



## Tannin-based rigid foams: A survey of chemical and physical properties

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### ARTICLE INFO

#### Article history:

Received 23 March 2009

Received in revised form 18 May 2009

Accepted 20 May 2009

Available online 2 July 2009

#### Keywords:

Tannins foams

Phenolic foams

Physical properties

Chemical resistance

### ABSTRACT

Tannin-based rigid foams, prepared from 95% natural material, are suggested for replacing synthetic phenol–formaldehyde foams in various applications. For that purpose, a few physical properties were measured and reported here: resistance to fire and chemicals, absorption of various liquids, permeability, thermal conductivity and mechanical (compressive and tensile) strength. Modifying the composition through the use of boric and/or phosphoric acid allowed substantial increase of fire resistance. The materials were also found to present good resistance to strong acid and bases, and to solvents. High affinity for water, but limited one for organic liquids, was also evidenced. Finally, slightly anisotropic mechanical properties were measured. The materials present a brittle behaviour, whether tested in compression or traction; nevertheless, their strengths, as well as their thermal conductivities, are fully comparable with those of their phenolic counterparts. We show that such materials of vegetable origins can compete with synthetic ones for most of traditional applications.

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### 1. Introduction

Structural thermoset foams are extensively used in transportation, packaging, cushioning, insulation, but also in building materials, automobiles, aircrafts and marine structures, as well as in electronic applications and flame retardants. For all these applications, flame, smoke and toxicity performances are critical. From that point of view, the performances of phenolic foams are much higher than those of polyurethane, polyvinyl chloride or polystyrene foams. Due to their good insulating properties, low density, outstanding fire characteristics, low smoke emission, no dripping of molten plastic when exposed to flame and low cost, phenolic foams bring a suitable solution as insulation and sandwich core materials. They are also highly resistant to chemicals and solvents. Finally, due to their brittle character, phenolic foams may dissipate energy irreversibly by damage and rupture of the skeleton, and find applications in the field of crash protection and packaging.

Foams based on natural products might replace industrial phenol–formaldehyde (i.e., phenolic resoles) foams in most of applications, as far as they present comparable properties. It is the purpose of the present work to show that thermoset tannin-derived foams are relevant materials for traditional applications of

phenolic foams. Especially, foamed phenolic resoles are customarily used as open-celled flower foams, closed celled insulation foam for civil engineering, foam for fire protection elements, filler for mining and tunnelling, etc. Such light materials might be replaced by vegetable tannins-based ones, given that tannins indeed combine high reactivity, “green” origin, and low cost (typically 650€ per metric ton). Mimosa (*Acacia mearnsii* formerly *mollissima*, De Wildt) bark tannin-based rigid foams have been known since 1994 (Meikleham and Pizzi, 1994). These tannin–furanic foams typically comprise 95% of natural products. Polyflavonoid tannins, representing more than 55% of the foam, are vegetable extracts derived from bark. Around 20% of the final weight of the foam is constituted by furfuryl alcohol which is obtained throughout catalytic reduction of furfural, a natural derivative obtained by hydrolysis of the sugars from several agricultural crops (Aguilar et al., 2002).

Tannin-based foams are prepared from a viscous liquid mixture of tannin–formaldehyde resin and furfuryl alcohol. The latter is used as a heat-generating agent through both its auto-polymerisation and for its reaction with the tannin under acid conditions; it also has an advantageous strengthening effect. Expansion of this liquid mixture to low-density foam is obtained by simultaneous cross-linking of the tannin–furfuryl alcohol mixture and evaporation of a low boiling-point solvent used as blowing agent (here diethyl ether). In the same time, polymerisation occurs because tannins quickly react with aldehydes, especially through the nucleophilic sites of their A ring.

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Characterisation of tannin-based rigid foams was just initiated in a recent work (Tondi and Pizzi, 2008). The present study reports further advances and more detailed information. Besides, significant improvements are reported here, through simple composition modifications of reference materials. Physical properties of the latter, such as liquid absorption and permeability, thermal conductivity and compressive and tensile resistance, are also measured and discussed. As far as the available data from the open literature allow it, systematic comparison of these properties with those of synthetic phenolic foams is made. It will be demonstrated that tannin-based foams present very similar performances, and can thus be considered as ecological, cheap, alternative materials. Finally, the measured properties are modelled on the basis of the foams' structure, and useful relationships are suggested for the first time, for predicting the behaviour of such materials as a function of their apparent density.

## 2. Experimental

### 2.1. Preparation of foams

Standard foams (i.e., without additives) were prepared as follows: furfuryl alcohol (5.2 g), formaldehyde 37% water solution (3.7 g) and water (3.0 g) were mixed with 15 g of tannin extract under mechanical stirring. When the mixture became homogeneous, diethylether (foaming agent: variable amount between 1 and 2 g) and then *para*-toluene-4-sulphonic acid (pTSA) 65% water solution (6.0 g) were added and mixed for 10 s. Diethyl ether was chosen among other blowing agents because of its very low boiling point (35 °C) and good miscibility with the other components of the foam. The mixture was then poured in a 6 × 6 cm plastic lab-made PET box. The resin foamed within 2 min of mixing, leading to black foam of density ranging from 0.04 to 0.12 g cm<sup>-3</sup>. The temperature rose to about 40 °C. After 10 min the skin of the foam was cut out and the remaining structure was left to age for at least 24 h. During this period, evaporation of residual blowing agent trapped into the foam occurred. Due to the rising of the gas vertically during foaming, the foams are orthotropic materials. They indeed present slightly elongated cells in the direction of cell growth, whereas the pores appear to be isotropic when observed in the orthogonal plane. Therefore, two measurement directions were defined: the so-called growing (or *z*-) direction, corresponding to the (vertical) direction of foaming, and the flat (*xy*-) direction, corresponding to the orthogonal (horizontal) plane.

Several modified foams have been prepared in order to increase their fire resistance: (a) foam modified with boron, prepared by addition of a solution of boric acid (H<sub>3</sub>BO<sub>3</sub>: 50.0 g L<sup>-1</sup>) instead of water; (b) foam modified with phosphorus, prepared by addition of 1.5 g of *ortho*-phosphoric acid (H<sub>3</sub>PO<sub>4</sub>: 85%) and 4.5 g of pTSA 65% water solution, instead of just 6.0 g of pTSA; Foam modified by both phosphorus and boron, prepared with the two, simultaneous, aforementioned modifications. For all these materials, the amount of diethylether was always kept constant at 1.5 g.

### 2.2. Characterisation of foams

#### 2.2.1. Porosity and surface area

Given their composition (mainly natural polymers cross-linked in aqueous solution), measuring their surface area through the traditional BET method based on nitrogen adsorption at 77 K is not possible. The materials indeed need to be outgassed by heat-treatment under vacuum, and continuously release volatile matters in these conditions. Thus, obtaining a sufficiently low working pressure in the adsorption apparatus is never possible. Therefore, the surface area can only be estimated, and compared with that of

carbon foams (obtained by pyrolysis in inert gas) having the same origin and the same pore structure.

Unpublished works from our group revealed, on the basis of SEM observations and tomography studies, that the pore structure may be modelled by a close packing of connected spherical pores. If the latter all have a radius *r*, then the specific surface area (m<sup>2</sup> g<sup>-1</sup>) reads:

$$S = \frac{3C}{dr} \quad (1)$$

*C* is the compacity and is equal to  $\pi\sqrt{2}/6 = 74\%$ , whether the close-packing is FCC or HCC type, and *d* is the bulk density, defined as the mass of material divided by the total volume it occupies. The pore-size distribution being shouldered at low pore diameters, about 10% of the total porosity is based on spherical pores having a radius typically *r*/10, and located between the bigger cells of radius *r*. The additional surface area brought by this narrower porosity is then:

$$S_{add} = \frac{3}{dr} \quad (2)$$

so the total surface area is  $S_{tot} = S + S_{add}$ , hence:

$$S_{tot} = \frac{3(1+C)}{dr} \quad (3)$$

The porosity was determined from the bulk density of the foam and from the skeletal density, *d<sub>s</sub>*, (i.e., the density of the polymer from which the foam is made), which was measured by helium pycnometry in a lab-made apparatus; *d<sub>s</sub>* was found to be 1.59 g cm<sup>-3</sup>, slightly higher than that of pure cured phenol-formaldehyde resin: 1.47. The porosity,  $\Phi$ , reads:

$$\Phi = 1 - \frac{d}{d_s} = 1 - d_r \quad (4)$$

where *d<sub>r</sub>* is the so-called relative density (dimensionless). The surface area could be calculated from average pore sizes, derived from the observation of a high number of cells by scanning electron microscope (SEM Hitachi S 4800).

#### 2.2.2. Resistance to fire and chemicals

Measuring such properties is of interest, given that these foams can be suitable materials for industrial thermal insulation in severe conditions. Resistance to fire was tested as follows. Foam samples of similar densities (around 0.058 g cm<sup>-3</sup>) and dimensions (2 × 2 × 2 cm) were exposed facially for 20 s to the oxidising flame of a Bunsen burner, and especially to the top of the blue cone of the flame (at least 1200 °C and 10 kW m<sup>-2</sup>). The flame was considered as extinguished when the generated glow disappeared and the foam reacquired its original black colour. During the 10 min test, the weight loss of each sample was measured as a function of time.

Tannin-based rigid foams might be used as filters for corrosive chemicals. For that reason, some tests of chemical resistance to acid and alkali media were achieved. Resistance to strong bases and acids was tested as follows. 30 × 30 × 15 mm foam samples of density 0.06 g cm<sup>-3</sup> were soaked for 24 h into either 33% H<sub>2</sub>SO<sub>4</sub> or 33% NaOH aqueous solutions. Samples were then dried by towel-paper and next during 12 h in air at 60 °C. The compressive strengths were finally measured once the samples were totally dry (see Section 2.2.6).

#### 2.2.3. Absorption of liquids

Absorption of water on one hand, and various organic fluids on the other hand, was investigated. In order to measure the maximum amount of water that can be absorbed by foams of different densities, cubic 2 × 2 × 2 cm samples were placed in an impregnation chamber filled with water. The pressure of the air above water was decreased to 10 mbar, which value was maintained for

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