

Lignin-based Foams: Production Process and Characterization

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Lignin foams are innovative materials obtained by the copolymerization of furanics with the spent liquor from the magnesite wood pulping process. In this study, the influence of the component amount in the formulation, as well as the effect of temperature on the final product, were elucidated. Several formulations, with various lignin/furanic ratios, blowing agents, and catalyst concentrations, exhibited good homogeneity and densities between 185 and 407 kg m⁻³. The mechanical properties, as well as the thermal conductivities, confirmed the strong dependence on density, and the results obtained were comparable to that of tannin foams. The leaching tests revealed that the lignin foams released a certain amount of catalyst within the first minutes of water dipping. However the pH of this leachate stabilized quickly, which suggests that the catalyst can be easily recovered.

Keywords: Insulation material; Lignin valorization; Natural foam; Renewable resource; Sustainable material

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INTRODUCTION

Pulping of wood is one of the most resource-consuming processes in the wood industry. In this process, only the celluloses in wood are properly exploited, while the lignin, which represents more than 25% of the dry constituents, is often just burned for energy recovery (Sixta 2006; Ek *et al.* 2009). Alternative uses for the spent liquor have been previously investigated, and one of the more attractive applications consists of its use as an additive for asphalt (Detroit 1979). Nevertheless, the great majority of the spent liquor is still used for energy production. The valorization of the spent liquor is a key-factor for significantly increasing the sustainability and also the turnover of the pulp and paper industries (Vishtal and Kraslawski 2011). Because the lignin present in this spent liquor is the largest renewable resource of aromatics, its use as a low-cost feedstock for the preparation of innovative materials would be very interesting. Indeed, using lignin combines the advantage of saving oil-derived resources with a decrease in the amount of CO₂ emissions, because of its disposal method.

With continuously increasing demand for energy and therefore increasing energy prices, the insulation of buildings plays a major role in the construction industry. The most used insulation materials in the market are polystyrene (expanded and extruded) and polyurethanes (cured or injectable), in addition to inorganic fibrous materials, such as glass and rock wool (Papadopoulos 2005). However, for several years the interest for more sustainable solutions has increased, and now natural alternatives are more often demanded.

More sustainable organic alternatives, including celluloses, natural wool, and expanded cork, are already available on the market (Sen *et al.* 2012; Zach *et al.* 2012), and other very valuable alternatives, based on bark, straw, and wood-leather composites have been thoroughly investigated and the results are very promising (Pires *et al.* 2010; Grünewald *et al.* 2013; Kain *et al.* 2014; Tondi *et al.* 2015a).

One disadvantage of these materials is their relatively high thermal conductivities, compared to traditional insulation materials, such as polystyrene. Still, bio-based materials that exhibit better performance qualities, in terms of thermal insulation purposes, are tannin foams. This material was deeply investigated in the last years (Tondi and Pizzi 2009; Link *et al.* 2011; Lacoste *et al.* 2013; Li *et al.* 2013; Sanchez-Martin *et al.* 2013; Tondi *et al.* 2015b).

Apart from their low thermal conductivity, tannin foams show high chemical and water stability, high resistance against fire (Tondi *et al.* 2008; Tondi *et al.* 2009a,b; Pizzi *et al.* 2012; Kolbitsch *et al.* 2012; Tondi *et al.* 2014) and low thermal conductivity. These properties can be explained by a compact rearrangement in its chemical structure (Pizzi *et al.* 2008; Tondi *et al.* 2015c).

The main hurdle in the commercialization of tannin foams is their high cost and the low availability of condensed tannin, which serves as the raw material. These factors inhibit their use in low-margin applications, such as insulation foam. Most flavonoid tannins used for these foams originate from tropical wood species, such as quebracho (*Schinopsis balansae*) and mimosa (*Acacia mearnsii*). In the countries that produce these tannins (principally Argentina, Brazil, Tanzania, and South Africa), these tannins are also exploited as leather tanning agents and adhesives. Hence, new phenolic resources like lignin could serve as a worthwhile alternative for the preparation of natural insulation materials. Therefore, in the present paper, lignin-furan-based foams, obtained from the copolymerization of lignosulfonates and a furan derivate, are investigated (Tondi *et al.* 2012).

EXPERIMENTAL

Materials

For the production of the lignin foams, the major raw material was spent liquor from a magnesium bisulfite pulping process using beech (*Fagus sylvatica*) wood. The spent liquor used for these experiments was “thick liquor” derived from Lenzing AG (Lenzing, Austria). This “thick liquor” was obtained prior to evaporation and pH adjustment of the cooking liquor. This thick liquor had a solid and ash content of 60.3% and 10.2%, respectively. For ease of understanding, the term spent liquor will be used throughout the text.

Technical-grade furfuryl alcohol supplied by International Furan Chemicals BV (Rotterdam, Holland) was used as co-monomer. Ethanol (96%) and sulfuric acid (32%) were used as the blowing agent and catalyst, respectively. Fractioned wood particles ($\phi=500$ to 1000 μm) were included in the formulations to regulate the initial viscosity. Alternative additives were lignosulfonate powder and polyvinylalcohol, purchased from Sigma-Aldrich (Taufkirchen, Germany), and mimosa tannin extract from Silva Chimica (S.Michele Mondoví, Italy).

Methods

Lignin foam preparation

Fifteen formulations were produced to study the influence of each component in the blowing process. The range in which the formulations were prepared is reported in Table 1.

Table 1. Range of Formulation Components for Lignin Foams

Formulations	Lignin (%)	Furfuryl Alcohol (%)	Water (%)	Catalyst (%)	Blowing Agent (%)	Additive (%)	Temperature (°C)
Minimum	24.2	18.8	23.7	4.0	4.6	4.7	120
Regular	28 to 33	19 to 25	25 to 30	4.5 to 6.5	5 to 8	6 to 12	120 to 160
Maximum	37.3	30.3	34.6	8.0	8.8	13.3	160

The spent liquor was mechanically stirred with furfuryl alcohol, water, additives, and the blowing agent for several minutes until a homogeneous solution was obtained. The acid catalyst was added to the batch and stirred again. The as-prepared formulation was then filled into the mould for foaming, which consisted of HDF (High density fiberboards) boxes of $10 \times 10 \times 2.5$ cm³, according to Link *et al.* (2011).

The samples were heated in a Höfler (HLOP 280) (Taiskirchen, Austria) hot-press with the press plates set at the range of temperatures between 120 and 160 °C for a variable blowing time of 8 to 20 min. The moulds were pre-heated for 2 min before formulation filling.

Afterwards, the HDF box was pulled out of the press and cooled for 24 h before removing the sides of the box. The porous material was then stored in a normative climate (20 °C/ 65% moisture content) for at least 48 h before being tested.

Evaluation of foam expansion and curing

Two phenomena occurred simultaneously during the formation of the lignin-furanic foams: (i) evaporation of the solvent and (ii) hardening of the resin (Tondi and Pizzi 2009). The blowing of the foam was evaluated considering the following aspects: volume of the foam obtained and distribution of the cells in the foam. The hardening was evaluated based on the rigidity of the copolymer.

Intrinsic properties

The bulk density was calculated as the registering weight, length, width, and thickness, according to the DIN EN 323 (1993) equation,

$$\rho = \frac{m}{l \times w \times t} \quad (1)$$

where m is the mass of the foam, and l , w , and t are the length, width, and thickness, respectively.

The homogeneity was initially evaluated optically, observing the four sides of each sample. The homogeneity was independently evaluated using five observers on a scale from 0 to 5, considering “5” to be of similar homogeneity to the commercial polyurethane foam, whereas “0” corresponds to very inhomogeneous foam. The homogeneity was then expressed as an average of the evaluation of each observer. An example is given in Fig. 1.

The dimension of the cells was measured with a field emission scanning electron microscopy (FE-SEM). The samples were coated with a thin layer of aluminum. The samples were examined by high-resolution scanning electron microscopy up to a 5000X magnification, with a Hitachi S4000 FE-SEM (Japan) using an acceleration voltage of 8 kV and a working distance of 13 mm.

Compression resistance

Compression resistance tests were performed in a Zwick-Roell Z250 (Ulm, Germany) universal testing machine, and the values reported are the average of at least 5 measurements. Samples of $50 \times 50 \times 25$ mm³ DIN 52185 (1976) were compressed towards the direction of growth, with a rate of 2 mm/min, and the compression strength of the samples was measured considering the maximal resistance end of the elastic region, when the first layer of the foam breaks.

Thermal conductivity

Two of the most interesting lignin-based foams were prepared on a larger scale to evaluate their λ -value and compared with tannin foams. Lignin-based foams with $250 \times 250 \times 22$ mm³ dimension were tested on a λ -Meter Lambda-Messtechnik EP500e (Dresden, Germany) device. The measurements were done by applying three different temperature ranges: 2.5 to 17.5 °C; 17.5 to 32.5 °C, and 32.5 to 47.5 °C.

Catalyst recovery

Three foams of $50 \times 50 \times 25$ mm³ produced with 4%, 6%, and 8% acid catalyst were immersed in three beakers, with 250 mL of deionized water. The pH of the solutions was controlled after 0.25, 1, 2, 4, 8, and 18 h. Then, the solutions were put under a vacuum of approximately 10 mbar for 10 min to allow the water to reach the core of the foam. The pH value of the water was measured after 1 h.

RESULTS AND DISCUSSION

The application of lignin fractions from the magnesite pulping process presents two tremendous advantages for the synthesis of innovative foam materials: (i) good availability and (ii) low-cost phenolic moieties. This study presents the preliminary investigations on furanic-copolymerized lignin foams, in which the influence of the most significant parameters for the production was evaluated.

The understanding of the relationship between the hardening process (HP) of the lignin-furanic polymer and the evaporation of the blowing agent (BP) is fundamental for the optimization of this process. The effects of the variation of the concentration of components, as well as the influence of temperature, were analyzed and will be described in detail below.

Interpretation of the graphics

The figures reported in the following paragraphs have the objective of describing the phenomena of hardening/curing of the resin (black lines) and the evaporation of the blowing agents (red lines) simultaneously, so that the effect of the different variables can be more easily visualized. In the x -axes the reaction time is reported, while in the y -axes the molecular mass of the lignin-furanic polymer (which indicates the hardening process)

and the amount of blowing agent evaporating (which indicates the blowing process) are reported. When the hardening line rises, it means that the molecular mass increases, whereas when the blowing process line rises, the blowing agent evaporates, and when the blowing agent is running out the blowing process line goes down. Successful foams occur if the hardening process (H.P.) occurs when the blowing process (B.P.) is also occurring.

Furfuryl alcohol:

This component is fundamental for the correct production of the foams because it is the co-monomer that forms the network between lignin moieties. It was observed that the applied amounts of furfuryl alcohol play an important role in hardening of the polymer, while less significant effects were observed in the blowing process. The limited effect on the expansion process was expected because of the higher boiling point of furfuryl alcohol (170 °C). The higher the ratio of furfuryl alcohol to lignin in the formulation, the higher the heat produced during the polymerization process and the higher the degree of crosslinking in the co-polymer. However, it has to be considered that the spent liquor is well mixable with furfuryl alcohol, and an excess of this component reduces the initial viscosity of the formulation.

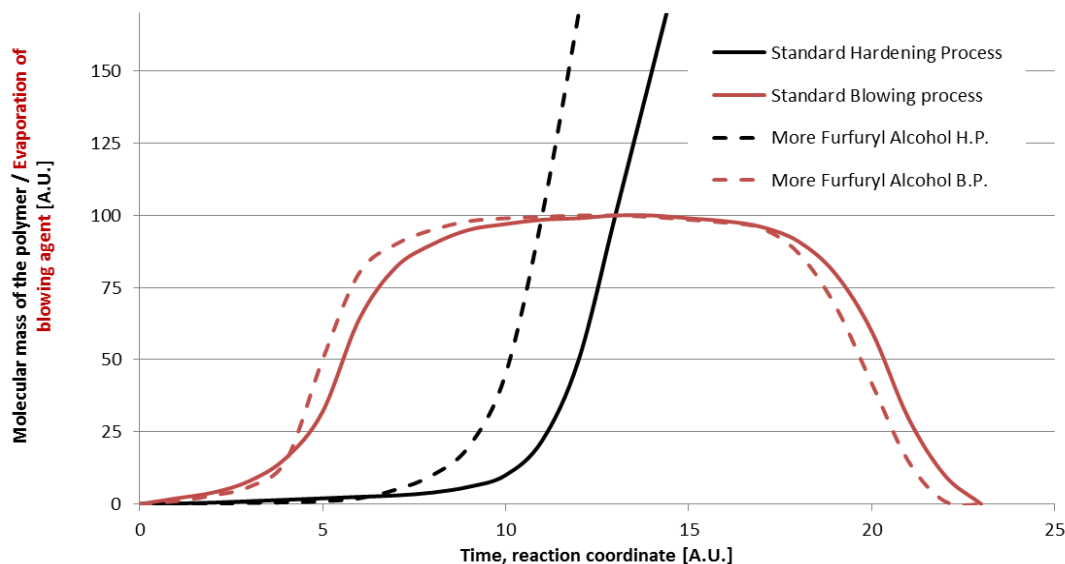


Fig. 1. Effect of the addition of furfuryl alcohol in the hardening process (HP) and the blowing process (BP)

Lower initial viscosity results in the ability to crosslink faster (*e.g.*, increased hardening), therefore, it involves in an increase in the viscosity and temperature. The blowing process is only slightly affected by a lower initial viscosity. However, because of the increased temperature originating from the condensation reaction, the blowing process will go faster and therefore it will finish earlier. This effect is visualized in Fig. 1.

Acid catalyst: Sulfuric acid (H₂SO₄) was chosen as the acid catalyst. Other acid catalysts will be part of further investigations. The presence of acid catalyzes the polymerization of furfuryl alcohol; hence, with increasing amount of acid, the reaction begins earlier. This component strongly affects the hardening of the polymer but also has an indirect role in the blowing process. If hardening occurs very fast, a large amount of heat is generated because of the exothermic polymerization. This heat increase allows for

a higher evaporation rate at the beginning of the process, and therefore the blowing process finishes earlier. In Fig. 2, the effect of an excess in catalyst is schematized.

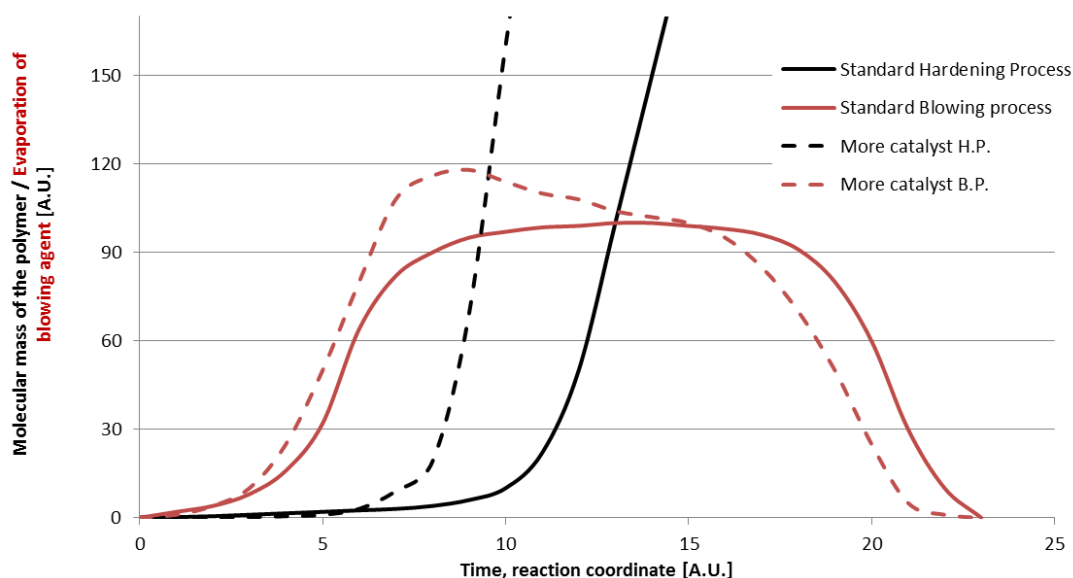


Fig. 2. Effect of the addition of catalyst in the hardening process (HP) and blowing process (BP)

An increase in the reaction velocity leads to an inhomogeneous distribution of the cells because of the lower time to distribute the heat in the reaction batch. Also, for the sulfuric acid, the same dilution effect at the beginning of the process can be observed as for the furfural alcohol. However, if the initial solution is too diluted, the hardening process can be delayed.

Blowing agents: These substances are required for ensuring the blowing of the foam. These molecules are responsible for the blowing because of their evaporation. For this reason, the use of non-reactive substances with a relatively low boiling point is required. The solvent plays a major role in the blowing process because the amount of gas evaporated is evidently higher. The hardening process is slightly affected because of the dilution effect already discussed. The influence of the addition of higher amounts of blowing agent is presented in Fig. 3.

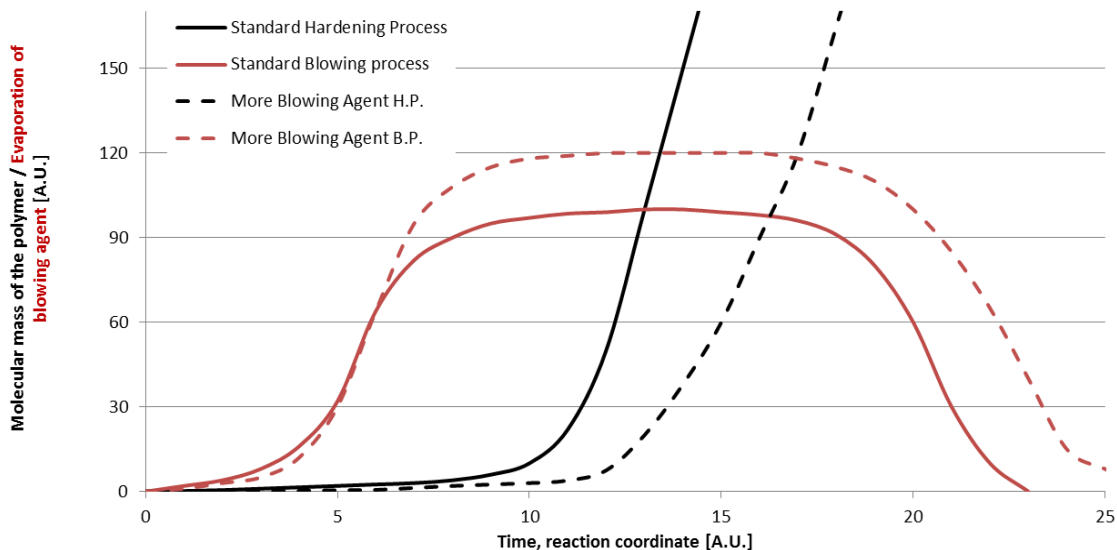


Fig. 3. Effect of the addition of the blowing agent in the hardening process (HP) and the blowing process (BP).

Another aspect to be considered is that blowing agents with low polarities require longer mixing times to obtain homogeneous solutions. This means that this component is highly dependent on the temperature applied. Therefore, the use of water as blowing agent can also be considered when the foaming temperature is high enough.

Additives: These substances are used to increase the initial viscosity of the formulation. Indeed, a higher initial viscosity guarantees (i) a slowing in the hardening and (ii) a more homogeneous blowing process. Some additives, such as lignosulphonates and tannin, can take part in the reaction; some other substances can be considered charged (e.g. PVA, wood powder, and recycled lignin foam). Especially those that are not taking part in the reaction lead to higher foam densities. The influence of additives is visualized in Fig. 4.

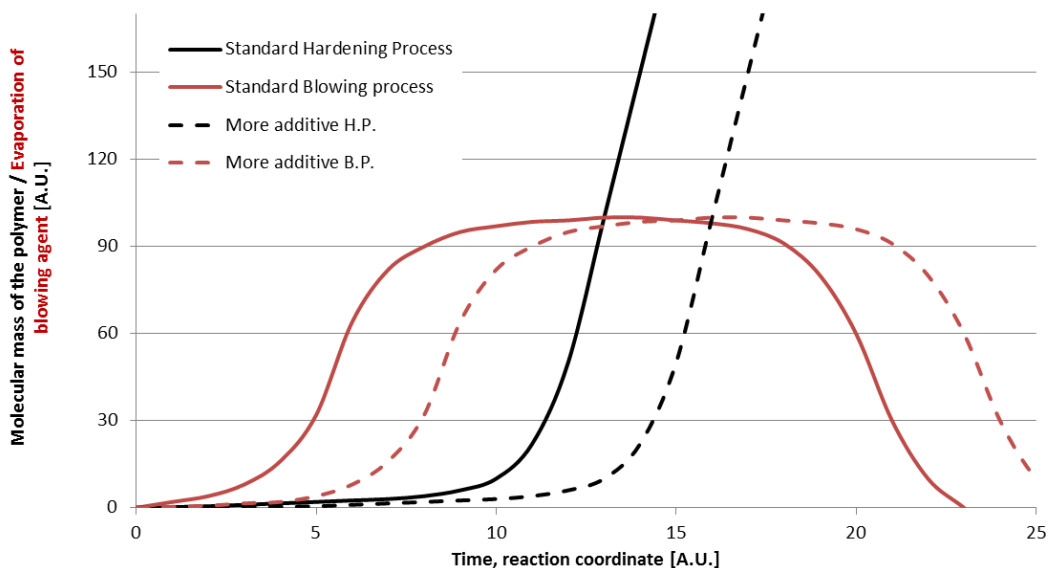


Fig. 4. Effect of the addition of the additives in the hardening process (HP) and the blowing process (BP).

The visual effect of producing foam, with and without wood particles as the additive, is observable in Fig. 5. The presence of the additive allows the production of smaller solvent bubbles, which results in a notable difference in terms of cell dimension and distribution.

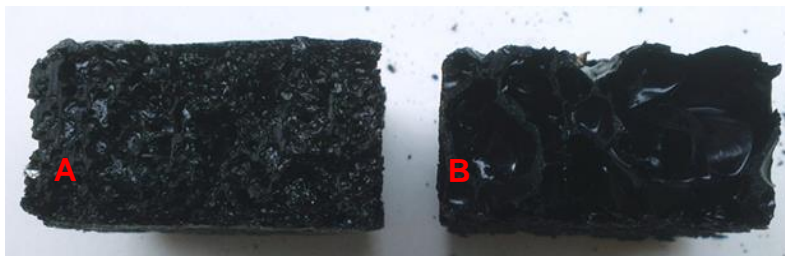


Fig. 5. Visual effect of the foams produced (a) with and (b) without wood particles

Temperature: A higher temperature produces notable effects: faster hardening and faster blowing (Fig. 6). The resulting cells are less homogeneous because the system has limited time for the homogenization with heating the entire reaction batch. Indeed, it was observed that the production of lignin foams at higher temperatures (160 °C) was not easy to be managed on the laboratory scale because the reaction happened too quickly. Moreover, reproducibility problems were observed. Conversely, very good results were achieved preparing the foams at 120 °C.

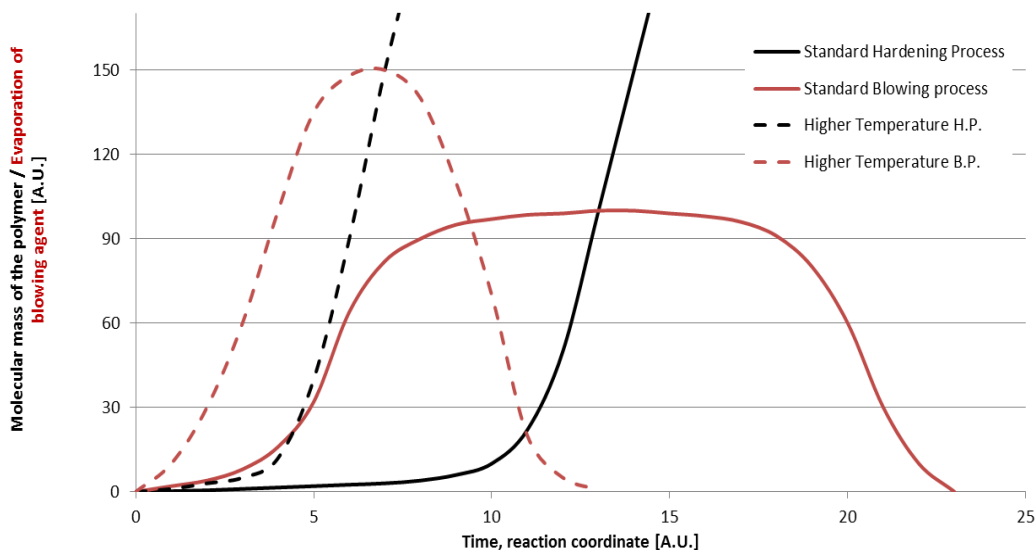


Fig. 6. Effect of increasing temperature on the hardening process (HP) and the blowing process (BP)

Because the production of foam is a simultaneous reaction of blowing and hardening, which are all influenced by the abovementioned parameters, the variables have to be correctly balanced to prepare good-quality foams. The amount of catalyst and the temperature needs to be balanced to allow a good blowing before the polymerization is complete.

After an initial screening of the formulation parameters, a number of good formulations were found. These were evaluated regarding their density, homogeneity, compression resistance, and thermal conductivity. The results are reported in Table 2.

Table 2. Summary of the Properties of the Lignin-Foams: Density, Homogeneity, Compression Resistance, and Thermal Conductivity

Range of features	Density (kg m ⁻³)	Homogeneity (#)	Compression Resistance (MPa)	Thermal Conductivity (mW m ⁻¹ K ⁻¹)*
Lower value	185	3.0	0.07	75
Mean/average	250 - 350	3.5-4.5	0.25-0.35	80-90
Higher value	407	4.6	0.45	95

Estimated scale from 0 to 5: 0 is very inhomogeneous; 5 is very homogeneous.

*= Measurement of foams at approximately 0.3 g cm⁻³

In the present study, 15 different formulations yielded satisfactory lignin-foams. They had different densities (between 200 and 407 kg m⁻³) and homogeneities (between 3 and 4.6). Two examples of foams are presented in Fig. 7.

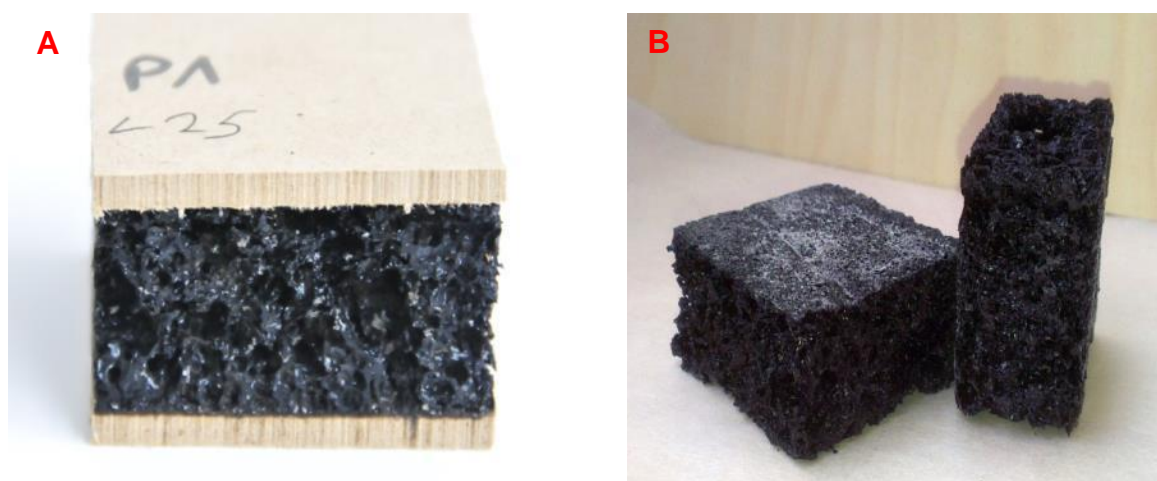


Fig. 7. Lignin-foams: a) after production in the HDF panel (h = 4.6); b) after removal from the reaction box (h = 4.3)

Formulations with higher densities yielded more homogeneous cell distribution. Indeed, only a few foams with densities higher than 300 kg m⁻³ reached the level of homogeneity of 4. This was attributed to the important effect of the additives in slowing down the hardening reaction, guaranteeing a more homogeneous cell distribution but also a denser product.

Another important aspect to be considered is the cell dimensions. For these materials, there was difficulty in determining an average value for the cell dimension because of their broad distribution, and therefore the homogeneity was evaluated further using a scanning electron microscope (SEM). An SEM image of foam with the homogeneity of 4.6 is reported in Fig. 8. These images show that the material is relatively homogeneous, as observed microscopically. Although a broad range of cell diameters (10 to 500 μ m) were observed, the variability of the cell dimensions depended on the distribution of the chemicals during the mixing phase. Even though the blend was always completely homogenized before filling into the mould, the local distribution of the

molecules and the local concentration of the heat in the box could not be controlled. However, better results could probably be obtained upon automation in an industrial plant (Tondi *et al.* 2016).

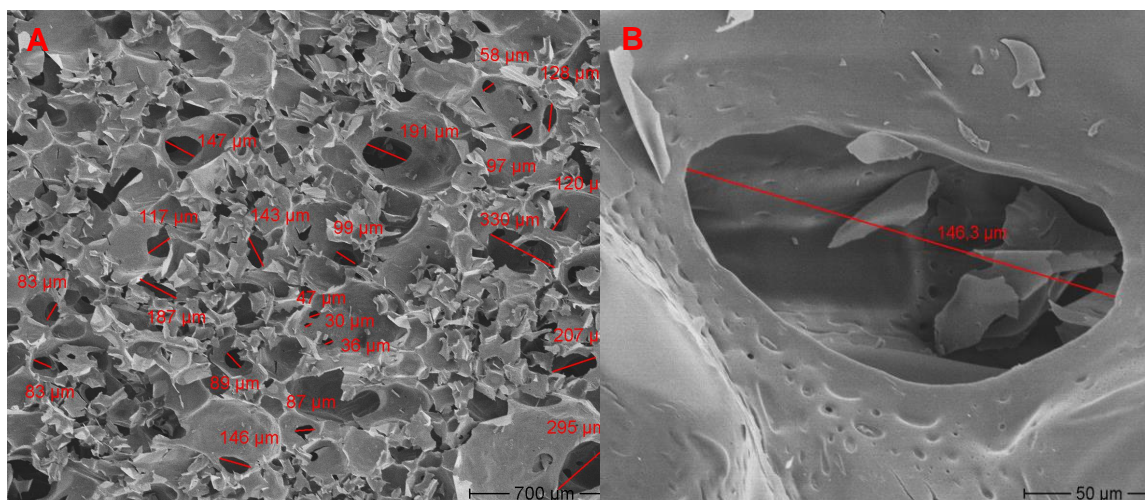


Fig. 8. SEM images of a lignin-foam with $d = 0.311 \text{ g cm}^{-3}$ and $h = 4.6$: a) with 40X and b) 700X magnification, respectively

From a mechanical standpoint, the typical direct proportionality between density and compression resistance was observed. In Fig. 9 the graphic presents the relation between the compression resistance and the density of various rigid foams.

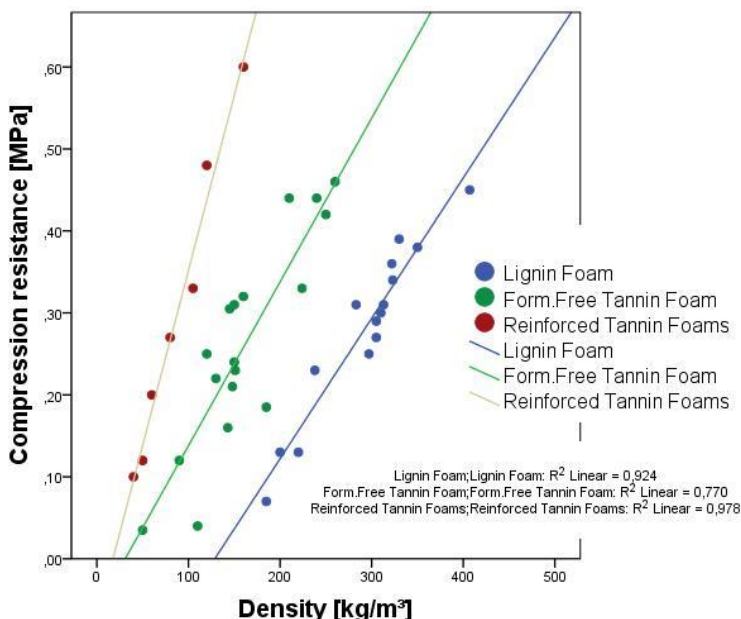


Fig. 9. Compression resistance vs. density behavior of lignin foams (blue) compared with tannin foams: reinforced with formaldehyde (red) and formaldehyde free (green)

The lignin foams exhibited similar trends to formaldehyde-free tannin foams, but their densities were higher. This can be explained by the lower interconnection between lignin and furanics. The lignin has a lower chemical reactivity than tannins for three reasons: (i) lignin fractions have less hydroxyl-groups directly bonded to the aromatic ring,

(ii) the aromatic rings have higher substitution degree (-methoxy groups principally), which renders the reactive positions sterically less available than in flavonoid tannins, and (iii) the spent liquor contains a high percentage of inorganic (ash), which contributes to an increase in the weight of the foam without improving its mechanical properties. The presence of charges, such as wood particles, does not actively participate to the network of the copolymer; hence, their replacement with more reactive materials is a positive perspective for improving the mechanical properties of the foams, especially the density. However, when reporting the values for the lignin foams in an Ashby plot (Ashby 1998), the material has the mechanical properties of rigid foam, similar to cork. This proves that even if the study is still in a preliminary stage, the material has very high potential. The lignin foam is generally a lightweight material that is natural and inexpensive. Therefore, the use of this material for insulation purposes is one of the most interesting alternatives for replacing commercial PS and PU foams. The thermal conductivity of some lignin foams was measured with a λ -meter for plates, and the results obtained are summarized in Fig. 10.

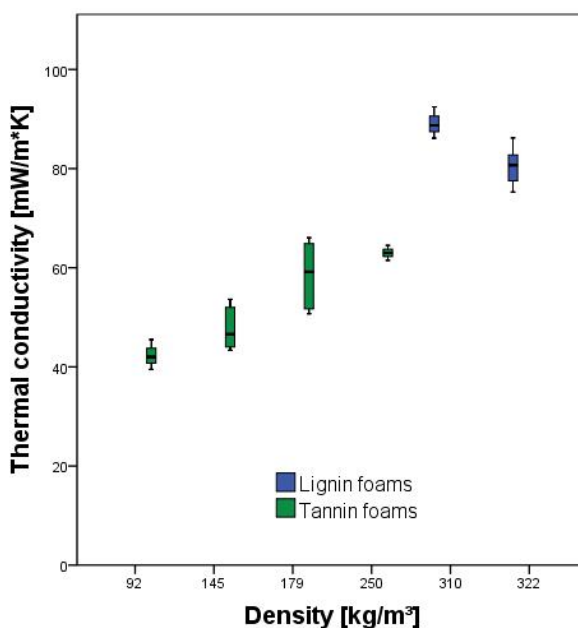


Fig. 10. Thermal conductivity (λ) vs. density behavior of lignin foams (blue) compared with tannin foams (formaldehyde-free) (green)

It is known that the thermal conductivity is inversely proportional to the density (Jarfelt and Ramnäs 2006) and therefore the production of lightweight foams involves a lower heat transferring rate. According to Table 2, the λ -value achieved by the lignin foams were in line with the measurements obtained for the tannin foams. Moreover, preliminary lab-scale burning tests showed that the lignin-foams did not burn. When small lignin foams samples ($20 \times 20 \times 20 \text{ mm}^3$) were exposed to a direct blue-roaring flame of a Bunsen burner for 30 seconds, only some glowing spots and some smoke development were observed afterwards. The foams, indeed, were self-extinguishing, and no flames were remaining a few seconds after the removal of the fire source. Interestingly, as the concentration of lignin in the foam increases, the time required for blowing out the glowing spots decreased up to 80 seconds (max. 250 s). The fire-proof behavior showed in these preliminary tests is

probably due to the good fire-properties of the furanic polymers and it represents a huge advantage compared to polystyrene foams, which need to be brominated to minimize their flammability.

Another interesting topic for the industrialization of these foams is their ability to recover the catalyst. Lignin foams produced with different amounts of catalyst were immersed in water and the pH was monitored. In Fig. 11, the leaching times at different catalyst concentrations and pHs are depicted.

Figure 11 shows that the greatest amount of acid was recovered within the first 15 min. This evidence suggests that once the foams are immersed in water they lose the acid catalyst within minutes. This catalyst cannot be embedded in the foam.

Consequently, foams with a higher amount of catalyst are also those that release more acid. Moreover, after 19 h of forcing the water penetration with a vacuum, the pH measurement confirms that the pH values remain constant.

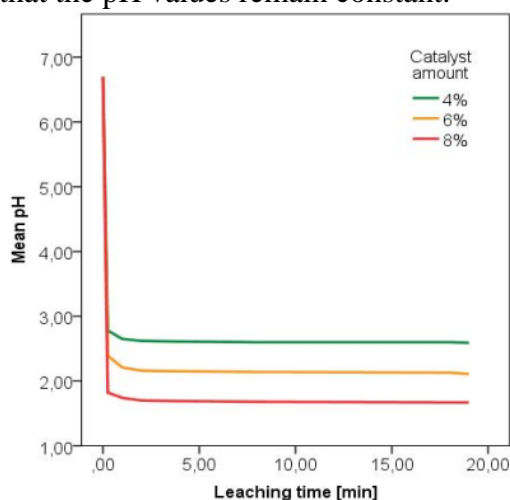


Fig. 11. pH variation of the leaching water of lignin foams prepared with different amounts of catalyst.

This means that the material is porous and the water can naturally reach the core of the foams without applying an external vacuum. Assuming that the pH is modified only by the catalyst, it is possible to estimate that the sulfuric acid recovery is between 7.5% (4% for foams prepared with low amount of acid) and 32.5% (8% for foams prepared with higher amount of catalyst).

CONCLUSIONS

1. Stable lignin foams were produced in this study. Because of their sustainable chemistry, their mechanical and thermal properties, as well as their fire-resistance, this material may have the potential to serve as an environmentally-friendly alternative for traditional insulation materials, such as polystyrene and polyurethane.
2. The kinetic evaluation of the process was studied, the effect of the concentration of each formulation component was evaluated, and a number of suitable formulations were discovered.
3. The lignin foams can be prepared with various densities as low as 185 kg m^{-3} . The lignin foams exhibited typical characteristics of porous materials, *i.e.*, the compression

resistances and thermal conductivities were directly proportional to the density. These properties show a similar trend to the previously observed characteristics of tannin foams.

4. It was observed that once the lignin-based foams were immersed in water they released part of the acid catalyst within the first minutes and then the pH remained unchanged, which suggests the possibility to recover up to 1/3 of the catalyst used.

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