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A new method for preparing tannin-based foams

A. Szczurek[a], V. Fierro[a], A. Pizzi[b,c], M. Stauber[d], A. Celzard[a,e,*,1]

[a] CNRS, Institut Jean Lamour, UMR 7198, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France
[b] Université de Lorraine, LERMAB, EA 4370, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex 9, France
[c] King Abdulaziz University, Jeddah, Saudi Arabia
[d] b-cube AG, Fabrikweg 2, 8306 Brüttisellen, Switzerland
[e] Université de Lorraine, Institut Jean Lamour, UMR 7198, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France

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ABSTRACT

Phenolic foams derived from natural precursors, condensed tannin extracts from mimosa trees, were prepared for the first time by curing and drying liquid foams obtained by aeration of tannin solutions containing surfactant and crosslinker. The materials derived from the new method were called tannin-based meringues in reference to the lightweight pastry made in a similar way by whipping egg whites. The new foams were compared with more standard cellular solids having very close composition but obtained by physical or chemical foaming. No significant differences were observed in terms of mechanical and thermal properties. The porous structure was also similar, except the cell sizes which were much higher in tannin-based meringues. The new method is not only easy, fast and cost-effective, but allows producing solid foams having a very broad range of bulk densities and cell sizes, which can be controlled by the concentration of tannin in the initial solution, all other things being equal.

1. Introduction

Phenolic foams are used for long in the fields of transportation, packaging, cushioning, insulation, but also in buildings, automobiles, aircrafts and marine structures, as well as in electronic applications and flame retardants. Such lightweight materials are especially appreciated because of their fire resistance, considerably higher than that of any other polymer foams (Haberstroh and Schlumm, 2006). In a former paper (Tondi et al., 2009a), some of the present authors showed how industrial phenol-formaldehyde chemical systems (i.e. phenolic resoles) can be advantageously replaced by natural condensed tannins.

Condensed tannins are composed of nontoxic flavonoid molecules of vegetable origin. Such polyphenols are mainly used for leatherwork but are also known in other fields of industry, e.g. in food industry and for manufacturing various kinds of adhesive resins used in the production of panels and particleboards (Pizzi and Mittal, 2003). They are known as potential substitutes of expensive resorcinol in sol–gel polycondensation reaction (Szczurek et al., 2011a,b), and have been shown to be excellent precursors of new carbon materials (Amaral-Labat et al., 2013a). And, of course, flavonoid tannins can also be used for producing rigid, insulating foams (Tondi et al., 2009a,b; Tondi and Pizzi, 2009; Celzard et al., 2011, 2013a,b; Basso et al., 2011, 2012, 2013; Pizzi et al., 2013; Lacoste et al., 2013a,b; Li et al., 2012a, 2013a; Meikleham and Pizzi, 1994; Zhao et al., 2010a,b).

Many physical properties of commercial phenolic foams and lab-made tannin-based foams are indeed fully comparable, at similar relative density. The exceptional fire resistance of tannin-based foams is even higher than that of other phenolic foams, as the latter have ignition time of around 2 min when submitted to a heat flux as high as 50 kW m^{-2}. The released heat, 12 kW m^{-2}, is much lower than what was required for burning them under the same radiant energy. Therefore, tannin foams slowly consume without flame if the heat flux is maintained and spontaneously self-extinguish as soon as the heat source is removed (Celzard et al., 2011).

Tannin-based rigid foams have been suggested as floral foams, internal insulating materials for interior and exterior wooden doors (Tondi et al., 2008) and as core materials for sandwich panels (Zhou et al., 2013). Their great advantage lies in their "green" character, since that up to 95% of their ingredients may have a natural origin. The base of the thermoset resin from which they are made is condensed tannin, a vegetal product obtained by spray-drying aqueous extracts from wood or tree barks. The most common commercial condensed tannin is the one extracted from mimosa barks (*Acacia mearnsii*), produced at around 220,000 tons per year, followed by quebracho tannin, extracted from *Schinopsis balansae* and *Schinopsi lorentzii* wood and produced at around 80,000 tons per year, followed by a variety of other tannins such as pine (*Pinus*

* Corresponding author at: Université de Lorraine, Institut Jean Lamour, UMR 7198, ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Epinal Cedex, France. Tel.: +33 329 29 61 14; fax: +33 329 29 61 38.
E-mail address: Alain.Celzard@univ-lorraine.fr (A. Celzard).
[1] Member of the Institut Universitaire de France.

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radiata), chestnut (*Castanea vesca*) and gambier (*Uncaria gambir*), extracted from barks, barks and timber, and shoot and leaves, respectively (Pizzi and Mittal, 2003). In the present work, only the results obtained with mimosa tannin are described, but successful trials have been made with the other families of condensed tannins.

Significant advances have been made in the recent past for producing many different kinds of tannin-based foams, using various formulations and different ways for producing the porosity. For example, foams without formaldehyde (Basso et al., 2011; Pizzi et al., 2013), using other aldehydes than formaldehyde (Lacoste et al., 2013a), based on a mixed chemical and physical foaming (Li et al., 2012a,b), using different kinds of blowing organic agents (Li et al., 2013a) or without blowing organic solvent at all (Basso et al., 2012, 2013) have been described. Different kinds of tannins have also been successfully used for the first time, leading to foams having different characteristics (Lacoste et al., 2013a,b; Celzard et al., 2013a). However, the panel of foaming methods was essentially limited to physical or chemical foaming, of both together, although the preparation of emulsion-templated cellular tannin-based organic (Celzard et al., 2013b) and carbon (Szczurek et al., 2013a) foams has just been reported.

In the present paper, a new way of producing tannin-based foams is described in detail. This method is inspired from the preparation of meringues from egg whites, and the corresponding materials are thus called tannin-based meringues (TBM). In the preparation of true meringues, egg whites, which typically comprise 90% of water and 10% of proteins, are severely beaten in a bowl. Doing this, the shear denaturates the proteins, allows the aeration of the liquid phase and the division of air bubbles into smaller ones. After a given time, the small air bubbles are stabilised and immobilised in the interlacing of uncoiled proteins, which act as surfactants by presenting their hydrophobic and hydrophilic parts to air and to aqueous phases, respectively. In the present case, liquid and stable foam was also obtained, but from an aqueous solution of tannin to which surfactant and crosslinker were added. We show that such a simple, fast and cost-effective method allows obtaining, after curing the liquid foam in an oven, new cellular thermoset materials. These new materials have properties and characteristics which are easy to control, and close to those of more traditional foams having similar compositions.

2. Experimental

2.1. Chemicals

Because of their phenolic nature, condensed tannins are known for undergoing some of the typical reactions of phenol such as polycondensation reaction with formaldehyde, or other aldehydes, under acid and alkaline conditions. Raw mimosa bark extract, known as FINTAN OP on the market, was used in this work and was

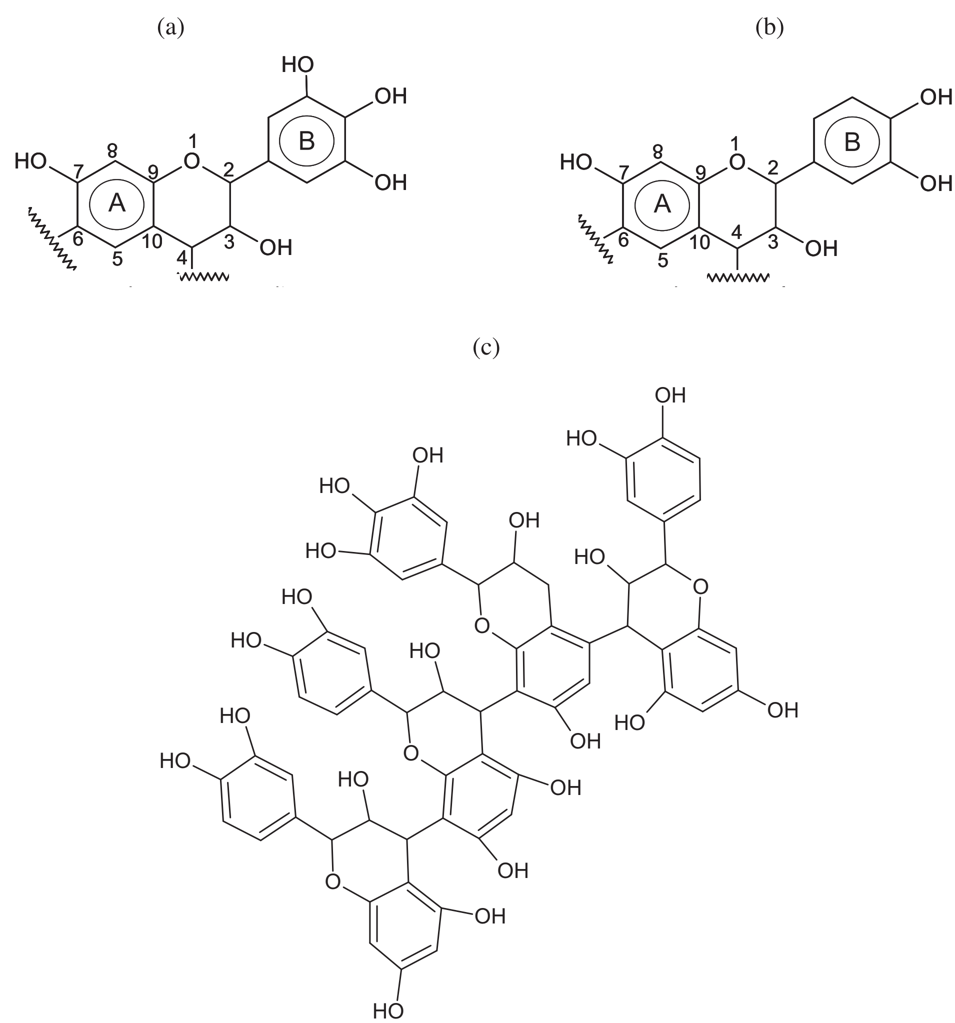

Fig. 1. Main chemicals used in the formulation of tannin-based meringues: (a) prorobinetinidin; (b) profisetinidin; (c) possible mimosa tannin oligomer based on 4 flavonoid units.