared to phenolic foams that ignited after 6 s flame exposure and Pizzi, (2019) reported that only at high temperatures around 3000 °C the foams start to decompose whereas exposed to a long period of time at a 1200 °C flame they do no burn. In the same way, no hazardous smoke occurred during the burning phase, just TB and TTB foam presented fumes after 30 s exposure, this exclusively by the presence of natural fibers in the formulations.

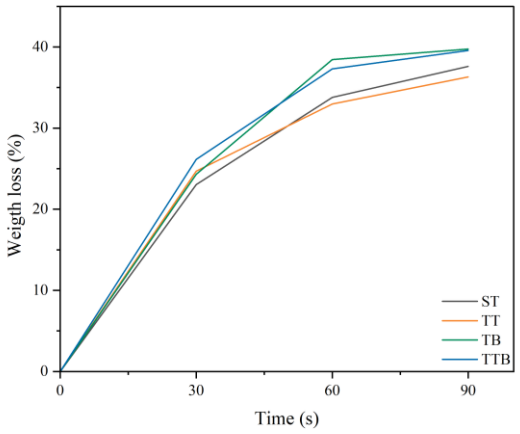


Figure 8: Mass loss of the of ST, TT, TB, and TTB foams during direct flame exposure.

The TT foam showed the lowest weight loss, slightly lower than that of the standard tannin foam, which can be explained by the presence of a surfactant in the mixture that modify the cell wall morphology forming a more homogeneous foam with narrow cell size distribution resulting in reduced flammability (Sarika et al., 2021). In concordance with TTB foam that contained tween 80 with bamboo fibers and exhibited slightly lower weight loss compared to TB foam that was prepared just adding fibers. In general, the tannin foams had very good fire resistance properties, mostly due to the benzene rings of the tannin structure regardless of the addition of modifiers in the mixture and other types of fire retardants (Mougel et al., 2019).

3.4.6 SEM images

The cell wall morphology and distribution of the tannin foams was evaluated by SEM analysis and the results are shown in Figure 9. Showing similar open-cell structure of these foams. In general, it was observed that the size of the cells was quite varied over the treatments. ST foam presented thick and more open cell walls, less porosity, and more empty spaces were observed; this foam presented a very brittle behavior and poor cellular structure due to the presence of cracked cells. This was consistent with the study of Hussain et al., (2020), where polyurethane foams prepared with unmodified condensed tannin, led to a higher number of broken or open cell walls. Overall, surfactant tween 80 used in TT and TTB foams lead to the formation of smaller pores, and the aspect of these foams were more homogeneous. In fact, the addition of a surfactant will lower the surface tension of the system, allowing the formation

of finer bubbles during the expansion and this will prevent the foam rupture or collapse (Sepperer et al., 2021).

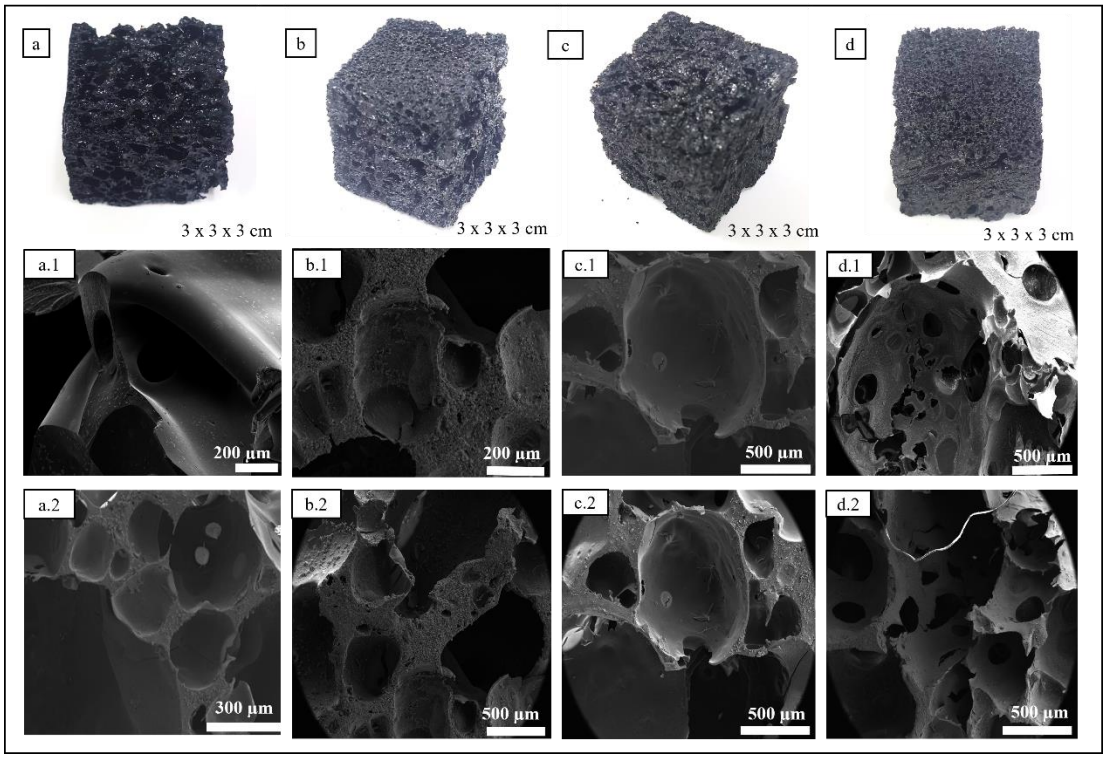


Figure 9: SEM images of tannin-based foams: a, a.1 and a.2 – Images of the ST foam; b, b.1 and b.2 – Images of the TT foam; c, c.1 and c.2 – Images of the TB foam; and d, d.1 d.2 – Images of the TTB foam.

The addition of bamboo fibers, had an effect on the cellular network and rigidity of foams, possibly due to the higher viscosity of the mixture, which may not improve the nucleation of bubbles, resulting in larger cell formation (Li et al., 2018). TB foam presented finer cell morphology and fewer broken (less perforated) cell walls, therefore, this can lead to superior mechanical strength and thermal insulating properties as mentioned by Li et al., (2018) with the addition of cork powder in the foam formulations. Moreover, some fibers can be observed unevenly distributed in the cell walls, noticing a not complete integration of the fibers in the foaming mixture; this can be attributed to the bamboo fiber size, possibly too large, that will increase the cell sizes as there is not a good nucleating effect in the foaming process (Saz-Orozco et al., 2015; Qiu et al., 2021).

Finally compared to the described treatments, the combination of bamboo fibers and tween 80 of TTB foam presented a more stable morphology with fewer irregular and broken cell walls, finer and smaller cells widely distributed over the network; however, breakages or debris still can be observed in the foam, resulting from the cut in the preparation of the sample before analysis.

3.4.7 Infrared spectroscopy (FTIR)

The FT-IR spectra of the foams are reported in figure 10, all the foams showed similar absorption bands, suggesting similar cellular structure. A broad absorption band between 3100 - 3700 cm^{-1} was observed, typical of hydroxyl groups, TB and TTB foams showed a more intense spectral peak OH stretching vibration which is mainly due to the numerous hydroxyl groups of the bamboo fibers incorporation; TT foam contained the lowest amount of O-H group due to possibly polycondensation reaction with the tween 80 added (Qiu et al., 2021). ST and TT foams presented peaks around 2924 and 2854 cm^{-1} corresponding to C-H stretching region from methylene (CH_2) and dimethylene ether (CH_2-O-CH_2) groups of the aliphatic chains and the aromatic rings, which lower the intensity in the TB and TTB foams (Hussain et al., 2020).

At around 1700 cm^{-1} the C=O bond stretching occurs, attributed to an incomplete scission of the ether linkage after furan ring opening (Tondi et al., 2015). The absorption band at 1610 cm^{-1} is attributed to the C=C vibration in the benzene ring of tannins present in all foams (Azadeh et al., 2022). The spectral region between 1608-1300 cm^{-1} presents C-H bending vibrations of the aromatic rings, with strong stretching at 1455 cm^{-1} band characteristic of phenolic compounds (Tondi et al., 2015; Li et al., 2018).

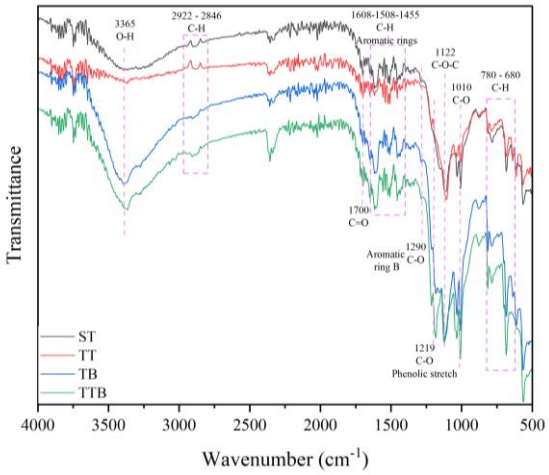


Figure 10: FTIR spectra of ST, TT, TB and TTB foams.

From 1300 to 950 cm^{-1}, C-O stretching vibrations are characteristic, in this region the TTB foam spectrum presented some differences compared to the other foams, with more intense bands occurring at 1122, 1035, and 1010 cm^{-1} attributed to C-O-C and C-O stretching vibrations due to the increasing amount of ether bridges obtained by the ether bonds formed by the reaction of glyoxal with furfuryl alcohol (Li et al., 2018). Finally, the region from 950 to 600 cm^{-1} bands are attributed to C-H bending of aromatic rings, 786 and 680 cm^{-1} peaks of TTB foam appeared to be more intense which can be attributed to the C-H vibration of the furan ring and to the C-C-C stretching of benzene rings, respectively (Tondi et al., 2015; Hussain et al., 2020).

3.4.7 Thermogravimetry (TG)

The thermogravimetric analysis (TGA) and DTG curves of the foams are shown in figure 11, describing the thermal stability behavior of the tannin-based foams formulations. Three similar degradation stages were observed for all foams, a first peak was observed between 30 and 100 °C, this initial mass loss was attributed to the volatilization of remaining water and light volatile compounds in the foams (Xi et al., 2020). The next stage took place between 150 and 400 °C range, where the initiation temperature of the foams was very close to about 200 °C and the mass loss was related to the degradation of the tannin bonds, the surfactant tween 80 in TT foam and decomposition of cellulose, hemicellulose and lignin in TB and TTB foams, providing better thermal stability (Qui et al., 2020; Chen et al., 2020).

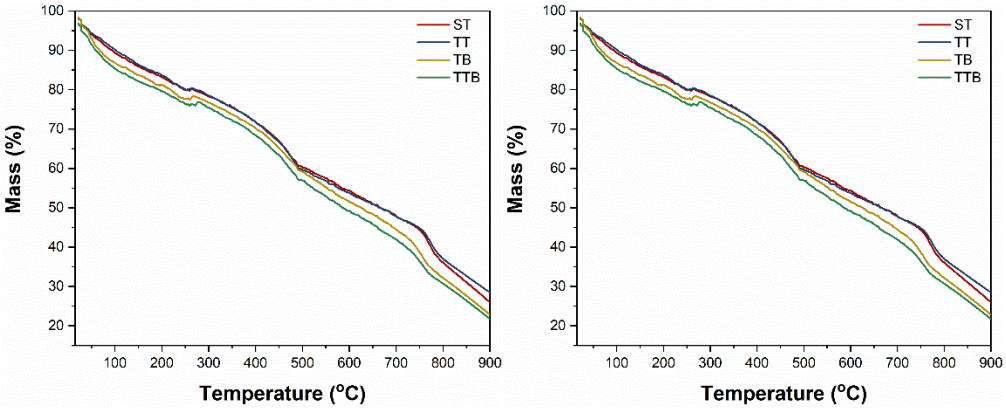


Figure 10: TGA and Derivative Thermogravimetry (DTG) curves of ST, TT, TB and TTB foams.

The third mass loss and the largest ranged from 550 to 750 °C, showing that 50 % of the mass loss occurred after 600 °C, attributed to the degradation of C-C bonds and the pyrolysis of any residual products. All the foams presented residual mass at 800°C, TB and TTB foams presented a similar residual mass of around 25 % and TT foam presented the highest residual mass of 32 % possibly attributed to the low crosslinking density and overall, indicating the good heat resistance of these foams (Xi et al., 2020; Chen et al., 2020; Li et al., 2018).

4. Conclusions

In general, A. peregrina tannins possessed desirable Stiasny index of 72,41% and condensed tannin content of 12,81% proving to be possible to use them tannins as phenolic sources for the production of bio-based free formaldehyde foams.

A. Peregrina tannin-based foams presented densities ranging from 0,12 to 0,19 g/cm^3, comparable to foams produced with other tannin species, however, the incorporation of the mentioned additives in this study tends to slightly decrease this parameter, whereas the porosity levels increased.

The water affinity of the foams that water absorption was related to the different cell morphology of the foam, it decreased with the incorporation of the additive tween 80, while shown to highly increase with the presence of bamboo fibers in the formulations due to their hydrophilic character; and the combination of both tend to stabilize this parameter.

The mechanical properties of the foams in this study were comparable to biomass-based insulation materials and were directly related to the cell wall morphology and the crosslinking density of the resin; the incorporation of surfactant tween 80 and bamboo fibers in the formulation showed little improvement in these properties.

All the A. peregrina tannin foams were flame resistant and presented self-extinguish behavior, even without the addition of any flame retardants in the formulation, and no hazardous fumes were released during combustion.

The SEM images confirmed the incorporation of the surfactant tween 80, producing more homogeneous, smaller pores cell wall morphology with higher mechanical resistance, compared with the treatments without surfactant that presented more brittle behavior.

Further studies regarding the development of these products are needed, with diverse natural additives, as low-cost, non-toxic substituents to replace non-environmental friendly petroleum-based insulating material.

References

Araujo E., Lorenço, M., Zidanes, U., Sousa, T., Mota, G., Reis, V., Silva, M. & Mori, F. (2021). Quantification of the bark *Myrcia eximia* DC tannins from the Amazon rainforest and its application in the formulation of natural adhesives for wood. Journal of Cleaner Production, vol. 280, part 1,124324. https://doi.org/10.1016/j.jclepro.2020.124324

Arbenz, A., & Avérous, L. (2015). Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures. *Green Chemistry*, *17*(5), 2626–2646. https://doi.org/10.1039/c5gc00282f

American Society for Testing Materials. (2010). ASTM D1621-10: Standard Test Method for Compressive Properties of Rigid Cellular Plastics. Philadelphia. ASTM International

American Society for Testing Materials. (2003). ASTM D1622-03: Standard Test Method for Apparent Density of Rigid Cellular Plastics. Philadelphia. ASTM International.

American Society for Testing Materials. (2000). ASTM C421-00: Standard Test Method for Tumbling Friability of Preformed Block-Type Thermal Insulation. Philadelphia. ASTM International.

Azadeh, E., Abdullah, U., Ali, N., Pizzi, A., Gerardin-Charbonnier, C., Gerardin, P., Samiun, W., Ashari, S. (2022). Development of Water Repellent, Non-Friable Tannin-Furanic-Fatty Acids Biofoams. Polymers, 14, 5025. https://doi.org/10.3390/ polym14225025

Bacelo, H. A. M., Santos, S. C. R., & Botelho, C. M. S. (2016). Tannin-based biosorbents for environmental applications - A review. *Chemical Engineering Journal*, *303*, 575–587. https://doi.org/10.1016/j.cej.2016.06.044

Basso, M. C., Giovando, S., Pizzi, A., Lagel, M. C., & Celzard, A. (2014). Alkaline tannin rigid foams. *Journal of Renewable Materials*, *2*(3), 182–185. https://doi.org/10.7569/JRM.2013.634137

Basso, M. C., Pizzi, A., Celzard, A., Fierro, V., Sánchez, M. C., & Franco, J. M. (2018). Industrial Crops & Products Projectable tannin foams by mechanical and chemical expansion. *Industrial Crops & Products*, *120*(March), 90–96. https://doi.org/10.1016/j.indcrop.2018.04.048

Bello, A., Virtanen, V., Salminen, J., & Leiviskä, T. (2020). Separation and Puri fi cation Technology Aminomethylation of spruce tannins and their application as coagulants for water clari fi cation. *Separation and Purification Technology*, *242*(December 2019), 116765. https://doi.org/10.1016/j.seppur.2020.116765

Borrero-López, A., Nicolas, V., Marie, Z., Celzard, A., & Fierro, V. (2022). A Review of Rigid Polymeric Cellular Foams and Their Greener Tannin-Based Alternatives. Polymers, 14, 3974. https:// doi.org/10.3390/polym14193974

Bouras, M., Chadni, M., Barba, F. J., Grimi, N., Bals, O., & Vorobiev, E. (2015). Optimization of microwave-assisted extraction of polyphenols from Quercus bark. *Industrial Crops and Products*, *77*, 590–601. https://doi.org/10.1016/j.indcrop.2015.09.018

Bule, M., Khanb, F., Nisard, M., & Niaz, K. (2020). Tannins (hydrolysable tannins, condensed tannins, phlorotannins, flavono-ellagitannins). Recent Advances in Natural Products Analysis. pp.132-146. ISBN: 9780128175194

Carneiro, A. (2006). Efeito da Hidrólise ácida e Sulfatacao de taninos de *Eucalyptus grandis* w. Hill ex Maiden e *Anadenanthera peregrina* Speg. Nas propriedades dos adesivos. Tese de doutorado do Programa de Pós-Graduação em Ciencia Florestal. UFV. Viçosa

Carneiro, A., Vital, B., Frederico, P., CARVALHO, A., & Vidaurre, G. (2009). Propriedades de Chapas de Aglomerado FabricaDAS com Adesivo Tânico de Angico-Vermelho (Anadenanthera Peregrina) e Uréia-Formaldeído. Revista Árvore. Viçosa-MG. V.33, n.3, p.521-531. https://doi.org/10.1590/S0100-67622009000300014

Carvalho, P. (2011). Espécies Arbóreas Brasileiras: Angico Vermelho. EMBRAPA. Recuperado de: https://www.alice.cnptia.embrapa.br/bitstream/doc/1137299/1/Especies-Arboreas-Brasileiras-vol-1-Angico-Vermelho.pdf

Celzarrd, A., Zhao, W., Pizzi, A., Fierro, V. (2010). Mechanical properties of tannin-based rigid foams undergoing compression. Materials Science and Engineering A 527 4438–4446. doi:10.1016/j.msea.2010.03.091

Celzard, A., Szczurek, A., Jana, P., Fierro, V., Basso, M., Bourbigot, S., Stauber, M., & Pizzi, A. (2014). *Latest progresses in the preparation of tannin-based cellular solids*. *7198*. https://doi.org/10.1177/0021955X14538273

Chemat, F., Rombaut, N., Sicaire, A. G., Meullemiestre, A., Fabiano-Tixier, A. S., & Abert-Vian, M. (2017). Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review. *Ultrasonics Sonochemistry*, *34*, 540–560. https://doi.org/10.1016/j.ultsonch.2016.06.035

Chen, X., Xi, X., Pizzi, A., Fredon, E., Zhou, X., Li, J., Gerardin, C., & Du, G. (2020). Preparation and characterization of condensed tannin non-isocyanate polyurethane (NIPU) rigid foams by ambient temperature blowing. *Polymers*, *12*(4). https://doi.org/10.3390/POLYM12040750 Chen, X., Li, J., Pizzi, A., Fredon, E., Gerardin, C., Zhou, X., & Du, G. (2021). Tannin-furanic foams modified by soybean protein isolate (SPI) and industrial lignin substituting formaldehyde addition. Industrial Crops and Products, vol. 168, 113607. https://doi.org/10.1016/j.indcrop.2021.113607

CNA Brasil. (2016). O Brasil é um dos maiores produtores de Florestas PlantaDAS do mundo. http://www.cnabrasil.org.br/o-brasil-e-um-dos-maiores-produtores-deflorestas-plantaDAS-do-mundo

Čop, M., LACOSTE, C., Conradi, M., Laborie, M., PIZZI, A., & Sernek, M. (2015). The effect of the composition of spruce and pine tannin-based foams on their physical, morphological and compression properties. Industrial Crops and Products, vol 74, pages 158-164.https://doi.org/10.1016/j.indcrop.2015.04.009

Das, A. K., Islam, M. N., Faruk, M. O., Ashaduzzaman, M., & Dungani, R. (2020). Review on tannins: Extraction processes, applications and possibilities. *South African Journal of Botany*, *135*, 58–70. https://doi.org/10.1016/j.sajb.2020.08.008

De Hoyos-Martínez, P. L., Merle, J., Labidi, J., & Charrier – El Bouhtoury, F. (2019). Tannins extraction: A key point for their valorization and cleaner production. *Journal of Cleaner Production*, *206*, 1138–1155. https://doi.org/10.1016/j.jclepro.2018.09.243

Delgado-Sanchez, C., Santiago-Medina, F., Fierro, V., Pizzi, A., & Celzard, A. (2018). Optimisation of " green " tannin-furanic foams for thermal insulation by experimental design. *Materials & Design*, *139*, 7–15. https://doi.org/10.1016/j.matdes.2017.10.064

Eckardt, J., Sepperer, T., Cesprini, E., Šket, P., & Tondi, G. (2023). Comparing Condensed and Hydrolysable Tannins for Mechanical Foaming of Furanic Foams: Synthesis and Characterization. Molecules, 28, 2799. https://doi.org/10.3390/molecules28062799

Feng, S., Cheng, S., Yuan, Z., Leitch, M., & Charles, C. (2013). *Valorization of bark for chemicals and materials : A review*. *26*, 560–578. https://doi.org/10.1016/j.rser.2013.06.024

Fraga-Corral, M., Otero, P., Echave, J., Garcia-Oliveira, P., Carpena, M., Jarboui, A., Nuñez-Estevez, B., Simal-Gandara, J., & Prieto, M. A. (2021). By-products of agri-food industry as tannin-rich sources: A review of tannins' biological activities and their potential for valorization. *Foods*, *10*(1). https://doi.org/10.3390/foods10010137

Gauler, M. & Grigsby, W. (2009). Thermal Degradation of Condensed Tannins from Radiata Pine Bark. Journal of Wood Chemistry and Technology, Vol. 29 - Issue 4, p. 305-321. https://doi.org/10.1080/02773810903165671

GVR. Grand view research. Tannin Market Size, Share & Trends Analysis Report By Sources (Plants, Brown Algae), By Product (Hydrolysable, Non-hydrolysable, Phlorotannins), By Application (Leather Tanning, Wine Production, Wood Adhesives), & Segment Forecasts, 2020 - 2025. Available in: https://www.grandviewresearch.com/industry-analysis/tannin-market

Hillig, É., Schneider, V. & Pavoni, E. (2009). Geração de resíduos de madeira e derivados da indústria moveleira em função DAS variáveis de produção. Produção, v. 19, n. 2, p. 292-303.

IBA. (2022). Indústria brasileira de árvores. Relatório Anual 2022. Available in: https://www.iba.org/datafiles/publicacoes/relatorios/relatorio-anual-iba2022-compactado.pdf

IBF, Instituto Brasileiro de Florestas. (2020). Angico Vermelho. Available in: https://www.ibflorestas.org.br/lista-de-especies-nativas/angico-vermelho

Issaoui, H., Sallem, F., Lafaille, J., Grassl, B., & Charrier–El Bouhtoury, F. (2021). Biosorption of Heavy Metals from Water onto Phenolic Foams Based on Tannins and Lignin Alkaline Liquor. *International Journal of Environmental Research*, *15*(2), 369–381. https://doi.org/10.1007/s41742-021-00313-5

Konai, N., Pizzi, A., Raidandi, D., Lagel, M.C., L'Hostis, C., Saidou, C., Hamido, A., Abdalla, S., Bahabri, F., Ganash, A. (2015). Aningre (Aningeria spp.) Tannin extract characterization and performance as an adhesive resin. Ind. Crop. Prod. 77, 225e231. https://doi.org/10.1016/j.indcrop.2015.08.053.

Konai, N., Raidandi, D., Pizzi, A., Girods, P., Lagel, M. & Kple, M. (2016). Thermogravimetric analysis of anningre tannin resin. Maderas, Cienc. tecnol. vol.18 no.2.http://dx.doi.org/10.4067/S0718-221X2016005000022

Lacoste, C., Basso, M. C., Pizzi, A., Laborie, M., Celzard, A., & Fierro, V. (2014). Pine tannin-based rigid foams : Mechanical and thermal properties. *Industrial Crops & Products*, *43*, 245–250. https://doi.org/10.1016/j.indcrop.2012.07.039

Lacoste, C., Basso, M., Pizzi, A., Celzard, A., Ebang, E. E., Gallon, N., & Charrier, B. (2015). Pine (P . pinaster) and quebracho (S . lorentzii) tannin-based foams as green acoustic absorbers. *Industrial Crops & Products*, *67*, 70–73. https://doi.org/10.1016/j.indcrop.2014.12.018

Li, J., Liao, J., Essawy, H., Zhang, J., Li, T., Wu, Z., Du, G., & Zhou, X. (2021). Industrial Crops & Products Preparation and characterization of novel cellular / nonporous foam structures derived from tannin furanic resin. *Industrial Crops & Products*, *162*(July 2020), 113264. https://doi.org/10.1016/j.indcrop.2021.113264

Li, X., Srivastava, V. K., Pizzi, A., Celzard, A., & Leban, J. (2013). *Nanotube-reinforced tannin / furanic rigid foams*. *43*, 636–639. https://doi.org/10.1016/j.indcrop.2012.08.008

Li, J., Zhang, A., Zhang, S., Gao, Q., Zhang, W., & Li, J. (2018). Larch tannin-based rigid phenolic foam with high compressive strength, low friability, and low thermal conductivity reinforced by cork powder. Composites Part B: Engineering, vol. 156, Pages 368-377, ISSN 1359-8368.https://doi.org/10.1016/j.compositesb.2018.09.005.

Link, M., Kolbitsch, C., Tondi, G., Ebner, M., Wieland,S., & Petutschnigg, A. (2011). Formaldehyde-Free Tannin-Based Foams And Their Use As Lightweight Panels. BioResources 6(4), 4218-4228.

Liu, B., Zhou, Y., Essawy, H., Feng, S., Li, X., Liao, J., Zhou, X., Zhang, J. & Xie, S. (2022). Formaldehyde Free Renewable Thermosetting Foam Based on Biomass Tannin with a Lignin Additive. Journal of Renewable Materials, 10 (11), 3009-3024. https://doi.org/10.32604/jrm.2022.019848

Marie, Z., Nicolas, V., Celzard, A., & Fierro, V. (2019). Industrial Crops & Products Experimental investigation of the physical foaming of tannin-based thermoset foams. *Industrial Crops & Products*, *138*(May), 111424. https://doi.org/10.1016/j.indcrop.2019.05.073

Marie, Z., Nicolas, V., Celzard, A., & Fierro, V. (2020). International Journal of Thermal Sciences First approach for modelling the physical

foaming of tannin-based thermoset foams. *International Journal of Thermal Sciences*, *149*(November 2019), 106212. https://doi.org/10.1016/j.ijthermalsci.2019.106212

Marques, S., Azevêdo, T., Castilho, A., Braga, R. & Pimenta, A. (2021). Extraction, Quantification, And FTIR Characterization Of Bark Tannins Of Four Forest Species Grown In Northeast Brazil. Revista Árvore, 45 - 4541. http://dx.doi.org/10.1590/1806-908820210000041

Martins, R., Gomes, I., Mendonça Telles, A., Kato, L., Souza, P., & Rodrigues Chaves, A. (2020). Molecularly imprinted polymer as solid phase extraction phase for condensed tannin determination from Brazilian natural sources. Journal of Chromatography A 1620 460977. https://doi.org/10.1016/j.chroma.2020.460977

Martinez de Yuso, A., Lagel, M., PIZZI, A., Fierro, V., & CELZARD, A. (2014). Structure and properties of rigid foams derived from quebracho tannin. Materials & Design. vol. 23, pages 208-212. https://doi.org/10.1016/j.matdes.2014.05.072

Merle, J., Birot, M., Deleuze, H., Mitterer, C., Carr´e, H., & Charrier-El Bouhtoury, F. (2015). New biobased foams from wood byproducts. Materials and Design. doi: 10.1016/j.matdes.2015.11.07

Mori, F., de Oliveira, C., Mendes, L., da Silva, J., & Melo, V. (2003). Influência do sulfito e hidróxido de sódio na quantificação em taninos da casca de barbatimão (Stryphnodendron adstringens). Floresta e Ambiente, Rio de Janeiro, v. 10, n. 1, p. 86-92, 2003

Mota, G., Sartori, C., Miranda, I., Quilhó, T., Mori, F., & Pereira, H. (2017). Bark anatomy, chemical composition and ethanol-water extract composition of *Anadenanthera peregrina* and *Anadenanthera colubrina*. PLoS ONE 12(12): e0189263. https://doi.org/10.1371/journal. pone.0189263

Mougel, C., Garnier, T., Cassagnau, P., & Sintes-Zydowicz, N. (2019). Phenolic foams: A review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer, vol. 164, Pages 86-117, ISSN 0032-3861. https://doi.org/10.1016/j.polymer.2018.12.050.

Mousavi, S., Zamani, M., Estaji, S., Tayouri, M., Arjmand, M., Jafari, S., Nouranian, S., & Khonakdar, H. (2022). Mechanical properties of bamboo fiber-reinforced polymer composites: a review of recent case studies. J Mater Sci (2022) 57:3143–3167. https://doi.org/10.1007/s10853-021-06854-6

Muhammad, A., Rahman, M., Hamdan, S., & Sanaullah, K. (2019). Recent developments in bamboo fiber-based composites: a review. *Polymer Bulletin.* **76**, 2655–2682. https://doi.org/10.1007/s00289-018-2493-9

Nurazzi, N., Norrrahim, M., Sabaruddin, F., Shazleen, S., Ilyas, R., Lee, S., Padzil, F., Aizat, G., Aisyah, H., Mohidem, N., Asyraf, N., Abdullah, N., Sapuan, S., Abdan, K., & Nor, N. (2022). Mechanical performance evaluation of bamboo fibre reinforced polymer composites and its applications: a review. Funct. Compos. Struct. 4, 015009. https://doi.org/10.1088/2631-6331/ac5b1a

Oliveira Mori, C., Mori, F., Mendes, L., Silva, J. (2007). Potencial da madeira de angico-vermelho para móveis. Revista da Madeira. N°108

Paes, J., Santana, G., Azevedo, T., Morais, R., & Júnior, J. (2010). Tannic substances present in several parts of Anadenanthera colubrina (Vell.) Brenan. var. cebil (Gris.) Alts.) tree. Sci. For., Piracicaba, v. 38, n. 87, p. 441-447.

Pagliaro, M., Albanese, L., Scurria, A., Zabini, F., Meneguzzo, F., & Ciriminna, R. (2021). Tannin: a new insight into a key product for the bioeconomy in forest regions. *Biofuels, Bioproducts and Biorefining*, 1–7. https://doi.org/10.1002/bbb.2217

Pantoja-Castro, A. & González-Rodríguez, H. (2012). Study by Infrared Spectroscopy and Thermogravimetric Analysis of Tannins and Tannic Acid. Rev. Latinoamer. Quím. 39/3.

Patil, P. D., Patil, S. P., Kelkar, R. K., Patil, N. P., Pise, P. V., & Nadar, S. S. (2021). Enzyme-assisted supercritical fluid extraction: An integral approach to extract bioactive compounds. *Trends in Food Science and Technology*, *116*(July), 357–369. https://doi.org/10.1016/j.tifs.2021.07.032

Pizzi, A. (2019). Tannin-based biofoams-A review. *Journal of Renewable Materials*, *7*(5), 477–492. https://doi.org/10.32604/jrm.2019.06511

Qiu, C., Li, F., Wang, L., Zhang, X., Zhang, Y., Tang, Q., Zhao, X., De Hoop, C., Peng, X., Yu, X. & Huang, X. (2021). The preparation and properties of polyurethane foams reinforced with bamboo fiber sources in China. Materials Research Express, vol 8, 45501. **DOI** 10.1088/2053-1591/abf1cd

Ricci, A., Olejar, K., Parpinello, G., Kilmartin, P., & Versari, A. (2015). Application of Fourier Transform Infrared (FTIR) Spectroscopy in the Characterization of Tannins. *Applied Spectroscopy Reviews* 50:5, 407-442, DOI: 10.1080/05704928.2014.1000461

Sánchez-Martín, J., Beltrán-heredia, J., Delgado-regaña, A., & Rodríguez-gonzález, M. A. (2013). *Adsorbent tannin foams : New and complementary applications in wastewater treatment*. *228*, 575–582. https://doi.org/10.1016/j.cej.2013.05.009

Sarika, P., Nancarrow, P., Khansaheb, A., Ibrahim, T. (2021). Progress in Bio-Based Phenolic Foams: Synthesis, Properties, and Applications. ChemBioEng Rev 2021, 8, No. 6, 612–632. DOI: 10.1002/cben.202100017

Sartori, C. (2012). Avaliação dos teores de compostos fenólicos nas cascas de *Anadenanthera peregrina* (angico-vermelho). Dissertação (mestrado)-Universidade Federal de Lavras, Programa de Pós-graduação em Ciência e Tecnologia da Madeira. p. 94.

Sartori, C., Castro, A. & Mori, F. (2014a). Teores de Fenóis Totais e Taninos nas Cascas de Angico-vermelho (Anadenanthera peregrina). Floresta e Ambiente. 21(3):394-400. https://doi.org/10.1590/2179-8087.061113

Sartori, C., Mori, F., Valle, M., Mendes, L., & Protásio, T. (2014b). Tannins Gravimetric Yield Condensed in *Anadenanthera Peregrina* Bark in Different Diameter Classes. Cerne, Lavras, v. 20, n. 2, p. 239-244. DOI: http://dx.doi.org/10.1590/01047760.201420021512

Saz-Orozco, B., Alonso, M., Oliet, M., Domínguez, J., & Rodriguez, F. (2015). Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Composites Part B: Engineering, vol. 75, Pages 367-372, ISSN 1359-8368. https://doi.org/10.1016/j.compositesb.2015.01.049.

Sepperer, T., Šket, P., PETUTSCHNIGG, A., & Hüsing, N. (2021). Tannin-Furanic Foams Formed by Mechanical Agitation: Influence of Surfactant and Ingredient Ratios. Polymers, 13, 3058. https:// doi.org/10.3390/polym13183058

Song, E., Jeong, S., Park, J., Kim, S., Kim, H., & Song, J. (2017). Polyurethane-Silica Hybrid Foams from a One-Step Foaming Reaction, Coupled with a Sol-Gel Process, for Enhanced Wound Healing. *Mater. Sci. Eng. C*, *79*, 866–874. https://doi.org/10.1016/j.msec.2017.05.041Get rights and content

Tondi, G., Zhao, W., Pizzi, A., Du, G., Fierro, V., & Celzard, A. (2009). Tannin-based rigid foams: A survey of chemical and physical properties. Bioresource Technology, vol. 100, Issue 21, pages 5162-5169. https://doi.org/10.1016/j.biortech.2009.05.055

Tondi, G., Fierro, V., Pizzi, A. Celzard, A. Tannin-based carbon foams. (2009). CARBON 47,1480 – 1492. doi:10.1016/j.carbon.2009.01.041.

Tondi, G., Link, M., Wei, C., & Petutschnigg, A. (2015). A Simple Approach to Distinguish Classic and Formaldehyde-Free Tannin Based Rigid Foams by ATR FT-IR. Journal of Spectroscopy. https://doi.org/10.1155/2015/902340

Tondi, G., & Petutschnigg, A. (2016). Middle infrared (ATR FT-MIR) characterization of industrial tannin extracts. Ind. Crop. Prod. 422e428 https://doi.org/10.1016/ j.indcrop.2014.11.005.

Varila, T., Romar, H., Luukkonen, T., & Lassi, U. (2019). Physical activation and characterization of tannin-based foams enforced with boric acid and zinc chloride. AIMS Materials Science, 6(2): 301–314. DOI: 10.3934/matersci.2019.2.301

Wu, X., Yan, W., Zhou, Y., Luo, L., Yu, X., Luo, L., Fan, M., Du, G., & Zhao, W. (2020). *Industrial Crops & Products Thermal , morphological , and mechanical characteristics of sustainable tannin bio-based foams reinforced with wood cellulosic fibers*. *158*(May). https://doi.org/10.1016/j.indcrop.2020.113029

Xi, X., Pizzi, A. Gerardin, C & Du, G. (2019). Glucose-Biobased Non-Isocyanate Polyurethane Rigid Foams. JRM, vol.7, no.3. DOI: 10.32604/jrm.2019.04174

Xi, X., Pizzi, A., Lei, H., Du, G., Zhou, X., Lin, Y. (2020). Characterization and Preparation of Furanic-Glyoxal Foams. Polymers. 12, 692; doi:10.3390/polym12030692

Yusuf, S., Syamani, F., Fatriasari, W., & Subyakto . (2018). Review on Bamboo Utilization as Biocomposites, Pulp and Bioenergy. IOP Conf. Series: Earth and Environmental Science, 141, 012039. doi :10.1088/1755-1315/141/1/012039

Zidanes, U., Dias, M., Lorenço, M., Araujo, E., Silva, M., Sousa, T., Ferreira, S., Ugucioni, J., Tonoli, G., Bianchi, M., & Mori, F. (2021). Preparation and characterization of tannin-based adhesives reinforced with cellulose nanofibrils for wood bonding. Holzforschung, 75 (2): 159-167. https://doi.org/10.1515/hf-2020-0033

Zhao, W., PIZZI, A., Fierro, V., Du, G., & Celzard, A. (2010). Effect of composition and processing parameters on the characteristics of tannin-based rigid foams . Part I : Cell structure. *Materials Chemistry and Physics*, *122*(1), 175–182. https://doi.org/10.1016/j.matchemphys.2010.02.062