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Projectable tannin foams by mechanical and chemical expansion

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ABSTRACT

A new formulation of quebracho tannin-based resin has been used to prepare bio-based rigid foams. The proposed foams were blown by using the simultaneous combination of two expansion methods by mechanical expansion as used for fire-fighting foams and by chemical expansion based on the release of water and other gases during the exothermal self-condensation of furfuryl alcohol. The combination of both methods allowed us to overcome certain limitations found in the preparation of foams exclusively based on mechanical expansion These were the resulting density (16% lower than that obtained by mechanical expansion) and the mechanical properties (compressive strength improved of about 11%). Resin chemorheology was characterized under stressed conditions using frequency and time sweeps as well as 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 processes were followed by the use of FOAMAT equipment and the resulting foams were characterized in terms of density (0.059–0.063 g/cm^3), mechanical properties (compressive strength of 0.090–0.144 MPa) and thermal conductivity (0.046–0.048 W m^{-1} K^{-1}).

1. Introduction

Condensed tannins are natural polyphenolic materials, which comprise a group of polyhydroxy-flavan-3-ol oligomers and polymers linked by carbon–carbon bonds between flavanol subunits (Schofield et al., 2001). They are used as one of the main components to prepare tannin-based rigid foams. These foams are a good substitute for commercial synthetic foams as they are environmentally friendly porous materials with excellent fire resistance properties and low thermal conductivity (Celzard et al., 2011; Tondi et al., 2008). They have also been used in other applications such as the preparation of lightweight sandwich panels (Tondi et al., 2016; Zhou et al., 2013). In addition, the improvement of hydrophobicity of tannin-based foams has been recently investigated (Delgado-Sánchez et al., 2016; Rangel et al., 2016).

Tannin-based foams can be prepared using different foaming systems. The most conventionally used foaming method is the physical one (Basso et al., 2015; Li et al., 2013). In the physical method, a solvent with low boiling point such as pentane or diethyl ether causes resin expansion due to solvent evaporation. The solvent boiling point is reached by the temperature increase caused by the exothermal self-condensation of furfuryl alcohol. Others foaming methods used in the preparation of tannin-based foams are chemical foaming (Basso et al., 2014), and mechanical foaming (Szczurek et al., 2014). The latter achieves the foaming of the tannin resin thanks to a surfactant and to the air introduced by energetic mechanical stirring. Finally, a last method of mechanical expansion based on firefighting foam systems has been recently developed (Santiago-Medina et al., 2018). All the foams obtained by these different methods tend to exhibit a common weakness: their mechanical properties are often inferior to those of the synthetic foams they are intended to replace. This is offset by the fact that they all employ sustainable, environmentally friendly additives and components.

Different rheological techniques have been successfully employed to mechanically characterize a large number of adhesives, coatings and related materials, such as polymeric adhesives (Mravljak and Šernek, 2011; Tenorio-Alfonso et al., 2017), polyurethane-based oleogels (Borrero-López et al., 2017; Gallego et al., 2013), bitumens (Carrera et al., 2014), tannin extracts (Garnier et al., 2001; Kim and Mainwaring, 1995), etc. These rheological characterizations give an insight on both, materials behavior under stressed conditions and their physical and

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mechanical stability by means of their viscous and viscoelastic responses, i.e. when viscous flow and oscillatory shear tests are applied to them. Moreover, oscillatory shear tests, frequency sweeps in particular, can be useful to obtain information about the molecular structure of the samples.

The decrease in thermal conductivity of foams, directly related to a decrease in their density, is one of the main challenges in the manufacture of tannin-based foams for insulation applications. Barriers to the decrease of the density of tannin foams prepared by mechanical foaming based on firefighting foams technology were found in previous works (Santiago-Medina et al., 2018). This research presents a new foam formulation where mechanical foaming, through the use of a foam concentrate, is combined with the chemical expansion provided by the self-condensation of furfuryl alcohol in acid medium to achieve a reduction in foam density. This approach generates a foam which could find application as a wall-projected foam, i.e. by directly spraying the foam on the wall. The resins used to prepare the foams have been characterized by rheological measurements (viscous flow, temperature ramp and frequency and time sweeps).

2. Material and methods

2.1. Materials

Sulphited quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) tannin extract, called Fintan T, was kindly supplied by SilvaChimica (S. Michele Mondovi, Italy). Furfuryl alcohol, Kolliphor ELP, glutarladehyde 50% water solution and glyoxal 40% water solution were provided by Sigma-Aldrich (France), and used as supplied. Phenolsulphonic acid 65% water solution was purchased at Capital Resin Corporation (Columbus, OH, USA). Ethoxylated oleyl amine, OAM-10, was supplied by Saibaba Surfactants Ltd (Gujarat, India) and the foaming agent used was SM2101, a proprietary product supplied by Condat (Chasse-sur-Rhone, France) mainly composed of alkyl glycols and modified fatty acid soaps.

2.2. Foam preparation

Foams formulations were prepared using the amounts of reagents listed in Table 1. The foams were made by mixing two components. The first component is formed by a homogeneous tannin resin (R1, which is composed by quebracho tannin, furfuryl alcohol, glutaraldheyde, glyoxal, and ethoxylated castor oil (Kolliphor ELP). Once the first component (R1) was prepared, the ethoxylated oleyl amine was added. The second component is a liquid mixture which contains the catalyst (acid or mixture of acids, as referred), the foam concentrate and the water. Using a special foaming blade stirrer as shown in Fig. 1, the second component was shaken at 2000 rpm during one minute to form a white liquid foam. The tannin resin was added immediately afterwards and the blend was stirred during 20 s with the same stirrer. When the blending step was finished, a homogeneous brown liquid foam was obtained which was poured in a mould. This foam quickly expanded and hardened into a rigid foam.

Table 1
Formulation components expressed in grams for each reactive.

Reactives (g)Samples	Standard	WEA	S10	S20
Tannin (Quebracho)	10	10	10	10
Furfuryl alcohol	16	16	16	16
Glutaraldehyde (50 wt.%)	5	5	5	5
Glyoxal (40 wt.%)	15	15	15	15
Ethoxylated castor oil (Kolliphor ELP)	1	1	1	1
Ethoxylated oleyl amine (OAM-10)	1.5	–	1.5	1.5
SM2101 (Foam concentrate)	2.6	2.6	2.6	2.6
Water	3	3	3	3
Phenolsulphonic acid (65 wt.%)	17	17	15.3	13.6
Sulfuric acid	–	–	1.7	3.4

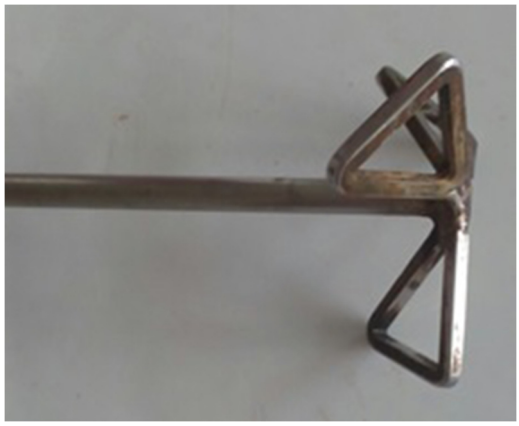

Fig. 1. Foaming blade.

The foam formulations described in Table 1 are: Standard, which was prepared using the above-mentioned method; WEA, the same that Standard foam but without using ethoxylated oleyl amine; S10, similar to Standard formulation but 10% of phenolsulphonic acid was replaced by 10% of sulfuric acid; and S20, where 20% of phenolsulphonic acid was replaced by 20% of sulfuric acid.

2.3. Rheological characterization of the resin

The tannin-based resin was rheologically characterized by using a controlled-stress rheometer Haake MARS II (Thermo Fisher Scientific, Waltham, Massachusetts, USA). Small-amplitude oscillatory shear (SAOS) tests were carried out within the linear viscoelastic region (LVR) in a frequency range from 0.01–100 rad/s, at 25 and 100 °C, using a cone-plate geometry (Ø 60 mm, 1°). The extension of the LVR was previously evaluated by performing stress sweep tests at 1 Hz. In addition, viscous flow tests were performed by imposing a stepped stress ramp in a stress range of 0.01 up to 100 Pa, at 25 °C. Curing process of the homogenous tannin resin was evaluated with the aid of time sweep tests, using the same cone-plate geometry, at 25 °C and 1 Hz. Finally, natural resin was submitted to a heating rate of 2 °C/min, from 25 to 100 °C and at 1 Hz, by using a Physica MCR501 (Anton Paar GmbH, Ostfildern-Scharnhausen, Germany) equipped with a Peltier temperature controller and a cone-plate geometry (Ø 50 mm, 0.1 mm gap, 1°). All the rheological results were presented as the arithmetic average of at least two replicates.

2.4. Characterization of the rigid foams

2.4.1. Bulk density

The samples were cut in 30 × 30 × 15 mm^3 specimens and, afterwards, they were dried at ambient temperature during one week after preparation. Then, the bulk density, ρ_b, was calculated as the weight/volume ratio of each sample. Average value of 5 samples for each foam is shown.

2.4.2. Thermal conductivity

The transient plane source method (Hot Disk TPS 2500S) (Hot Disk AB, Gothemburg, Sweden) was used to carry out the thermal conductivity measurements. This method to calculate the thermal conductivity is based on a transiently heated plane sensor, which acts both as a heat source and as a dynamic temperature sensor, consisting of an electrically conducting pattern in the shape of a double spiral, which has been etched out of a thin nickel foil and sandwiched between two thin sheets of Kapton®. The plane sensor was fitted between two identical parallelepiped samples. The sensor used was C5501 with radius