

## First Tools for Tannin-Furanic Foams Design

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Formaldehyde-free quebracho tannin foams were prepared for the first time. Several simple formulations have been presented in order to study the capital influence of each component on foaming and therefore on the characteristics of the obtained foams. Incorporation of a non-ionic surfactant leads to smaller cells and a more homogeneous cell size distribution. Cross-linking agents improve the mechanical properties of foams. A combination of different catalysts allows control of the ratio between the expansion/hardening processes. The understanding of the roles and interactions of the different components of formulation make possible the design of tannin foams having specific properties.

*Keywords:* Quebracho tannin foams; Without formaldehyde; Reactive effects; Specific properties; Expansion-hardening processes; Formulation design

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### INTRODUCTION

In the framework of sustainable development, biosourced materials represent an attractive alternative to products derived from petrochemical resources (Kaplan 1998; Gardziella *et al.* 2000; Raqueza *et al.* 2010). Tannin/furanic foams are approximately 95% composed of natural raw materials. Condensed polyflavonoid tannins are vegetal products obtained by water extraction from the wood and bark of trees, and furfuryl alcohol is obtained from agricultural waste after hydrolysis and catalytic reduction (Aguilar *et al.* 2002). These green, cheap, lightweight, cellular materials are prepared from a liquid resin mainly based on tannin and furfuryl alcohol dissolved in water, with a cross-linking agent and 4-paratoluene sulfonic acid as catalyst. A low boiling point solvent is used as the blowing agent (physical foaming) (Meikleham and Pizzi 1994; Tondi and Pizzi 2009; Basso *et al.* 2013a,b).

Polyflavonoid tannin-furanic foams have been extensively described and tested for a number of different applications showing great potential for replacing commercial, synthetic phenolic foams in most applications (Meiklenham and Pizzi 1994; Pizzi *et al.* 2008; Tondi *et al.* 2008a,b, 2009; Tondi and Pizzi 2009; Lacoste *et al.* 2013a,b).

Foam design, and thus the formulation of appropriate combinations of materials to achieve the properties wanted for particular applications, requires the understanding of (i) the influence of the different process variables, (ii) the role of each reactant during foaming, and (iii) the knowledge of the interactions of the different components involved. Recently, in this context, some research works have presented dynamic and kinetic studies of foaming for different formulations, describing in detail the foaming process

itself while correlating its parameters with the characteristic properties of mimosa and pine bark tannins (Basso *et al.* 2013a,b,c; Lacoste *et al.* 2013c).

In the present work, a formaldehyde-free quebracho tannin foam was prepared according to a base formulation. Several simple modifications were introduced to this starting formulation to show their influence on foaming, and consequently on the characteristics of the foams obtained, while discussing in detail the role played by each reactant. The aim of this work was to give some basic first principles for the appropriate formulation and design of tannin-furanic foams with desirable characteristics. This approach is not only descriptive of the foam but also predictive of the characteristics of the foams obtained, allowing foam design on demand.

## EXPERIMENTAL

### Materials

Quebracho (*Schinopsis lorentzii* and *balansae*) wood extracts were provided by Silva Chimica (S. Michele Mondovi', Italy). Furfuryl alcohol, glyoxal, and pentane were purchased at Acros Organics (Geel, Belgium), phenol sulfonic acid 65% water solution at Capital Resin Corporation (CRC 605, Columbus, OH, USA), silicone surfactant at Dow Corning (Xiameter OFX193, Paris, France), and para-toluene sulfonic acid at Sigma Aldrich (Saint-Louis, Missouri).

### Foams Preparation

The formaldehyde-free quebracho foams were prepared according to the mixture of components shown in Table 1 at  $32 \pm 2$  °C in an open plastic mould.

**Table 1.** Composition of Free-Formaldehyde Quebracho Tannin Foams

Sample name	TA	TB	TC	TD	TE
Tannin (g)	30	30	30	30	30
Furfuryl alcohol (g)	14	14	14	14	14
Water (g)	9	9	9	9	9
Pentane (g)	4.5	4.5	4.5	4,5	4.5
Phenol sulfonic acid (65%) (g)	8	8	8	8	-
Para-toluene sulfonic acid (65%) (g)	-	-	-	-	8
Silicone surfactant (g)	-	1	9	1	1
Glyoxal (g)	-	-	-	4,5	-
Apparent density (g/cm <sup>3</sup> )	0.042	0.031	0.041	0.037	0.041
Thermal conductivity (W/mK)	0.047	0.035	0.042	0.036	0.041
Average cell size (µm)	>500	~100	~100	~100	~500
Compression strength at 20% strain (MPa)	0.11	0.05	0.07	0.09	0.08

First, a liquid mixture was prepared and mechanically stirred for 20 s at room temperature. The liquid mixture was composed of furfuryl alcohol, silicone surfactant (except for the TA foam), and water. The tannins in powder form were then added to the mixture and strongly stirred for 90 s. Afterward, the glyoxal (TD foam) and subsequently the blowing agent, namely the pentane, and the acid catalyst were added by stirring for 15 s after the addition of each reagent to ensure homogenization. Finally, the mixtures were put in a ventilated oven preheated at  $32 \pm 2$  °C where foaming and hardening were carried out. After 30 min, the tannin-furanic foams obtained were dried at room

temperature. Before analysis, the samples were put in a climate chamber at 20 °C with a relative humidity of 65% for one week.

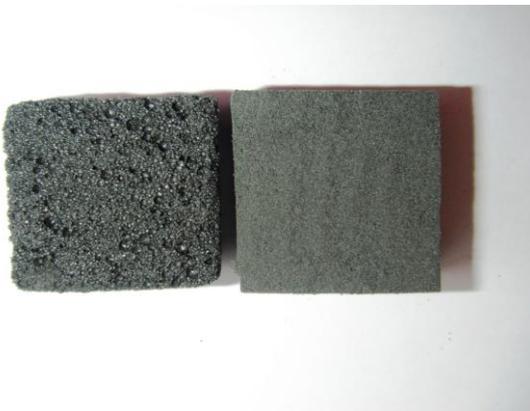
### Foams Characterization

Blocks of foam with dimensions of 3×3×1.5 cm were weighed to obtain the bulk density. The cellular morphologies of the foams were obtained by Hitachi S 520 Scanning Electron Microscope (SEM, Tokyo, Japan) at 30x magnification (TA and TE foam) and 200x magnification (TB, TC, and TD foam). Different magnifications were applied due to great differences in cell sizes of the evaluated samples. The thermal conductivity of the foam samples with dimensions of 3×3×1.5 cm was measured by the transient plane source method (Hot Disk TPS 2500, Piscataway, USA) at room temperature. The mechanical resistance to compression was investigated with an Instron 4467 universal testing machine (Norwood, MA, USA) at a load rate of 2.0 mm min<sup>-1</sup>. No significant differences in results were noticed within the specimens coming from the four repetition foams prepared for each case.

## RESULTS AND DISCUSSION

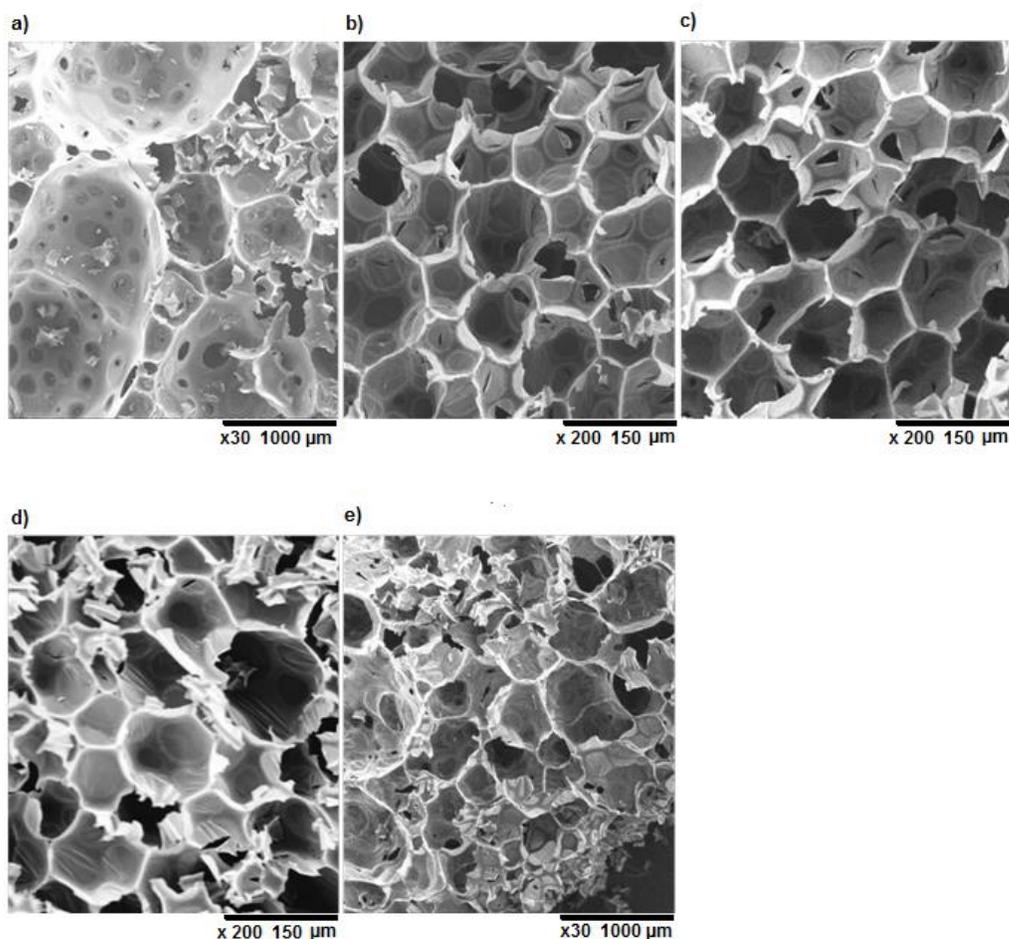
All of the mixtures presented in Table 1 yielded foams based on quebracho tannin and were completely formaldehyde-free. Thus, they are much more environmentally acceptable than the first quebracho tannin foams previously presented (Martinez de Yuso *et al.* 2014). These new tannin-furanic foams are rather lightweight (density lower than 0.1 g/cm<sup>3</sup>) and grey-coloured. Their measured thermal conductivities indicate good insulation properties, and they are comparable or better than those reported for other foams based on mimosa or pine tannins (Tondi *et al.* 2008b; Lacoste *et al.* 2013a) and other phenolic or lignophenolic foams (Shutov 1984, De Carvalho *et al.* 2003).

In particular, the TA foam is rigid, brittle, and has a cell distribution that is uneven and irregular. The TB foam, containing a small amount of a non-ionic surfactant, presents a density (0.031 g/cm<sup>3</sup>) lower than that of the TA foam (0.042 g/cm<sup>3</sup>), hence also presents a lower thermal conductivity (Table 1). Furthermore, at the macroscopic level, the aspect of these foams is very different (Fig. 1); namely the TB foam is more homogeneous, with finer and smaller cells than the TA foam which does not contain any surfactant.



**Fig. 1.** Free-formaldehyde Quebracho tannin based-foam samples. From left to right: without surfactant; with surfactant.

Scanning electron microscopy (SEM) also shows this same trend (Fig. 2a and b, Table 1). Such differences can be explained by the triple function of the surfactant: (i) to improve the compatibility of the reactants, mainly of the non-polar hydrophobic blowing agent with the resin and catalyst; (ii) to lower the surface tension of the system, thereby forming finer bubbles, and (iii) to prevent the cell wall from becoming thin and unstable during foaming, *i.e.* to prevent the developing foam from collapsing or rupturing (Iwasaki 1995; Zhang *et al.* 1999; Gardziella *et al.* 2000).

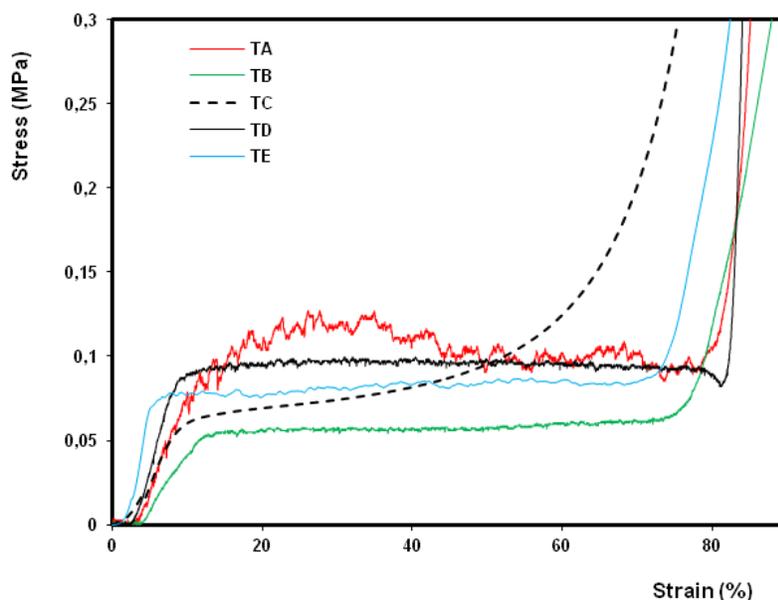


**Fig. 2.** SEM pictures of free-formaldehyde quebracho based-foam samples (a) TA foam; (b) TB foam; (c) TC foam; (d) TD foam; (e) TE foam

It is thus interesting that although it has a lower density, the cell size of the TB foam is lower than for the TA foam. This can be explained because the rise temperature is lower and later when a surfactant is used; curing process shows the same trend (Basso *et al.* 2013b). In this way, TB foam (with surfactant) becomes rigid more slowly than TA foam; then TB is more expanded, and so it is lighter than TA. Thus, the inclusion of a surfactant in the foam composition allows for the modification of the cell size independently of the density of the material, contrary to what was found by Zhao *et al.* (2010), Lacoste *et al.* (2013a), and Martinez de Yuso *et al.* (2014) for mimosa, pine, and quebracho tannin foams, respectively, who were limited to the variation of the blowing agent proportion. As a consequence, the capacity of achieving independence from the

other foaming parameters greatly increases formulation possibilities and the range of materials that can be developed, hence their greater diversity of properties and applications.

Figure 3 shows the compression resistance curves for the TA and TB foams. The former presents a higher mechanical resistance (Table 1) which is consistent with its greater density. The TB foam is instead more elastic as shown by the shape of its compression curve. This behaviour could depend on the temperature, hence the internal pressure generated during foaming, decreasing when a surfactant is included in the formulation (Basso *et al.* 2013). Thus, the foam with the surfactant is more elastic and less brittle.



**Fig. 3.** Stress-strain curves of free-formaldehyde quebracho based-foams

This same trend has been observed (examples not shown in Table 1) when used in the foam composition small proportions (0.2 to 2 g) of either castor oil 35OE and 40OE, Pluronic PE6800 (blocks copolymers of polypropylene glycol-polyethylene glycol), or Tegostab B8406 and Tegostab B8244, two silicone surfactants currently used for the manufacture of polyurethane foams. All of these products are non-ionic surfactants.

Conversely, inclusion of other types of surfactants must be evaluated for each specific case. Adding anionic surfactants that are strongly hydrophilic, particularly sodium dodecylbenzenesulphonate or laureth sulphate (not reported in Table 1), provides a lack of compatibility with the pentane blowing agent and leads to collapse and destruction of the cellular structure. Such types of additives, often used in floral foams (dry flowers conservation, hydroponic cultures), must be combined with non-ionic surfactants which ease the emulsion formation for all the components of the formulation.

The TC foam (Table 1) containing a much higher proportion of non-ionic surfactant presents a structure as homogeneous as the TB foam due to the emulsion effect of the surfactant allowing for better mixing of the system components. Its cellular structure (Fig. 2c, Table 1) is similar to that of the TB foam. Nonetheless, its density is greater as well as its mechanical resistance and thermal conductivity. When a high proportion of surfactant is used, this compound acts as a plasticizer (Gardziella *et al.*

2000). Using plasticizers decreases the internal temperature of the foams, which decreases their internal foaming pressure and their rate of expansion (Basso *et al.* 2013a; Lacoste *et al.* 2013c). Such an effect would explain why the TC foam has a higher density than the TB foam as well as a certain degree of elasticity (Fig. 3). The foam density and its mechanical properties are then controlled by the proportions of surfactant used. In this way, the TC foam hardening is slower than for the TA and TB foams. For formulations TA and TB, the foams are sufficiently hardened 15 min after the catalyst addition and can be cut neatly with a knife. However, the TC foam remains semi-liquid and needs at least 20 to 25 min to solidify. This longer hardening time is due to a certain degree of elasticity (Fig. 3).

It has been shown that adding surfactant in proportions higher than those in Table 1 causes foam shrinking. This can be explained by the greater out of phase difference between foaming and hardening (Basso *et al.* 2013a), for which the structure of the foam while foaming is not sufficiently solid to support its cooling. This occurrence can be avoided by using moulds made with insulating materials, possibly closed or by increasing the outer temperature or by incorporating additives favouring polymerization.

Increasing the proportion of furfuryl alcohol in the formulation in order to limit foam shrinkage is not a valid approach, as it contributes even more to such an undesirable effect. An increase in the proportion of furfuryl alcohol, the heat generated by self-polymerisation of the foam system, would further exacerbate the time difference between foaming and hardening (Basso *et al.* 2013a,c). Thus, after a rather sharp temperature peak leading to an abrupt foam expansion, the system undergoes rapid cooling before the material can present a sufficiently solid structure in absence of either a cross-linker such as formaldehyde or a sufficiently high curing temperature. Furthermore, in addition to the shrinking problem, too quick an expansion is harmful to the integrity of the foam and hence to the mechanical properties of the final foam. In principle, it is preferable to control the kinetics of foam expansion by the external temperature used.

To improve the mechanical performance of the TB foam, a cross-linker other than the environmentally unacceptable formaldehyde has been added to the formulation obtaining the foam TD (Table 1). In particular, the addition of the non toxic and non-volatile glyoxal (Ballerini *et al.* 2005; El-Mansouri *et al.* 2007a,b), improves the foam's mechanical resistance and renders it more rigid (Table 1 and Fig. 3). This is because it favours polymerisation and cross-linking by forming new tannin-aldehyde and furan-aldehyde bonds (Lacoste *et al.* 2013b). The same effect is obtained by adding glutaraldehyde (Li *et al.* 2013 & 2014) and 1,6 diaminohexane to the TB formulation. All of these additives favour cross-linking and polymerisation.

By the use of different additives it is possible to give the foam its desired characteristics. For example, a foam of improved mechanical resistance can be obtained by including a cross-linker in the formulation and the increased rigidity induced by this can be counterbalanced by the addition of an appropriate amount of a non-ionic surfactant. Finally, replacing the phenol sulfonic acid used as a catalyst in the TB foam with p-toluen sulfonic acid (pTSA) leads to obtaining the TE foam (Table 1). These two acid catalysts, which are currently used for the preparation of synthetic phenol-formaldehyde foams, both react and are included in the final foam structure (Gardziella *et al.* 2000; Tondi *et al.* 2008a; Basso *et al.* 2014). However, the composition and the characteristics of the catalyst as well as the curing/foaming relationship appear to determine the characteristics of the final foam.

The TE foam is denser and consequently presents both a higher mechanical resistance and a higher thermal conductivity than the TB foam (Table 1 and Fig. 3). TE foam hardening is slow (contrary to the TB foam); thus it cannot be cut with a knife after 15 minutes as in the case of foam TC. Moreover, it has larger cells than the TB foam (Fig. 2e, Table 1) and it shrinks because the pTSA used as catalyst favours more rapid foam expansion rather than polymerisation and cross-linking. Conversely, phenol sulfonic acid favours these last processes, *i.e.*, the curing foam. The molar weights of pTSA and phenol sulfonic acid are similar (172 and 174 g/mol, respectively), but the first is used as powder monohydrate (molecular weight 190 g/mol, 99% extra pure), while the phenol sulfonic acid is purchased as a 65% water solution including 2% sulphuric acid.

While the TC and TE foams suffer from some shrinkage due to their slower hardening, the cell size of the TC foam is not greater than for the TB foam because the excess surfactant decreases the foaming temperature of the system and thus slows down its expansion. For the TE foam, the lack of a plasticizer/surfactant leads to enlarged cells.

An interesting possibility is to combine the two acid catalysts in different proportions to obtain foams presenting specific characteristics by the precise control of the degrees of polymerisation/cross-linking and the equilibrium between the rate of foam expansion and hardening. For example, the pTSA acid could be combined with either the phenol sulfonic acid, another stronger organic acid, or even a very moderate proportion of sulphuric acid. In the case that alkaline catalysis is desired instead, the formulation needs to be changed by substituting the furfuryl alcohol with another hardener/cross-linker (Basso *et al.* 2014). In order to allow such foam expansion and hardening, the external temperature of the operation will need to be higher, due to the lack of the heat generated by the acid self-polymerisation of furfuryl alcohol.

## CONCLUSIONS

1. Incorporation of a small proportion of non-ionic surfactant leads to a more homogeneous cell size distribution and smaller cells in tannin/furanic foams.
2. Tannin foams having a high proportion of non-ionic surfactant present a certain degree of elasticity.
3. The mechanical performance of foams can be improved by using a cross-linking agent, such as an aldehyde.
4. The combination of different catalysts allows for controlling the ratio between the expansion/hardening processes.
5. The appropriate combination of different components and additives in the formulations leads to achieve specific properties for the obtained tannin foams.

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