

Review

Innovations in Tannin-Based Phenolic Foams: A Review of the Research

António G. Abreu ^{1,2,†}, Joana J. Costa ^{1,2,*,†}, P. Filipe Santos ³, Abel J. Duarte ^{1,2} , Elizabeth S. Vieira ^{3,*} and Felismina T. C. Moreira ^{1,2,*} 

¹ CIETI—LabRISE, ISEP, Polytechnic of Porto, Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal; agvsa@isep.ipp.pt (A.G.A.); ajd@isep.ipp.pt (A.J.D.)

² School of Engineering of the Polytechnic School of Porto, Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal

³ Prudêncio Impermeabilizações, Parque Industrial Sete Fontes, R. dos Pedreiros 14, 4710-553 Braga, Portugal; filipe@prudencio.pt

* Correspondence: jjdca@isep.ipp.pt (J.J.C.); elizabeth@prudencio.pt (E.S.V.); ftm@isep.ipp.pt (F.T.C.M.)

† These authors contributed equally to this work.

Abstract

Research on tannin-based foams has shown promising results. However, all developments in this field have not been addressed from different perspectives, in a systematic way, and with an emphasis on sustainability. This work discusses different formulations, emphasizing their bio-based components and how modifications influence key properties. It examines life cycle assessment (LCA) studies through a sustainability lens and identifies major commercial phenolic products to highlight the practical use of tannin foams for thermal insulation. The type of tannins, as well as their sources, influences the key properties of these foams. The replacement of formaldehyde, a crosslinking agent known for its health risks, is possible, particularly through more sustainable alternatives that allow for foams with better properties than those obtained with formaldehyde. Substitution of diethyl ether with less hazardous alternatives results in foams with improved thermal and mechanical performance. The elimination of the blowing agent—the green alternative—also leads to foams with good performance. The presence of additives (surfactants, plasticizers, and fillers), some of which are sustainable, improves the mechanical properties of the foams. The performance in fire-related applications, already promising, is also enhanced by the presence of additives. An increase in understanding, combined with the sustainable nature of the various alternatives, makes tannin-based foams promising candidates for next-generation insulation and structural materials in construction.

Keywords: tannin–furfuryl alcohol resin; bio-based foam; lignocellulosic biomass; flame retardancy; thermal insulation; sustainable materials; phenolic foams



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1. Introduction

The European Green Deal, announced in 2019, aims to make the European Union (EU) a climate-neutral continent by 2050. It is the EU's strategy to create a sustainable economy by turning climate and environmental challenges into opportunities [1] (Figure 1). Among the elements included in the European Green Deal is building and renovation in an energy- and resource-efficient way [1], where the EU emphasizes the need to reduce the energy consumption of buildings (around 40% of total energy consumption in Europe [2]) and

their high greenhouse gas (GHG) emissions (around 36% of the EU's energy-related GHG emissions come from buildings [3]).

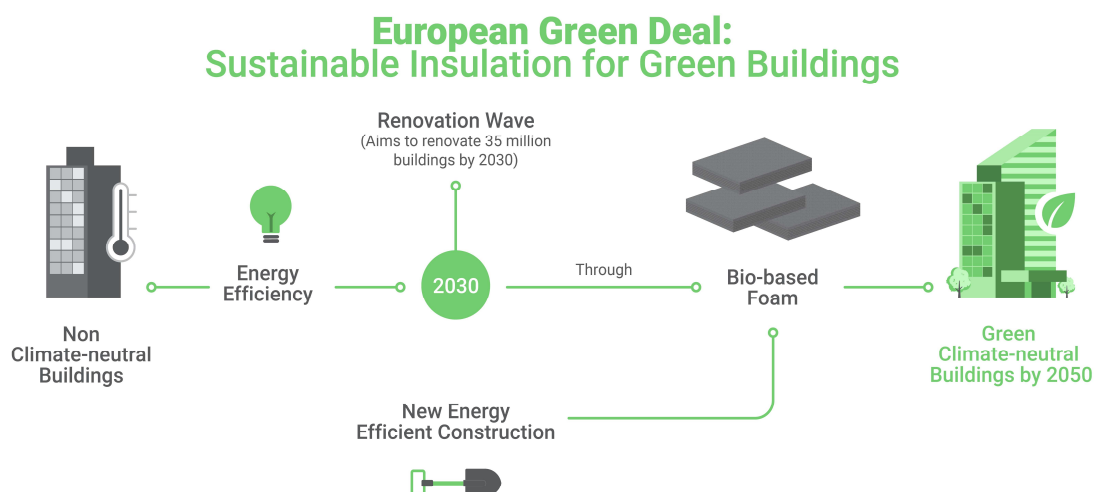


Figure 1. Pathway to climate-neutral buildings: energy efficiency and Renovation Wave.

Given the energy inefficiency of buildings in Europe and the potential of renewable energy, along with individual measures such as the installation of thermal insulation and replacement of old windows and doors with new, more energy-efficient ones, the EU is promoting a Renovation Wave to achieve greater energy and resource efficiency [3]. The Renovation Wave aims to renovate 35 million buildings by 2030 according to requirements that ensure better energy performance of buildings. These requirements are set out in the Energy Performance of Buildings Directive [4] and Energy Efficiency Directive [5], which emphasize insulation of the building envelope for renovated and new constructions.

Currently, among the many options for insulation, foams are widely used for thermal and acoustic insulation. Most are mineral-based (e.g., rock wool and glass wool) or petroleum-based (e.g., expanded polystyrene (EPS), extruded polystyrene (XPS), polyurethane (PUR), polyisocyanurate (PIR), and phenolic foams).

The attractiveness of these materials lies in their (i) low thermal conductivity, which reduces heating and cooling needs; (ii) moisture resistance, which prevents mold growth and performance deterioration over time; (iii) lightness and rigidity, which allow easy handling, transport, and installation; (iv) great versatility in application, as they can be cut and shaped to fit surfaces such as walls, roofs, and floors; and (v) the excellent fire performance offered by some materials, such as phenolic foams (e.g., [6–9]).

Phenolic foams were first used in the industry in the early 1940s in Germany [10]. However, as other foams with better mechanical performance emerged, mainly concerning friability, such as PUR (Table 1), phenolic foams became less popular [11].

Table 1. Density, thermal conductivity, compressive strength, limiting oxygen index (LOI) for combustion, and friability for different foams.

Foam	Density [kg m^{-3}]	Thermal Conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	Compressive Strength [MPa]	LOI (%)	Friability (Mass Loss, %)	References
Phenolic foams	43–54	0.036–0.039	0.05–0.25	28–51	6–32.2	[12–19]
Polystyrene foam (XPS or EPS)	24–63	0.031–0.038	0.06–0.29	17–18	-	[20–24]
Polyurethane foam (PUR or PIR)	35–60	0.025–0.038	0.15–0.46	19–20	8–11	[13,14,16,20,25–31]

However, the excellent fire properties of phenolic foams—low flammability, low peak heat release rate, no dripping during combustion, and low smoke density and toxicity [11,19,32]—and the good thermal insulation properties are seen as driving forces that provide opportunities in the market for phenolic foams [9] and are responsible for the growing interest of the scientific community in these foams [6].

The growth in market volume for phenolic foam insulation boards between 2024 and 2033 is shown in [9]. In 2024, the market size was USD 1.23 billion, and by 2033, the value is estimated to reach USD 2.45 billion, corresponding to a compound annual growth rate of 8% between 2024 and 2033. An increase in the number of publications, as evident in Figure 2, especially since 2005–2009, describing phenolic foams may be noted.

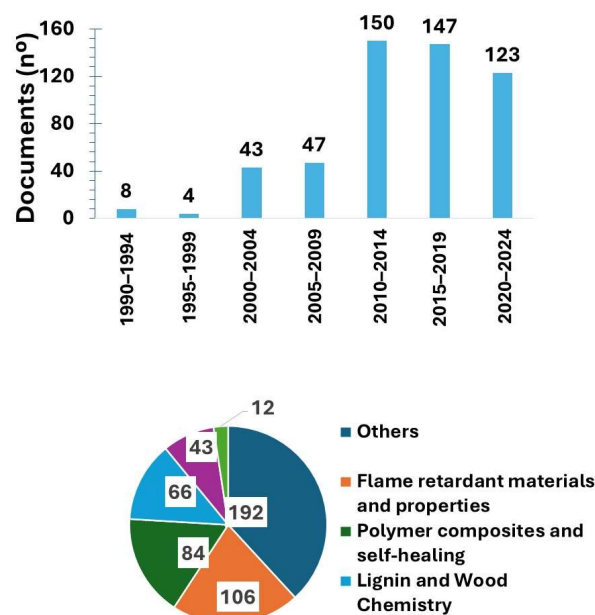


Figure 2. Evolution of the number of documents addressing phenolic foams and the main topics researched. The documents are those indexed in OpenAlex and published between 1990 and 2024 (see the Supplementary Material for more details).

However, the distribution of topics is very skewed; 62% of the documents reflect most aspects of these materials (Figure 2). Fire properties of phenolic foams have been most frequently assessed, with 21% of all documents addressing flame-retardant materials and properties. The use of bio-based materials has been noted, with 13% of all documents classified under the topic of lignin and wood chemistry, reinforcing the concern for sustainable alternatives.

Despite the interesting properties of phenolic foams, the expected increase in consumption, and the growing development, these foams display deficiencies. Most phenolic foams are made from petroleum-based raw materials, which is a major disadvantage due to environmental pollution, fluctuating prices of petrochemical products, and the depletion of petroleum resources. In addition, formaldehyde is widely used in the production of these foams as a key reactant with phenol to form the thermosetting resin that gives the foam its structure and properties. However, formaldehyde is known for its health and environmental risks [33–35].

The use of bio-based materials to fully or partially replace petroleum-based raw materials has been explored. Lignin, tannins, cardanol, and bio-oils, may be used to produce phenolic foams with interesting properties (e.g., [36–44]).

Because of the need for energy-efficient buildings, safe fire-resistant materials, and increasingly sustainable alternatives, an overview of the use of tannins as an alternative to

petroleum-based raw materials in the generation of phenolic foams is appropriate. Tannins are characterized by their low cost, wide availability, and high extraction quality [45,46]. Therefore, it is important to review current understanding and outline future directions.

The most recent dedicated work is by Pizzi (2019), which provides an extensive review of changes in formulations and production processes of tannin foams up to 2019 [47]. However, in the paper, the research or results aimed at addressing one of the major limitations of these foams is not addressed: their poor mechanical strength. The remaining documents [6,48,49] include brief sections on research related to these foams within broader review articles. Furthermore, none of these documents address LCA to quantify the sustainability of these foams. This article contributes to the literature on this topic by providing a comprehensive description of the research on this type of foam, covering different formulations, physicochemical, mechanical, and fire-resistance properties, as well as sustainability, and a description of the products on the market, thereby addressing limitations found in existing documents. The various formulations are discussed, highlighting the bio-based nature of the components and the effects that modifications have on key properties. LCA studies are also examined from a sustainability perspective, along with a mention of the main phenolic products on the market, to highlight possible practical applications of tannin foams as thermal insulation materials. An in-depth exploration of the mechanisms occurring in different formulations is beyond the scope of this article.

2. Tannin-Composed Foams: The Workflow

The first tannin-based foam was produced from a bio-based viscous liquid mixture containing tannin, formaldehyde, furfuryl alcohol (FA), a low-boiling blowing agent, and an acid catalyst. This formulation exhibits self-foaming behavior, where the controlled combination of chemical crosslinking and physical expansion leads to the formation of a rigid cellular structure [48] (Figure 3).

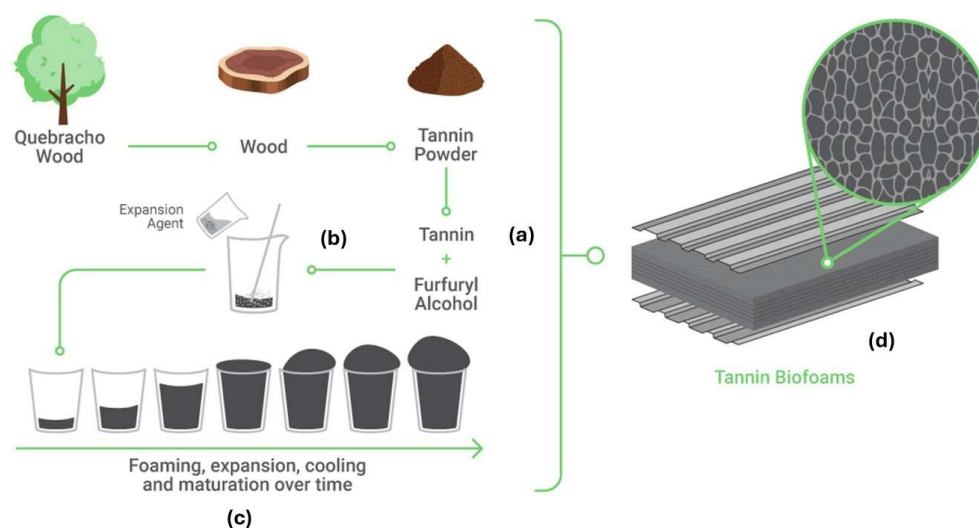


Figure 3. Schematic representation of the preparation process for tannin-based foams. (a) Initial mixture of components: quebracho tannins, FA, and formaldehyde. (b) Stirring with the addition of a foaming agent and p-TSA to promote foam expansion. (c) Time-lapse sequence showing formulation, expansion driven by foaming agent vaporization, cooling, and foam maturation, accompanied by heat generation from the exothermic reaction. (d) Tannin biofoam.

The expansion of the liquid mixture into a low-density foam occurs through two main mechanisms that act simultaneously: crosslinking of the polymer matrix and evaporation of the blowing agent. Crosslinking results from the polycondensation of tannins and

formaldehyde, as well as the self-condensation and copolymerization of FA with tannin in an acidic medium [46,50,51]. The high reactivity of tannins with aldehydes promotes the rapid formation of a three-dimensional network of polymer chains [50]. In parallel, the heat generated by the exothermic reactions of FA with tannin causes the blowing agent to boil [46,51]. This expansion phase creates bubbles within the fluid matrix, enabling the development of a porous structure. Simultaneous crosslinking ensures dimensional stabilization of the foam, preventing the collapse of the formed cells and promoting the final curing of the material [48,51]. Overall, balancing the thermal evolution of the reactions and the evaporation rate of the blowing agent is essential for producing a homogeneous, low-density foam with structural integrity.

2.1. Phenol–Formaldehyde (PF) Resin Formulation: Chemistry, Components, and Bio-Derived Innovations

Phenolic resins are thermosetting polymers formed by the polycondensation reaction between phenol and formaldehyde. The specific type of resin produced, either *resole* or *novolac*, depends on the molar ratio of formaldehyde to phenol (F/P) and the catalytic conditions (Table 2). The F/P ratio significantly affects the resin’s reactivity, crosslink density, viscosity, and final performance. A higher F/P ratio generally results in increased hydroxymethylation, which enhances the resin’s ability to form a dense and rigid network. However, excessive formaldehyde can also cause brittleness and increase the free formaldehyde content, raising health and environmental concerns [52].

Table 2. Key differences between resole-based and novolac-based phenolic resins.

Resin Type	F/P Molar Ratio	Catalyst Type	Curing Behavior	Properties	Applications
Resole	F/P > 1	Basic (e.g., NaOH)	Self-curing (heat or acid)	Fast curing, high crosslinking density, more brittle at high F content	Insulation foams, adhesives, laminates
Novolac	F/P < 1	Acidic (e.g., HCl)	Needs hardener (e.g., hexamine)	Thermoplastic before curing, stable storage, flexible pre-cure	Molding compounds, coatings, abrasives

2.1.1. Phenol Substitutes—A Tannin-Based Approach

Environmental and health concerns associated with conventional PF resins, particularly the toxicity of formaldehyde and the non-renewable origin of phenol, have prompted significant research into sustainable alternatives. Bio-based resins, derived from natural polyphenols and renewable aldehydes, offer a promising way to reduce dependence on petrochemical resources while maintaining desirable mechanical and thermal properties. Among these, tannins and lignin [53], FA, cardanol, and soy derivatives have emerged as natural precursors [54,55]. These biomolecules exhibit inherent reactivity toward crosslinking agents and contribute to the development of resins with tailored biodegradability, reduced emissions, and lower toxicity. Tannin-based resins have attracted considerable attention as sustainable alternatives to conventional PF systems due to their natural polyphenol structure and high reactivity with aldehydes [38,50,56]. They are widely distributed throughout the plant kingdom, occurring in leaves, fruits, bark, and especially in the wood of trees. These secondary metabolites play a crucial role in plant defense against parasitic organisms such as insects, fungi, and bacteria. Traditionally, tannins were used in the leather industry. However, their abundance, biodegradability, and ability to form rigid thermosetting networks make them ideal candidates for various applications, including

wood adhesives, metal coatings, pharmaceuticals, and, more recently, the production of bio-based materials such as thermal and acoustic insulation foams [49,57–59].

Tannins are categorized into two main types: condensed and hydrolysable tannins (Table 3), each with distinct chemical structures and reactivity profiles [47,48]. Condensed tannins, also known as proanthocyanidins, consist of flavonoid units, mainly *catechin*, *epicatechin*, and *proflisetinidin*, linked by carbon–carbon bonds. These structures are highly stable and resistant to hydrolysis. A high phenolic content and reactive hydroxyl groups make them suitable for adhesive and resin synthesis, particularly as substitutes for phenol in PF systems. Their structure is based on two aromatic rings: ring A, which can be of the resorcinol type (one OH group) or phloroglucinol type (two OH groups), and ring B, which can be of the catechol (two OH groups) or pyrogallol type (three OH groups) [36,46] (Figure 4). The reactive properties of tannins are strongly associated with the configuration of these rings. Common sources include *Acacia mearnsii* (mimosa), *Schinopsis balansae* (quebracho), *Pinus radiata* (pine bark), and *Larix decidua* (larch) [49] (Table 3). Extraction is usually performed on the bark or heartwood, with the material first crushed and extracted in hot water with sulfites. The resulting extract is then filtered and spray-dried, producing a fine brown powder rich in tannins [48]. These extracts are not pure compounds; in addition to the flavonoid units, they contain small amounts of unpolymerized precursors such as monoflavonoids, simple sugars (hexoses, pentoses, and disaccharides), hydrocolloid gums, hydrolyzed hemicellulose oligosaccharides, and trace amounts of amino acids [47].

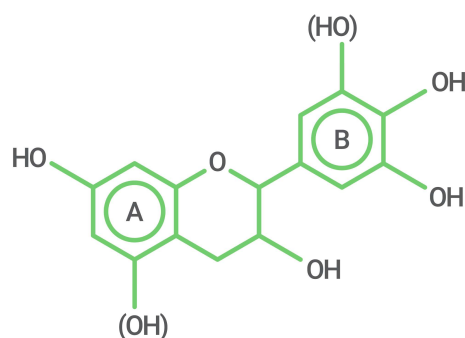


Figure 4. General chemical structure of flavonoid monomer. Adapted from ref. [47], Journal of Renewable Materials, 2019.

Hydrolysable tannins are esters of gallic acid (gallotannins) or ellagic acid (ellagitannins) with a central sugar molecule, typically glucose. Despite possessing antioxidant and antimicrobial properties, their lower chemical reactivity (Table 3) and structural fragility limit their use in thermosetting resins. However, studies have attempted to incorporate them as substitutes for synthetic phenols in PF resins or isocyanates in polyurethane (PUR) resins [48,60,61]. Typical sources include *Castanea sativa* (chestnut) and *Quercus* sp. (oak) (Table 3).

Distinctive structural characteristics of condensed and hydrolysable tannins enable targeted functionalization, making each class of tannin valuable for specific industrial applications (Table 3). Condensed tannins are generally preferred in industrial resin and foam production due to their higher chemical reactivity, superior thermal conductivity and compressive strength, and better compatibility with common crosslinkers such as formaldehyde or FA compared to hydrolysable tannins [61]. In contrast, hydrolysable tannins are more suitable for applications where biodegradability, antioxidant capacity, and bioactivity are desirable, particularly in sectors like biomedicine, packaging, and environmental technologies.

Table 3. The type of tannins, botanical origin, main components, reactivity, and industrial use according to the tannin source.

Tannin Source	Type	Botanical Origin	Main Components	Reactivity	Industrial Use	Key References
Mimosa	Condensed	<i>Acacia mearnsii</i>	Profisetinidin/ flavan-3-ols	High	Adhesives, foams; wood panels	[49,62]
Quebracho	Condensed	<i>Schinopsis balansae</i>	Profisetinidin derivatives	High	Leather tanning; adhesives	[49,63,64]
Pine bark	Condensed	<i>Pinus radiata</i> , others	Catechin/epica- techin units	Very High	Resin synthesis; composites	[56,65]
Larch	Condensed	<i>Larix decidua</i>	Taxifolin, flavonoids	Moderate	Less common in resin use	[66]
Chestnut	Hydrolysable	<i>Castanea sativa</i>	Gallic acid esters (ellagitannins)	Low	Leather, limited resin applications	[67–69]
Oak	Hydrolysable	<i>Quercus</i> sp.	Ellagitannins	Low	Aging of wine/spirits, not resin-use	[70,71]
Spruce	Condensed or mix	Industrial formulations	Mixed polyphenols	Tailored	Resin/foam applications	[72,73]

The main differences between foams produced with tannin-based resins and those with synthetic PF resins are highlighted below, based on studies that present and examine the formulations of both types of foams simultaneously. A cross-study comparison is not conducted, as the procedures and methods used for foam production and analysis of key characteristics are not always consistent across studies. These procedures may influence the properties of the final foams.

Using mimosa tannin to completely replace synthetic phenol produced foams with lower compressive strength and less smoke and odor than synthetic phenolic foams [74]. The partial substitution of synthetic phenol with (1) chestnut tannin showed that the cure reactions of these resins differ from those of non-modified *novolacs* in both kinetic values and final chemical structure [75], (2) hydrolysable tannins produced foams with higher thermal conductivity, improved mechanical properties, and greater water resistance than pure phenolic foams [60], and (3) larch tannins resulted in foams with lower apparent density and compressive strength and higher thermal conductivity, water resistance, and LOI values than synthetic phenolic foams [76].

Mimosa tannin foams have a lower density than quebracho tannin foams, as well as higher water absorption, compression strength, and auto-extinguishing time [36]. In another study, the opposite result was observed for density and compression strength, although the values for the two foams are similar [77]. For low values of apparent density, mimosa tannin foams have lower thermal conductivity than quebracho tannin foams [77]. Also, mimosa tannin foams have a higher total heat release than quebracho tannin foams [51]. When comparing mimosa tannin with pine tannin foams, the former have higher thermal conductivity, and at low densities, their compressive strength is higher [37,77]. For high densities, the behavior concerning compressive strength is the opposite.

2.1.2. Formaldehyde Substitutes

Formaldehyde, a raw material used in the production of PF resins (Table 2), acts as a crosslinking agent. The condensation polymerization reaction involves the addition of

formaldehyde to phenol at specific sites (ortho and para positions) on the benzene ring, followed by the formation of methylene or ether bridges between phenol molecules. The reaction is typically catalyzed by either an acid or a base (Table 2). However, there are several limitations concerning the use of formaldehyde: (1) it is mainly obtained from petroleum resources, and therefore it is not a sustainable alternative; (2) it presents a risk to health during manufacture and end use (e.g., [33,35]); and (3) it is harmful to the environment [34]. These concerns led to research aimed at safer alternatives. Previous studies on tannin-based formulations have proposed the elimination of aldehydes entirely, which is counterbalanced by an increase in FA [37,51,75,76,78]; the use of bio-based options such as glyoxal, furfural, vanillin, soybean protein isolate, cellulose nanofibrils, and humins [38,79–87]; the use of glutaraldehyde [38,88]; the use of hexamine [89,90]; and a steam-driven foaming process [91].

The studies addressing tannin-based foams with and without formaldehyde (the absence of formaldehyde compensated with FA) showed that (1) the bulk or apparent density of foams with formaldehyde is higher than that without it [37,51,76], (2) the total heat release and the heat release capacity of foams with formaldehyde are lower than those without it [51], (3) the thermal conductivity of foams with formaldehyde is higher than that without it [51,75], and (4) the elastic behavior of foams with formaldehyde is lower than that without it [37,78,92].

Glyoxal as a substitute for formaldehyde resulted in (1) slower hardening than with formaldehyde, and (2) the thermal conductivity and compressive strength are similar to those observed in foams with formaldehyde [38].

The partial substitution of formaldehyde by furfural reduced the content of free formaldehyde and improved thermal stability [86]. The complete substitution of formaldehyde with furfural and vanillin produced interesting results; however, benchmarking is limited, as it does not provide a comparable formulation of a tannin-based foam with formaldehyde [87]. For the same formulation, those with vanillin showed lower apparent density, compressive strength, and thermal conductivity, and higher pulverization ratio and porosity than foams with furfural. Compared with other formulations of tannin-based foams with formaldehyde in the literature, foams with vanillin have lower thermal conductivity, while foams with furfural have higher thermal conductivity. Both foams, with vanillin and furfural, have higher densities.

The use of soybean protein isolate as a crosslinking agent produced foams with higher density, lower pulverization ratio, higher specific compressive strength, greater flame retardancy, and reduced smoke generation compared to foams with formaldehyde [82].

Cellulose nanofibrils as a substitute for formaldehyde enabled the production of foams with lower density and higher compressive strength than those made with formaldehyde, as well as improved heat and flame resistance [80].

The preparation of tannin–furanic foams with FA and humins showed that humins react well with condensed tannins; however, they react more slowly than FA. The stress–strain study of the different foams revealed higher compressive strength for both the foam with the lowest and the highest proportion of humins, indicating that dominant proportions of either FA or humins were responsible for this effect [81].

Glutaraldehyde in pine-tannin-based foams is not suitable as a crosslinking agent due to its lower reactivity with pine tannin [38]. However, glutaraldehyde combined with quebracho tannin allows for foams for horticultural/hydroponics and floral applications [88]. These foams have comparable or superior performance to commercial phenolic foams used as a reference (benchmarking using a similar formulation for foams obtained with formaldehyde is not provided in this study).

The slower reaction rate between tannin and hexamine, compared to conventional tannin–furfuryl alcohol polymerization, implies a different strategy for generating the porous structure. In this approach, foam formation does not result from the evaporation of a blowing agent but from the mechanical incorporation of air into the tannin–hexamine resin through intensive agitation. To ensure that the foam structure remains stable during the time required for the polymer network to fully cure, surfactants are added, playing an essential role in stabilizing the dispersed gas phase. Foams obtained using this method exhibit mechanical properties of the same order of magnitude as conventional tannin-based foams, whose expansion is promoted by controlled solvent volatilization [89].

Tannin-based foams prepared without blowing and crosslinking agents, using steam-driven foaming, resulted in larger cell size, thicker cell walls, lower apparent density, lower pulverization ratio, lower thermal conductivity, lower compressive strength, and greater flame resistance than foams with formaldehyde, highlighting a novel foaming strategy [91].

In summary, recent research on replacing formaldehyde [80–82,91] shows that bio-based components and water vapor can serve as the sole agents to produce the resin. The resulting foams have desirable properties, including low density, higher compressive strength, and improved heat and flame retardance compared to tannin-based foams with formaldehyde.

2.2. Furfuryl Alcohol

FA is a bio-based compound with high potential in tannin–phenolic foam formulations, due to its dual role as a reactive agent and a heat source for foaming. FA can be produced industrially by the catalytic reduction of furfural, which is derived from the hydrolysis of C5 sugars found in hemicelluloses from lignocellulosic residues [36,48]. In phenolic foams, FA reacts with phenolic groups of tannins (Figure S1) and self-polymerizes (Figure 5) in exothermic reactions. The heat released by these reactions is sufficient to vaporize the physical foaming agent present in the formulation, promoting the cellular expansion of the foam. Simultaneously, the FA contributes to the crosslinking of the polymer matrix, reinforcing the three-dimensional structure of the foam [48,50]. Additionally, FA reacts with formaldehyde to form highly reactive intermediates (Figure 5). These compounds help extend the polymer network, improving the thermal and mechanical properties of the final material [48].

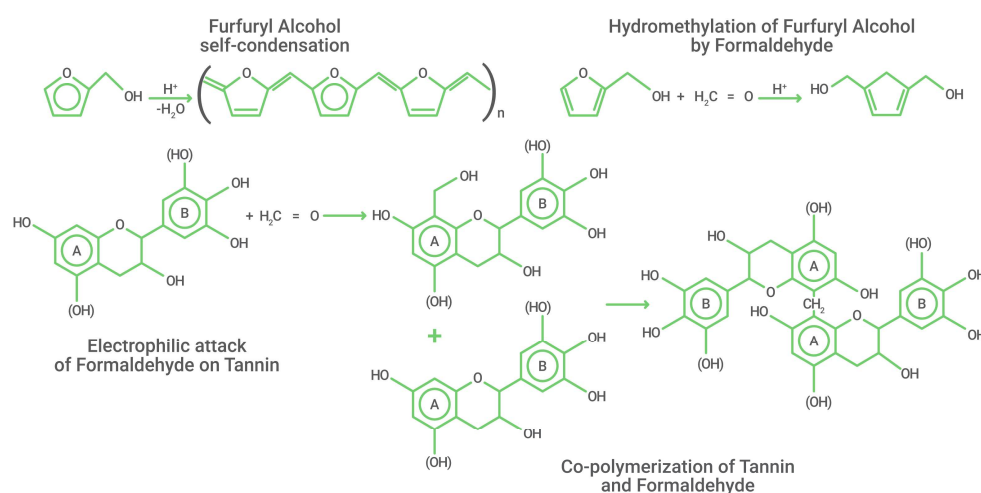


Figure 5. Reaction schemes illustrating all the possible reactions that occur between the mixture of furfuryl alcohol, formaldehyde, and tannins. Adapted from ref. [47], Journal of Renewable Materials, 2019.

2.3. Blowing Agent

The blowing agent is essential to the cellular structure of tannin-based phenolic foams. It acts as a low-boiling volatile solvent that vaporizes in coordination with exothermic polymerization reactions, ensuring that foaming and curing occur simultaneously and enabling controlled volumetric expansion of the resin [36]. The final cell morphology depends strongly on the choice of blowing agent and the kinetic control of the curing reaction. High internal gas pressures or accelerated reaction rates tend to cause cell wall rupture, resulting in open-cell foams with high permeability. Conversely, more moderate pressures and slower polymerization rates favor the formation of closed cells, in which the gas remains trapped, providing better thermal insulation properties [93]. Therefore, careful selection of the blowing agent and proper balance between blowing and curing parameters are crucial for obtaining tannin-based foams with optimized structural and functional properties.

The first formulations of tannin-based foams used diethyl ether (DE) as the blowing agent [74], due to its low boiling point (34 °C) and chemical inertness relative to the other components in the system [48]. However, the need to use less harmful substances led to the exploration of others, such as pentane (e.g., [37,88,94]), which is also applied in synthetic phenolic foams [95]. A greener and more sustainable alternative has been explored: tannin-based foams without blowing agents [78]. More recently, petroleum ether was also applied as a blowing agent [96]. The reader is invited to look at Table 4 for examples of studies using distinct blowing agents in tannin-based foams.

Foams obtained with DE have the lowest density, ranging from 30 to 80 kg/m³, while those with pentane have the highest density, ranging from 120 to 180 kg/m³. Foams made from a mixture of DE and pentane have densities ranging from 80 to 120 kg/m³ [94]. At the same relative density, the thermal conductivity of DE foams is slightly higher than that of pentane, and the compressive strength does not vary significantly among foams [94]. Foams produced with petroleum ether showed higher bulk density and compressive strength (for similar densities) and lower porosity, orthotropicity, and thermal conductivity than those with DE [96]. In the case of DE, increasing the concentration lowered the apparent density of the foams [97]. The production of foams without a blowing agent resulted in foams with a higher density than those with a blowing agent, lower thermal conductivity, and greater compressive strength [78].

As an alternative to conventional blowing agents, it was shown that water can act as a pseudo-blowing agent, promoting the formation of phenolic foams with comparable thermal properties, albeit with less structural uniformity [94,98]. In this case, expansion occurs through the vaporization of wastewater, requiring strict management of the system's heat balance to ensure reaction kinetics compatible with the formation of a stable porous structure. Sufficient heat generation to promote this expansion can be achieved by various strategies: (i) increasing the concentration of acid catalysts or FA, as well as reducing the water content in the formulation; (ii) applying heat from external sources; or (iii) partially or completely replacing formaldehyde with other aldehydes or crosslinking agents of equivalent reactivity. Producing foams with higher proportions of catalyst or FA, or with less water, not only achieves thermal conductivity equivalent to foams expanded by volatile solvents but also contributes to greater mechanical stability, a direct result of the increased density of the polymer matrix. As external heat sources, air circulation ovens, heat presses, microwaves, or infrared emitters can be used, with hot presses being particularly relevant in industrial processes, as they allow the continuous production of sandwich panels incorporating a central layer of rigid tannin–furan foam [89].

2.4. Catalyst

In the production of tannin-based foams, selecting and controlling the catalyst are crucial steps to ensure efficient polymerization under appropriate pH conditions. In this context, two main approaches stand out: the use of acidic catalysts, which is widely practiced, and the use of alkaline catalysts, which is less common [48]. The most widely used method is based on the acid condensation between tannins and formaldehyde, a reaction favored by the addition of strong organic acids such as para-toluenesulfonic acid (e.g., [37,99]) and phenol sulfonic acid [88]. These catalysts enhance the formation of methylene bonds and methylene ethers, which are essential for the resin's three-dimensional structure. Among the organic catalysts, benzenesulfonic acid and xylenesulfonic acid also stand out [93], usually in phenolic petroleum-based formulations.

In addition to organic catalysts, several inorganic acids—namely hydrochloric acid, phosphoric acid, sulfuric acid, and nitric acid (Table 4)—are used as curing agents and also provide high efficiency in promoting the crosslinking reaction [89].

In formulations based on alkaline conditions, sodium hydroxide is commonly added to the initial resin. Although this approach is less common overall, it allows modulation of the condensation mechanism for urea–formaldehyde resins or even hybrid systems involving isocyanates, expanding the application possibilities [48].

The curing catalyst plays a decisive role in foaming kinetics by regulating the resin's hardening rate. This is crucial for stabilizing the cellular structure and affects the average pore size, distribution, apparent density, mechanical strength, and overall porosity of the foam. Bio-based phenolic systems, such as tannin-based foams, have lower reactivity than conventional synthetic resins. Therefore, a higher catalyst dosage is often required to prevent the formation of excessively large pores and to ensure a sufficiently cross-linked polymer network. Insufficient catalyst dosage compromises structural integrity, resulting in foams with lower strength and poor performance [93].

The choice of catalyst type, as well as its concentration, directly influences critical properties such as hydrophilicity, thermal stability, and mechanical performance of the foams [93]. Thus, catalyst optimization—whether in its nature, concentration, or mode of addition—remains a critical parameter for developing tannin-based foams with properties competitive with their petrochemical counterparts.

Lastly, a constant concern with the use of an acid catalyst is the need to neutralize the residual acidity [6,88]. Dolomite, calcium carbonate, calcium hydroxide, and vermiculite have been used to eliminate residual acidity in foams for horticultural, hydroponic, and floral applications. The resulting foams are not phytotoxic and are suitable for preserving fresh cut flowers. The results showed performance comparable to or better than commercial synthetic phenolic floral foam used as a control [88]. The same subject is addressed in the patent application US20070232785A1 [100].

More recently, the use of nitric acid as a catalyst has enabled the production of foams with physical properties similar to standard tannin-based foams, demonstrating that it is possible to obtain materials using sulfur-free catalysts, whose presence has previously discouraged the upscaling of this type of foam [96].

2.5. Additives: Surfactants

The development of tannin-based foams has benefited significantly from the incorporation of additives, which has expanded the range of applications for these materials by enabling controlled modification of their physicochemical properties. These additives can be grouped into various categories according to their function in foam formulation. This section is limited to the use of surfactants.

To optimize the cellular structure and reduce the foam's apparent density, the formulation may include surfactants. These additives play a key role in reducing the surface tension between the polymer matrix—often composed of tannin, formaldehyde, and FA—and the blowing agent, promoting a more homogeneous mixture and efficient bubble formation during the expansion phase [56]. In short, the surfactant ensures that tannin foams are easy to generate, stable long enough to cure, and have a uniform cellular structure. A wide range of synthetic, semi-synthetic, and bio-based surfactants have been explored (e.g., DC-193, Triton X100, Tween 80, and castor oil ethoxylate).

Among sodium dodecyl sulfate (anionic, SDS), Triton X-100 (non-ionic), Tween 80, Brij 35 (non-ionic), and Pluronic F127 (non-ionic), only SDS and Tween 80 produced acceptable foams for further characterization. Subsequent analysis showed that the presence of SDS results in foams with lower bulk density, porosity, and compressive strength than foams with Tween 80 [101].

In foams with castor oil ethoxylate, internal temperature, pressure, and induction time decreased, while expansion time increased compared to tannin-based foams without surfactants. Additionally, higher surfactant dosages resulted in lower densities [56]. As for Tween 80, it has been shown that the higher the dosage, the lower the density [102]. Regarding fire properties, it has been shown that foams with surfactants have a higher heat release rate and a shorter ignition time than tannin-based foams without these additives [51].

Table 4. Resin formulations, additives, and end use in tannin-based foams.

Resin	Crosslinking Agent	Blowing Agent	Catalyst	Additives	End Use	Ref.
Quebracho-tannin-based (AF-Tannin)	Glutaraldehyde	Pentane	Phenol sulfonic acid	Ethylene glycol, sodium laureth sulfate, dolomite, vermiculite, Tween 80	Hydroponics	[88]
Mimosa/quebracho/pine-tannin-based (AF-Tannin)	Formaldehyde	DE	p-toluenesulfonic acid	PUR adhesive, Triton X100e	Thermal insulation	[36]
Pine/mimosa-tannin-based (AF-Tannin)	With and without formaldehyde	DE and pentane	p-toluenesulfonic acid	Polyethylene glycol	Thermal insulation	[37]
Tannin-based (AF-Tannin)	Formaldehyde		p-toluenesulfonic acid	Tween 80	Thermal insulation	[99]
Prorobinetinidin/profisetinidin type tannins-based (AF-Tannin)	With and without formaldehyde	With and without DE	p-toluenesulfonic acid	Polyethylene glycol, 4,4-diphenylmethane diisocyanate (pMDI)	Thermal insulation	[78]
Mimosa/quebracho/chestnut-based	Not specified	Water	Sulfuric acid	Tween 80, diethylene glycol	Thermal insulation	[61]
Tannin- and lignin-based (AF-Tannin)	Hexamine, glyoxal	Mechanical foaming	Nitric acid	Tween 80	Heavy metal adsorption	[90]
Mimosa-tannin-based (AF-Tannin)	-	DE, propanol	Sulfuric acid	Not specified	Lightweight panels	[103]
Mimosa/quebracho-tannin-based (AF-Tannin)	Formaldehyde and hexamine	DE, mechanical foaming	p-toluenesulfonic acid, Phenol sulfonic acid	Polyethylene glycol, SM2101-1, Tween 80, Pluronic PE 7400, Triton X-100, Cremophor ELP	Thermal insulators	[51]
Mimosa-tannin-based (AF-Tannin)	Formaldehyde	DE, pentane	p-toluenesulfonic acid		Not specified	[94]
Pine-tannin-based (AF-Tannin)	Glyoxal, glutaraldehyde	DE	p-toluenesulfonic acid	Polyethylene glycol	Thermal insulation	[38]

Table 4. Cont.

Resin	Crosslinking Agent	Blowing Agent	Catalyst	Additives	End Use	Ref.
Phenol- and chestnut-tannin-based	Formaldehyde	Pentane, 4,4'-diphenylmethane diisocyanate (pMDI)	65% solution of phenol sulfonic acid in ethylene glycol, 65% solution of phenol sulfonic acid in water, 65% solution of phenol sulfonic/sulfuric acids [50/50] in ethylene glycol	Cremophor ELP, DC 193	Not specified	[60]
Wood bark (AF-Tannin)	Formaldehyde	-	p-toluenesulfonic acid	Tween 80	Thermal Insulation	[99]
Quebracho wood (AF-Tannin)	Formaldehyde	DE	p-toluenesulfonic acid	Tween 80, wood cellulosic fiber	Not specified	[104]
Mimosa (AF-Tannin)	-	DE	p-toluenesulfonic acid	Boric acid, phosphoric acid, montmorillonite, soybean protean isolate	Thermal Insulation	[105]
Larch-tannin-based phenolic resin	Formaldehyde	Petroleum ether	p-toluenesulfonic acid	Phosphoric acid, hydrochloric acid, Tween 80, cork powder	Not specified	[76]
Mimosa (AF-Tannin)	-	DE, pentane, and petroleum ether	Sulfuric acid and nitric acid	Tween 80	Not specified	[96]

3. Mechanical, Fire, and Thermal Performance

When comparing synthetic phenolic foams with tannin-based foams (both produced with similar formulations and processes), synthetic foams have a wider range of densities and a higher compressive strength [74,76]. Tannin-based foams have slightly higher thermal conductivity [76], and they also exhibit significantly higher fire resistance compared to synthetic phenolic foams, even without the addition of flame retardants, since the energy required to initiate combustion corresponds to severe conditions [51,74]. As outlined in the preceding sections, the mechanical performance and fire behavior of tannin-based foams are influenced by the nature and proportion of their constituents (type and source of tannin, crosslinking agents, catalysts, and surfactants). Each component serves a distinct function within the formulation, directly or indirectly shaping the resulting properties. In Table 5, the physicochemical properties and mechanical performance of foams obtained in several studies are shown.

This section examines studies focused on the purposeful modification of the mechanical and fire-resistance characteristics of these foams through the incorporation of targeted additives. The mechanical performance of tannin foams can be influenced by a wide range of additives. The relationship between density and compressive strength in foams is described by the Gibson–Ashby model (e.g., [38]). For example, additives designed to achieve a uniform cellular structure, such as surfactants, produce foams with a density correlated to their compressive strength. Additives that intercalate within the tannin chains, such as plasticizers, increase the elasticity of the foams and improve the compressive strength when added in the correct proportion (excess plasticizer has the opposite effect). Finally, incorporating reinforcements, such as fillers, allows for a more uniform distribution of stress, enhancing mechanical performance.

Plasticizers primarily function is to increase the elasticity of naturally rigid foams. Glycerol and PEG400 have been widely used (Table 4). Glycerol facilitates the relative sliding of macromolecular chains, increasing the flexibility of the polymer network and promoting more elastic mechanical behavior. The use of glycerol resulted in more flexible foams and, therefore, a broader range of final applications [106]. However, compared to standard tannin foams, they have higher density (0.073 versus 0.053 g/cm³) and higher thermal conductivity (0.061 versus 0.044 W/m·K). The PEG400 made the foams more elastic than those without PEG400 (about 0.5 versus 0.6 MPa). As the dosage of PEG400 increases, both the elastic modulus and shrinkage increase [56]. There is also an increase in gel time and curing time. For foams with and without PEG400, those containing PEG400 have higher density and lower thermal conductivity (0.043 versus 0.049 W/mK) [56,78].

Nanotubes [97], nanofibers [107], cork [76], wood flour [104], and poplar wood fibers have been explored as fillers [87].

The addition of multiwall carbon nanotubes (CNTs) to tannin-based foams resulted in foams with higher compressive strength [97]. For 0.37% CNTs (0.20 g of CNTs), this variable increased by about 32% compared to standard foams. However, there is a limit, as foams with a higher proportion of CNTs cannot be produced due to the significant increase in viscosity (>0.20 g of CNTs).

By utilizing the dispersibility of nano-sized cellulose fiber slurry in hydrophilic tannin-furanic resin, it has been shown that foams containing cellulose nanofibers (CNFs) have a higher density than standard tannin-based foams [107]. The compressive strength (approximately 250 kPa and 90 kPa for foams containing cellulose nanofibers and standard tannin-based foams, respectively) is also higher, including the specific strength, based on which it was concluded that the improved performance is due to both increased density and reinforcement in the cell wall and strut. The increase in thermal conductivity (from 0.045 to 0.049 W/mK for the standard tannin foam and CNF foam, respectively) is considered

insignificant by the authors. Regarding flammability, the LOI was about 32% for foams with and without CNFs.

In preparing larch-tannin-based foams with cork, it was found that these foams exhibit excellent cell morphology and high compressive strength. Compared to larch-tannin-based foams without cork, the compressive strength and modulus of the reinforced foams increased by 14.84% (93.63 kPa) and 16.18% (2216 kPa), respectively. Improved performance is due to the smaller cell size and higher cell density compared to unreinforced tannin-based foams [76]. Foams containing cork have lower thermal conductivity than those without cork (0.0294 and 0.0325 W/mK, respectively). However, when more than 1 wt.% cork powder was added, thermal conductivity increased further with additional cork (0.0415 W/mK). The LOI values of foams with cork decreased slightly but still maintained excellent flame retardancy (about 45%).

In foams with wood cellulosic fiber, cell size decreases and cell density increases. Mechanically, the reinforced foams have higher compressive strength than the unreinforced foams. The maximum value observed was 1.22 MPa, which is 2.39 times higher than that of the unreinforced foams. The compressive modulus is also higher, at 5.54 times that of the unreinforced foams [104]. All foams exhibited excellent flame retardancy, as the LOI values were higher than 27%. Although the reinforced foam had a higher LOI than the unreinforced foam (42.5% versus 41.3%), the results also indicate that for wood cellulosic fiber contents above 2 wt%, the LOI is lower than that of the unreinforced foam. Regarding thermal conductivity, the results are similar for both reinforced and unreinforced foams.

Tannin-based foams reinforced with poplar wood fiber had a 33–63% lower pulverization ratio and a 50–65% higher specific compressive strength [87]. The inclusion of poplar wood fiber resulted in foams with a peak heat release rate 5–12.7% lower than that of unreinforced foams.

The addition of bio-based fillers produces foams with enhanced mechanical properties. However, the improvements do not increase linearly with the amount of filler added. Generally, performance improves up to a certain point, after which it declines. These fillers slightly reduce fire resistance, but the foams remain highly attractive in this area.

When studying the flammability of standard tannin-based foams and tannin-based foams with additives such as boric acid and phosphoric acid, no significant difference was observed in fire retardance among foams [46]. A very low heat release rate (12 kW/m²) has been recorded, as well as a high time to ignition for heat fluxes (below 50 kW/m²) compared to most polymers. In another study, adding boric and phosphoric acids to tannin-based foams showed synergistic effects. Partially replacing para-toluenesulfonic acid with phosphoric acid significantly improved ignition resistance and extended self-extinguishing time, while adding boric acid reduced crack formation under prolonged flame exposure [50].

Regarding the presence of plasticizers and, more importantly, the initial water content in the foam formulation, it has been shown that tannin-based foams with plasticizers have a higher heat release rate and a shorter ignition time than tannin-based foams without such an additive [51]. Additionally, increased water content causes greater weakening of the polymeric structure as water evaporates, thereby facilitating the thermal degradation of foams when exposed to fire.

The range of thermal conductivity values is broad (Table 5). Changes in formulations—such as eliminating or substituting formaldehyde and blowing agents or introducing surfactants and fillers—cause variations in this property. However, it is impossible to generalize these changes, as described below.

Table 5. Physicochemical properties and mechanical performance of different tannin-based foams.

Foam: Tannin Type	Density (kg/m ³)	Compressive Strength (MPa)	Thermal Conductivity (W·m ⁻¹ ·K ⁻¹)	Compression Resistance (MPa)	Auto- Extinguish Time (s)	LOI (%)	Ref.
Mimosa	30–80	0.21	0.037	-	-	-	[94]
Pine	35–70	0.028–0.058	0.076–0.037	-	-	-	[37,38]
Pine	50	0.08	0.0388	-	-	-	[38]
Commercial tannin	90–115	0.17–0.28	0.073–0.086	-	-	-	[60]
Larch	36–38	0.07–0.81	0.032–0.043	-	-	45	[36,76]
Mimosa	50–120	-	-	0.14–0.66	40–200	-	[36]
Mimosa	136–306	-	-	1.04–3.97	0–382	-	[50]
Mimosa	140–200		0.044–0.055	0.15–0.5	-	45	[76,108]
Mimosa	150–260	-	-	0.15–0.57	-	-	[50,109]
Chestnut	310–350	-	-	0.32–0.91	275–345	-	[108,110]
Tannin acid	50–290	-	-	0.1–0.55	-	-	[109,111]
Quebracho	90	-	-	0.24	-	-	[77,110]
Wood bark	78	0.183	0.0239			24.51	[99]
Quebracho wood	70–150	0.167–0.640	0.0366–0.0445	0.17–1.03		42.5	[104]
Commercial mimosa (<i>Acacia mearnsii</i>)	48–70		0.046–0.049	-		32	[107]
Commercial mimosa condensed tannin extract (<i>Acacia mearnsii</i>)	82–122	0.2–0.35	0.026–0.064	-		37.33–49.05	[105]
Mimosa	62.3–83.8	0.03–0.24	0.033–0.041				[96]

Adding fillers to improve mechanical properties resulted in foams with a thermal conductivity that was higher [110], lower [76], or similar [111] to foams without these fillers. Adding a surfactant, SDS, produced foams with higher thermal conductivity compared to classical tannin-based foams. Eliminating both the blowing agent and formaldehyde resulted in foams with lower thermal conductivity compared to those containing formaldehyde and DE [78]. Changing the catalyst to nitric acid produced foams with lower thermal conductivity than classical tannin-based foams [100]. Foams in which DE was replaced by petroleum ether and pentane exhibited lower thermal conductivity [100].

4. Phenolic Foam Market Applications

The physicochemical properties of final phenolic systems, including cell size distribution, open or closed cell ratio, density, mechanical integrity, and friability, depend intrinsically on the formulation (such as resin type, surfactants, blowing agents, and fillers) and the foaming process used (batch, continuous, or semi-continuous methods). These

processing parameters determine the morphology and functional performance of the material in target environments. This structural flexibility allows the design of foam systems tailored for specific applications, such as thermal and acoustic insulation, structural reinforcement, liquid absorption, and fire protection. As a result, phenolic foams are used in various sectors, including construction, transportation, floriculture, and medical support devices [112].

Currently, tannin-based insulation materials are not available on the market due to challenges in the production process (foaming control, viscosity and curing process, and moisture sensitivity). However, the review presented in this paper shows that when tannins are used as an alternative to fossil-fuel-derived (synthetic) phenolic compounds, tannin-based foams outperform synthetic phenolic foams in parameters such as water resistance and fire resistance (smoke and odor release and LOI values).

Given the attractiveness of these results and the current unavailability of tannin-based insulation materials on the market, this section presents some of the phenolic foams used in walls, roofs, and floors, highlighting parameters such as thermal conductivity, sustainability, and mechanical performance, among others, to identify potential market opportunities.

Wall insulation:

Several manufacturers now offer commercial solutions, each introducing specific innovations.

Kingspan Group, through the Kooltherm line, provides rigid phenolic foam boards with high compressive strength and aluminum foil facings that improve vapor resistance and long-term thermal stability [113]. In these products, thermal conductivities are in the range of 0.019–0.022 W/m·K, compressive strength values around 100 kPa, and fire performance ratings ranging from A2-s1, d0 (Kooltherm K112) to C-s2, d0 (e.g., Kooltherm K5). Additionally, some of the products are manufactured with a blowing agent that has zero ozone depletion potential and low global warming potential [114].

Asahi Kasei has introduced ultrathin phenolic boards suitable for modern architectural systems with a thermal conductivity of 0.020 W/(m K) free of CFC [115].

Xiamen UNT Duct Technology markets fiber-reinforced phenolic foams tailored for wall insulation in HVAC and building envelopes, prioritizing fire safety and minimal smoke emission [116].

Unilin Insulation has developed the Safe-R line of phenolic foams, which includes several products for walls [117]. These insulations are faced with low-emissivity materials on both sides and have a λ value as low as 0.020 W/m·K. Regarding fire performance, ratings ranging from B-s1, d0 (e.g., SR/TB-MF) to D-s1, d0 (e.g., SR/FB) are available. Compressive strength values of 100 kPa are reported.

Roof insulation:

Phenolic foams can also be used beneath roof structures, where their thermal insulation capacity helps reduce energy consumption and improve indoor comfort in both cold and warm climates.

Companies such as Kingspan Group have become market leaders, particularly with products like Kooltherm K107, designed for pitched roofs. This solution offers high insulation performance with significantly reduced thickness, which is especially beneficial in energy-efficient retrofits and buildings with space constraints [118]. Kooltherm K107 has a thermal conductivity of 0.019 W/(m·K) and a compressive strength of 100 kPa.

In Unilin Insulation's Safe-R range of phenolic foams, the SR/PR option is available for pitched roofs, featuring composite foil facing with a thermal conductivity between 0.020 and 0.021 W/m·K, a compressive strength of 100 kPa, and a fire performance rating of C-s1, d0 [119]. The manufacturer highlights as advantages reduced thermal bridging and risk

of condensation, as well as the low emissivity of the aluminum facing, which improves thermal performance.

Flooring systems:

Phenolic foams also find applications in floors. Leading solutions include Kingspan's Kooltherm K103 floorboard, which offers a thermal conductivity as low as 0.019 W/m·K, a compressive strength of 120 kPa, C-s2,d0 fire classification, and high vapor resistance for use under concrete or timber floors [120]. The SR/UF product, from Unilin Insulation, is another widely used phenolic underfloor board, with a thermal conductivity between 0.020 and 0.021 W/mK, a D-s1,d0 fire rating, a compressive strength of 100 kPa, and aluminum foil facings for moisture control [121].

Despite these advancements, several technical challenges remain unresolved and present opportunities for future development. First, phenolic foams are inherently brittle, especially in thin cross-sections, which limits impact resistance during installation and necessitates reinforced facings. Second, although the core foam resists water uptake, moisture ingress at cut edges and panel joints can degrade performance over time. Third, most products still rely on petrochemical-based phenol and formaldehyde, raising concerns about sustainability and indoor air quality. Fourth, phenolic foams still have a higher cost per square meter compared to PIR or mineral wool, which restricts their widespread adoption in budget-sensitive projects. Despite these unresolved challenges, the European Phenolic Foam Association, of which Kingspan Group and Unilin Insulation are members, highlights the low thermal conductivity of this type of material, the excellent strength at high density values, the very low flame spread with negligible smoke emission, and the possibility of achieving the Euroclass Bs1, d0 rating in an appropriate form [122].

5. Life Cycle Assessment of Tannin-Based Foams

This section covers works, including LCA studies, which, despite not explicitly including tannin-based phenolic foams, provide a robust benchmark for evaluating the potential environmental positioning of these emerging materials. Although LCA studies specifically focused on tannin-based foams are limited, existing research provides relevant information through LCAs of insulating foam materials and tannin extraction processes reported in the literature. Together, these studies contribute to understanding the environmental performance of tannin-derived systems compared with conventional fossil-based alternatives.

The substitution of petrochemical phenol with tannin-based extracts is generally associated with a reduction in fossil resource depletion and, in many cases, a lower global warming potential (GWP). These benefits are primarily attributed to the renewable nature of tannins and the presence of biogenic carbon in plant-derived feedstocks [71]. However, the environmental performance of tannin-based foams is strongly dependent on the extraction and processing routes used to obtain tannins, including solvent use, water demand, energy intensity, and geographical origin of the biomass [123].

A major limitation in current LCA studies of tannin-based materials is the lack of dedicated life cycle inventory (LCI) datasets for tannins. As a result, most assessments rely on proxy datasets such as wood extractives or generic biomass-derived chemicals. While this is acceptable in a review context, it introduces uncertainty and underscores the need for primary, process-specific inventory data [93]. Dedicated LCA studies on tannin extraction have provided important insights into upstream environmental hotspots. Assessments of hot water extraction of tannins from spruce bark have shown that evaporation is a dominant contributor to environmental impacts due to its high energy demand. Multi-extraction batch processes have particularly low environmental performance, whereas strategies to reduce water use—such as flow-through extraction systems—or to replace evaporation with ultrafiltration show potential for significant improvements. These findings underline

that the environmental benefits of tannin-based foams cannot be evaluated independently of extraction and purification strategies [124].

Beyond the phenol source, formaldehyde remains a critical contributor to human toxicity impacts in conventional phenolic systems and a major driver for regulatory pressure, particularly in indoor construction products. Tannin–phenolic foams containing formaldehyde may show reduced fossil-based impacts compared to fully petrochemical phenolic foams; however, toxicity-related indicators often remain comparable due to the continued presence of formaldehyde. Formaldehyde-free systems, including self-condensed tannin networks or alternative crosslinkers, offer clear advantages in human-health-related impact categories, although the energy intensity of alternative aldehyde production may partially offset climate-related benefits depending on system boundaries [123].

Insights from cradle-to-grave LCA studies on phenolic resin components produced at an industrial scale further support these trends. For example, recent assessments of phenolic resin knobs for household appliances demonstrated that resin production, energy consumption during processing, and end-of-life assumptions dominate environmental impacts. The substitution of virgin phenolic resin with recycled material fractions significantly reduced fossil resource use and climate change impacts, highlighting the relevance of circularity strategies for phenolic-based materials, including foams [124].

A broader comparative perspective is provided by LCA studies evaluating multiple insulation materials using midpoint indicators such as climate change, ozone depletion potential (ODP), primary energy demand, and water scarcity. In terms of climate change, polymer-based foams generally exhibit the highest impacts. Polystyrene foam slabs show the greatest GWP, with values around 4.2 kg CO₂ equivalent per kilogram, followed by urea–formaldehyde foam slabs (≈ 3.8 kg CO₂ eq) and glass wool mats (≈ 3.5 kg CO₂ eq). Foam glass exhibits intermediate values (≈ 2.5 kg CO₂ eq), while stone wool consistently presents the lowest climate change impact among insulation materials, at approximately 2.0 kg CO₂ eq per kilogram. These differences are largely attributed to the petrochemical origin of polymer foams and the energy-intensive expansion and curing processes, in contrast to mineral-based insulation materials [125]. Ozone depletion potential further discriminates between insulation options beyond GWP. Glass wool mats exhibit the highest ODP, followed by polystyrene foam slabs, while urea–formaldehyde foams show moderate values. Stone wool displays negligible ODP, making it particularly advantageous in contexts where ozone depletion is a binding constraint. In ReCiPe-based assessments, these impacts are largely driven by upstream emissions associated with historical or current use of halogenated compounds in energy and material supply chains [125].

Primary energy demand and water scarcity indicators support these hierarchies and reveal potential burden-shifting effects. Polystyrene foam slabs have the highest fossil and nuclear energy demand, often exceeding 90 MJ per kilogram, while stone wool remains below 30 MJ. Urea–formaldehyde foam slabs have the highest water scarcity impacts among insulation materials, reflecting water-intensive chemical synthesis and curing stages. In contrast, stone wool consistently has the lowest water footprint [125,126]. These trends are particularly relevant when considering tannin-based phenolic foams, as water and energy demand during tannin extraction may significantly influence their overall performance in these categories.

Tannin-based and formaldehyde-free phenolic foams may be expected to outperform conventional polymer foams in fossil resource depletion and human toxicity, while their competitiveness with mineral-based insulation materials such as stone wool will largely depend on process optimization, energy sourcing, and end-of-life management. While tannin-based foams contain renewable carbon, they should not be assumed to be biodegradable. Nevertheless, their higher bio-based carbon content may result in reduced

fossil carbon emissions during incineration compared to conventional phenolic foams. Comprehensive end-of-life assessments specifically addressing tannin-based phenolic foams remain scarce and represent a key research gap [124].

The end-of-life pathways for tannin-based foams are still being defined, with research pivoting between material circularity and functional repurposing. Beyond partial recycling into new foam formulations [127], current trends investigate their potential in thermal recovery [128] and their degradation in soil environments [129].

Overall, LCA evidence and end-of-life studies suggest that tannin-based foams hold significant potential to reduce fossil resource dependence and human health impacts relative to conventional phenolic foams. However, when compared to alternative insulation materials, particularly mineral-based systems such as stone wool, their environmental advantages may not be consistent across all impact categories. These findings highlight the need for systematic, cradle-to-grave LCA integration in the design and optimization of next-generation bio-based insulation materials to ensure that increased bio-based content results in genuinely sustainable solutions.

6. Conclusions and Future Perspectives

Tannin-based phenolic foams have emerged as promising bio-based alternatives to conventional petroleum-derived insulation materials, offering a compelling combination of sustainability, fire resistance, and thermal performance. Their formulation leverages the natural reactivity of condensed tannins with aldehydes, enabling the development of rigid, thermally stable foams suitable for various applications, particularly in the construction sector.

Recent research (2019–present) continues to focus on formaldehyde-free foams, although these foams began to be explored several years ago, as well as modifying formulations by introducing new components to improve the mechanical properties and friability of foams. Substituting formaldehyde with safer, renewable crosslinking agents such as furfuryl alcohol, glyoxal, vanillin, and soy protein isolate represents a significant step toward environmentally friendly and health-conscious materials. The properties of the resulting foams are superior to those of foams containing formaldehyde. Using bio-based materials to improve mechanical properties is feasible and enables the production of foams with higher compressive strength and lower friability than foams without these materials, although an increase in density was observed in some cases.

Despite these advances, several challenges remain, including friability, moisture sensitivity at panel edges, and variability in mechanical properties depending on the tannin source and processing methods. Standardizing production techniques and optimizing formulations are essential to ensure consistent performance and commercial viability.

Evidence from market-available synthetic phenolic foams suggests that, once formulations and industrial manufacturing are optimized, tannin-based foams offer the functional versatility required for diverse construction applications, such as walls, floors, and roofs.

The future of tannin-based phenolic foams is set for significant progress, driven by sustainability and innovation. A primary focus will be industrial scale-up, as researchers and manufacturers work to develop cost-effective, continuous production methods for large-scale applications such as sandwich panels and modular insulation systems.

Equally important is the shift to fully bio-based formulations, replacing all petrochemical-derived components with renewable alternatives including catalysts, blowing agents, and functional additives to ensure these foams are sustainable throughout their lifecycle.

Beyond traditional uses, tannin-based foams are expected to find advanced applications in diverse fields. Promising areas under exploration include biomedical innovations

such as wound dressings and tissue scaffolds, eco-friendly packaging solutions, automotive components, and environmental remediation projects.

Another promising direction is the development of hybrid materials. By combining tannin foams with natural fibers, nanocellulose, or graphene, researchers can create high-performance (bio)composites with superior mechanical strength and enhanced functional properties. To broaden their applicability, it is essential to understand performance under extreme conditions. Studies will focus on how these foams behave in environments with high humidity, temperature fluctuations, and chemical exposure, critical factors for the infrastructure and transportation sectors.

Comprehensive life cycle assessments are necessary and will play a pivotal role in validating the environmental benefits of tannin-based foams compared to conventional synthetic alternatives. Together, these research directions underscore the potential of tannin-based phenolic foams to become a cornerstone of sustainable material innovation, aligning with global goals for climate neutrality, a circular economy, and safer construction practices.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/macromol6010010/s1>, Figure S1: Evolution of the number of documents addressing phenolic foams and the main topics researched. The documents are those indexed in OpenAlex and published between 1990 and 2024.

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