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# Mechanically blown wall-projected tannin-based foams

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## ABSTRACT

Condensed flavonoid tannin-based foams from quebracho tannin extract have been developed using a new method of expansion based on 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 stability of the as-obtained liquid foam and the influence of the amount of catalyst are reported. 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. Bulk density (0.069–0.080 g/cm$^3$), mechanical (compressive strength of 0.034–0.13 MPa) and thermal (0.045–0.047 W m$^{-1}$ K$^{-1}$) properties and morphological appearance of the foams have been characterised and reported.

## 1. Introduction

A broad range of rigid foams is commercially available today, such as phenolic or polyurethane foams. These foams are used for a wide variety of applications, such as packaging in transportation, electronic applications, flower preservation, flame retardant or in building applications, e.g. for roofing, flooring or as insulation materials. However, as they are derived from petrochemical resources, their development from biosourced, renewable materials is gaining in importance.

Tannin-based foams are approximately 95% composed of natural raw materials and have shown potential as alternative to phenolic foams (Li et al., 2013; Tondi et al., 2009; Zhao et al., 2010; Zhou et al., 2013). The main component of those foams is tannin, which is a non-toxic complex of polyflavonoids generally extracted from tree bark. This natural material has been shown to impart exceptional fire-resistant properties to the foams from it (Celzard et al., 2011). Moreover, tannin foams self-extinguish when the flame and the heat source are removed (Celzard et al., 2011). The second main component of these foams, at a 20% level by weight, is furfuryl alcohol. The latter is also a biosourced material, being obtained by catalytic reduction of furfural, a natural derivative obtained by carbohydrate hydrolysis from agricultural waste (Aguilar et al., 2002).

Tannin-based rigid foams prepared from mimosa bark extract (*Acacia mearnsii*) are known since 1994 (Meikleham and Pizzi, 1994). Most recently, similar materials have been developed to obtain relevant properties for different applications, such as floral preservation (Basso et al., 2016), and thermal (Tondi et al., 2008) or acoustic (Lacoste et al., 2015a) insulation. In addition, these foams could be prepared from condensed tannins extracted from different trees, such as mimosa (*Acacia mearnsii*, formerly *mollissima*, de Wildt) (Tondi et al., 2009), quebracho (*Schinopsis lorentzii* and *balansae*) (Basso et al., 2015; Martinez de Yuso et al., 2014), as well as pine (*Pinus radiata* (Lacoste et al., 2013a) and *Pinus pinaster* (Lacoste et al., 2014)). Many different formulations have already been developed, and the resultant materials have been prepared using different foaming methods. The most used methods are: chemical foaming (Basso et al., 2014b), physical foaming (Basso et al., 2015; Li et al., 2013), both of them together (Li et al., 2012; Li et al., 2012a) and even formulations without blowing agent (Basso et al., 2013a). Moreover, cellular tannin-based materials have been also obtained by a mechanical method (Szczurek et al., 2014). For improving the properties of the foams, different crosslinkers have been studied under acidic conditions, such as formaldehyde (Tondi et al., 2009), other aldehydes (Lacoste et al., 2013b) or without any of them (Basso et al., 2011). Foams under alkaline conditions have also been developed (Basso et al., 2014a).

On the other hand, a firefighting foam is a stable mass of small bubbles used for fire suppression. It can extinguish a liquid fire by the combined mechanisms of cooling, separating the flame or the ignition source from the product surface, thus preventing its contact with oxygen resulting in the suppression of the combustive, and suppressing

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vapours and smothering the fire. Firefighting foams are classified in various types as a function of the kind of fire or risks incurred. Such foams are a combination of foam concentrate, water and air. The foam concentrate is a liquid foaming agent, which mixed with the recommended amount of water and air produces a foam. The mechanically-stirred foams, currently the most used for firefighting, are generated through a two-step process. In the first step, the foam concentrate is injected in the desired ratio into the water through the proportioning device. The foam proportioner, generally an eductor, works on the Venturi principle. The water flow through a reduced section creates then a pressure drop that picks up and introduces the foam concentrate from its tank into the water pipe. In the second step, the foam solution reaches the foam nozzle, within which air is injected into the foam solution. The foam solution and the air travel up to the outlet, where a properly expanded foam exits the nozzle.

The present work explains the preparation and the properties of tannin-based foams based on the firefighting or in-tunneling foams principle. For this new method, a tannin-furanic resin was mixed with an aqueous solution of foam concentrate and a catalyst. Through vigorous mechanical stirring, a large amount of air was then introduced into the mixture, leading to a fast expansion of the liquid foam. After curing at room temperature, a cellular material was obtained. This work is part of a research project dealing with tannin-based wall-projected foams. The foams presented in this publication should be considered as a first step in the development of foams with a natural origin for their adaptation to an application as projectable foams for thermal or acoustic insulation of buildings. Firstly, what is needed is an adaptation to a laboratory scale and then, an adaptation to a real field application such as those used in the application of polyurethanes foams by projection. These are the further steps to follow in the development of this material. The development of these foams is of interest because in addition to having a direct industrial application, it is the first time that tannin foams have been developed by simultaneous mechanical foaming and polymerization at room temperature. So far, tannin based foams had only been obtained by physical foaming either (i) without an additional external heat source – which renders foaming much more difficult to control; or (ii) by mechanical foaming where an external heat input during 24 h was necessary for polymerization of the foam – which is not very practical for its application–.

## 2. Experimental

### 2.1. Materials

Quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) tannin extract, called Fintan T on the market, was provided by SilvaChimica (S. Michele Mondovi, Italy). Furfuryl alcohol, ethylene glycol and Kolliphor ELP were purchased from Sigma-Aldrich (France) and used as supplied. Phenolsulphonic acid 65% water solution was purchased at Capital Resin Corporation (Columbus, OH, USA). Ethoxylated tallow amine with the commercial name Noramox S11 was supplied by Arkema (Châteauroux, France) and the ethoxylated oleyl amine, OAM-10, was supplied by Saibaba Surfactants Ltd (Gujarat, India). The foaming agent used was SM2101-l, a proprietary product supplied by Condat (Chasse-sur-Rhone, France) mainly composed of alkyl glycols and modified fatty acid soaps.

### 2.2. Foam preparation

The new mechanically expanded tannin foams were prepared by vigorous stirring of a tannin resin solution with a solution of foam concentrate (SFC hereinafter). In a first step, a tannin resin containing 46.7 wt.% of tannin, 37.4 wt.% of furfuryl alcohol, 9.4 wt.% of water, 3.4 wt.% of ethylene glycol and 3.1 wt.% of ethoxylated castor oil was mixed by strong mechanical stirring until achieving a homogeneous mixture. This resin was prepared using a metallic paddle blade stirrer. Then, a 14 wt.% of foam concentrate in water was added to the prepared resin at a ratio SFC/resin of 0.6 and stirred at 2000 rpm for 5 min. Other resin to foaming surfactant ratios have been tried, giving a more unstable liquid foam (see below). For stirring and thus mechanically blowing the mixture into a foam, a special foaming blade stirrer (Fig. 1) was used. The unusual shape of this blade favours the incorporation of air in the mixture, decreasing the stirring time needed. In few seconds, after the stirring has begun, a liquid foam was formed increasing its volume progressively as more air was incorporated. Finally, the acid (14 g) was added under stirring, continued for 30 s more. After that, the foam was left to cure at room temperature. The stable liquid foam obtained just before the addition of acid and the final rigid foam are both shown in Fig. 2. The polycondensation between the different components was induced under acidic conditions by the exothermal self-condensation of the furfuryl alcohol in the mixture. Contrary to other foams formulation, in the present case there is not expansion due to the release of gases during furfuryl alcohol self-condensation. The temperature in the foam increases while, simultaneously, the liquid foam hardens by crosslinking of the tannin-furfuryl alcohol system (Foo and Hemingway, 1985; Pizzi, 2016), turning the colour of the foam from light brown to black. This method has been used for a number of cases varying the quantity of acid as indicated in Table 1. Furthermore, three additional samples have been prepared using two non-ionic surfactants, an ethoxylated tallow amine (NSA3 and NSA6 formulations) and an ethoxylated oleyl amine (NSO formulation). All the formulations are detailed in Table 1.

**Fig. 1.** Foaming blade.

### 2.3. Expansion and stability of the liquid foam

Liquid tannin foams are not stable for a too long period. In general, the lifetime of a foam can be split into two main regions, as shown in Fig. 3 (Lunkenheimer et al., 2004; Rafati et al., 2016). The first region corresponds to the foaming, where the liquid foam grows up progressively until the maximum volume. After stirring is stopped, the second region, the decay one, starts and the maximum volume is kept during a deviation time, $t_{de}$. When the deviation time is exceeded, the bubbles begin to collapse, while a liquid phase starts to drain and accumulates at the bottom of the vessel, separating the liquid foam in two well-defined phases. The destabilization events that can take place on a liquid tannin foam are explained more in detail elsewhere (Delgado-Sánchez et al., 2017). Drainage can be, therefore, used to study the stability of the foam through the transition time, $t_{tr}$, or half-life of the foam in respect to its maximum volume. Thus, the longer the transition time, the more stable is the liquid foam (Lunkenheimer et al., 2004; Rafati et al., 2016). However, taking the transition time as a reference is not the best option in our case. The objective is indeed obtaining homogeneous rigid foams before a significant decay takes place at the point at which liquid foams are already destabilized. Therefore, a