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ORIGINAL ARTICLE

Valorization of Kraft black liquor and tannins via porous material production



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Abstract Macroporous polymeric monoliths were prepared using, as main raw material, mixtures of hydrolysable and condensed tannins and Kraft black liquor from pulp industry. The process consists of mechanical frothing of aqueous solutions constituted with the different polyphenols, a hardener, and in the presence of a surfactant that maintains the foam stable before curing. The aim of this work was to study the contribution in the formulations of Kraft black liquor on physical properties for the foams. This objective was justified by the significantly lower cost of black liquor as compared with that of tannins. The target application is the thermal and sound insulation in the building industry. The materials obtained were characterized by scanning electronic microscopy, mercury porosimetry and mechanical, thermal and acoustical measurements.

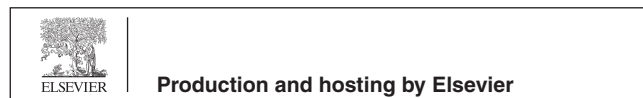
Solid, self-standing foams with an average porosity of 90% and an average cell diameter between 170 and 329 μm were obtained. The measured values of compression modulus ranged from 1.8 up to 21.6 MPa and the thermal conductivity was around $40 \text{ mW}\cdot\text{K}^{-1}\text{m}^{-1}$. The materials showed also good sound absorption characteristics at medium frequencies with coefficients of 0.5 (500 Hz) and 0.8 (1000 Hz) and at high frequencies with coefficients of 0.7 (2000 Hz) and 0.8 (4000 Hz).

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1. Introduction

The need to find new materials made out of renewable resources becomes more pressing with the decline in the amount of oil. To avoid the use of agricultural products that can be used in the food industry, it is possible to turn to the waste and byproducts from wood transformation industries such as lignin (Alekhina et al., 2015) or tannins (Lee and Lan, 2006). The work presented here investigates the possibility of converting the waste from different industries (pulp and paper, wood, etc.) into new materials. Wood

and paper industries generate several by-products such as tannins and lignins. We know that such materials as foams have a wide range of applications since they have a variety of properties compared to non-foam materials. The use of polymeric foams is extremely widespread. We find them in sports and leisure products, in military applications, vehicles, aircraft, and at home. Most people encounter polymer foams every day in one form or another, either in furniture, packaging, in their car, etc. (Eaves, 2004). Among the most popular applications there are packaging and impact protection (energy absorbing), decrease in structures weight and the thermal insulation and sound absorption in the field of construction (Ashby and Gibson, 1999; Gibson and Ashby, 1997).

If we consider waste from wood and paper industries, foams can be produced from condensed tannins (Celzard et al., 2010; Sánchez-Martín et al., 2013; Tondi et al., 2009) or lignins (Pan and Sessler, 2013; Stevens, 2010). Some works have focused on replacing petrochemical polyols by lignin in polyurethane foams (Chung and Washburn, 2012; Hatakeyama et al., 2008) or replacing phenol by tannin in phenolic foams (Link et al., 2011; Meikleham and Pizzi, 1994). In a previous work we developed an original process based on mechanical frothing allowing the manufacture of foam from hydrolysable and condensed tannins mixed with lignosulfonate (Merle et al., 2016). Preliminary tests revealed the high potential of our product for building insulation applications. In the present work, we aimed to optimize the formulation of the foams with the objective to use as much black liquor as possible for a potential used as thermal and sound insulation in buildings. Indeed, black liquor from the Kraft process can be considered as one of the cheapest and most available renewable waste worldwide. The Kraft process has the advantage over other pulping processes of accepting all types of softwood and hardwood. In 2009, around 130 million tons of Kraft pulp were produced (Tran and Vakkilainen, 2009). The main by-product of the Kraft process is black liquor: 1.3 billion tons of dilute black liquor (15% in water) are industrially produced every year, resulting in 200 million tons of dry black liquor being burned (Clay, 2008). Kraft black liquor is essentially composed of alkali lignin, wood acids and polysaccharides inorganic salts, resins, fatty acids, and methanol. When this black liquor is burned, it releases sulfur compounds and methanol. Black liquor represents therefore a material available in large quantities around the world, inexpensive and whose use as “energy recovery” leads to volatile compounds such as sulfur compounds that can have health effects. Indeed, pulp and paper industries can have important impacts on environment and health. In North America, it is one of the most polluting industries (Ritchlin and Johnston, 1999; Sources, 1998). Therefore, it is important to treat this waste to reduce environmental impact while promoting a product with great potential.

Previous works showed that it was possible to make porous materials from concentrated emulsions using unmodified Kraft black liquor as the main starting biopolymer (Foulet et al., 2016, 2015). In the present work we intend to study the replacement of lignosulfonates by black liquor in the mechanical frothing of porous materials previously developed (Merle et al., 2016). This method has already been known for years (Pugh, 2005; Weaire et al., 1995), particularly in food science (Davis et al., 2004; Yankov and Panchev, 1996). It was also used to prepare biobased foams from mimosa tannin (Szczurek et al., 2014, 2013). As far as we know, no study has been carried out on the preparation of foams containing both tannins and unmodified black liquor from Kraft process.

In this work, results were compared with tannin and lignin foams results but also results of phenolic foams since tannins and lignins are polyphenols. Finally, comparisons were also made with polyurethane foams since they represent the largest market share in terms of polymeric foams. In addition, the last two mentioned polymers are found in the field of construction (Eaves, 2001).

The resulting foams were discriminated according to their porous structure, compression tests, thermal conductivity and sound absorption.

2. Materials – experimental

2.1. Materials

The condensed tannin was a commercial extract from mimosa (*Acacia mearnsii*) kindly supplied by Tanac S. A. (Brazil), under the commercial name Tanfood (T1). Oak tannin (T2), hydrolysable tannin was kindly supplied by Silvachimica (Silvateam, Italy) under their respective commercial names Tan'activ QP (T2). Crude Kraft black liquor collected from a local paper mill (Smurfit Kappa, Cellulose du Pin Kraft paper mill, Biganos, France) was used as received. Its major physicochemical properties were as follows: dry matter amount = 50 wt%; dynamic viscosity $\mu = 7000$ MPa s at 23 °C; density $\rho = 1.3$ g/mL; pH = 14 (solution diluted to 5 wt% dry matter). Hexamethylenetetramine (Hexamine), adipic acid, phthalic acid, 1,3-octanediol and Tween 80 were purchased from Fisher Scientific (France). All the products were used as received.

2.2. Foam preparation

Firstly, tannin powders were mixed manually. The mixture was then dissolved in water, together with the Kraft black liquor. Hexamine and additives were then added and the solution was mechanically stirred in a jacketed reactor at 60 °C, obtained by water circulation. The stirring was performed using an overhead motor at 250 rpm for 5 min and then at 500 rpm for another 5 min in order to obtain a homogeneous mixture. Surfactant (Tween 80) was then added dropwise before a final stirring, at 1800 rpm for 30 min, which enables the formation of air bubbles. Finally, the foam is poured into a mold placed in an oven at 85 °C for 24 h. After removal from the oven, the cured foams were left at room temperature until complete drying.

This approach was used to foam eight different aqueous formulations containing the following: condensed tannin (Mimosa/T1), hydrolysable tannin (Oak/T2), Kraft black liquor, hexamine as curing agent, Tween 80 as surfactant. The percentage of weight composition of these formulations is reported in Table 1.

Previous studies showed that hexamine can harden phenolic resins based on condensed tannin through benzylamine bridges (Peña et al., 2006; Pichelin et al., 1999; Pizzi and Tekely, 1995).

Regarding additives, adipic acid is an aliphatic dicarboxylic acid ($C_6H_{10}O_4$). It has been used for decades in nylon 6.6 production and as plasticizer (Castellan et al., 1991). This acid, which was produced from benzene (a volatile carcinogen), can now be synthesized from D-glucose (Niu et al., 2002). The 1,8-octanediol is also an aliphatic compound ($C_8H_{18}O_2$). Together with adipic acid they are used to make aliphatic polyester (Mahapatro et al., 2003; Vouyiouka et al., 2013). This combination was supposed to give more elasticity to the foams and avoids cracks. With this addition, the issue was the loss of mechanical properties. Indeed without phthalic acid, it wasn't possible to handle the foams, which collapse easily. Phthalic acid is an aromatic dicarboxylic acid ($C_8H_6O_2$) used for the production of polyester such as poly(ethylene terephthalate) (PET) (Guimarães et al., 2007). Aromatic compounds enhanced mechanical properties.

Table 1 Formulation of the different foams.

Sample	M1	M2	M3	M4	M5	M6	M7	M8
T1 (wt%)	14.2	10.2	10.2	7.9	20.3	15.8	15.8	12.9
T2 (wt%)	14.2	10.2	20.3	15.8	10.2	7.9	15.8	12.9
Black liquor (wt%)	7.1	15.2	5.1	11.9	5.1	11.9	4	9.7
Water (wt%)	53.3	53.3	53.3	53.3	53.3	53.3	53.3	53.3
Hexamine (wt%)	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
Adipic acid (wt%)	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
Phthalic acid (wt%)	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
1,8-octanediol (wt%)	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
Tween 80 (wt%)	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

2.3. Foam characterization

2.3.1. Electron microscopy investigations

The morphology of the foams was observed by scanning electron microscopy (SEM) using a Hitachi TM-1000 microscope. Foam samples were manually broken in sections of about 0.5 cm² before being placed on a carbon tab to ensure a good conductivity. Metallization of the foam was carried out by sputtering a thin layer of gold-palladium onto the sample prior to analysis.

Micrographs were taken at several different magnifications between $\times 50$ and $\times 200$.

Two-dimensional (2D) circular cross-sectional cell diameter was estimated from SEM micrographs after image processing with ImageJ freeware (NIH, USA). Experimental data were obtained by manual measurements of diameters from a population of at least 150 cells, which represent between 15 and 20 micrographs for each foam. Several methods have been devised to find a simple factor to convert the mean size of such 2D size distribution to the actual 3D mean size of the spheres without a consensus. A standard assumption in the stereology literature (Russ, 1986) assumes that the distance between the center of a given sphere and a random plane that intersects it has a uniform distribution on $[-x, x]$, where x is the radius of the sphere. An approximate solution from this entirely theoretical approach leads to the result that the ratio of the mean diameter of a set of spheres (d_{3D}) to that of its 2D intercept (d_{2D}) is $d_{3D}/d_{2D} = 4/\pi \approx 1.27$, irrespective of the particular distribution of the 3D sizes (Kong et al., 2005). This correction factor was used in this work to estimate the mean corrected diameter (d_m). The mean corrected diameter (d_m) and the uniformity factor (U) were calculated from the following relations: $d_m = \sum n_i d_i / \sum n_i$, $U = (1/d^*) \times (\sum |d^* - d_i| \times n_i d_i^3 / \sum n_i d_i^3)$ where n_i is the number of cells of diameter d_i and d^* is the median diameter (the diameter for which the cumulative undersize volume fraction is equal to 0.5).

This factor is usually used to obtain insight about droplets homogeneity in an emulsion. Here, its determination provides information concerning the dispersion of cell size. According to Schmitt et al. (2003) an emulsion can be considered monodisperse when U is smaller than 0.25.

2.3.2. Mercury porosimetry

Mercury intrusion porosimetry analysis was carried in a Micromeritics Autopore IV 9500 porosimeter with the following parameters: contact angle = 130°, mercury surface

tension = 485 mN/m, maximum intrusion pressure = 124 MPa. This analysis was performed only once for each foam and measured the bulk (apparent) density (ρ_a), the average interconnection diameter and the total open porosity (Φ). The apparent density is defined as the mass of the material divided by the total volume it occupies. ρ_s , was also calculated from the relationship ($\Phi = 1 - \rho_a/\rho_s$) and represents the density of the solid, without porosity.

2.3.3. Mechanical properties

Compression testing was carried out on a texture analyser TA-XT2. A 250N load-cell was used with a crosshead speed of 0.1 mm/s and a specimen size of 50 mm \times 50 mm \times 20 mm. The probe was cylindrical with a diameter of 12.70 mm giving a surface area of 126.62 mm². The given values were averaged from tests carried out on 3 replicates for each foam.

2.3.4. Thermal properties

Samples with dimensions of 20 mm \times 20 mm \times 10 mm were placed for 20 s in contact with a flame of a Bunsen burner. The time needed for the glow to disappear was measured. Each foam was tested 5 times. Thermal conductivity measurements were carried out using a Hot Disk TPS 1500 (ThermoConcept, France) based on the transient plane source method. The method uses a plane sensor that acts as both a heat source and a dynamic temperature sensor. The plane sensor was fitted between two identical samples. The thermal conductivity was calculated by the Hot Disk software.

2.3.5. Acoustic absorption

Acoustic absorption coefficients α were measured with an impedance Kundt tube. The samples were submitted to a planar acoustic wave emitted by a loudspeaker. The absorption coefficient was derived from the transfer function between the pressures measured by the microphone. The frequency generator was a RIGOL DG1022 and the oscilloscope a RIGOL DS1102E. The tube had an interior diameter of 35 mm and the microphone that crosses the wave had a diameter of 10 mm. For each foam formulation, 3 replicates with a cylindrical shape and a thickness of 15 mm were tested. The main issue with a Kundt tube is the shape of the sample that must perfectly fit the tube.

A sample of commercial insulator such as wood fiber was tested to control the impedance Kundt tube and to evaluate the foams.

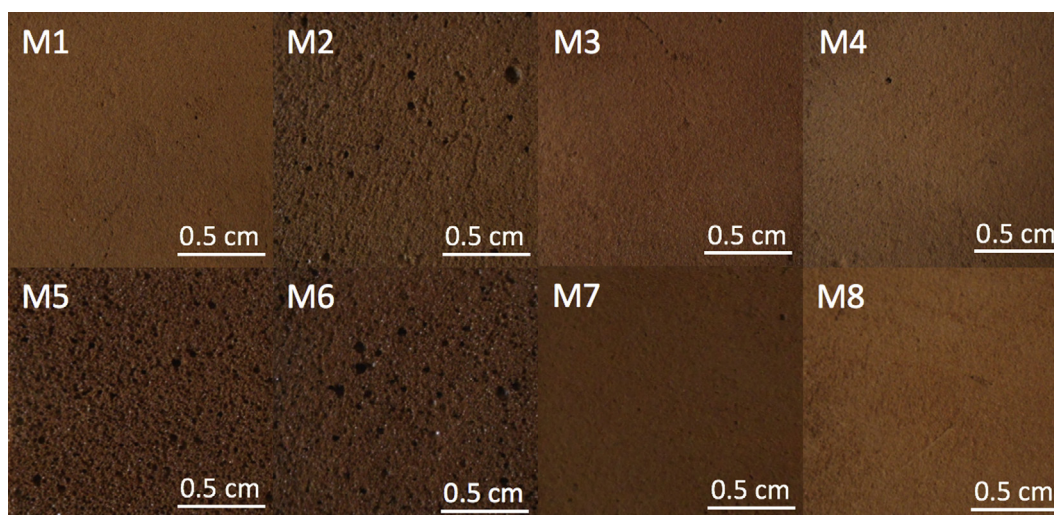


Figure 1 Optical photographs of foams after curing and drying.

3. Results and discussion

3.1. Solid foam preparation and characterization

3.1.1. Preparation

A dispersion such as a foam or an emulsion system is not thermodynamically stable over time, leading to a separation of the components of the composition (Kitchener, 1964; Lam et al., 2014). To overcome this problem, the formulation was heated during foaming in order to prevent a too rapid coalescence by a sufficient increase in the viscosity at the temperature of curing.

Mechanical frothing through high shear mixing in the presence of air is a well-known process to prepare polyurethane foams (Barron and Dunlap, 1974; Gribble et al., 2001). This process, particularly easy to implement, has been recently applied to the preparation of biobased foams (Lee et al., 2011). The high speed stirring will cause the formation of air bubbles in the aqueous solution, stabilized by the surfactant. These bubbles are the template of the porosity of the foam. Curing of the foam is obtained by hexamine before drying. Pictures of foams after curing and drying are shown in Fig. 1 (only one picture was taken for each foam).

After curing, it was observed that drainage occurred. Indeed, under each foam a viscous liquid was observed.

First, one can notice that there is no crack in the foam. Then, after drying, we can already see a difference between the structures of different formulations. Indeed, M2, M5 and M6 have cells with larger sizes than the other samples.

3.1.2. Electron microscopy investigations

The morphology of the foams was analyzed by SEM. In all cases, an open macroporous cellular morphology was observed, as can be seen in Fig. 2.

The dimensions of the cells and interconnections are reported in Table 5. The diameter of the cells varies from 170 to 329 μm . For comparison, phenolic foams have cell diameter from 70 μm (Del Saz-Orozco et al., 2014) to 100–200 μm (Aquad et al., 2007; Kim and Lee, 2008). Tannin foams with an average cell size between 94 and 396 μm have

been reported before (Szczurek et al., 2014; Tondi and Pizzi, 2009). Polyurethane foams were produced with cell size ranging from 100 to 150 μm (Van Hooghten et al., 2014). Lignin foam has voids around 100–1000 μm (Stevens, 2010).

From the measurements in the SEM micrographs, (Fig. 2), it was possible to estimate the cell diameter distribution. The average cell size does not exceed 329 μm , whatever the sample. The size of the cells from each material is shown in Table 5.

The uniformity factor (U) is used to characterize emulsions. U gives a good indication of the dispersity of the droplets. An emulsion is considered monodisperse when U is smaller than 0.25 (Schmitt et al., 2003; Van Hooghten et al., 2014). The U values of the cells of the solid foams were calculated from the diameter measurements for each sample and are also presented in Table 5. These values are the smallest for M2 and M7, which means they are the best materials in terms of size dispersion. Overall, the best dispersions are obtained when the quantities of tannins are equivalent (M1, M2, M7 and M8).

As shown previously (Merle et al., 2016), the foams obtained formed a multitude of beads stuck to each other (Fig. 2). Cells are empty with air between cells, which should give good thermal and acoustical properties. Reported examples of such foams having the appearance of beads stuck to each other and not connected through a solid matrix are aluminum spheres (Gibson and Ashby, 1999), macroscopic silica beads (Castrodeza and Mapelli, 2009), PLA or polyurethane foams (Mosanenzadeh et al., 2015) or inorganic monoliths (Carn et al., 2004).

The main difference is that our foams have mostly interconnected porosity when aluminum foams are closed cell materials. The areas of contact between adjacent cells are a continuous polymer film that forms the walls that enclose the cells. Those walls are extremely thin (from 1 to 2 μm).

If we consider cell sizes, it gives some information about the reactivity of the raw material.

In Table 2, the influence of black liquor is shown and it had an effect on cell size when the amount of condensed tannin is below 14.2 wt%. It gives higher cell diameters for the higher quantity of lignin, whatever the amount of hydrolysable

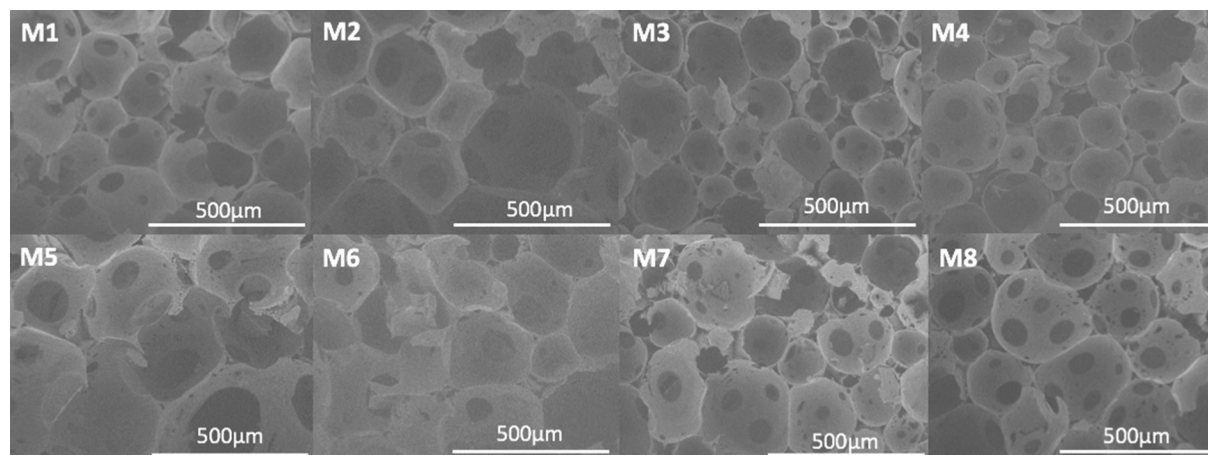


Figure 2 SEM micrographs of M1 to M8.

Table 2 Influence of the amount of lignin between two formulations on cell diameters and compression modulus (M1–M2, M3–M4, M5–M6 and M7–M8).

Kraft black liquor	Average cell diameter (μm)	Compressive modulus (MPa)
M1 \rightarrow M2	+	–
M3 \rightarrow M4	\approx	\approx
M5 \rightarrow M6	+	\approx
M7 \rightarrow M8	\approx	\approx

tannin. However, when it comes to compressive modulus, the impact of the amount of lignin is only obvious between M1 and M2. We can conclude that higher amount of hydrolysable tannin reacts with the lignin.

Table 3 shows the influence of the hydrolysable tannin on the formulation. Regarding the diameters, it tends to reduce the cell size, which is consistent with the fact that the condensed tannin is the most reactive compound in the mixture (Merle et al., 2016). Concerning M6 and M8, it doesn't influence the cell size. In M6 formulation there is a better interaction between all polyphenols leading to stabilization of the cell diameter, whatever the amount of condensed tannin. However this is true only for cell diameter since the compressive modulus is higher for M8. This shows that increasing condensed tannin leads to a better crosslinking. Again there is an exception and it concerns M3, which has almost the same modulus as M1.

Table 3 Influence of the amount of condensed tannin between two formulations on cell diameters and compression modulus (M1–M2, M3–M4, M5–M6 and M7–M8).

Condensed tannin	Average cell diameter (μm)	Compressive modulus (MPa)
M1 \rightarrow M3	–	\approx
M2 \rightarrow M4	–	+
M5 \rightarrow M7	–	+
M6 \rightarrow M8	\approx	+

Finally, Table 4 shows the influence the hydrolysable in tannin. Increasing the amount of hydrolysable tannin increases the cell sizes, except for M6.

For the compression modulus a higher amount of hydrolysable tannin tends to decrease the mechanical properties, except for M6. This results show us that with the good proportion of hydrolysable tannin and Kraft black liquor, a crosslinking occurs.

Regarding the shape of the cells this structure is different from most foams available. Indeed, polyurethane foams and phenolic foams also have well distinct cell but there are no voids between cells and the walls are thinner than the walls of our foams (Del Saz-Orozco et al., 2014; Gu et al., 2013; Sousa et al., 2014; Yang et al., 2012).

Closed and open cells are important in terms of thermal conductivity. Some phenolic foams give the same results as foams presented here, in terms of open-cell structure, thermal conductivity and density (Kim and Lee, 2008), whereas commercial phenolic foams have close cell structure with much lower thermal conductivity and density (Auaud et al., 2007; Eaves, 2001).

3.1.3. Mercury porosimetry analysis

The porous structure of the foams was investigated using mercury porosimetry. The overall results are reported in Table 5. One important property in foam is the apparent density (Housel, 2004). According to Ashida and Iwasaki (1995), most physical properties of plastic foams, both flexible and rigid, are proportional to their density. They give examples of flexible urethane foams and phenolic foams where density impacts

Table 4 Influence of the amount of hydrolysable tannin between two formulations on cell diameters and compression modulus (M1–M2, M3–M4, M5–M6 and M7–M8).

Hydrolysable tannin	Average cell diameter (μm)	Compressive modulus (MPa)
M1 \rightarrow M5	+	–
M2 \rightarrow M6	\approx	+
M3 \rightarrow M7	+	–
M4 \rightarrow M8	+	–

Table 5 Morphological and physical characteristics of the foams.

	M1	M2	M3	M4	M5	M6	M7	M8
Average cell diameter ^a (μm)	236 \pm 75	315 \pm 74	170 \pm 54	186 \pm 51	329 \pm 130	292 \pm 107	257 \pm 68	260 \pm 74
Uniformity factor ^a (U)	0.35	0.26	0.48	0.39	0.52	0.48	0.29	0.35
Apparent density ^b (g/cm^3)	0.18	0.15	0.14	0.13	0.18	0.25	0.15	0.13
Average interconnection diameter ^b (μm)	27	42	24	33	58	32	28	48
% porosity ^b	88	89	90	91	89	80	89	91
Auto-extinguished time (s)	299 \pm 3	160 \pm 1	329 \pm 3	284 \pm 3	142 \pm 1	198 \pm 2	277 \pm 3	260 \pm 2
Thermal conductivity ($\text{mW}\cdot\text{K}^{-1}\text{m}^{-1}$)	40.3 \pm 1.6	41.8 \pm 1.1	40.3 \pm 1.2	41.8 \pm 1.2	41.4 \pm 2.8	42.9 \pm 0.9	41.4 \pm 2.1	40.6 \pm 1.1

^a From SEM image analysis.

^b Estimated by mercury porosimetry (the relative uncertainty is 2–5%).

on properties such as compressive strength, tensile strength, flexural strength or even thermal conductivity. Nasirzadeh et al. reported that absorption energy is also function of the density (Nasirzadeh and Sabet, 2014).

Apparent density of the foams prepared in this work is in the range 0.13–0.25 g/cm^3 . These values are close to some phenolic foams found in the literature, from 0.12 to 0.20 g/cm^3 (Del Saz-Orozco et al., 2015). Concerning porous material based on concentrated emulsions of Kraft black liquor, densities obtained were between 0.38 and 0.76 g/cm^3 (Foulet et al., 2015). The lowest density is 0.13 g/cm^3 for samples **M4** and **M8**. Density is important when working on large volumes. Indeed, in the field of construction, the best materials have the best physical properties with the lowest density.

3.1.4. Mechanical tests

Mechanical properties of the resulting rigid foams were investigated by uniaxial compression tests. Results are shown in Table 6. Usually, polymer foams show a compression stress-strain curve corresponding to three behaviors of the material (Eaves, 2004): first, the linear part is the elastic domain controlled by cell wall bending. In the second region, the cells collapse and a plateau is observed. Finally, when all the cell walls are collapsed, a third phase occurs: densification.

The compressive strength of foams (except for **M2**) is higher than 100 kPa, which is a sufficient value for many rigid PU foam applications (Belgium, 2006).

Materials with the lowest compressive modulus (below 5 MPa) are **M2**, **M5** and **M6**. In these samples, the black liquor and/or hydrolysable tannins weight fractions exceed than those of condensed tannin. If we consider that poor mechanical properties are related to low cross-linking, this can explain why those three foams have higher cell diameters. Indeed, before curing, all components were mixed in a jacketed reactor at 60 °C. Heat and acids are known to act as catalysts and cross-linking is supposed to start before curing. If the kinetic of cross-linking is slow, the viscosity of the mixture will need more time to increase, and the ripening phenomena will occur more easily, which explains cell sizes of samples **M2**, **M5** and **M6**, which have the lowest proportion of condensed tannin. Then, **M7** and **M8** have the same compressive modulus around 11 MPa. In both cases, the proportion of black liquor has no influence on the compressive modulus. Finally, testing **M1**, **M3** and **M4** gives modulus higher than 15 MPa. To summarize, the mechanical properties are better if the weight fraction of condensed tannin is greater than those of black liquor and

hydrolysable tannin. This is consistent with previous studies indicating that condensed tannins are very reactive with hexamine (Merle et al., 2016; Tondi et al., 2012). To get the best mechanical results, the weight fraction of hydrolysable tannin should not be greater than that of condensed tannin. At best, both weight fractions may be identical.

In this work, unexpectedly, foams having the highest densities are not necessarily those with the best results in compression tests. The compressive modulus is higher with the highest content of condensed tannin (**M3**, **M4**), with densities between 0.13 and 0.14 g/cm^3 . Furthermore, unlike previous work (Eaves, 2004; Tu et al., 2008) compressive properties of foams are not influenced by densities. As another example, **M4** and **M8** have the same densities (0.13 g/cm^3) but compressive modulus of **M4** (21.6 MPa) is higher than that of **M8** (11.4 MPa).

M3 and **M4** contain greater proportions of condensed tannin and studies showed that they react together to form phenolic resins (Peña et al., 2006; Pizzi and Tekely, 1995). Higher percentage of condensed tannin gave lower cell diameter and the foams obtained have the highest mechanical properties. We can conclude that in these cases the cross-linking was faster than in the other foams (lowest cells size) and with a greater extend (higher mechanical properties).

3.1.5. Thermal properties

Auto-extinguished time of foams after exposure to a Bunsen flame has been estimated and results are shown in Table 5. No clear correlation appears between density and time of extinction of the incandescence. Indeed, with an equivalent apparent density ($\rho_a = 0.13 \text{ g}/\text{cm}^3$), the estimated extinguishing times for **M4** and **M8** are 284 s and 260 s respectively. For **M2** and **M7** ($\rho_a = 0.15 \text{ g}/\text{cm}^3$) the values are 160 s and 277 s respectively. Finally, for **M1** and **M5** ($\rho_a = 0.18 \text{ g}/\text{cm}^3$) extinguishing times are 299 s and 142 s respectively. The best result is observed for the **M3** ($\rho_a = 0.14 \text{ g}/\text{cm}^3$) sample which obtained the longest extinguishing times (329 s).

3.1.6. Thermal conductivity

Thermal conductivity measurements have been conducted on the different foams prepared and results are shown in Table 5. The thermal conductivity is similar for all samples having the same cell size. Again, there is no clear correlation appears between density and thermal conductivity.

According to Eaves (2004), when density decreases the conductivity decreases.

Table 6 Mechanical properties.

Sample	M1	M2	M3	M4	M5	M6	M7	M8
Compressive modulus (MPa)	16.5 ± 2.5	1.8 ± 0.5	19.1 ± 3.7	21.6 ± 3.1	2.7 ± 0.6	3.8 ± 1.1	11.1 ± 3.1	11.4 ± 3.6
Maximum compressive stress (MPa)	0.38 ± 0.10	0.062 ± 0.003	0.59 ± 0.13	0.51 ± 0.03	0.10 ± 0.06	0.13 ± 0.04	0.33 ± 0.16	0.30 ± 0.11
Maximum force (N)	47.8 ± 12.7	31.5 ± 1.4	78.8 ± 16.2	64.3 ± 3.3	12.9 ± 7.8	16.6 ± 5.1	41.6 ± 19.6	38.0 ± 14.1

Moreover, the porosity of foams varies from 80% to 91%. Yet, this difference may be due to two different phenomena: the porosity decreases if the volume of expansion of the foam decreases, and hence the thermal conductivity increases, which could be the case for M6, and the total porosity is 80%, with the higher density and thermal conductivity (0.25 g/cm^3 and $42.9 \text{ mW}\cdot\text{K}^{-1} \text{ m}^{-1}$). The second phenomenon may be due to the fact that if more cells are closed, this would decrease the total open porosity and decrease the thermal conductivity. This last hypothesis is unlikely given that the pressure reached in the mercury porosimeter is 124 MPa and the cell walls collapse between 0.1 and 0.59 MPa.

Even if we take into account these assumptions it is still not possible to explain the difference between the densities of foam and thermal conductivity. This suggests that the solid material itself has a different thermal conductivity depending on the formulation.

These new kinds of biobased foams can be considered for thermal insulation since thermal conductivity of most common insulation materials ranges between 20 and 50 mW/K (Belgium, 2006). An optimization of the formulation and a better control of the final structure would give a better thermal conductivity. Indeed, through the MEB micrographs, we can see that all the foams are mainly open-cell foams and they are filled with air. Open-cell foams exhibit high absorption properties but closed cell foams have very good thermal insulation properties (Cornick, 2010). Our foams exhibit a thermal conductivity around $40 \text{ mW}\cdot\text{K}^{-1} \text{ m}^{-1}$ with a porosity around 90% and an open-cell structure. If we can formulate a close cell structure the thermal conductivity should drop significantly.

3.1.7. Acoustic absorption

A good sound absorption is an important property of materials for building conception, and the foams were tested and compared to a commercial sound absorber (Pavatex). Results are reported in Table 7. Only samples M1, M3, M4, M7 and M8 did not crack until the end of the measurements. Other

samples did not resist the shaping necessary for the measurements.

Results reported in Table 7 indicate that M1, M4, M7 and M8 samples show acoustic absorption coefficient values close to the commercial material, except for 2000 Hz. The differences between formulations do not induce a significant difference in terms of acoustic behavior between samples. The materials developed in this work have good acoustic insulation properties in medium range frequencies (500–1000 Hz) and also in high frequencies (2000–4000 Hz). However, M3 shows slightly lower performances at 1000 Hz and 4000 Hz with coefficients of 0.72 and 0.74 respectively, and M7 has the lowest coefficient at 2000 Hz (0.67). Considering acoustic absorption, the best choices are M1, M4 and M8 that have similar coefficients but different densities. The most interesting material is the one giving the best acoustic results while being the lightest, such as M4 and M8, with a density of 0.13 g/cm^3 .

4. Conclusion

Insulating foams were already prepared based on lignosulfonate. The use of Kraft black liquor was justified by the need to find raw sources worldwide. This study showed that it is possible to value the industrial Kraft lignin by integrating it directly and without modification into porous material formulations. Indeed, modifying or purifying the liquor involves costs, that is why a direct use was considered. The results reported here represent a promising and innovative approach toward new kind of biobased insulating foams from lignin, and condensed and hydrolysable tannins. The open-cell macroporous biobased foams were prepared from low cost raw materials by mechanical frothing and curing. Various combinations of formulation have been tested to determine the optimal contribution of each phenolic compound. The apparent density of the final foams varies from 0.13 to 0.25 g/cm^3 . Thermal conductivities are around $40 \text{ mW}\cdot\text{K}^{-1} \text{ m}^{-1}$, acoustical properties vary from 0.5 to 0.91 in medium and high frequencies and mechanical properties are between 1.8 and 21.6 MPa.

Results are promising since those foams can be considered as thermal insulating (REF), even if we are far from petro-sourced phenolic foam with density range of 0.04 – 0.05 g/cm^3 and a thermal conductivity around $18 \text{ mW}\cdot\text{K}^{-1} \text{ m}^{-1}$ (Cornick, 2010).

Table 7 Absorption coefficient of the foams between 500 and 4000 Hz.

	500 Hz	1000 Hz	2000 Hz	4000 Hz
Pavatex	0.52 ± 0.02	0.84 ± 0.03	0.89 ± 0.005	0.89 ± 0.01
M1	0.50 ± 0.01	0.90 ± 0.004	0.75 ± 0.001	0.81 ± 0.01
M3	0.50 ± 0.03	0.72 ± 0.01	0.74 ± 0.005	0.74 ± 0.005
M4	0.47 ± 0.02	0.84 ± 0.02	0.73 ± 0.002	0.80 ± 0.01
M7	0.47 ± 0.01	0.83 ± 0.0001	0.67 ± 0.001	0.82 ± 0.005
M8	0.52 ± 0.01	0.91 ± 0.02	0.70 ± 0.005	0.85 ± 0.0001

Values determined with 15 mm thickness foam.

Small variations in the weight fractions of the three components of the formulation provide significant variations in the morphological and physical properties of the final dried foams. Kraft black liquor should be in weight proportion lower than condensed tannin in order to obtain good physical properties. Regarding hydrolysable tannin, its weight proportion can be as high as or lower than condensed tannin.

The results of the tests conducted on the different formulations, indicate overall the best samples in terms of physical properties are those with the highest weight level of condensed tannins. One of the main reasons of introducing black liquor into the foam formulation was its very low cost. The results obtained during this work show that, in order to maintain mechanical and thermal properties of the foam, the highest possible percentage of black liquor to introduce in tannins foam formulations is 12 wt%.

Finally, the best formulation for the foam appears to be that of sample **M4**, i.e. condensed tannin (15.8 wt%), hydrolysable tannin (7.9 wt%) and black liquor (11.9 wt%) (water, surfactant and additives qsp 100 wt%). Indeed, this formulation leads to low density foam having the best physical properties and the highest proportion of Kraft black liquor.

If a possible application of the materials developed in this study is the insulation of buildings, an optimization on the formulation as well as the process should be done in order to decrease the density of the final materials while maintaining good mechanical and thermal properties. Another issue is drainage. Indeed, the mixture is too liquid before curing, but using a shear-thinning liquid such as alginate should solve the problem.

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References

- Alekshina, M., Ershova, O., Ebert, A., Heikkinen, S., Sixta, H., 2015. Softwood kraft lignin for value-added applications: fractionation and structural characterization. *Ind. Crop. Prod.* 66, 220–228. <http://dx.doi.org/10.1016/j.indcrop.2014.12.021>.
- Ashby, M.F., Gibson, L.J., 1999. Introduction. In: *Cellular Solids: Structure and Properties*. second ed. Cambridge University Press.
- Auad, M.L., Zhao, L., Shen, H., Nutt, S.R., Sorathia, U., 2007. Flammability properties and mechanical performance of epoxy modified phenolic foams. *J. Appl. Polym. Sci.* 104, 1399–1407. <http://dx.doi.org/10.1002/app.24405>.
- Barron, B., Dunlap, J., 1974. Air frothed polyurethane foams. US3821130 A.
- Belgium, B., 2006. Thermal insulation materials made of rigid polyurethane foam. *Assoc. Fed. Eur. Rigid Polyurethane Foam*, pp. 1–33.
- Carn, F., Colin, A., Achard, M.-F., Deleuze, H., Sellier, E., Birot, M., Backov, R., 2004. Inorganic monoliths hierarchically textured via concentrated direct emulsion and micellar templates. *J. Mater. Chem.* 14, 1370–1376. <http://dx.doi.org/10.1039/b400984c>.
- Castellan, A., Bart, J.C.J., Cavallaro, S., 1991. Industrial production and use of adipic acid. *Catal. Today* 9, 237–254.
- Castrodeza, E.M., Mapelli, C., 2009. Processing of brass open-cell foam by silica-gel beads replication. *J. Mater. Process. Technol.* 209, 4958–4962. <http://dx.doi.org/10.1016/j.jmatprotec.2008.12.009>.
- Celzard, A., Zhao, W., Pizzi, A., Fierro, V., 2010. Mechanical properties of tannin-based rigid foams undergoing compression. *Mater. Sci. Eng. A* 527, 4438–4446. <http://dx.doi.org/10.1016/j.msea.2010.03.091>.
- Chung, H., Washburn, N.R., 2012. Improved lignin polyurethane properties with lewis acid treatment. *ACS Appl. Mater. Interf.* 4, 2840–2846. <http://dx.doi.org/10.1021/am300425x>.
- Clay, D.T., 2008. *Evaporation principles and black liquor properties*. TAPPI Kraft Recover. TAPPI Press, pp. 1–6. Short Course.
- Cornick, M., 2010. Foam. In: Pilato, L.A. (Ed.), *Phenolic Resins: A Century of Progress*, pp. 188–208.
- Davis, J.P., Foegeding, E.A., Hansen, F.K., 2004. Electrostatic effects on the yield stress of whey protein isolate foams. *Colloids Surf. B. Biointerf.* 34, 13–23. <http://dx.doi.org/10.1016/j.colsurfb.2003.10.014>.
- Del Saz-Orozco, B., Alonso, M.V., Oliet, M., Domínguez, J.C., Rodríguez, F., 2015. Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. *Compos. Part B Eng.* 75, 367–372. <http://dx.doi.org/10.1016/j.compositesb.2015.01.049>.
- Del Saz-Orozco, B., Alonso, M.V., Oliet, M., Domínguez, J.C., Rodríguez, F., 2014. Effects of formulation variables on density, compressive mechanical properties and morphology of wood flour-reinforced phenolic foams. *Compos. Part B Eng.* 56, 546–552. <http://dx.doi.org/10.1016/j.compositesb.2013.08.078>.
- Eaves, D., 2001. *Polymer Foams Trends in Use and Technology*. Rapra technology.
- Eaves, D., 2004. Foam fundamentals. In: Eaves, D. (Ed.), *Handbook of Polymer Foams*. Harbury, UK. Rapra technology, pp. 1–8.
- Foulet, A., Birot, M., Backov, R., Sonnemann, G., Deleuze, H., 2016. Preparation of hierarchical porous carbonaceous foams from Kraft black liquor. *Mater. Today Commun.* 7, 108–116. <http://dx.doi.org/10.1016/j.mtcomm.2016.04.005>.
- Foulet, A., Birot, M., Sonnemann, G., Deleuze, H., 2015. The potential of kraft black liquor to produce bio-based emulsion-templated porous materials. *React. Funct. Polym.* 90, 15–20. <http://dx.doi.org/10.1016/j.reactfunctpolym.2015.03.006>.
- Gibson, L.J., Ashby, M.F., 1999. *Cellular Solids Structure and Properties*. Cambridge University Press.
- Gibson, L.J., Ashby, M.F., 1997. The mechanics of foams: basic results. In: *Cellular Solids: Structure and Properties*, second ed. Cambridge University Press, pp. 175–234.
- Gribble, M.Y., Tabor, R.L., Jakubowski, J.J., Schrock, A.K., Belleghem, P.C.J.M., Van Kennedy, J.G., 2001. Froth dispersion, stabilization and preparing polyurethanes. US6271276 B1.
- Gu, R., Sain, M.M., Konar, S.K., 2013. A feasibility study of polyurethane composite foam with added hardwood pulp. *Ind. Crops Prod.* 42, 273–279. <http://dx.doi.org/10.1016/j.indcrop.2012.06.006>.
- Guimarães, D.H., de Meireles Brioude, M., da Paz Fiúza, R., de Almeida Prado, L.A.S., Boaventura, J.S., José, N.M., 2007. Synthesis and characterization of polyesters derived from glycerol and phthalic acid. *Mater. Res.* 10, 257–260. <http://dx.doi.org/10.1590/S1516-14392007000300007>.
- Hatakeyama, H., Kosugi, R., Hatakeyama, T., 2008. Thermal properties of lignin- and molasses-based polyurethane foams. *J. Therm. Anal.* 92, 419–424.
- Ashida, K., Iwasaki, K., 1995. Thermosetting foams. In: Landrock, Arthur H. (Ed.), *Handbook of Plastic Foams – Types, Properties, Manufacture and Applications*. New Jersey. Landrock in Noyes Publications, pp. 11–140.
- Kim, B.G., Lee, D.G., 2008. Development of microwave foaming method for phenolic insulation foams. *J. Mater. Process. Technol.* 201, 716–719. <http://dx.doi.org/10.1016/j.jmatprotec.2007.11.143>.
- Kitchener, J.A., 1964. Foams and free liquid films. In: Danielli, J.F., Pankhurst, K.G.A., Riddiford, A.C. (Eds.), *Recent Progress in Surface Science*, vol. 1. Academic Press Inc., pp. 51–93.
- Kong, M., Bhattacharya I, R.N., James, C., Basu, A., 2005. A statistical approach to estimate the 3D size distribution of spheres from 2D size distributions. *Geol. Soc. Am. Bull.* 117, 244–249.

- Lam, S., Velikov, K.P., Velev, O.D., 2014. Pickering stabilization of foams and emulsions with particles of biological origin. *Curr. Opin. Colloid Interface Sci.* 19, 490–500. <http://dx.doi.org/10.1016/j.cocis.2014.07.003>.
- Lee, K., Wong, L.L.C., Blaker, J.J., Hodgkinson, J.M., Bismarck, A., 2011. Cutting-edge research for a greener sustainable future Green Chemistry Bio-based macroporous polymer nanocomposites made by mechanical frothing of acrylated epoxidised soybean oil. *Green Chem.* 13, 3117–3123. <http://dx.doi.org/10.1039/c1gc15655a>.
- Lee, W., Lan, W., 2006. Properties of resorcinol – tannin – formaldehyde copolymer resins prepared from the bark extracts of Taiwan acacia and China fir. *Bioresour. Technol.* 97, 257–264. <http://dx.doi.org/10.1016/j.biortech.2005.02.009>.
- Link, M., Kolbitsch, C., Tondi, G., Ebner, M., Wieland, S., Petutschnigg, A., 2011. Formaldehyde-free tannin-based foams and their use as lightweight panels. *Bioresources* 6, 4218–4228.
- Mahapatro, A., Kalra, B., Kumar, A., Gross, R.A., 2003. Lipase catalyzed polycondensations: effect of substrates and solvent on chain formation, dispersity, and end group structure. *Biomacromolecules* 4, 544–551. <http://dx.doi.org/10.1021/bm0257208>.
- Meikleham, N.E., Pizzi, A., 1994. Acid- and alkali-catalyzed tannin-based rigid foams. *J. Appl. Polym. Sci.* 53, 1547–1556. <http://dx.doi.org/10.1002/app.1994.070531117>.
- Merle, J., Birot, M., Deleuze, H., Mitterer, C., Carré, H., Charrier-El Bouhtoury, F., 2016. New biobased foams from wood byproducts. *Mater. Des.* 91, 186–192. <http://dx.doi.org/10.1016/j.matdes.2015.11.076>.
- Mosanenzadeh, S.G., Naguib, H.E., Park, C.B., Atalla, N., 2015. Functionally graded porous membranes for effective sound absorption. *Soc. Plast. Eng.*, 10–12.
- Nasirzadeh, R., Sabet, A.R., 2014. Study of foam density variations in composite sandwich panels under high velocity impact loading. *Int. J. Impact Eng.* 63, 129–139. <http://dx.doi.org/10.1016/j.ijimpeng.2013.08.009>.
- Niu, W., Draths, K.M., Frost, J.W., 2002. Benzene free synthesis of adipic acid. *Biotechnol. Prog.* 18, 201–211.
- Pan, X., Sandler, J.N., 2013. Effect of replacing polyol by organosolv and Kraft lignin on the property and structure of rigid polyurethane foam. *Biotechnol. Biofuels* 6, 12. <http://dx.doi.org/10.1186/1754-6834-6-12>.
- Peña, C., Martín, M.D., Tejado, A., Labidi, J., Echeverría, J.M., Mondragon, I., 2006. Curing of phenolic resins modified with chestnut tannin extract. *J. Appl. Polym. Sci.* 101, 2034–2039. <http://dx.doi.org/10.1002/app.23769>.
- Pichelin, F., Kamoun, C., Pizzi, A., 1999. Hexamine hardener behaviour: effects on wood glueing, tannin and other wood adhesives. *Holz als Roh- und Werkst* 57, 305–307. <http://dx.doi.org/10.1007/s001070050349>.
- Pizzi, A., Tekely, P., 1995. Mechanism of polyphenolic tannin resin hardening by hexamethylenetetramine: CP-MAS ¹³C NMR. *J. Appl. Polym. Sci.* 56, 1645–1650.
- Pugh, R.J., 2005. Experimental techniques for studying the structure of foams and froths. *Adv. Colloid Interf. Sci.* 114–115, 239–251. <http://dx.doi.org/10.1016/j.cis.2004.08.005>.
- Ritchlin, J., Johnston, P., 1999. Zero discharge: technological progress towards eliminating Kraft pulp mill liquid effluent, minimising remaining waste streams and advancing worker safety. *Environ. Sci. Pollut. Res.* 6, 1–50. <http://dx.doi.org/10.1007/BF02987611>. pdf.
- Russ, J.C., 1986. *Practical Stereology*. Plenum, New York.
- Sánchez-Martín, J., Beltrán-Heredia, J., Delgado-Regaña, A., Rodríguez-González, M.A., Rubio-Alonso, F., 2013. Optimization of tannin rigid foam as adsorbents for wastewater treatment. *Ind. Crops Prod.* 49, 507–514. <http://dx.doi.org/10.1016/j.indcrop.2013.05.029>.
- Schmitt, V., Leal-Calderon, F., Bibette, J., 2003. Preparation of monodisperse particles and emulsions by controlled shear. *Top. Curr. Chem.* 227, 195–215. <http://dx.doi.org/10.1007/b10839>.
- Sources, W.S.A.T., 1998. *Chemical Pulp Mills Kraft Pulping*. Rapra technology, pp. 1–10.
- Sousa, A.F., Matos, M., Pinto, R.J.B., Freire, C.S.R., Silvestre, A.J.D., 2014. One-pot synthesis of biofoams from castor oil and cellulose microfibrils for energy absorption impact materials. *Cellulose* 21, 1723–1733. <http://dx.doi.org/10.1007/s10570-014-0229-z>.
- Stevens, E.S., 2010. Starch-lignin foams. *Express Polym. Lett.* 4, 311–320. <http://dx.doi.org/10.3144/expresspolymlett.2010.39>.
- Szczurek, A., Fierro, V., Pizzi, A., Celzard, A., 2013. Mayonnaise, whipped cream and meringue, a new carbon cuisine. *Carbon N.Y.* 58, 245–248. <http://dx.doi.org/10.1016/j.carbon.2013.02.056>.
- Szczurek, A., Fierro, V., Pizzi, A., Stauber, M., Celzard, A., 2014. A new method for preparing tannin-based foams. *Ind. Crops Prod.* 54, 40–53. <http://dx.doi.org/10.1016/j.indcrop.2014.01.012>.
- Housel, T., 2004. Flexible polyurethane foam. In: Eaves, D. (Ed.), *Handbook of Polymer Foams*. Shawbury, Shrewsbury, Shropshire, pp. 85–122.
- Tondi, G., Pizzi, A., 2009. Tannin-based rigid foams: characterization and modification. *Ind. Crops Prod.* 29, 356–363. <http://dx.doi.org/10.1016/j.indcrop.2008.07.003>.
- Tondi, G., Wieland, S., Lemenager, N., Petutschnigg, A., Pizzi, A., Thevenon, M.-F., 2012. Efficacy of tannin in fixing boron in wood: fungal and termite resistance. *Bioresources* 7, 1238–1252.
- Tondi, G., Zhao, W., Pizzi, A., Du, G., Fierro, V., Celzard, A., 2009. Tannin-based rigid foams: a survey of chemical and physical properties. *Bioresour. Technol.* 100, 5162–5169. <http://dx.doi.org/10.1016/j.biortech.2009.05.055>.
- Tran, H., Vakkilainen, E.K., 2009. *The Kraft chemical recovery process*. TAPPI Kraft Recover. TAPPI Press, pp. 1–8. Short Course.
- Tu, Y.-C., Suppes, G.J., Hsieh, F.-H., 2008. Water-blown rigid and flexible polyurethane foams containing epoxidized soybean oil triglycerides. *J. Appl. Polym. Sci.* 109, 537–544.
- Van Hooghten, R., Gyssels, S., Estravis, S., Rodriguez-Perez, M.A., Moldenaers, P., 2014. Understanding the effect of particle surface free energy on the structural and mechanical properties of clay-laden rigid polyurethane foams. *Eur. Polym. J.* 60, 135–144. <http://dx.doi.org/10.1016/j.eurpolymj.2014.08.029>.
- Vouyiouka, S.N., Topakas, E., Katsini, A., Papaspyrides, C.D., Christakopoulos, P., 2013. A green route for the preparation of aliphatic polyesters via lipase catalyzed prepolymerization and low temperature postpolymerization. *Macromol. Mater. Eng.* 298, 679–689. <http://dx.doi.org/10.1002/mame.201200188>.
- Weaire, D., Coughlan, S., Fortes, A.M., 1995. The modeling of liquid and solid foams. *J. Mater. Process. Technol.* 55, 178–185. [http://dx.doi.org/10.1016/0924-0136\(95\)01951-0](http://dx.doi.org/10.1016/0924-0136(95)01951-0).
- Yang, H., Wang, X., Yuan, H., Song, L., Hu, Y., Yuen, R.K.K., 2012. Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. *J. Polym. Res.* 19. <http://dx.doi.org/10.1007/s10965-012-9831-7>.
- Yankov, S., Panchev, I., 1996. Foaming properties of sugar-egg mixtures with milk protein concentrates. *Food Res. Int.* 29, 521–525. [http://dx.doi.org/10.1016/S0963-9969\(96\)00048-8](http://dx.doi.org/10.1016/S0963-9969(96)00048-8).