

Tannin-Based Biofoams-A Review

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Abstract: This review details the development of tannin-based biofoams for fire resistance and acoustic insulation and details the different varieties of these foams that have been developed, from tannin-furanic self-blowing foams to tannin-furanic polyurethanes and finally non-isocyanate tannin-based-carbohydrates polyurethanes (NIPU).

Keywords: Biofoams; tannins; tannin-furanic; tannin-carbohydrates, non-isocyanate polyurethanes (NIPU)

1 Introduction

The word foams rhymes in general with polyurethanes, this application being one of the main one for these materials. In general, industrial practice polyurethanes are prepared by reacting a polyol with an isocyanate. In general too, when partially biobased polyurethanes are described these are formed by reaction of a biobased polyol reacted, still with an isocyanate, a synthetic material. Many of these semi-biosourced polyurethanes are used for foams or other applications and are described, even recently, in the literature [1-19]. This approach has been applied to foams derived from such semi-biosourced polyurethanes, even recent literature being quite consequent on this subject [12-17]. Many different renewable materials are used to prepare the polyols of these semi-biosourced polyurethanes and their derivate foams [1-17]. More recently, foams derived, totally or partially, from renewable raw materials have attracted attention as well, these been based mainly on lignin, proteins [18,19] or tannins, this latter being the subject of this review, being a more advanced technology. These tannin-furanic foams can be of different types. Thus, in this category, tannin-furanic non-polyurethane foams, tannin-furanic polyurethane foams and even non-isocyanate polyurethane (NIPU) tannin foams have been developed. Other materials have also been used for these latter ones too [18-20].

Tannins are natural materials that are fairly ubiquitous in the vegetable world. They can be and are extracted from the bark and wood of certain trees, as well as from grape and other fruit skins. They have been traditionally extracted industrially for the manufacture of heavy leathers but have in the last decades acquired more importance for many other industrial uses. Other than for leather, their other main alternative use has been for wood adhesives [21], but extensive research on their utilisation has led to a variety of other possible utilisations, such as metal primers, pharmaceuticals and many other uses. Among these, one of the more interesting applications is for biobased foams for thermal and acoustic insulation and other uses. This review is a rapid summary of this particular application for which further developments are likely to occur.

First of all, tannins are divided into two main classes, namely hydrolysable tannins and condensed or polyflavonoid tannins. Extensive reviews on their chemistry exists. Other than the short introduction to these two classes of tannins presented here the reader should consult extensive reviews on their structure and chemistry [21].

1.1 Hydrolysable Tannins

Hydrolysable tannins, are derivatives of gallic acid and they are classified according to the products obtained from their hydrolysis. Thus, they are divided into gallo-tannins (comprised of gallic acid and glucose) and ellagitannins (comprised mainly of digallic and ellagic acids and penta-galloyl-glucose). They are composed of a great variety of combinations the main components being oligomers of n-galloyl-glucose and of their rearrangement derivatives such as vescaline and vescalagin [22-25].

1.2 Condensed (Polyflavonoid) Tannins

Condensed tannin extracts, consists of flavonoid units that have undergone varying degrees of condensation. They are invariably associated with their immediate precursors (flavan-3-ols, flavan-3,4-diols), other flavonoid analogs [26,27], carbohydrates and traces of amino- and imino-acids [28]. Monoflavonoids and nitrogen-containing acids are present in concentrations which are too low to influence the chemical and physical characteristics of the extract as a whole. However, the simple carbohydrates (hexoses, pentoses and disaccharides) and complex glucuronates (hydrocolloid gums) as well as oligomers derived from hydrolysed hemicelluloses are often present in sufficient quantity [21]. Equally, carbohydrate chains of various length [29-31] are also sometime linked to flavonoid units in the tannin.

2 Tannin-Based Fire Resistant Foams

The first records of tannin-based foams date from the early 1970s when a basic formulation was developed by a collaboration between D. Grey and D. G. Roux with A. Pizzi and A. Ryder in South Africa [32]. These foams had severe problems and at that time, although a considerable effort was expended on them for many years by successive researchers, they did not achieve a good enough performance. Furthermore, they did not seem to interest industry then totally dominated by synthetic foams, also because their relative performance/cost structure seemed unfavourable at that time, in the public opinion, to totally biosourced materials. The first public record of a formulation that appeared to work well was published by Meikleham and Pizzi in 1994 [33]. This notwithstanding, interest in these materials came to the fore only in the late years 2000s [34]. While these tannin foams are non-isocyanate, phenolic-like foams, other research groups also tried from the early 1990s to develop tannin-isocyanate foams in which the tannin functioned just as the polyol. [35-37].

There are several systems used to prepare the tannin-based phenolic-like foams, these varying from within foam chemical reactions in presence or not of a blowing agent, foaming under the impulse of the exotherm generated by a chemical reaction or by simply heating the mix, and foams created by simple mechanical agitation/stirring, as well as mixed systems. Tannin-furanic foams are no exception to this type of classification. The various systems developed will be briefly described.

2.1 Tannin-Furanic Foams by Chemical Reaction Exotherm

Initially, and for quite a time afterwards, tannin-furanic foams powered by an exothermic reaction were the only one studied (Fig. 1). The early efforts used diethyl ether as a blowing agent and the exotherm allowing foaming was based on the acid autocondensation of furfuryl alcohol [33]. In this early work acid and alkali-catalysed rigid foams of comparable properties to synthetic phenolic rigid foams were prepared. The fluid polymer phase was based on a tannin-formaldehyde resin. Expansion (foaming) was brought about by a physical blowing agent, whereas dimensional stabilisation was achieved through cross-linking to the desired density. In the case of the acid-catalysed foam the heat-generating agent was the self-condensation of furfuryl alcohol. Tannin-furan copolymers were generated in the reaction. These foams moreover did not give any quantity of toxic gasses on carbonization [38]. While this system worked well, when this research was taken up again in the late years 2000 the first problems that was necessary to solve were (i) the substitution of diethyl ether with a less dangerous and volatile solvent, and (ii) the elimination of formaldehyde. These foams were abundantly characterized. Mimosa tannin bark

extract, pine bark tannin and quebracho tannin wood extract were used as building blocks together with furfuryl alcohol. Modifications by addition of up to 20% hydroxymethylated lignin, or smaller proportions of polyurethane, isocyanate [39] and an industrial surfactant were also characterised [34]. Physical tests such as water absorption, compression resistance, direct flame behaviour and measure of foam cells dimensions were carried out [34]. A ^{13}C -NMR analysis contributed to the chemical characterisation of these foams.

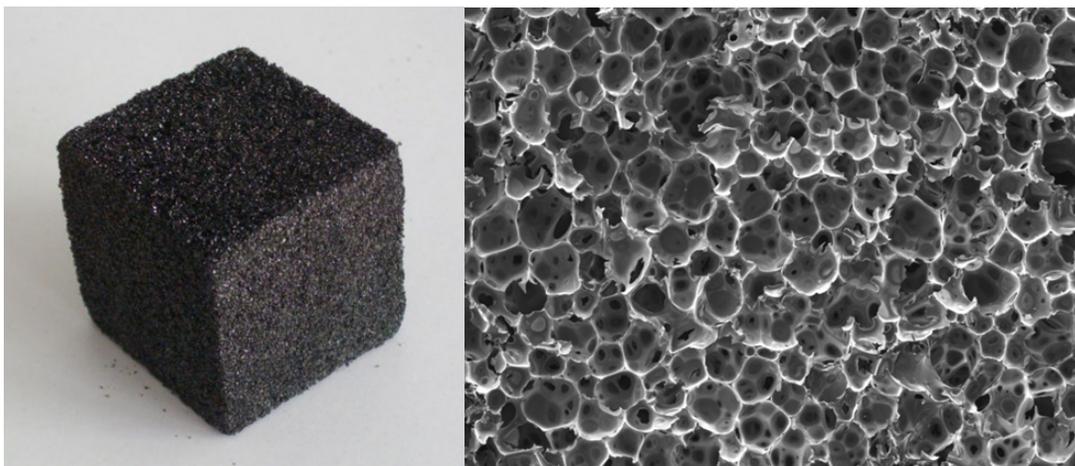


Figure 1: An example of a tannin-furanic rigid foam (left) and of its structure as observed at the scanning electron microscope

Equally, resistance to fire and chemicals, absorption of various liquids, permeability, thermal conductivity and mechanical (compressive and tensile) strength were tested. Modifying the structure by addition of boric acid and/or phosphoric acid allowed a substantial increase in fire resistance. These early foam formulations produced rigid foams presenting good resistance to strong acid and bases, and to solvents [40]. High affinity for water, but limited one for organic solvents was also put into evidence. Finally, slightly anisotropic mechanical properties were measured. The foams presented a brittle behaviour either in compression or in tension. However, their strength as well as their thermal conductivity were fully comparable with those of their synthetic phenolic counterparts. These early foams were also examined by X-ray microtomography [41-43]. This gave by image treatment additional useful informations on physical characteristics such as porosity, fraction of open cells, connectivity, tortuosity, and pore size distribution as a function of the foam's density.

To conclude, the great interest in these foams resided in their phenomenal fire resistance and potential thermal insulation [44]. They do not burn at all for whatever period when exposed at a flame of 1200°C or of higher temperatures. Only at 3000°C they start decomposing. The multiple uses for which they were tested will be discussed later, and will then become evident to a reader that just thinking of these materials only in term of thermal insulation would be limiting their much wider area of application.

The first modification implemented on these foams was to substitute the unacceptable diethyl ether with a much safer solvent, namely pentane, the same solvent as used for synthetic phenolic foams. This entailed a rebalancing of the formulation due to the higher boiling temperature of pentane.

The first fundamental foam reformulation was dictated by the need to eliminate formaldehyde from the formulation, formaldehyde having become unacceptable for health reasons [45,46]. Formaldehyde was eliminated and the new materials so obtained had, compared to the first generation of tannin-based foams, lower density, lower thermal conductivity, lower hydrophilicity but were also much less brittle due to a much higher flexibility. Such significantly improved characteristics could be obtained through the

replacement of formaldehyde with furfuryl alcohol, also a renewable chemical, and a higher amount of blowing agent [47,48]. This was followed by the further modification of eliminating both formaldehyde and solvent (pentane) to render the foams even greener, greener at 98% [26]. Comparison of kinetic curves describing the simultaneously-measured foams expansion, hardening, temperature and pressure variation as a function of time allowed to show the differences in process and foaming parameters as a function of time by the differences in formulation between the experimental and control foams and optimisation of the foaming and hardening parameters involved [49,50].

It was at this same time that the first successful try to prepare elastic tannin furanic foams occurred [51]. In this first successful approach flexible tannin foams as opposed to the rigid tannin foams already prepared, were obtained by the addition of an external (non-reacted) plasticizer, namely glycerol. Glycerol was chosen for its high boiling temperature and the lack of evaporation, coupled to its 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 foams containing formaldehyde and without glycerol have been shown to reach a stress plateau indicative of structure crushing. Tannin foams without formaldehyde but without glycerol too, become very fragile, brittle and rigid just two months after their preparation again presenting structure crushing with ageing. Instead, tannin foams without formaldehyde but with glycerol added do not show any change of flexibility with time and remain truly flexible [51]. Their glass transition temperature was measured by thermomechanical analysis.

Furthermore, open cell foams obtained by the simultaneous coreaction of condensed flavonoid tannins with an alcoxylated fatty amine and polymeric diphenylmethane isocyanate yielded highly flexible/elastic polyurethane foams [52]. Copolymerised amine/isocyanate/tannin oligomers were identified by ^{13}C 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 tannin present slows down burning, some of them can be made flame self-extinguishing and if burning they neither flow nor asperge flaming material around, contrary to what occurs with normal polyurethanes. This limits the possibility of transmitting fire to other materials in the same environment. Cyclic compression tests were carried out showing that after 50 cycles foam recovery was in excess of 80%.

Tannin based rigid foams were also modified with a hyperbranched synthetic polymer, namely hyperbranched poly (acylamide-ester) polyol prepared by reaction of diethanolamine with succinic anhydride by a "one step" method [53]. The hyperbranched poly (acylamide-ester) polyol prepared was acetalized by reaction with glutaraldehyde, and the product so obtained used to modify the tannin-based foams. It was found that when 3.5wt% acetalized poly (acylamide-ester) polyol was added, the compressive strength of the tannin-based foam was improved by 36.6%. This occurred without any side effect to the other properties of the foam.

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 [54-57]. The high reactivity of pine tannins in relation to other tannins induced fundamental changes in the tannin foam formulations in order to coordinate foam resin hardening, reaction exotherm and solvent blowing allowing the formation of a rigid foam. For this work, an equipment named FOAMAT was used to record simultaneously temperature, pressure, velocity and dielectric polarization during foaming. The results highlight the role of surfactant (castor oil ethoxylate) and plasticizer (Polyethylene glycol) during foam formation: polymerization, expansion, hardening, and shrinkage. In this work, foam density - and its physical properties-are either surfactant or plasticizer-controlled. With polyethylene glycol and castor oil ethoxylate, homogeneous microstructure foams were obtained but polyethylene glycol made the foams more elastic and presenting lower shrinkage. Finally, pine tannin foams with and without formaldehyde were prepared. Their characteristics were tested as regards stress-strain curves, thermal conductivity, Young's modulus, compression strength, densification, densification rate and energy absorbed under

compression. In most properties the pine tannin foams with formaldehyde have properties similar to mimosa tannin foams, in some case slightly lower in others slightly higher. Pine tannin foams without formaldehyde showed lower mechanical strength and more elastic behaviour. This work permitted clearly the application of such type of tannin-furanic foam formulations to the whole class of very reactive procyanidin tannins, not only different species of pine tannins [54-57] but also spruce tannins [58-61], and others. Formaldehyde-free, in reality any-aldehyde-free pine tannin foams have also been developed but present lower mechanical resistance undergoing compression. Thus, formaldehyde-free pine tannin/furanic rigid foams were successfully prepared by a new approach, namely using alternative non-toxic [45,46], non-volatile aldehydes as hardeners: glyoxal or glutaraldehyde [54-56]. Furthermore, open cells structure tannin-furanic foams prepared using pine bark tannin and mimosa/quebracho type tannins have been shown to give good sound absorption/acoustic insulation characteristics at medium and high frequencies (1000-4000 Hz) with coefficient of acoustic absorption of 0.85-0.97 [62]. In this range they were superior to polyurethane foams, melamine foams, fibreglass and mineral wool acoustic insulations. Their acoustic absorption coefficient was lower, 0.40-0.60 at lower frequencies (250-500 Hz). Compared with commercial foams, tannin-furanic foams have the same typical behaviour of light porous materials. The more open-cell is the foam the better is its sound absorption, with thicker samples absorbing better at medium frequencies.

One of the last problems to be solved has been the surface friability of these foams. One of their main drawbacks is the absorption of water within the foam itself. Another problem is the rather friable surface, which is a definite drawback for some potential applications. These two problems are minimized or eliminated by introducing a component of oil-grafted tannin in the foam formulation. The incorporation of fatty chains markedly decreased foam friability and increased water repellency in the body of the foams [63].

Such foams were used also to prepare lightweight sandwich panels with a tannin-furanic foam core and wood veneers or hardboard thin panels as surfaces bonded on to the foam core [64,65] (Fig. 2).

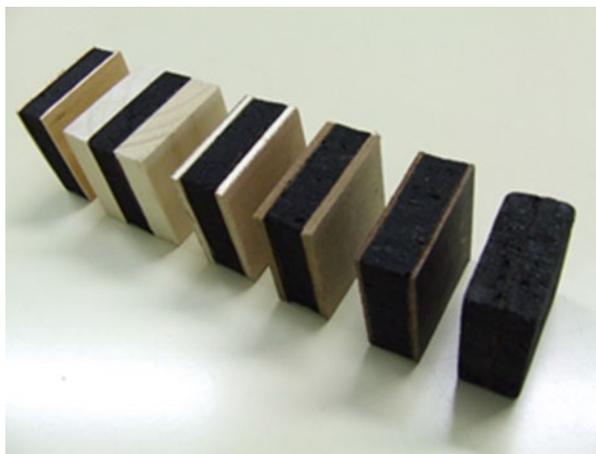


Figure 2: Foam cores sandwiched from top left to bottom right between surfaces formed of wood veneers, thick solid wood boards, thin plywood surfaces, thick and thin hardboard surfaces, and not sandwiched (just foam core)

Considering that procyanidin tannins are the greater repository and source of condensed tannins in the world all these were very important results to allow any future diffuse utilisation of tannin foams.

The considerable amount of research dedicated to these foams has allowed also to fairly clearly codify which are the essential parameters to consider when designing new tannin-furanic foams [66]. It constitutes a guide for further progress in this field to anyone that cares to work in it.

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 [67-71] have also been prepared recently [72]. It is of interest to note that upscaling to pilot plant level of the preparation of these types of foams has also been reported [73].

Recently some more progress on the chemical analysis of this foam has also been made, with Raman spectroscopy and ATR-FTIR approaches [74,75]. Research groups have also been active both on the preparation processes of these tannin-furanic foams [76-78] as well on the range of different applications possible, the more notable one in the medical field [79]. This latter one using tannin-furanic foams to form a tannin-hydroxyapatite scaffold of stem cells for bone reconstruction without using any synthetic materials [79].

2.2 Tannin Foams by Formation of Mixed Tannin-Furanic and Tannin-Based Polyurethanes

While phenolic foams can be clearly substituted to good effect with tannin-furanic 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 a plant trial [80]. A variety of different copolymerization oligomers were formed. Urethanes appeared to have been formed with two flavonoid tannin sites, mainly at the flavonoid hydroxyl group at C3, but also, although less, on the phenolic hydroxyl groups of the flavonoid oligomers. Urethanes are also formed with (i) glyoxal in the formulation, be it pre-reacted or not with the tannin, (ii) with phenolsulfonic acid and (iii) with furfural. This latter one, however, greatly favours reaction with the A-ring of the flavonoids through a methylene bridge rather than reaction with the isocyanate groups to form urethanes [80]. All of the materials appeared to have co-reacted in a manner to form urethane and methylene bridges between all of the main components used. Thus, the tannin, the furfuryl alcohol, the isocyanate, the glyoxal and even the phenol sulfonic acid hardener formed a number of mixed species linked by the two bridge types. Several mixed species comprised of 2, 3 and even 4 co-reacted different components were observed.

The more interesting result here, however, was an unusually different approach from the other interesting one taken to use tannins as polyols for polyurethanes that involve tannin oxypropylation [81,82], thus an additional reaction step. The unusual result obtained was especially interesting because the results were obtained on an industrial plant line trial. Effectively what mainly 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, a remarkably useful outcome [80]. Thus, species of the type shown in Fig. 3 were present.

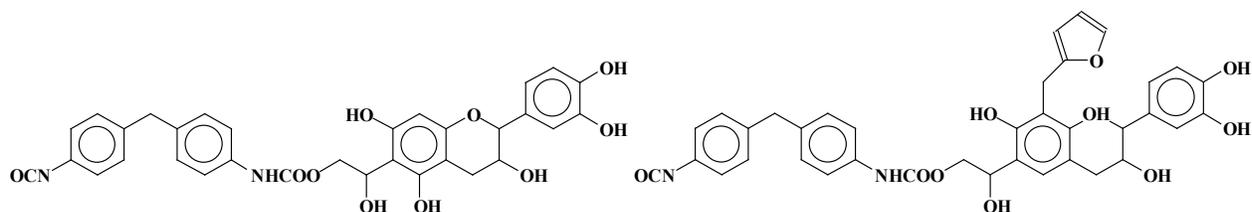


Figure 3: Example of mixed tannin polyurethanes obtained by the reaction of the isocyanate group on the glyoxal groups pre-reacted with flavonoid tannin units. The reaction can be carried out simultaneously also, as used under industrial conditions

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 $-CH_2OH$ groups formed by the reaction of formaldehyde with tannins, and also with synthetic phenolic and amino resins [83-85].

3 Alkaline Tannin Foams by Application of External Heat

All the foam formulations described up to now, however, rely on the acid-catalyzed exothermal self-condensation reaction of furfuryl alcohol to provide blowing of the mixture to form the foam itself. They are all, then, without exception, tannin/furanic foams. The catalyst of all these foams is invariably a strong acid such as para-toluene sulfonic acid; hence the foams themselves are strongly acidic due to the strong acid catalyst used. Some self-neutralisation systems originating from other tannin technologies [86] have been successfully tested. However, the fact remains that at some important stage of the process the mix is strongly acidic and that acid can still be released in service. Such strong acidity, either permanent or transitory (as in self-neutralisation) can be rather damaging in some applications where the loose acid might seep through and damage materials with which the foam is in contact, such as for instance wood.

Thus, the next major variations of condensed flavonoid tannin foams were the formulation of foams capable to be prepared under alkaline conditions [87]. This entailed the elimination of furfuryl alcohol from these formulations, as under alkaline conditions, foam preparation could not rely on the heat generated by the self-condensation of furfuryl alcohol, which occurs only under strongly acidic conditions. The approach used to formulate the alkaline foam then was: (i) the total elimination of furfuryl alcohol from the formulation, (ii) coupled with the use of an aldehyde hardener different from formaldehyde (for environmental reasons) and (iii) the application of moderate heat to allow foaming. These were not tannin/furanic foams as their acid-curing counterparts, but tannin only foams. The open cell foams were evaluated for apparent density, compressive strength, thermal conductivity and fire resistance. Their characteristics were similar to the acid-curing tannin/furanic foams.

4 Mechanically Blown and Mixed Mechanically/Chemically Blown Tannin Foams

Condensed flavonoid tannin-based foams from quebracho tannin extract have been developed using a new method of expansion based on what done for fire-fighting or tunneling foams, where a foam concentrate forms a stable liquid foam. This new mechanical method of expansion allows obtaining a solid porous material after curing and hardening at room temperature, through a liquid foam formed by a tannin resin and an aqueous solution of surfactant. The use of this new approach for preparing tannin-based rigid foams avoids the problem of shrinkage presented by many other formulations where physical or chemical foaming is employed. Non-ionic surfactants have also been used in the formulation to obtain smaller cells and improve the structure of the new material. Apparent density, mechanical and thermal properties and morphological appearance of the foams have been characterized and reported [88,89]. Equally a mixed mechanical-chemical blowing approach has been taken. These foams needed the reaction with polyamines [90] to stiffen relatively quickly to avoid that the liquid projected foams pours/drips and breaks under the effect of gravity.

These latter foams are made using the combination of two expansion methods, one by mechanical expansion and the other method based on the release of water and other gases during the self-condensation of furfuryl alcohol (chemical expansion). The combination of both methods has allowed to overcome certain limitations found in the preparation of foams exclusively based on mechanical expansion, as the resulting density or the mechanical properties. The resin was characterized under stressed conditions by means of several rheological techniques, such as frequency and time sweeps and temperature ramps. The evolution of the linear viscoelastic functions during the reaction clearly showed the transition from viscous to strong gel-like behavior. The foaming and hardening process have been followed kinetically as well, and the resulting foams have been characterized in terms of density, mechanical properties and thermal conductivity [91].

5 Tannin Based Monolith Foams

Three types of monoliths-type foams can also be prepared with condensed tannins. The term monolith is preferred rather than foams in this case because their porous structure is not developed by traditional foaming. They can be obtained by emulsion-templating, or by whipping the emulsion until stiff,

or by whipping an aqueous phase of resin in the presence of a surfactant, until a liquid, stable foam is obtained [92,93].

Albumin/tannin-based monolith foams were also prepared under alkaline or acid conditions [94]. They were prepared by whipping up a water solution of a protein, egg albumin, mixed with a second water solution of condensed flavonoid tannins. Monolith foam formulations with 4 different condensed tannin bark extracts and different relative proportions of protein and tannin were developed with a rapid process where the protein has a double function: co-reagent and surfactant as well. Physical properties such as mechanical performance, thermal conductivity, and porous structure were characterized to identify the large potential of applications of these new cellular monolith foams, fully bio-based and probable of easier biodegradability. Moreover, some albumin-based monolith foams were found to be completely flexible under certain conditions.

6 Tannin-Associated Carbohydrates Non-Isocyanate Polyurethane (NIPU) Foams

Non-isocyanate polyurethanes (NIPU) have been developed fairly recently to try to eliminate toxic isocyanates from their preparation by the reaction of synthetic polyols with cyclic or bicyclic carbonates followed by reaction with diamines [95-107] some of which constitute the seminal approach and pioneer work of this important technique [95,97,98,102,105]. Through this route not only synthetic materials but also a number of rather different biobased materials have been used to prepare NIPUs [108-110]. However very few of these NIPUs approaches has ventured up to the preparation of NIPUs foams, with some rare notable exception either with synthetic materials [111] or with natural materials [112].

Tannins have been used recently to lead to non-isocyanate polyurethanes (NIPU) for a number of applications, but mainly for surface coatings [113-115]. The reaction to polyhydroxyurethanes is based on the reaction of a tannin extract with dimethyl carbonate (or with more complex cyclic carbonates) followed by reaction of the carbonated tannin with a diamine (Fig. 4).

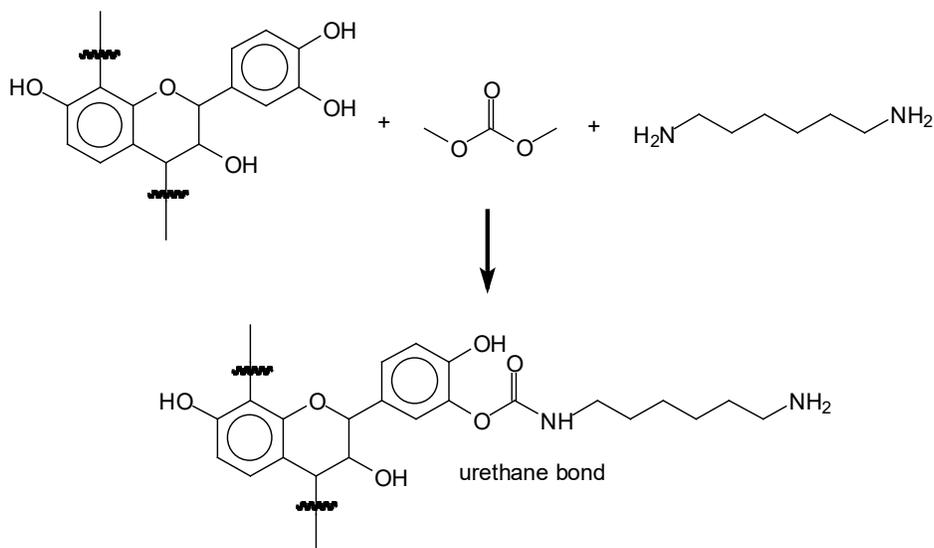


Figure 4: Schematic representation of the reaction of preparation of tannin-based non-isocyanate polyurethanes (NIPUs) obtained by reaction of hydroxyl groups of flavonoid tannin units with dimethyl carbonate followed by reaction with hexamethylenediamine

During this work, especially in the case of the hydrolysable tannins [113] the backbone of which is rich in carbohydrates it was observed that not only the tannins but also the carbohydrates themselves in the tannin extracts reacted to form NIPUs (Fig. 5).

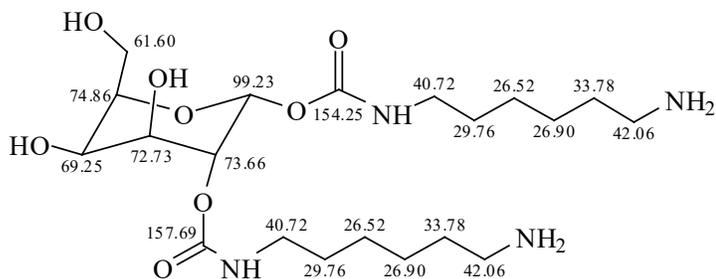


Figure 5: NIPUs formed by reaction of carbohydrates found in hydrolysable tannin extracts with dimethyl carbonate and hexamethylene diamine

This observation has subsequently led to trying to obtain NIPUs from glucose and sucrose, and to apply these for different applications [116]. Thus, mostly biosourced non-isocyanate polyurethanes (NIPU) were prepared from glucose and sucrose, by reaction with dimethyl carbonate and hexamethylene diamine and the NIPU oligomers obtained were determined. Linear and branched NIPU (Fig. 6) were formed.

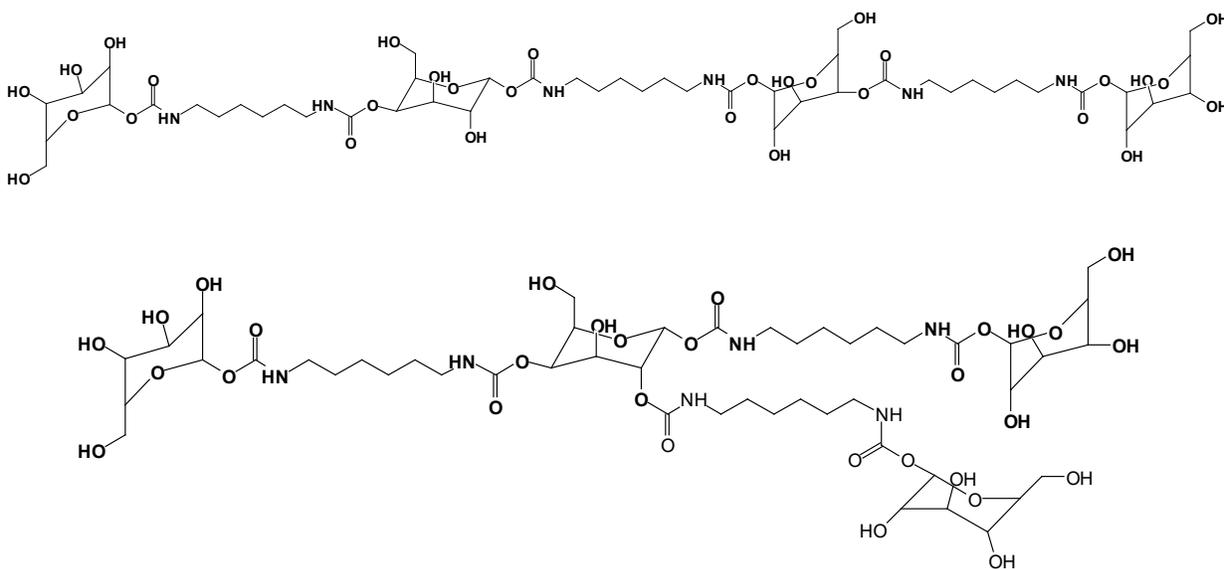


Figure 6: Linear and branched NIPUs formed by reaction of glucose with dimethyl carbonate and hexamethylene diamine

The glucose-derived NIPU were applied as wood and steel surface coatings with very encouraging results [116]. The glucose NIPU resins were also tested as thermosetting wood joint adhesives [116] and the sucrose NIPUs for wood particleboard adhesives [117] again with most encouraging results.

Glucose-based non-isocyanate polyurethanes (NIPU) were also used to prepare partially biobased polyurethane foams by reaction with NaHCO_3 as a blowing agent and addition of a silane coupling agent [112]. The foams were foamed and hardened by applying heat. Differently from the tannin-furanic foams described earlier these foams presented very limited fire resistance indicating that as for synthetic polyurethane foams the eventual use of a fire retardant appears to be really necessary. More characteristic is their stress strain behaviour. While compression does indeed flattens the cell walls nonetheless the cellular structure is maintained and the cell walls have not been destroyed. This indicates a certain level of elasticity in the cell walls of formulations containing NaHCO_3 . In effect the macro-appearance of this foams, confirms this explanation.

This NIPU foams development described above opens a number of new perspectives in biofoams based on tannins, carbohydrates and on other natural materials such as lignin and others, and even more interestingly on a number of variations in foams obtained by the mixing of these different natural materials.

The different foams dealt with in this review present similar but different characteristics according to their system of preparation and their type. Typical ranges of some properties are given in Tab. 1.

Table 1: Typical range of physico-mechanical values for different tannin-based and related foams [40, 42, 54, 57, 80, 92-94, 112]

Foam type	Apparent density (g/cm ³)	Compressive strength (MPa)	Thermal conductivity (W m ⁻¹ K ⁻¹)
Tannin-furanic	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
Tannin-furanic-isocyanate	0.040-0.050	0.08-1.20	0.036-0.040
Monoliths	0.025-1.20	0.04-1.00	0.040-0.060
NIPU glucose	0.075-0.09	0.20-0.40	-
	0.300	5.00	-

7 Conclusions

Tannin based rigid foams appear suitable for a wide range of applications. Other than thermal insulation and acoustic insulation, obviously two of the more interesting areas, a third area is also of particular topical interest. This latter is one being the carbonization of tannin foams to form carbon foams for a variety of applications, an area in which a considerable amount of research has been done in the last three years. A considerable literature on the subject exists already and the readers is invited to consult some of the initial basic work in this very interesting area as well as some of the more recent works on this subject [118-124].

Another area of application of interest for the natural tannin-furanic foams is the field of hydroponics [125]. Formaldehyde-free quebracho tannin foams were developed for horticultural/hydroponics and floral applications. These foams included in their composition a wetting agent and at least one compound able to neutralize the residual acidity derived from acid catalysts. This was necessary to bring the pH in line with what plants required. Their densities were between 0.048 and 0.066 g/cm³ and compression strength between 0.07 and 0.09 MPa. Scanning electron microscopy (SEM) images showed open porosity and average cell size of 125-250 µm. Water absorption peaked at 98% (vol.), while residual pH value was 5. These new tannin foams do not result to be phytotoxic and are apt to the conservation of fresh cut flowers and as support matrices for horticulture and hydroponics. They have shown performances comparable or superior to commercial synthetic phenolic floral foam used as reference. It is clear that a number of other applications can be thought and are likely to be developed in future especially with the new perspective of tannin-carbohydrate NIPUs foams.

References

1. Guo, A., Javny, I., Petrovic, Z. (2000). Rigid polyurethane foams based on soybean oil. *Journal of Applied Polymer Science*, 77(1), 467-473.
2. Campanella, A., Bonnaillie, L. M., Wool, R. P. (2009). Polyurethane foams from soyoil-based polyols. *Journal of Applied Polymer Science*, 112(4), 2567-2578
3. Jacob, J., Bhattacharya, M., Turner, R. B. (2002). Characterization of polyurethane foams from soybean oil. *Journal of Applied Polymer Science*, 86(6), 3097-3107.
4. Hu, S., Luo, X., Li, Y. (2014). Polyols and polyurethanes from the liquefaction of lignocellulosic biomass. *Chemistry and Sustainability (ChemSusChem)*, 7(1), 66-72.
5. Hu, S., Li, Y. (2014). Two-step sequential liquefaction of lignocellulosic biomass by crude glycerol for the production of polyols and polyurethane foams. *Bioresource Technology*, 161, 410-415.
6. Hu, S., Li, Y. (2014). Polyols and polyurethane foams from base-catalyzed liquefaction of lignocellulosic biomass by crude glycerol, Effects of crude glycerol impurities. *Industrial Crops and Products*, 57(6), 188-194.
7. Rattanapan, S. (2016). *Preparation and properties of bio-based polyurethane foam prepared from modified natural rubber and poly(ϵ -caprolactone)* (PhD Thesis). Université du Maine, Le Mans, France.
8. Ionescu, M., Wan, X., Bilić, N., Petrović, Z. S. (2012). Polyols and rigid Polyurethane foams from cashew nut shell liquid. *Journal of Polymers and Environment*, 20, 647-658.
9. Suresh, K. I. (2013). Rigid polyurethane foams from cardanol, synthesis, structural characterization, and evaluation of polyol and foam properties. *American Chemical Society Sustainable Chemistry and Engineering*, 1(2), 232-242.
10. Nadji, H., Bruzzèse, C., Belgacem, M. N., Benaboura, A., Gandini, A. (2005). Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols. *Macromolecular Materials and Engineering*, 290, 1009-1016.
11. Narine, S. S., Kong, X., Bouzidi, L., Sporns, P. (2007). Physical properties of polyurethanes produced from polyols from seed oils, elastomers. *Journal of the American Oil Chemists Society*, 84(1), 65-72.
12. Palaskar, D. V., Boyer, A., Cloutet, E., Alfos, C., Cramail, H. (2010). Synthesis of biobased polyurethane from oleic and ricinoleic acids as the renewable resources via the AB-type self-condensation approach. *Biomacromolecules*, 11(5), 1202-1211.
13. Rojek, P., Prociak, A. (2012). Effect of different rapeseed-oil-based polyols on mechanical properties of flexible polyurethane foams. *Journal of Applied Polymer Science*, 125(4), 2936-2945.
14. Faruk, O., Mohini, S. (2013). Continuous extrusion foaming of lignin enhanced thermoplastic polyurethane (TPU). *Journal of Biobased Materials and Bioenergy*, 7 (3), 309-314.
15. Mora-Murillo, L. D., Orozco-Gutierrez, F., Vega-Baudrit, J., González-Paz, R. J. (2017). Thermal-mechanical characterization of polyurethane rigid foams, effect of modifying bio-polyol content in isocyanate prepolymers. *Journal of Renewable Materials*, 5(3-4), 220-230.
16. Brenes-Granados, D., Cubero-Sesin, J. M., Orozco Gutiérrez, F., Vega-Baudrit, J., Gonzalez-Paz, R. (2017). Variation of physical properties of rigid polyurethane foams synthesized from renewable sources with different commercial catalysts. *Journal of Renewable Materials*, 5(3-4), 280-289.
17. Hatakeyama, H., Hatakeyama, T. (2013). Advances of polyurethane foams derived from lignin. *Journal of Renewable Materials*, 1(2), 113-123.
18. Basso, M. C., Pizzi, A. (2017). New closed- and open-cell, aldehyde-free protein foams. *Journal of Renewable Materials*, 5(1), 48-53.
19. Santiago-Medina, F. J., Basso, M. C., Pizzi, A., Delmotte, L. (2018). Polyurethanes from kraft lignin without using isocyanates. *Journal of Renewable Materials*, 6(4), 413-425.
20. Santiago-Medina, F. J., Pizzi, A., Basso, M. C., Delmotte, L., Abdalla, S. (2017). Polycondensation resins by lignin reaction with (poly) amines. *Journal of Renewable Materials*, 5(5), 388-399.
21. Pizzi, A. (1983). Tannin based adhesives. In: A.Pizzi ed., *Wood adhesives chemistry and technology*, pp. 178-246. Marcel Dekker. New York.

22. Pasch, H., Pizzi, A. (2002). On the macromolecular structure of chestnut ellagitannins by MALDI-TOF mass spectrometry. *Journal of Applied Polymer Science*, 85, 429-437.
23. Pizzi, A., Pasch, H., Rode, K., Giovando, S. (2009). Polymer structure of commercial hydrolysable tannins by MALDI-TOF mass spectrometry. *Journal of Applied Polymer Science*, 113, 3847-3859.
24. Radebe, N., Rode, K., Pizzi, A., Giovando, S., Pasch, H. (2013). MALDI-TOF-CID for the microstructure elucidation of polymeric hydrolysable tannins. *Journal of Applied Polymer Science*, 128, 97-107.
25. Giovando, S., Pizzi, A., Pasch, H., Pretorius, N. (2013). Structure and oligomers distribution of commercial tara (*Caesalpinia spinosa*) hydrolysable tannin. *ProLigno*, 9(1), 22-31.
26. Drewes, S. E., Roux, D. G. (1963). Condensed tannins. 15. Interrelationships of flavonoid components in wattle-bark extract. *Biochemistry Journal*, 87, 167-172.
27. Roux, D. G., Paulus, E. (1961). Condensed tannins. 8. The isolation and distribution of interrelated heartwood components of *Schinopsis* spp. *Biochemistry Journal*, 78, 785-789.
28. Saayman, H. M., Roux, D. G. (1965). The origins of tannins and flavonoids in black-wattle barks and heartwoods, and their associated 'non-tannin' components. *Biochemistry Journal*, 97, 794-801.
29. Drovou, S., Pizzi, A., Lacoste, C., Zhang, J., Abdalla, S. et al. (2015). Flavonoid tannins linked to long carbohydrate chains - MALDI ToF analysis of the tannin extract of the african locust bean. *Industrial Crops and Products*, 67, 25-32.
30. Abdalla, S., Pizzi, A., Ayed, N., Charrier, F., Bahabry, F. et al. (2014). MALDI-TOF and ¹³C NMR analysis of tunisian *Zyzyphus jubjuba* root bark tannins. *Industrial Crops and Products*, 59, 277-281.
31. Abdalla, S., Pizzi, A., Ayed, N., Charrier-El-Bouthoury, F., Charrier, B. et al. (2014). MALDI-TOF analysis of Aleppo pine (*Pinus halepensis*) bark tannin. *Bioresources*, 9(2), 3396-3406.
32. Roux, D. G., Ferreira, D., Hundt, H. K. L., Malan, E. (1975). Structure, stereochemistry, and reactivity of natural condensed tannins as basis for their extended industrial application. *Applied Polymer Symposia*, 335-353.
33. Meikleham, N., Pizzi, A. (1994). Acid and alkali-setting tannin-based rigid foams. *Journal of Applied Polymer Science*, 53, 1547-1556.
34. Tondi, G., Pizzi, A. (2009). Tannin based rigid foams, characterisation and modification. *Industrial Crops and Products*, 29, 356-363.
35. Ge, J. J., K Sakai, K. (1993). Compressive properties and biodegradabilities of polyurethane foams derived from condensed tannins. *Mokuzai Gakkaishi*, 39(7), 801-806.
36. Ge, J. J., K Sakai, K. (1998). Decomposition of polyurethane foams derived from condensed tannin II, Hydrolysis and aminolysis of polyurethane foams. *Journal of Wood Science*, 44(2), 103-105.
37. Ge, J., Shi, X., Cai, M., Wu, R., Wang, M. (2003). A novel biodegradable antimicrobial PU foam from wattle tannin. *Journal of Applied Polymer Science*, 90(10), 2756-2763.
38. Tondi, G., Pizzi, A., Masson, E., Celzard, A. (2008). Analysis of gasses emitted during carbonization degradation of polyflavonoid tannin/furanic rigid foams. *Polymer Degradation and Stability*, 93, 1539-1543.
39. Li, X., Basso, M. C., Fierro, V., Pizzi, A., Celzard, A. (2012). Chemical modification of tannin/furanic rigid foams by isocyanates and polyurethanes. *Maderas*, 14, 257-265.
40. Tondi, G., Zhao, W., Pizzi, A., Fierro, V., Celzard, A. (2009). Tannin-based rigid foams, a survey of chemical and physical properties, *Bioresource Technology*, 100, 5162-5169.
41. Tondi, G., Blacher, S., Leonard, A., Pizzi, A., Fierro, V. et al (2009). X-ray microtomography studies of tannin-derived organic and carbon foams, *Microscopy and Microanalysis*, 15, 395-402.
42. Zhao, W., Fierro, V., Pizzi, A., Du, G., Celzard, A. (2010). Effect of composition and processing parameters on the characteristics of tannin-based rigid foams. Part 2, Physical properties. *Materials Chemistry and Physics*, 123, 210-217.
43. Zhao, W., Pizzi, A., Fierro, V., Du, G., Celzard, A. (2010). Effect of composition and processing parameters on the characteristics of tannin-based rigid foams. Part 1, Cell structure. *Materials Chemistry and Physics*, 122, 175-182.

44. Celzard, A., Fierro, V., Amaral-Labat, G., Pizzi, A., Torero, J. (2011). Flammability assessment of tannin-based cellular materials. *Polymer Degradation and Stability*, 96, 477-482.
45. [NIOSH] (2000). National Institute for Occupational Safety and Health, Registry of Toxic Effects of Chemical Substances. National Institute for Occupational Safety and Health, Washington, DC, USA.
46. [NTIS] (1977). National Technical Information Service, Publication AD-A125-539. National Technical Information Service, Washington, DC, USA.
47. Basso, M. C., Li, X., Giovando, S., Fierro, V., Pizzi, A. et al. (2011). Green, formaldehyde-free foams for thermal insulation. *Advanced Materials Letters*, 2(6), 378-382.
48. Pizzi, A., Basso, M. C., Celzard, A., Fierro, V., Giovando, S. et al. (2016). Composition for manufacturing a tannin-based foam material, foam material obtainable from it, and manufacturing process thereof. US patent 9,302,413.
49. Basso, M. C., Giovando, S., Pizzi, A., Celzard, A., Fierro, V. (2013). Tannin/furanic foams without blowing agents and formaldehyde *Industrial Crops and Products*, 49, 17-22.
50. Basso, M. C., Pizzi, A., Celzard, A. (2013). Influence of formulation on the dynamics of preparation of tannin based foams. *Industrial Crops and Products*, 51, 396-400.
51. Li, X., Pizzi, A., Cangemi, M., Fierro, V., Celzard, A. (2012). Flexible natural tannin-based and protein-based biosourced foams *Industrial Crops and Products*, 37, 389-393.
52. Basso, M. C., Giovando, S., Pizzi, A., Pasch, H., Pretorius, N. et al. (2014). Flexible-elastic copolymerized polyurethane-tannin foams. *Journal of Applied Polymer Science*, 131.
53. Li, X., Essawy, H., Pizzi, A., Delmotte, L., Rode, K. et al. (2012). Modification of tannin based rigid foams using oligomers of a hyperbranched poly(amine-ester). *Journal of Polymer Research*, 19, 21-29.
54. Lacoste, C., Basso, M. C., Pizzi, A., Laborie, M. P., Celzard, A. et al. (2013). Pine tannin-based rigid foams, mechanical and thermal properties. *Industrial Crops and Products*, 43, 245-250.
55. Lacoste, C., Basso, M. C., Pizzi, A., Laborie, M. P., Garcia, D. et al. (2013). Bioresourced pine tannin/furanic foams with glyoxal and glutaraldehyde. *Industrial Crops and Products*, 45, 401-405.
56. Lacoste, C., Pizzi, A., Basso, M. C., Laborie, M. P., Celzard, A. (2014). *Pinus pinaster* tannin/furanic foams, Part 1, formulations. *Industrial Crops and Products*, 52, 450-456.
57. Lacoste, C., Pizzi, A., Basso, M. C., Laborie, M. P., Celzard, A. (2014). *Pinus pinaster* tannin/furanic foams, Part 2, physical properties. *Industrial Crops and Products*, 61, 531-536.
58. Lacoste, C., Cop, M., Kampainen, K., Giovando, S., Pizzi, A. et al. (2015). Biobased foams from condensed tannins from Norway spruce (*Picea abies*) bark. *Industrial Crops and Products*, 73, 144-153.
59. Cop, M., Laborie, M. P., Pizzi, A., M. Sernek, M. (2014). Curing characterisation of spruce tannin-based foams using the advances isoconversional method. *Bioresources*, 9(3), 4643-4655.
60. Cop, M., Lacoste, C., Conradi, M., Laborie, M. P., Pizzi, A. et al. (2015). The effect of the composition of spruce and pine tannin-based foams on their physical, morphological and compression properties *Industrial Crops and Products*, 74, 158-164.
61. Cop, M., Gospodaric, B., Kempainen, K., Giovando, S., Laborie, M. P. et al. (2015). Characterization of the curing process of pine and spruce tannin-based foams by different methods. *European Polymer Journal*, 69, 29-37.
62. Lacoste, C., Basso, M. C., Pizzi, A., Celzard, A., Ella Bang, E. et al. (2015). Pine (*Pinus pinaster*) and quebracho (*Schinopsis lorentzii/balansae*) tannin based foams as green acoustic absorbers. *Industrial Crops and Products*, 67, 70-73.
63. Rangel, G., Chapuis, H., Basso, M. C., Pizzi, A., Delgado-Sanchez. et al. (2016). Improving water repellency and friability of tannin-furanic foams by oil-grafted flavonoid tannins. *Bioresources*, 11, 7754-7768.
64. Zhou, X., Pizzi, A., Sauget, A., Nicollin, A., Li, X. et al. (2013). Lightweight tannin foam/composites sandwich panels and the coldset tannin adhesive to assemble them. *Industrial Crops and Products*, 43, 255-260.
65. Link, M., Kolbitsch, C., Tondi, G., Ebner, M., Wieland, S. et al. (2011). Formaldehyde-free tannin based foams and their use as lightweight panels, *Bioresources*, 6(4), 4218-4228.
66. Basso, M. C., Lagel, M. C., Pizzi, A., Celzard, A., Abdalla, S. (2015). First tools for tannin-furanic foams design. *Bioresources*, 10(3), 5233-5241.

67. Meikleham, N., Pizzi, A., Stephanou, A. (1994). Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates, Part 1, ^{13}C NMR, ^{29}Si NMR, x-ray and polarimetry studies and mechanism. *Journal of Applied Polymer Science*, 54, 1827-1845.
68. Pizzi, A., Meikleham, N. (1995). Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates - Part III, CP-MAS ^{13}C NMR of different tannins and models. *Journal of Applied Polymer Science*, 55, 1265-1269.
69. Pizzi, A., Meikleham, N., Dombo, D., Roll, W. (1995). Autocondensation-based, zero-emission, tannin adhesives for particleboard. *Holz Roh Werkstoff*, 53, 201-204.
70. Garcia, R., Pizzi, A. (1998). Polycondensation and autocondensation networks in polyflavonoid tannins, Part 1, final networks. *Journal of Applied Polymer Science*, 70, 1083-1091.
71. Garcia, R., Pizzi, A. (1998). Polycondensation and autocondensation networks in polyflavonoid tannins, Part 2, polycondensation vs. autocondensation. *Journal of Applied Polymer Science*, 70, 1093-1110.
72. Szczurek, A., Fierro, V., Medjahdi, G., Celzard, A. (2019). Carbon aerogels prepared by autocondensation of flavonoid tannin. Carbon Resources Convention, 2, 72-84.
73. Tondi, G., Link, M., Kolbitsch, C., Lesacher, R., Petutschnigg, A. (2016). Pilot plant up-scaling of tannin foams. *Industrial Crops and Products*, 79, 211-218
74. Tondi, G., Link, M., Oo, C. W., Petutschnigg, A. (2015). A simple approach to distinguish classic and formaldehyde-free tannin based rigid foams by ATR FT-IR. *Journal of Spectroscopy*, 1-8.
75. Reyer, A., Tondi, G., Berger, R. J. F., Petutschnigg, A., Musso, M. (2016). Raman spectroscopic investigation of tannin-furanic rigid foams. *Vibrational Spectroscopy*, 84, 58-66.
76. Kolbitsch, C., Link, M., Petutschnigg, A., Wieland, S., Tondi, G. (2012). Microwave produced tannin-furanic foams, *Journal of Materials Science Research*, 1(3), 84.
77. Tondi, G., Johansson, M., Leijonmarck, S., Trey, S. (2015). Tannin based foams modified to be semi-conductive, synthesis and characterization, *Progress in Organic Coatings*, 78, 488-493.
78. Tondi, G., Link, M., Kolbitsch, C., Petutschnigg, A. (2013). Infrared-catalyzed synthesis of tannin-furanic foams *Bioresources*, 9(1), 984-993.
79. Abdalla, S. M. S., Al-Marzouki, F., Pizzi, A., Bahabri, F. S. (2018). Bone graft with a tannin-hydroxyapatite scaffold and stem cells for bone engineering. US Patent number 10,155,069.
80. Basso, M. C., Pizzi, A., Lacoste, C., Delmotte, L., Al-Marzouki, F. A. et al. (2014). Tannin-furanic-polyurethane foams for industrial continuous plant lines. *Polymers*, 6, 2985-3004.
81. Garcia, D. E., Fuentealba, C. A., Salazar, J. P., Perez, M. A., Escobar, D. et al. (2016). Mild hydroxypropylation of polyflavonoids obtained under pilot-plant scale *Industrial Crops and Products*, 87, 350-362.
82. Garcia, D. E., Glasser, W. G., Pizzi, A., Paczkowski, S., Laborie, M. P. (2015). Hydroxypropyl tannin from *Pinus pinaster* bark as polyol source in urethane chemistry. *European Polymer Journal*, 67, 152-165.
83. Pizzi, A. (1994). *Advanced Wood Adhesives Technology*, Marcel Dekker, New York.
84. Pizzi, A., Walton, T. (1992). Non-emulsifiable, water-based diisocyanate adhesives for exterior plywood, Part 1, novel reaction mechanisms and their chemical evidence. *Holzforschung*, 46, 541-547.
85. Pizzi, A., Valenzuela, J., Westermeyer, C. (1993). Non-emulsifiables, water-based, diisocyanate adhesives for exterior plywood, Part 2, industrial application. *Holzforschung*, 47, 69-72.
86. Pizzi, A., Vosloo, R., Cameron, F. A., Orovan, E. (1986). Self-neutralizing acid-set PF wood adhesives. *Holz Roh Werkstoff*, 44, 229-234.
87. Basso, M. C., Giovando, S., Pizzi, A., Lagel, M. C., Celzard, A. (2014). Alkaline tannin rigid foams. *Journal of Renewable Materials*, 2, 182-185.
88. Santiago, F. J., Delgado, C., Basso, M. C., Pizzi, A., Fierro, V. (2018). Mechanically blown wall-projected tannin-based foams. *Industrial Crops and Products*, 113, 316-323.
89. Delgado, C., Santiago, F. J., Fierro, V., Pizzi, A., Celzard, A. (2018). Optimisation of "green" tannin-furanic foams for thermal insulation by experimental design. *Materials and Design*, 139, 7-15.
90. Santiago, F. J., Pizzi, A., Basso, M. C., Delmotte, L., Celzard, A. (2017). Polycondensation resins by flavonoid tannins reaction with amines. *Polymers*, 9(2), 37-52.

91. Santiago, F. J., Tenorio-Alfonso, A., Delgado, C., Basso, M. C., Pizzi, A. et al. (2018). Projectable tannin foams by mechanical and chemical expansion. *Industrial Crops and Products*, 120, 90-96.
92. Szczurek, A., Fierro, V., Pizzi, A., Stauber, M., Celzard, A. (2014). A new method for preparing tannin-based foams. *Industrial Crops and Products*, 54, 40-53.
93. Celzard, A., Szczurek, A., Jana, P., Fierro, V., Basso, M. C. et al. (2015). Latest progresses in tannin-based cellular solids. *Journal of Cellular Plastics*, 51(1), 89-102.
94. Lacoste, C., Basso, M. C., Pizzi, A., Laborie, M. P., Celzard, A. (2015). Natural albumin/tannins cellular foams. *Industrial Crops and Products*, 73, 41-48.
95. Rokicki, G., Piotrowska, A. (2002). A new route to polyurethanes from ethylene carbonate, diamines and diols. *Polymer*, 43(10), 2927-2935.
96. Peng, Y., Zheng, Z., Sun, P., Wang, X., Zhang, T. (2013). Synthesis and characterization of polyphenol-based polyurethane. *New Journal of Chemistry*, 37, 729-734.
97. Kihara, N., Endo, T. (1993). Synthesis and properties of poly(hydroxyurethane)s. *Journal of Polymer Science, Part A*, 31, 2765-2773.
98. Kihara, N., Kushida, Y., Endo, T. (1996). Optically active poly(hydroxyurethane)s derived from cyclic carbonate and L-lysine derivatives. *Journal of Polymer Science, Part A*, 34, 2173-2179.
99. Tomita, H., Sanda, F., Endo, T. (2001). Structural analysis of polyhydroxyurethane obtained by polyaddition of bifunctional five-membered cyclic carbonate and diamine based on the model reaction. *Journal of Polymer Science Part A*, 39, 851-859.
100. Tomita, H., Sanda, F., Endo, T. (2001). Model reaction for the synthesis of polyhydroxyurethanes from cyclic carbonates with amines, substituent effect on the reactivity and selectivity of ring-opening direction in the reaction of five-membered cyclic carbonates with amine. *Journal of Polymer Science Part A*, 39, 3678-3685.
101. Birukov, O., Potashnikova, R., Leykin, A., Figovsky, O., Shapovalov, L. (2009). Advantages in chemistry and technology of non-isocyanate polyurethane. *Journal of Scientific Israel-Technology Advances*, 11, 160-167.
102. Figovsky, O., Shapovalov, L. (2002). Features of reaction amino-cyclocarbonate for production of new type polyurethanes. *Macromolecular Symposia*, 187, 325-332.
103. Camara, F., Benyahya, S., Besse, V., Boutevin, G., Auvergne, R. et al. (2014). Reactivity of secondary amines for the synthesis of nonisocyanate polyurethanes. *European Polymer Journal*, 55, 17-26.
104. Blattmann, H., Fleischer, M., Bähr, M., Mülhaupt, R. (2014). Isocyanate- and phosgene-free routes to polyfunctional cyclic carbonates and green polyurethanes by fixation of carbon dioxide. *Macromolecular Rapid Communications*, 35, 1238-1254.
105. Kim, M. R., Kim, H. S., Ha, C. S., Park, D. W., Lee, J. K. (2001). Syntheses and thermal properties of poly(hydroxy) urethanes by polyaddition reaction of bis(cyclic carbonate) and diamines. *Journal of Applied Polymer Science*, 81(11), 2735-2743.
106. Fleischer, M., Blattmann, H., Mülhaupt, R. (2013). Glycerol-, pentaerythritol- and trimethylolpropane-based polyurethanes and their cellulose carbonate composites prepared via the non-isocyanate route with catalytic carbon dioxide fixation. *Green Chemistry*, 15, 934-942.
107. Nohra, B., Candy, L., Blanco, J. F., Guerin, C., Raoul, Y. (2013). From petrochemical polyurethanes to biobased polyhydroxyurethanes. *Macromolecules*, 46(10), 3771-3792.
108. Besse, V., Auvergne, R., Carlotti, S., Boutevin, G., Otazaghine, B. (2013). Synthesis of isosorbide based polyurethanes, An isocyanate free method. *Reactive and Functional Polymers*, 73, 588-594.
109. Cornille, A., Auvergne, R., Figovsky, O., Boutevin, B., Caillol, S. (2017). A perspective approach to sustainable routes for non-isocyanate polyurethanes. *European Polymer Journal*, 87, 532-552.
110. Tryznowski, M., Świdarska, A., Żółek-Tryznowska, Z., Gołofit, T., Paweł, G. et al. (2015). Facile route to multigram synthesis of environmentally friendly non-isocyanate polyurethanes. *Polymer*, 80, 28-236.
111. Cornille, A., Dworakowska, S., Bogdal, D., Boutevin, B., Caillol, S. (2015). A new way of creating cellular polyurethane materials, NIPU foam. *European Polymer Journal*, 66, 129-138.
112. Xi, X., Pizzi, A., Gerardin, C., Du, G. (2019). Glucose-based non-isocyanate polyurethane biofoams. *Journal of Renewable Materials*, 7(3), 301-312.

113. Thebault, M., Pizzi, A., Dumarcay, S., Gerardin, P., Fredon, E. et al. (2014). Polyurethanes from hydrolysable tannins obtained without using isocyanates. *Industrial Crops and Products*, 59, 329-336.
114. Thebault, M., Pizzi, A., Essawy, H., Baroum, A., Van Assche, G. (2015). Isocyanate free condensed tannin-based polyurethanes. *European Polymer Journal*, 67, 513-523.
115. Thebault, M., Pizzi, A., Santiago, F. J., Al-Marzouki, F. M., Abdalla, S. (2017). Isocyanate-free polyurethanes by coreaction of condensed tannins with aminated tannins. *Journal of Renewable Materials*, 5, 21-29.
116. Xi, X., Pizzi, A., Delmotte, L. (2018). Isocyanate-free polyurethane coatings and adhesives from mono- and di-saccharides. *Polymers*, 10, 402-422.
117. Xi, X., Wu, Z., Pizzi, A., Gerardin, C., Lei, H. et al. (2019). Non-isocyanate polyurethane adhesive from sucrose used for particleboard. *Wood Science and Technology*, 53(2), 393-405.
118. Tondi, G., Pizzi, A., Pasch, H., Celzard, A. (2008). Structure degradation, conservation and rearrangement in the carbonization of polyflavonoid tannin/furanic rigid foams-a MALDI-TOF investigation. *Polymer Degradation and Stability*, 93, 968-975.
119. Tondi, G., Fierro, V., Pizzi, A., Celzard, A. (2009). Tannin-based carbon foams. *Carbon*, 47, 1480-1492.
120. Szczurek, A., Amaral-Labat, G., Fierro, V., Pizzi, A., Masson, E. et al. (2011). The use of tannin to prepare carbon gels, part 1. carbon aerogels. *Carbon*, 49, 2773-2784.
121. Szczurek, A., Amaral-Labat, G., Fierro, V., Pizzi, A., Celzard, A. (2011). The use of tannin to prepare carbon gels, part 2. Carbon cryogels. *Carbon*, 49, 2785-2794.
122. Szczurek, A., Fierro, V., Pizzi, A., Stauber, M., Celzard, A. (2013). Carbon meringues derived from flavonoid tannins. *Carbon*, 65, 214-237.
123. Celzard, A., Tondi, G., Lacroix, D., Jeandel, G., Monod, B. et al. (2012). Radiative properties of tannin-based, glasslike, carbon foams. *Carbon*, 50, 4102-4113.
124. Grischechko, L., Amaral-Labat, G., Szczurek, A., Fierro, V., Pizzi, A. et al. (2013). New tannin-lignin aerogels. *Industrial Crops and Products*, 41, 347-355.
125. Basso, M. C., Pizzi, A., Al-Marzouki, F., Abdalla, S. (2016). Horticultural/hydroponics and floral foams from tannins. *Industrial Crops and Products*, 87, 177-181.