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Chapter

Furanic Rigid Foams, Furanic-Based Bioplastics and Furanic-Derived Wood Adhesives and Bioadhesives

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Abstract

In this chapter, we discuss pure furanic foams and tannin-furanic foams as fire-resistant, environmentally friendly, rigid biofoams. We also examine furanic wood adhesives in which a major furan portion is coupled with either synthetics or bioadhesives. In the case of furanic wood bioadhesives, the formulations developed were 90–100% biosourced. Equally, furanic rigid plastics of considerable mechanical resistance have also been developed and applied to angle-grinder discs and automotive brakes with very encouraging results.

Keywords: furanic foams, tannin-furanic foams, tannin-furanic adhesives, tannin-furanic plastics, tannin-furanic films

1. Introduction

Biosourced furan derivatives such as furfural, furfuryl alcohol, and hydroxymethyl furfural have been a focus of research in the last 10 to 15 years in several different application fields. This chapter deals with three topics: (1) fire-resistant furan-based foams, (2) the co-reaction to prepare wood panel bioadhesives of furanic materials with renewable and environmentally friendly materials, and (3) the preparation of hard plastics by reacting different natural and environmentally friendly renewable materials with furanics. A considerable level of research activity has been recorded in all these areas.

2. Fireproof furanic rigid foams

2.1 Tannin-furanic foams by chemical exothermal reactions

In this section we discuss the preparation of almost totally biobased tanninfuranic foams via expansion/blowing of the foam by chemical exothermal reactions caused by the heat generated under acid conditions of the self-condensation of furfuryl alcohol. Then, we discuss tannin-furanic foams in which isocyanate is added in the minority to the tannin-furanic mix. We also address the applicability of these foams to isocyanate-based polyurethane foam factories. Synthetic isocyanate-based polyurethane foams, even those using biopolyols, are not generally fire resistant unless some fire-retardant is used. Although the foams presented here are intrinsically fire resistant, like phenolic foams, but without their pollution characteristics.

Pure furanic foams are prepared by polycondensation of furfuryl alcohol under acid conditions [1–3]. Furanic foams are commonly used in foundries, because of their high resistance to heat and their relatively low cost, to bind the sand of molds or cores for casting engine heads or other kinds of steel tools [4, 5]. A study on the formation of pure furanic foams and the conservation and modification of their structure after carbonization is described in [6]. Ambient temperature catalysis of furfuryl alcohol with para-toluen sulphonic acid (pTSA) is the method used to prepare pure furanic foams. This research shows that the furfuryl group is the main repeating unit/motive from which derive the whole variety of structures observed in the polymer network formed (**Figures 1** and 2), with structures shown in **Figure 2** been present.

The same work [6] studied the type of structures that remain in a furanic foam after carbonization at 900°C. The research shows that many polynuclear aromatic hydrocarbons are present after carbonization (**Figure 3**). The average molecular weight of the fragments increases during carbonization because of the rearrangement of the furanic structures. Gasification during carbonization makes the signal



Figure 1. *Structure of the linear furanic oligomers formed by the self-condensation of furfuryl alcohol.*



Methylene and methylene ether bridges linking furanic nuclei in furanic oligomer structures found in linear oligomers from the self-condensation of furfuryl alcohol (FA). Top: reaction of the $-CH_2OH$ of FA with the furanic ring of a second FA molecule. Bottom: reaction of the $-CH_2OH$ of FA with the $-CH_2OH$ of another molecule of FA. Both reactions are obtained by elimination of water.



Figure 3. Example of rearranged structures formed during carbonization of furanic foams [6].

of the pTSA catalyst derivates disappear by degrading to toluene and SO2 not surviving carbonization. However, certain furanic oligomers survive carbonization; these are mostly cyclic compounds with 4–6 or more furan rings. Thus, even if most of the constituents are transformed to more stable aromatic structures, some of the starting chemical species survive intact or partly transformed to carbonization even if most structures are converted to more stable aromatic structures (**Figure 3**). This shows the stability of some furanic oligomers that are not degraded or rearranged by carbonization. Molecular mechanics calculation of their relative energies appeared to confirm that these structures are cyclic furanic oligomers.

Tannin-furanic foams were mentioned for the first time in the literature in the early 1970s when Grey, Roux, Pizzi, and Ryder developed a foam formulation in South Africa [7]. This formulation had some severe problems and its performance was unacceptable. Moreover, industry did not appear to have any interest in the foam, as there was more focus on the dominant synthetic oil-derived foams at the time. In addition, the public opinion of the relative cost structure/performance relationship of these foams and of the biomaterials used also appeared to be unfavorable. The first tannin-furanic biofoam formulation that appeared to work well was published in the literature in 1994 by Meikleham and Pizzi [8]. Nonetheless, even then there was no interest in these materials; interest in them materialized only in the late 2000s [9].

Ambient temperature, self-blowing tannin-furanic foams were the first researched for a relatively long period, these being chemically foamed and set by the exothermic acid self-condensation of furfuryl alcohol (Figure 4). In earlier times, diethyl ether was used as a blowing agent [8]. The foams prepared with this early research were either catalyzed by an acid or a base but showed characteristics and performance comparable to synthetic phenolic foams. The liquid polymer phase was a tanninformaldehyde resin. Foaming occurred by the forced evaporation of a physical blowing agent, while cross-linking rendered the foams dimensionally stable and with the goal target density. Acid-catalyzed foams expanded by evaporating the blowing agent due to the heat-surge agent produced by the self-condensation of furfuryl alcohol. Tanninfuran copolymers were so obtained. No toxic gasses on these foams' carbonization were detected [9, 10]. This formulation worked, but when this research was again started up in the late 2000s several problems remained that needed to be solved. These were (1) the elimination of formaldehyde, used up to then to improve cross-linking and (2) the elimination of diethyl ether by substituting it with a less volatile and less dangerous blowing agent. In-depth characterization of these foams ensued. Different condensed tannins, namely, mimosa tannin bark extract, pine bark tannin, and quebracho tannin wood extract, were coupled to furfuryl alcohol as foam building blocks. Hydroxymethylated lignin up to a level of 20% by weight, and even smaller proportions of polyurethane, isocyanate [11], and industrial surfactant [9], were added



Figure 4.

An example of a tannin-furanic rigid foam (left) and of its structure as observed at the scanning electron microscope (right).

successfully to modify these foams. Physical tests such as water absorption, compression resistance, direct flame behavior, and measure of foam cells' dimensions were carried out [9]. These foams were chemically characterized by 13C-NMR analysis.

Equally, these tannin-furanic foams' resistance to fire and chemicals (e.g., resistance up to 1200°C and higher), absorption of and resistance to various liquids (e.g., ethanol, 33% sulphuric acid, and organic and mineral acids), permeability, thermal conductivity (e.g., between 0.024 and 0.044 W/m K), and mechanical (compressive and tensile) strength were tested. Boric acid and/or phosphoric acid were added to modify the foams' structure while improving substantially their fire resistance (**Figure 3**). Rigid foams resisting well to strong acid, bases, and solvents were prepared with these early formulations [12]. High affinity for water, but limited affinity for organic solvents, was also put into evidence. Slightly anisotropic mechanical properties were measured. These foams were brittle in tension and compression, but their thermal conductivity and mechanical performance fully compared with those of synthetic phenolic foams. X-ray microtomography was also used to examine these early foams [13–16]. This provided additional and useful information regarding their physical characteristics such as porosity, pore size distribution, proportion of open and closed cells, connectivity, and tortuosity.

These foams garnered considerable interest for their phenomenal fire resistance and hence their heat insulation potential [16]. Even when exposed to a flame 1200°C or higher, they do not burn for whatever length of time. The red color induced on the area where the flame is applied is automatically and immediately self-extinguishing on subtracting the flame. These tannin-furanic foams only begin to decompose at 3000°C. We will discuss the multiple uses for which they were tested later in the chapter. These include, for example, thermal insulating materials, fire-resistant filling for hollow doors and wood sandwich structures [17], green acoustic absorption materials [18], support for cut flowers [19] and hydroponic cultures [19], and flexible and rigid polyurethane-tannin-furanic mixed foams [20, 21].

The substitution of diethyl ether as a blowing agent with a much safer solvent was the first modification introduced in these tannin-furanic foams. The blowing agent chosen was n-pentane in synthetic phenolic foams. A necessary formulation rebalancing ensued, as pentane boils at a temperature higher than diethyl ether.

The first necessity was to eliminate formaldehyde from the formulation, formaldehyde having been declared unsuitable for sanitary reasons [22, 23]. With the elimination of formaldehyde, the new foams that were obtained presented lower density, thermal conductivity, hydrophilicity, and brittleness, and thus greater flexibility than the first generation of tannin-furanic foams. Formaldehyde was replaced with more furfuryl alcohol and a greater proportion of blowing agent, significantly improving the characteristics previously described [24, 25]. **Table 1** shows the characteristics of these foams regarding their range of compressive strength and thermal conductivity as a function of their apparent density. **Table 1** shows that as the apparent foam density increases the compressive strength sharply improves; however, the thermal conductivity increases, which is less acceptable as regards insulation.

Next, both formaldehyde and solvent (pentane) were eliminated, rendering the foams 98% "green." Comparison of kinetic curves describing the simultaneously measured foams' expansion, hardening, temperature, and pressure variation as a function of time illustrated the differences in process and foaming parameters as a function of time by the differences in formulation between the experimental and control foams and optimization of the foaming and hardening parameters involved [26, 27].

A first encouraging attempt to prepare elastic tannin-furanic foams occurred at this time [28]. In this first successful approach, flexible tannin-furanic foams, rather than the rigid ones prepared up to then, were obtained by the addition of

Apparent density (g/cm ³)	Compressive strength (MPa)	Thermal conductivity (W $m^{-1} K^{-1}$)
0.016	0.03	0.024–0.030
0.040-0.080	0.12-0.45	0.040-0.050
0.10–1.30	0.65–1.10	0.050–0.060

Table 1.

Typical range of physico-mechanical values for tannin-furanic-based foams [12, 14, 30, 33, 54].

glycerol as an external (unreacted) plasticizer. The choice of glycerol was dictated by its high boiling temperature, lack of evaporation, and lack of toxicity. Flexibility and spring-back of these experimental foams when subjected to a cyclic compression force followed by spring-back and compression again was quantified by both thermomechanical analysis at different temperatures as well as by compression/ spring-back hysteresis cycle tests in a universal testing machine. Tannin-furanic foams with formaldehyde and no glycerol reached a stress plateau indicative of structure crushing. Tannin-furanic foams without both formaldehyde and glycerol become very fragile, brittle, and rigid just two months after their preparation. They also show structure crushing with ageing. Tannin-furanic foams with no formaldehyde but with glycerol remain instead equally and truly flexible in time [27, 28].

Furthermore, open cell foams obtained by the simultaneous co-reaction of condensed flavonoid tannins with an alkoxylated fatty amine and polymeric diphenylmethane isocyanate yielded highly flexible/elastic polyurethane foams [28]. Copolymerized amine/isocyanate/tannin oligomers were identified by ¹³C NMR and MALDI-TOF spectroscopy. In general, between 30% and 50% of natural tannins is added to the components used to polymerize the polyurethane. The characteristic of these new, partially biosourced polyurethanes is that the presence of the tannin slows down burning; some of them can be made flame self-extinguishing and if burning they neither flow nor sprinkle flaming material around, contrary to what occurs with normal polyurethanes. This limits transmitting the fire to other materials in the same environment. Cyclic compression tests were carried out showing that after 50 cycles foam recovery was more than 80%.

Hyperbranched poly (acylamide-ester) polyol synthesized reacting in one step succinic anhydride with diethanol amine was also used to modify tannin-furanic foams [29]. Glutaraldehyde was reacted with the hyperbranched poly (acylamideester) polyol to acetalize it, and the dendrimer so prepared was used to modify the tannin-based foams. It was found that the compression strength of the tanninfuranic foam improved by 36.6% with the addition of 3.5 wt% of acetalized poly (acylamide-ester) polyol without affecting the other foam properties.

Pine bark tannins are much more reactive than mimosa and quebracho tannins experimented with up to 2012. Pine bark tannin-furanic foams were prepared for the first time in 2013 [30–33]. The tannin-furanic foam formulations underwent fundamental changes due to the greater pine tannin reactivity. This had to be implemented to coordinate foam hardening, reaction exotherm, and solvent blowing to obtain a rigid foam. This work was achieved using the FOAMAT, an equipment able to simultaneously monitor during foaming the variation of temperature, pressure, velocity, and dielectric polarization. This allowed for determining the function of the surfactant (castor oil ethoxylate) and the plasticizer (polyethylene glycol) during foam formation and thus to monitor their polymerization, expansion, hardening, and shrinkage. Foam density and its physical properties were found to be either surfactant- or plasticizer-controlled in this research work. Foams presenting a homogeneous microstructure were obtained with castor oil ethoxylate and polyethylene glycol. However, polyethylene glycol made the foams more elastic but with lower shrinkage. Pine tannin-furanic foams both with and without formaldehyde were also prepared and tested to determine their stress–strain curves, thermal conductivity, Young's modulus, compression strength, densification, densification rate, and energy absorbed under compression. These pine tannin-furanic foams with formaldehyde had properties similar to mimosa tannin-furanic foams. At very low densities, mimosa foams are more mechanically resistant than pine foams. Mimosa foams with formaldehyde have a greater Young's modulus less than 0.10 g cm⁻³ and a greater compressive strength less than 0.14 g cm⁻³ than pine tannin foams. Pine tannin-furanic foams without formaldehyde were more elastic and had lesser mechanical strength. However, on a comparative test, pine tannin foams are a better insulation material with an average thermal conductivity of 0.030 W/m/K for pine foam without formaldehyde, 0.034 W/m/K for pine foam with formaldehyde at a density of 0.031 g cm⁻³.

The reformulation undertaken for these pine tannin-furanic foams allowed to develop such foams for the whole class of very reactive procyanidin tannins and not only different species of pine tannins [30–33] such as spruce tannins [34–37], and others. Pine tannin-furanic foams free of any aldehyde, and of formaldehyde, have also been developed, but their main drawback is their lower resistance to compression. Consequently, formaldehyde-free pine tannin-furanic rigid foams were successfully obtained by using non-volatile aldehydes [22, 23], namely glyoxal or glutaraldehyde, as alternative non-toxic hardeners [30–32]. All the open-cell pine tannin-furanic foams and mimosa–/quebracho-type tannin-furanic foams have also yielded medium and high frequencies (1000–4000 Hz) and good sound absorption/acoustic insulation with acoustic absorption coefficients of 0.85–0.97 [17]. They were better than polyurethane foams, melamine foams, fiberglass, and mineral wool acoustic insulations within this frequency range [17]. Their acoustic absorption coefficient decreased to 0.40–0.60 at lower frequencies of 250–500 Hz.

Tannin-furanic foams have shown typical characteristics comparable to synthetic commercial foams as light porous materials. Open-cell foams result in better sound absorption with thicker samples performing better in the medium frequency range.

Surface friability of tannin-furanic foams was a drawback for such potential applications, but this problem was also solved. A second main drawback is absorption of water within the foam itself. Both these drawbacks have been eliminated or at least minimized by adding to the formulation a small percentage of an oil-grafted tannin. The fatty chains introduced in the foam markedly decreased foam friability and increased water repellency in the foam's body [38]. Also, adding small amounts of soy protein hydrolysate decreased surface friability of these foams [18].

Lightweight sandwich panels with a tannin-furanic foam core and wood veneers or hardboard thin panels as surfaces bonded on to the foam core were also prepared (**Figure 5**) [39, 40].

As procyanidin tannins are the world's predominant potential source of condensed tannins the development outlined for pine tannins-furanic foams are of considerable importance as they allow any future diffuse utilization of tannin foams anywhere.

The determinant parameters when designing new tannin-furanic foams have been clearly identified and codified [41]. Further progress in this field can be achieved by anyone who would care to follow these parameter guidelines.

Tannin-based carbon aerogel foams innovatively based on the ionic and radical autocondensation of tannins under alkaline conditions promoted by their reaction with silica and silicates [42–46] have also been prepared [47]. Upscaling to pilot plant level of the preparation of these types of foams has also been reported [48].

Recently, some more progress on the chemical analysis of this foam has also been made using Raman spectroscopy and attenuated total reflection–Fourier transform



Figure 5.

Foam cores sandwiched from top left to bottom right between surfaces formed of wood veneers, thick solid wood boards, thin plywood surfaces, thick and thin hardboard surfaces, and not sandwiched (just foam core).

infrared spectroscopy (ATR–FTIR) approaches [49, 50]. Research groups have also been active in the preparation processes of these tannin-furanic foams [51–53] as well on the range of different applications possible, the most notable being in the medical field [21]. For example, tannin-furanic foams can be used in medicine to form a tannin-hydoxyapatite scaffold of stem cells for bone reconstruction without using any synthetic materials [21].

3. Tannin foams by formation of mixed tannin-furanic and tannin-based polyurethanes

While phenolic foams can be clearly substituted to good effect with tanninfuranic foams, the market is particularly interested in the use of biobased polyurethane foams. This interesting situation came to the fore with an industrial plant trial for a plant where isocyanate had to be compulsorily used, otherwise the plant could not run. This was furthermore quite a sizeable polyurethane foam panels line (approx. 18 thousand tons/year). Mixed phenolic-polyurethane-type rigid foams were developed using tannin-furfuryl alcohol natural materials co-reacted with polymeric isocyanate in the proportions imposed by the limitations inherent to the continuous industrial plants for polyurethane foams and used in the plant trial [54]. Chemical analysis of the final foams identified several different copolymerization oligomers having been generated. Urethane linkages were generated by reaction of the isocyanate with two flavonoid tannin reactive sites, mainly at the flavonoid aliphatic hydroxygroup at C3, and less so on the phenolic hydroxygroups of the tannin flavonoid units. Urethane linkages also formed by isocyanate reaction with (1) glyoxal both alone or pre-reacted with the tannin, (2) the phenolsulfonic acid catalyst, and (3) with furfural. This latter reagent does react preferentially through formation of a methylene bridge with the A-ring of the flavonoid units of the tannin rather than reacting with the isocyanate to form urethanes [54]. All the materials appeared to have co-reacted to form a mix of urethane linkages and methylene bridges between all the main components used. Thus, the tannin, furfuryl alcohol, isocyanate, glyoxal, and even the phenolsulfonic acid catalyst formed a variety of mixed species linked by the two bridge types. Several mixed species constituted of 2, 3, and even 4 co-reacted different components were observed.



Figure 6.

Example of mixed tannin polyurethanes obtained by the reaction of the isocyanate group on the glyoxal groups pre-reacted with flavonoid tannin units. The reaction can be carried out simultaneously as well, as used under industrial conditions.

The more interesting result here, however, was that this approach was unusually different from the approach of oxypropylating tannins to render them more apt polyols for reaction with isocyanates [55, 56], hence using an additional reaction step. The unusual results [54] were especially interesting because they were obtained on an industrial plant line trial. Effectively, what occurred was that the glyoxal easily reacted with the tannin during the trial producing –OH groups much more easily approached by the isocyanate, thus forming a glyoxalated tannin polyurethane in a single step, which is a remarkably useful outcome [54]. Thus, species of the type shown in **Figure 6** were present.

The reaction of glyoxal with the tannin and then with isocyanates to form urethanes closely repeat the same reaction already used for wood adhesives but using the –CH₂OH groups formed by the reaction of formaldehyde with tannins and with synthetic phenolic and amino resins [57–59]. As regards the fire resistance of these foams the preponderance of the tannin phenolic groups and furanic nuclei gives a certain level of fire resistance due to the inclusion of tannins in standard polyurethane formulations [20], but fire resistance is expected to be lower than the standard tannin-furanic foams described earlier in the chapter.

4. Wood and fiber adhesives

The potential of using tannin-furfuryl alcohol resin for biobased composites using vegetal fiber reinforcement has also been investigated [60–62]. Results showed that a mix of 54% furfuryl alcohol, 45% modified quebracho tannin extract, and 0.9% pTSA as a catalyst yields a resin with which one can prepare lightweight composites by working as bonding and solidifying matrix of a nonwoven flax fiber. The composite panels so prepared, once tested for tensile and flexural modulus and strength, water resistance, and thermo-degradation, presented good mechanical properties and a very short curing time in a hot press.

Tannin-furfuryl alcohol resins reacting under alkaline conditions to minimize self-condensation of furfuryl alcohol and force its reaction with tannins have proved to be another alternative for formaldehyde-free, environmentally friendly adhesives from renewable materials [63]. An indication of the reactivity of tannin with furfuryl alcohol to harden an adhesive composed of these two materials is given in **Figures 7** and **8** where it is shown that the mixture of the two materials gels at pH levels of less than 2–2.5 and greater than 8–9 according to the reactivity of the tannin

itself, with pine tannin being more reactive than mimosa tannin. At the acid pH, the reaction is both reaction of tannin with furfuryl alcohol as well as self-condensation of furfuryl alcohol, whereas under rather alkaline conditions furfuryl alcohol cannot really self-condense and thus is forced to react with the tannin. It must be pointed out that the reactivity of the tannin even with aldehydes progressively increases from pH 4 (minimum reactivity) towards a more acidic pH, with the tannin being progressively more reactive as the pH become progressively lower. The same is true under alkaline conditions where the reactivity of the tannin increases and gel time decreases as one progresses to higher pH. The resins were prepared by mixing 100 parts of tannin with 100 parts of water and reacting this with 50 and 75 parts of furfuryl alcohol. The results were monitored by gel time measurements and thermomechanical analysis (TMA). The laboratory particleboard bonded with this resin under standard laboratory conditions and the dry internal bond (IB) strength was tested according to European Norm EN 312, 1995. The results confirmed that tannin extracts and furfuryl alcohol react with each other and do cross-link in the total absence of formaldehyde (**Table 2**).

For the mimosa tannin-furfuryl alcohol particleboards, the dry IB strength satisfies only marginally the requirements of the relevant European norm. However, for the pine tannin-furfuryl alcohol particleboards the dry IB strength satisfies the relevant EN 312 requirements.

Ten-ply and twenty-ply high continuous-type pressure paper laminates were prepared by impregnating filter paper with a mimosa-tannin solution mixed with



Figure 7.

Gel time of mimosa tannin reacted with furfuryl alcohol at pH ranging from 1 to 11. The gel time at pH 3, 4, 5, and 8 cannot be attained [63].



Figure 8.

Gel time of pine tannin reacted with furfuryl alcohol at pH ranging from 1 to 9. The gel time at pH 3, 4, and 5 cannot be attained [63].

	Gel time (s)	TMA max MOE (MPa)	Board density (kg/m ³)	IB strength (MPa)
Mimosa tan + 100%FA, pH 11	260	1929 ± 81	_	_
Mimosa tan + 50%FA, pH 11	500	2177 ± 82	_	_
Mimosa tan + 100%FA, pH 10	400	2332 ± 112	_	_
Mimosa tan + 50%FA, pH 10	600	2401 ± 97	716	0.34 ± 0.02
Pine tannin + 50% FA, pH 8	150	2430 ± 100	697	0.35 ± 0.02
Pine tannin + 75%FA, pH 8	110	3034 ± 130	715	0.40 ± 0.02
)E = modulus of elasticity; IB = in	ternal bond.			

Table 2.

Results for wood particleboard panels bonded with furanic-tannin-based wood adhesives.

furfuryl alcohol and a formurea concentrate [64]. Crosscut, abrasion resistance, and water vapor resistance measurements were done. The effect of bonding 10-ply paper laminates on plywood shear strength was also determined. The 10-ply paper laminates with mimosa tannin-furfuryl alcohol resin appeared to increase the plywood dry shear strength while reducing its absorption of water. When pressed at 140°C temperature at 120 kg cm² pressure for 600 s, the 10-ply paper laminates gave the best appearance compared to other laminates.

The syntheses of difurfuryl diisocyanates [e.g., ethylidenebis (2,5-furandiylmethylene) diisocyanate (EDFI)] with formula shown in **Figure 9** have been reported in the literature [65].

Difurfuryl diisocyanates (**Figure 9**) are structurally similar to diphenylmethane diisocyanate (MDI), hence they can be equally good adhesives for bonding wood composites. The EDFI adhesive is synthesized from biomass-derived chemicals, contrary to the petroleum-derived MDI. The mechanical performances of MDI- and EDFI-bonded aspen flakeboards were compared. Flakeboards bonded with MDI showed results only marginally better than those bonded with EDFI. The difference has been ascribed to EDFI having greater viscosity than MDI. This has been thought to have caused a less optimal distribution of EDFI during spraying on the wood flakes, causing the slight difference in strength properties. The dry IB strength values of EDFI-bonded flakeboards showed dry IB strengths of 0.97 MPa, hence a value significantly greater than the 0.41 MPa required by the American National Standards Institute for type-2 medium-density particleboard when compared to MDI yielding 1.13 MPa.

Furfuryl alcohol, a biosourced material, is widely used in the foundry industry and in adhesives as additives or modifiers. However, furanic resins have not been reported as being used alone as wood panel adhesives. Furfuryl alcohol-aldehyde resins were nonetheless recently prepared for wood panel adhesives by reacting furfuryl alcohol with three different aldehydes: formaldehyde, glyoxal, and glutaraldehyde [66]. p-Toluene sulfonic acid coupled with an acid self-neutralizing system to minimize any damage to the wood substrate was used as a resin hardener to prepare plywood panels and to determine their bonding performances. In this adhesive system, formaldehyde and glyoxal reacted with furfuryl alcohol and the resin so prepared had excellent performance. The reaction of glutaraldehyde with furfuryl alcohol instead seemed difficult, the furfuryl



Figure 9. Structural formula of difurfuryl diisocyanate.



Schematic representation of the formation of the reactive species hydroxymethyl furfural and furan 2,5-dialdehyde from carbohydrate exudates of several African trees and their reaction to cross-link tannins.

alcohol autocondensation predominating instead. The curing agent acidity greatly influences the resin bonding performance. The furfuryl alcohol-glyoxal resin showed a good bonding strength and water resistance greater than the standard requirements (≥ 0.7 MPa), even when using an acid self-neutralizing system as a hardener. This resin performed particularly well, considering that no formaldehyde was used.

Furfural and more recently hydroxymethyl furfural (HMF) are well-known upgraders of formaldehyde-based synthetic resins. An excellent review on this exists and the reader is addressed to it [67]. Even early literature and patents are known on this subject. The use of hydroxymethyl furfural is less known in synthetic resins where formaldehyde has been totally eliminated. Recent examples of the increased interest in HMF are the resins based on the coupling of glyoxal with HMF. Glyoxal is an aldehyde that is both nonvolatile and nontoxic. It can be used to substitute formaldehyde to prepare melamine-glyoxal (MG) resins for the wood industry. Due to the lower reactivity of glyoxal compared to formaldehyde, the MG resins performance is not as good as could be expected. Thus, 5-hydroxymethyl furfural (HMF) was used as a modifier to improve the properties of MG resins to prepare a hydroxymethyl furfural modified melamine-glyoxal (HMFMG) adhesive for bonding plywood [68]. The structure of the oligomers formed was determined along with the thermomechanical properties of the resins. The HMFMG resin presented a lower curing activation energy than the MG resin, yielding a much better bonded and water-resistant plywood.

Some fully biobased carbohydrate extracts from African trees have shown to release both hydroxymethyl furfural and furan 2,5-dialdehyde as hardeners [69, 70] during hot-pressing. **Figure 10** shows an example of the reactions involved.

This approach also fits with the adhesives based on the reaction of the reactive procyanidins of pine bark tannin with hydroxymethyl furfural [69] also yielding encouraging wood bonding results.

5. Furanic-based hard thermoset plastics

A 100% biosourced thermoset material based on condensed tannin-furfuryl alcohol thermoset resins has been used as the resin matrix of solid abrasive wheels by using pTSA as a catalyst [62, 71–73]. The system is based on two reactions: the reaction of furfuryl alcohol with the tannin and the acid-induced self-condensation of the furfuryl alcohol (**Figure 11**). The co-polymerization reactions were studied by ¹³C NMR and MALDI-ToF mass spectrometry; they are shown in **Figure 11**.

The 100% renewable bioresourced tannin–furanic thermosetting resin was found to have a glass transition temperature as high as 211°C, and a 95% weight loss temperature of 244°C and 240°C in nitrogen and in air atmosphere, respectively.

The char yield is as high as 52%. Moreover, this new thermoset material showed excellent mechanical properties: a Brinell hardness of 23 HBS, which is higher than commercial acrylic, polyvinyl chloride and a little lower than that of solid (not foamed) polystyrene. The compressive break strength was found to be as high as 194.4 MPa, thus higher than that of filled phenolic resins and much higher than that of solid polystyrene and acetal resins (**Table 3**). **Figure 12** shows its appearance and the repetition of the resin stress vs. strain curves.

This hard thermoset resin was produced by a simple process that is easily industrialized. Abrasive wheels held together with this resin bonding different mineral and organic abrasive powders were developed and characterized. The main abrasive powder used was aluminum trioxide Al₂O₃ of different grit levels (**Figure 13**). Hard nutshell powders were also tried but did not give sufficiently good results. These abrasive wheels showed excellent abrasiveness properties when compared to commercial abrasive wheels [71].

Angle-grinder's cutting and grinding discs based on this green resin were also used for bonding abrasive particles of aluminium trioxide of different sizes and of different grits level (**Figure 13**). These discs were characterized and showed excellent abrasiveness and cutting properties. Their mechanical resistance was found to be comparable to that of commercial grinding discs bonded with synthetic phenolic resins. They tolerated well the severe stresses induced on them at 11,000 revolutions per minute (rpm) by operation in an angle grinder when grinding or cutting steel [72].

The same hard resin was used as a resin matrix for automotive brake pads. These experimental automotive brake pads based on this green resin showed excellent braking properties and wear resistance when used in a real car under full-scale test conditions. Their mechanical resistance was found to be comparable to that of commercial automotive brake pads bonded with synthetic phenolic resins. They tolerated well the severe stresses induced by strong braking, such as emergency braking at 50 km/h (31 mph) until complete standstill and showed braking distances comparable or even shorter than commercial brake pads [73].



Figure 11.

Schematic representation of the reaction of furfuryl alcohol with tannin to form hard thermoset plastics.

Resin name	Breaking strength (MPa)	Young's modulus (GPa)	
Tannin–furanic plastic	194.4 + 2.3	2.16 + 0.09	
Solid Polystyrene	106	3.88	
Acetal resin	100	3.28	
Filled phenolic resin	158	6.82	

^aNote: the values of the other resins are cited from ASTM_D695-10.

Table 3.

Breaking strength and Young's modulus of tannin–furanic resin under compression.^a



Figure 12.

Top: examples of rigid plastic specimens prepared by the reaction of tannin and furfuryl alcohol. Bottom: plot of the stress/strain curves of the tannin-furfuryl rigid plastic, the two curves showing its behavior repeatability.



Figure 13.

Left: example of angle grinder disc formed by a tannin-furfuryl rigid plastic matrix and aluminium oxide abrasive. Right, example of a steel tube cut with the same type of disc but with different abrasive grits [72].

The same technology led to the preparation of both highly flexible films and strongly adhering non-scratch surface finishes by reacting partially aminated polyflavonoid tannins with furfuryl alcohol in the presence of plasticizers such as glycerol or polyethyleneimine. Chemical analysis showed partial amination of the tannin under the conditions used and even the formation of some -N bridges between flavonoid units, although these were shown to be rare. Oligomers formed

by the reaction of furfuryl alcohol with the flavonoid units and the simultaneous self-condensation of furfuryl alcohol were detected. Linear methylene–furanic chains were also found to be linked to flavonoid reactive sites. Side condensation reactions of furfuryl alcohol led to the formation of methylene ether bridges between furanic nuclei, followed by rearrangement to methylene bridges with liberation of formaldehyde. The latter reacted with both the flavonoid units and furan ring reactive sites to yield $-CH_2OH$, $-CH_2^+$ groups and methylene bridges [74].

6. Conclusion

Furanic resins either alone or in combination with other renewable biosourced materials have come of age in fields where they were never considered before, either because of their dark color or high cost. Their biosourced, renewable materials-derived label has changed this perception in a world looking for materials that are not oil-derived. Thus, from their traditional industrial applications, namely, in foundry sand shell molds for metal casting, they are starting to be used other areas such as fire-resistant, thermally insulating, and sound absorbent foams, as wood panel adhesives, hard rigid plastics, resistant matrix resins for abrasive aggregates, and even for the formation of flexible films and non-scratch surface finishes. These biomaterials are attracting the interest of researchers to develop new uses for them. Thus, their future expansion to a variety of products appears now to be assured.

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Conflict of interest

The authors declare no conflict of interests.



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