Infrared-Catalyzed Synthesis of Tannin-Furanic Foams

Gianluca Tondi,* Martin Link, Christian Kolbitsch, and Alexander Petutschnigg

Formaldehyde-free tannin-based furanic foams were prepared by applying infrared radiation (IR) as an alternative energy source. Up to now, tannin-based rigid foams have been produced *via* heat conduction or microwave radiation energy. The present innovative heating system allows for the production of extra-light products with low density (≤ 50 kg/m³). The IR-produced lightweight tannin foams (IR-TF) exhibited similar properties to those made by hot pressing (HP-TF), but IR-TF can be synthesized with much shorter production time. Although microwave-produced foams (MW-TF) can be obtained with even shorter production times, the IR-TFs are much more homogeneous. Therefore, the IR radiation-based process resulted in the most suitable compromise between foam properties and production time. Overall, IR-TF showed very competitive structural characteristics, such as high homogeneity, high porosity, and limited orthotropicity, which was similar to that shown by the hot press-produced foams. The mechanical properties and material costs are rather similar, but the production time for IR-TF is considerably shorter.

Keywords: Formaldehyde-free; Tannin foams; Infrared beam; Light materials; Orthotropicity

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INTRODUCTION

During the previous century, petroleum-based plastic products have dominated the market, and at present, the need for such plastics has become indispensable. One of the fields that is dominated by oil-derived polymers is that of insulation materials, in which polystyrene and polyurethane play a major role. Due to limitations in the availability of petroleum, the price of plastics is continuously increasing, and this is causing the industry to consider more eco-compatible and sustainable alternatives (Jerez *et al.* 2007; Gonzalez-Gutierrez *et al.* 2010; Singh and Mohanty 2007; Siracusa *et al.* 2008; Imam *et al.* 2008; Grigsby and Kadla 2013). In this context, some of the most intriguing materials developed in the last few years are tannin-based rigid foams (Tondi and Pizzi 2009) developed from the work of Meikleham and Pizzi (1994). These materials are constituted, for almost 70% of their skeleton, of condensed tannins (Tondi *et al*. 2009a) that are obtained by water extraction of wood (bark) chips and for around 20 to 25% of furanic derivatives obtainable by hydrolysis and dehydrogenation of hemicelluloses, which are particularly abundant in crops such as corn and sugar cane (Aguilar *et al.* 2002; Tong *et al.* 2010). The tannin foams have shown high performance in terms of thermal conductivity and fire resistance, as well as dimensional, chemical, and mechanical stability. However, tannin-based rigid foams have the main drawback of containing around 5% formaldehyde (Tondi *et al.* 2008; Pizzi *et al.* 2008). The presence

of formaldehyde has significantly hindered the industrialization of tannin foams due to the fact that formaldehyde has been classified as a carcinogenic substance (IARC 2006).

This particular drawback has been recently overcome, and now tannin-furanic foams can be produced without formaldehyde as a hardening agent. Conduction heat *via* hot-plate presses (Link *et al.* 2011) or *via* radiative energy through microwaves (Kolbitsch *et al.* 2012), or increasing the amount of the furanic component (Basso *et al.* 2011) of tannin-furanic foams have been used; these alternative production methods have increased the market's interest in these products, and their production has soared again (Link 2013).

In this paper, we present an additional alternative method for producing formaldehyde-free tannin foams by applying infrared radiation as the external energy source. An evaluation of the properties of the infrared-produced tannin foams is presented, and they are compared with other formaldehyde-free tannin foams.

EXPERIMENTAL

Materials

The chemicals used for the production of the formaldehyde-free tannin-furanic foams were as follows: Mimosa (*Acacia mearnsii*) tannin extract provided by Silva Chimica (Italy); furfuryl alcohol (FOH) (99%) from Merck; ethanol (99%) from Australco; and diethylether (99%) and sulfuric acid (32%) supplied by Roth. For some formulations wood chips of the core layer fraction for particleboads provided by Kaindl GmbH were also used.

The foams were synthesized in high-density foam, HDF (850 kg/m^3), boxes of dimension 10 x 10 x 2.5 cm with external energy supplied by a Krelus-Mini (248 x 248 mm) infrared heater manufactured by Krelus (Hirschthal, Switzerland); the infrared energy was varied from 3.2 to 16 kW/m^2. The distance from the bottom of the box and the IR source was 12 cm, and the exposure time was varied from 180 to 300 s to ensure the correct development of the foam. Figure 1 shows the apparatus.

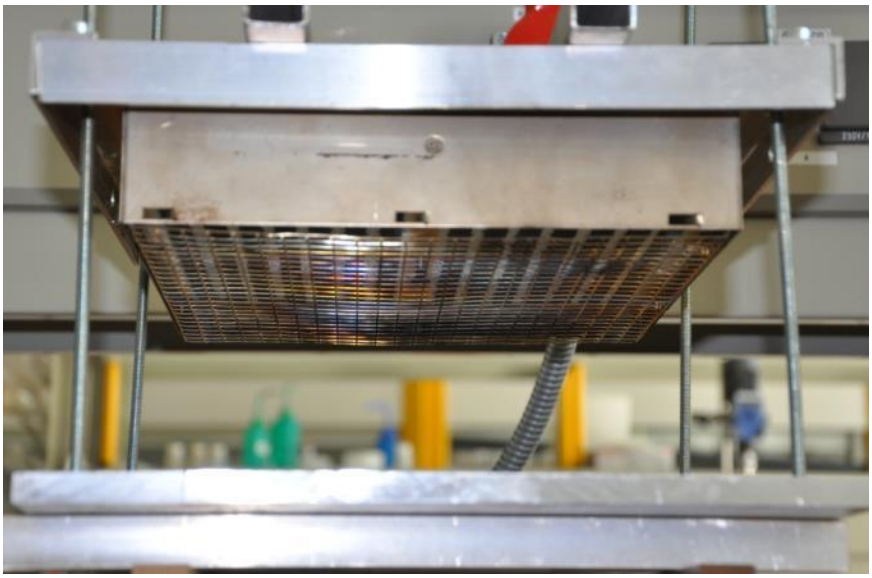

Fig. 1. Infrared radiation heating device

Methods

Sample production

The components of the formulations are described in Table 1. Blowing agents and furfuryl alcohol (FOH) were mixed in a beaker with the tannin powder and stirred until a homogenous viscous suspension was obtained. The catalyst was added and homogeneously stirred in a second step immediately before discharging the formulation into the HDF box. The latter was then placed in the sample compartment, which was exposed to the IR source at a distance of 8 cm.

Table 1. Overview of the Synthesized Formulations

Formulation	Tannin	FOH	Catalyst	Blowing agents		
			H_2SO_4	Water	Ethanol	Diethylether
	[g]	[g]	[g]	[g]	[g]	[g]
A	30	7.5	10	7.5	-	2
B	30*	7.5	10	7.5	-	2
C	30	15	14.3	11	4.4	-

* = 5 g wood chips added.

The energy of the infrared radiation was regulated according to the chemicals used for the production of the foams. The infrared radiation ranged between 3.2 and 16 kW/m², while the exposure time varied between 180 and 300 s. The temperatures reached during this process were dependent on the energy of the radiation and in every case between 120 and 200 °C.

After production, the samples were stabilized in a climate chamber at a temperature of 20 °C and 65% humidity for 24 h. The samples were successively cut into 50 x 50 x 20 mm pieces. These samples contained foam that was in direct contact with the HDF forming box; thus, only the inner core of the formed foam was tested.

Bulk density

The bulk density (ρ) was determined according to DIN EN 323 after stabilization of the sample,

$$\rho = \frac{m}{(l*w*h)} \quad (1)$$

where m is the mass of the sample and l, w, and h are length, width and height, respectively.

Porosity

The porosity (φ) of the foam was calculated based on the bulk density of the material (ρb) compared to the skeletal density (ρs) of the unblown polymer of 1590 kg/m³ (Tondi *et al.* 2009b) according to the following formula:

$$\varphi = \frac{\rho s - \rho b}{\rho s} \quad (2)$$

Density profile

The density profile was determined with a DenseLabX device from Electronic Wood Systems (EWS), with a step rate of 100 μm along the thickness of the foam.

Microscopy investigation

The foams were cut parallel to the growing direction into 1.5-mm-thick slices and were fixed in a glass support prior to being analyzed with a Nikon eclipse E200 optical microscope. Each sample was observed at 10 and 50 times magnification.

The dimensions of the foam cells were estimated, selecting 50 cells randomly chosen from transversal slices of foam. The heights and thicknesses of the cells were measured. The degree of geometric orthotropicity was defined by the following formula,

$$o = \frac{h}{t} \quad (3)$$

where o is the degree of orthotropicity and h and t are the height and the thickness of the cell, respectively.

Homogeneity

The local homogeneity was optically evaluated according to the following classification: a value of 1 when the sample's homogeneity was the highest, and a value of 5 when the sample was completely inhomogeneous.

Compression resistance

Foam compression tests were carried out with a Zwick Roell Z250 device in accordance with the DIN 52185 (1976) test method. Samples of each foam formulation were tested along the direction of foam growth by applying a compression rate of 2 mm/min. The test ended when the sample reached 75% of its original height. The maximum compressive strength (σ_{cp}) was determined by use of the following equation, which represented the moment where the elastic behavior of the foam reached its maximum (*i.e.*, collapse of the first layers of cells),

$$\sigma_{cp} = \frac{F_{max}}{A} = [\frac{N}{mm^2}] \quad (4)$$

where F_{max} is the maximum measured compression force and A is the area of the foam sample subjected to the force.

RESULTS AND DISCUSSION

The batch of samples whose properties are reported in Table 1 were evaluated for their intrinsic properties and for their mechanical behavior; these values were then compared with two formaldehyde-free tannin-based foams produced with a hot-press (HP-TF) or with the help of microwave radiation (MW-TF).

Figure 2 shows representative images of formaldehyde-free tannin foam prepared with the infrared radiation heating system.

Fig. 2. Formaldehyde-free tannin foam produced with infrared radiation heating system

Density and Porosity

Tannin foams produced by infrared radiation (IR-TF) exhibited a density between 50 and 200 kg/m³. This range of densities was similar to those obtained with the hot-press process and was slightly lower than that of microwave-produced foams. The porosity of the IR-TF varied between 87 and 97%. These values were comparable to the most common porous insulation foams that dominate the present market (Al-Homoud and Mohammad 2005).

However, the bulk density gives only a partial outlook of the distribution of mass with respect to the volume; the samples were therefore scanned with the DenseLabX device to evaluate the distribution of the mass along the height of each foam. In Fig. 3, the density profile of the infrared foam (solid line) produced with formulation B exposed at 16 kW/m² for 300 s is compared to similar foams produced with microwaves (dashed) and hot pressing (dotted).

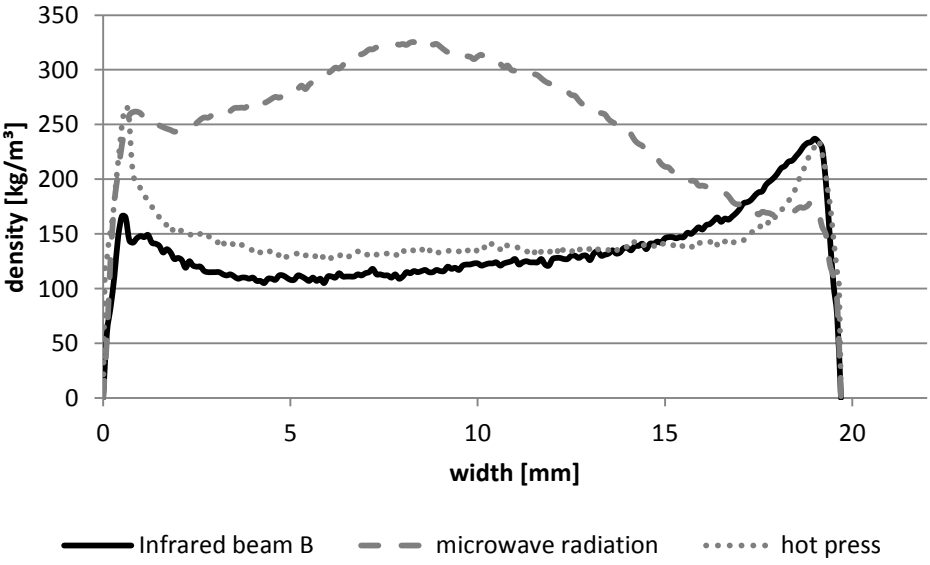

Fig. 3. Density profile of infrared-produced tannin foam compared with similar foams produced with microwave radiation and hot press technology

The distribution of the polymer over the profile of the IR-TF was very similar to that of HP-TF. The cores of the samples were very homogeneous, while the external layers were denser because of the accumulation of mass that occurs during the process of foam formation. Infrared and hot-press production systems had the heating device positioned along the direction of growth of the foam, and the distribution of material was therefore similar. Conversely, the MW-TF specimens were produced with an energy source perpendicular to the growth of the foam, and the distribution of the mass was therefore dissimilar to that of the other two foams. In particular, the skeleton of the material is concentrated in the core because of the high amount of gasses produced during microwave heating. These gasses will then accumulate in the outer shell of the material resulting in lower density of the surface layers. Next, the materials were examined by optical microscopy to more completely characterize the mass distribution of the foams.

Microscopy

In Fig. 4, the foams produced with the three heating techniques are shown. Although the foams had similar densities (115 to 149 kg/m^3), the foams had considerable differences in their observable structures.

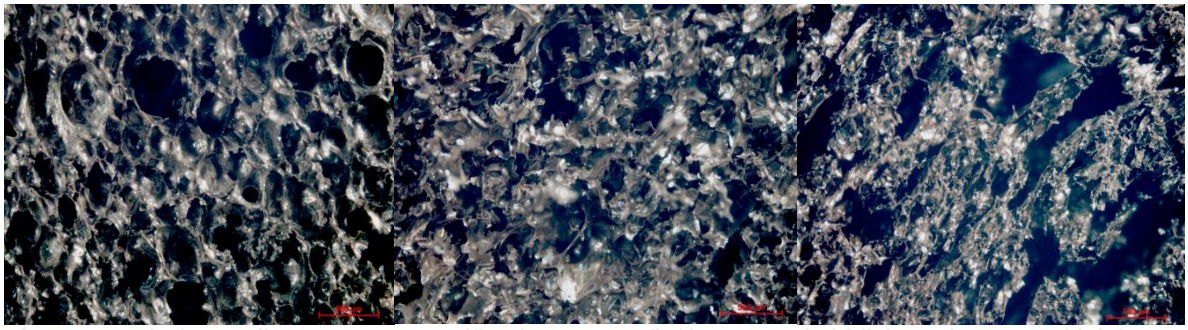

Fig. 4. Tannin foam slices at 40x magnification: IR-TF (left), HP-TF (middle), and MW-TF (right)

The IR-TF presented regular and defined cells, while the HP-TF presented a jagged surface having more irregular borders; both production methods yielded very homogeneous foams. Conversely, the MW-TF presented some larger irregular cells along with numerous smaller non-structured cells.

Table 2 presents the structural properties of the formaldehyde-free tannin foams produced with an infrared radiation source; these results are compared with tannin foams produced by the hot-press and microwave processes.

The formulations produced with infrared radiation as the heating source yielded variable homogeneity. The more significant observations were that (i) almost every one of the presented formulations was more homogeneous than the MW-TF, and (ii) some foams (IR-1 and IR-3) had comparable homogeneity to the HP-TF sample. The cells obtained with the infrared rays appeared to be more regular, but in terms of dimensions, they were slightly larger than the hot-press-produced one. Also, the infrared radiation production system oriented the cells vertically; thus, the properties of the foam will vary when measured in different directions. This results in an anisotropic material with two perpendicular symmetry axes, also known as orthotropicity. Specifically, the orthotropic IR-TF exhibited two perpendicular symmetry axes: the growing direction axis and its perpendicular axis.

Table 2. Structural Properties of Formaldehyde-Free Tannin Foams Produced with Infrared Radiation Compared to Other Production Technologies

Label	Formulation	Energy	Time [s]	Density [kg/m³]	Homogeneity [1]	Cell dimensions [μm]	Degree of Orthotropicity (*o*)
Press*	Specific*	120°C	600	152	1.3	50-500	1.3
μw**	Specific**	600 W	120	149	2.3	50-1000	1.9
IR-1	A	3.2 kW/m²	180	50	1.7	200-500	1.5
IR-2	B	3.2 kW/m²	180	125	2.0	200-500	1.3
IR-3	B	16 kW/m²	300	115	1.3	200-400	1.4
IR-4	C	16 kW/m²	180	183	3.0	100-800	1.2

[1] Homogeneity degree defined as: 1 = highest homogeneity and 5 = completely inhomogeneous
* Hot-press-produced foam (HP-TF): Link *et al.* 2011
** Microwave-produced foam (MW-TF): Kolbitsch *et al.* 2012

According to the microscopy observations, it was possible to quantify the degree of geometric orthotropicity of these materials by calculating the ratio between the dimensions of the cells. This value was always between 1.2 and 1.5 for the IR-TF, and therefore, they were perfectly comparable with the HP-TF. The MW-TF were significantly different; for these foams, the degree of orthotropicity was much higher (1.9). In particular, it was observed that the orientation of cells was not aligned with the growth of the foam, but especially in the central part of the material, the cells were perpendicularly oriented.

Finally, Table 2 highlights the possibility of producing highly homogeneous foams by the infrared radiation heating process. In particular, foams IR-1, IR-2, and IR-3 were highly homogeneous, had very similar ranges of cell dimensions, and also had similar degrees of orthotropicity (*o*) to the tannin foams produced *via* the hot-press process.

Compression Resistance

The IR-produced foams IR-2 and IR-3 had comparable compression resistance to that of the foams produced with the other production methods (Fig. 5).

Also, the extra-light foam, IR-1, had similar mechanical properties to the corresponding HP-TF (*e.g.*, HP-TF with a density of 50 kg/m³ had compression resistance of around 0.02 N/mm²).

The only data that showed a considerable variance to the classical behavior were for IR-4 foams. Despite having a higher density value, its mechanical properties were significantly lower than expected. This fact can be explained by the higher amount of furfuryl alcohol and catalyst used in the formulation, which resulted in an excessively rigid polymer.

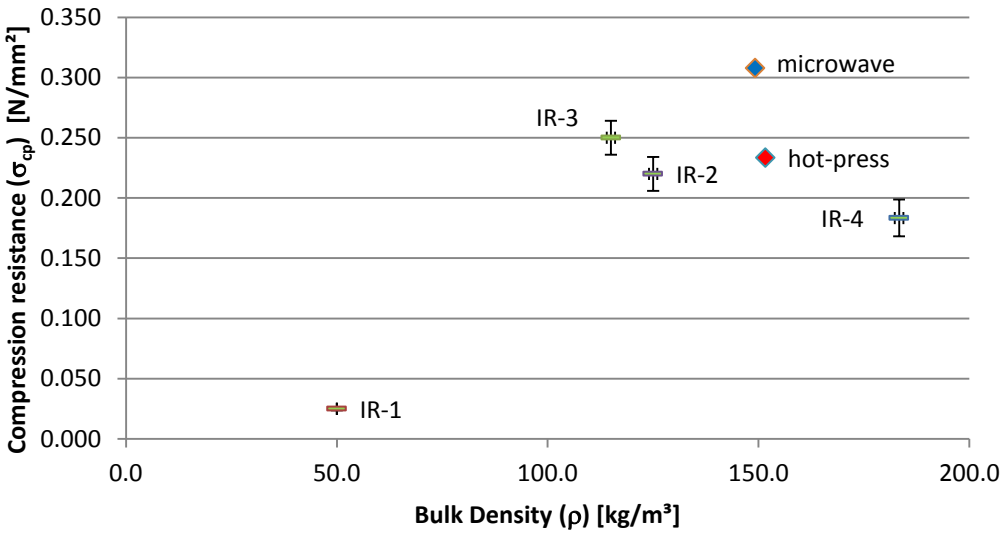

Fig. 5. Compression resistance of IR-TF compared with similar densities of foam samples of HP-TF and MW-TF

Material and Cost Estimation

The formulations of formaldehyde-free tannin foams may vary considerably with different heating sources. Table 3 shows some examples of formulations that allow estimation of the material costs.

Table 3. Calculation of Material Costs for the Production of Foams with Similar Densities

Production method	Tannin (%)	Furfuryl alcohol (%)	Solvent (%)	32% Sulfuric acid (%)	Water (%)	Cost (€/kg)
Hot-press	46.9	15.6	11	15.6	11	1.020
Microwave radiation	52	13	7	19		0.986
Infrared radiation	40.1	20	5.9	19	14.7	0.984

The cost for the production of the foams did not change much in terms of the raw material costs; therefore, a significant parameter for the selection of the blowing technique is the production time for the foam. Considering this aspect, it should be noted that the IR-TF can be defined as fully blown within 3 to 5 min, while the HP-TF treatment needed longer blowing time (5 to 8 min). The MW-TF had slightly shorter blowing time (2 min), but the products obtained were not always homogeneous. Thus, the infrared process represented a good compromise for producing homogeneous foams in a relatively short time.

CONCLUSIONS

1. Tannin foams produced with infrared radiation can be prepared with a considerable variety of densities from very light (50 kg/m³) up to relatively heavy (183 kg/m³).
2. These materials exhibited a good homogenous structure with a porosity between 87 and 97%. The cells had variable dimensions, with the average diameter in the range between 100 and 500 µm. The cells presented a relatively sharp profile, which resulted in a foam with limited orthotropicity.
3. All the IR foams exhibited similar intrinsic properties to the HP-TF and had the advantage of requiring around half of the production time compared to conventional thermal processing.
4. The mechanical properties of these foams are generally proportional to the bulk density, although when excess FOH and catalyst are used, the compression resistance decreases.
5. The material costs for the IR-produced foams, MW-TF, and HP-TF are rather similar, but the energy costs for producing highly homogenous products are lower because of the shorter production time.

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