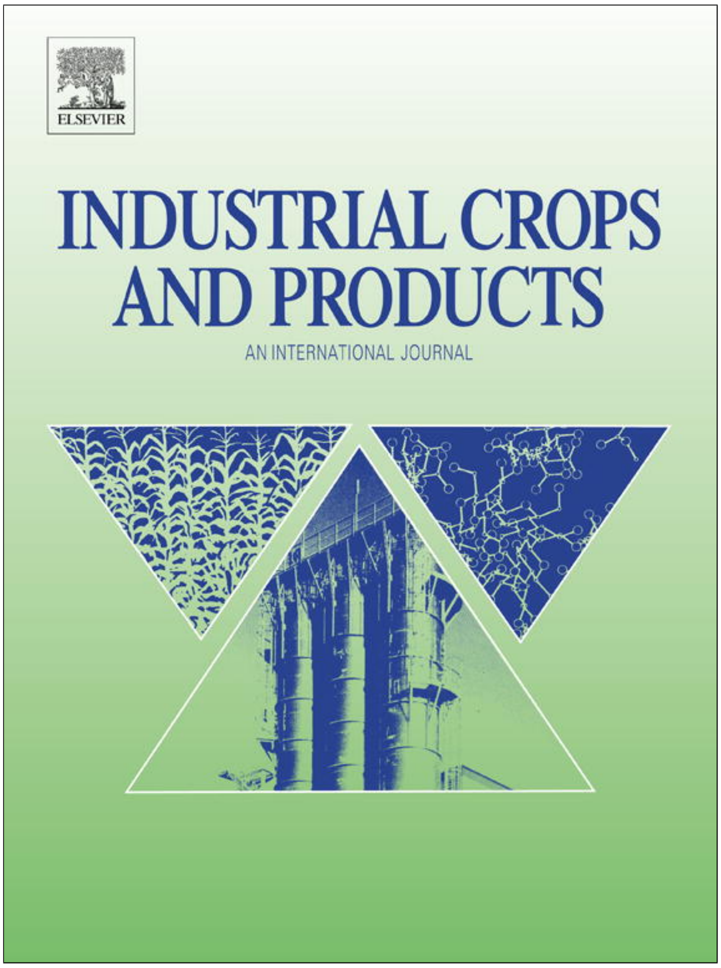

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Pine tannin-based rigid foams: Mechanical and thermal properties

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ABSTRACT

Pine bark tannin foams were prepared for the first time. The high reactivity of pine tannins in relation to other tannins induced the change in the tannin foam formulations in order to coordinate foam resin hardening, reaction exotherm and solvent blowing allowing the formation of a rigid foam. Pine tannin foams with and without formaldehyde were prepared. Their characteristics were tested as regards stress–strain curves, thermal conductivity, Young's modulus, compression strength, densification, densification rate and energy absorbed under compression. Mostly, properties the pine tannin foams with formaldehyde have properties similar to mimosa tannin foams, in some cases slightly lower and in others slightly higher. Pine tannin foams without formaldehyde showed lower mechanical strength and more elastic behaviour.

1. Introduction

Tannin based rigid foams are obtained from natural products; they are resistant to fire to the same extent as synthetic phenolic foams. They are already known for their application as floral foams (Meikleham and Pizzi, 1994). Recent studies have shown that these foams can be also used in metal ion adsorption (Tondi et al., 2008) and as internal insulating materials for interior and exterior wooden doors (Tondi et al., 2008).

Natural products constitute approximately 95% of these tannin/furanic foams. Furfuryl alcohol is obtained throughout catalytic reduction of furfural which is obtained by hydrolysis of the sugars from several agricultural crops. Polyflavonoid tannins are vegetal products obtained by water extraction from the wood and bark of trees.

Condensed polyflavonoid tannins, due to their phenolic nature, can undergo some of the typical reactions of phenol such as reaction with formaldehyde, or other aldehydes, under acid and alkaline conditions. The condensed flavonoid tannins used up to now for tannin/furanic foams are based on commercial tannins for leather, namely mimosa (*Acacia mearnsii*) bark tannin extract or quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) wood tannin extract. These tannins are principally composed of profisetinidin and porobinetinidin oligomeric chains (Fig. 1) and since the first formulation of these foams these and structurally similar condensed tannins have been used. Thus, for mimosa tannin resorcinol A-ring and pyrogallol B-ring (i.e. a robinetinidin flavonoid unit) are the main patterns at about 90% of the phenolic content of the tannin itself (Pizzi and Mittal, 2003). For quebracho tannin resorcinol A-ring and catechol B-ring (i.e. fisetinidin flavonoid unit) are the main patterns constituting more than 80% of the phenolic content of the tannin itself (Pizzi and Mittal, 2003).

The extraction of these types of tannin at present available in the world is not higher than 220,000 tons/year, thus a very limited resource. A resource instead that is immense and can be exploited for tannin extraction to satisfy world needs in phenolic type resins are the extensive softwood/conifers plantations that exist all around the world. Extraction of pine and spruce barks and other conifer species has been shown to give economical yields of condensed tannins (Sealy-Fisher and Pizzi, 1992; Pizzi et al., 1998). Unfortunately these tannins have a slightly different structure than those described above. They are based on a phloroglucinol A-ring and a catechol B-ring (i.e. they are procyanidin type tannin.) or on a phloroglucinol A-ring and a pyrogallol B-ring (i.e. they are prodelphinidin-type tannin.) (Fig. 1). Consequently, the A-rings of these condensed tannins are far more reactive than the A-rings of mimosa and quebracho-type tannins, namely about 6–7 times more reactive (Pizzi and Mittal, 2003). Thus, the simultaneous combination of foam bowing and foam hardening (Tondi and

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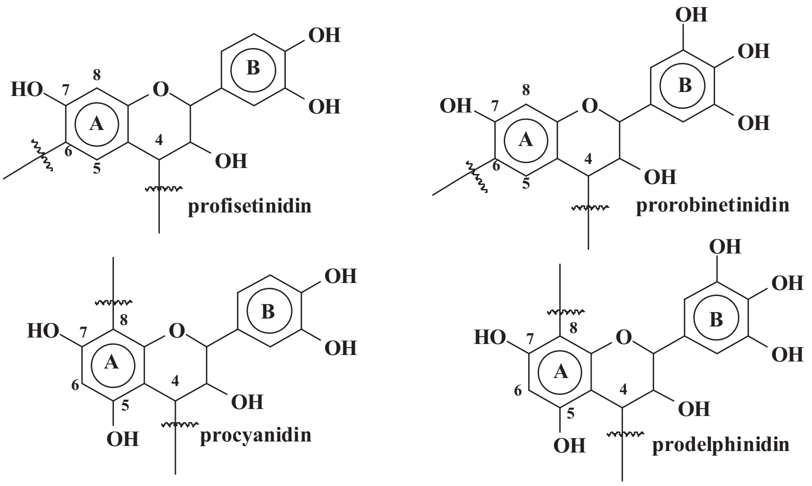

Fig. 1. Repeating units in profisetinidin (quebracho) type tannin, prorobinetinidin (mimosa) type tannin, and prodelphinidin and procyanidin (pine) type tannin.

Pizzi, 2009) and the foam formulations presented up to now cannot be used when one of these tannins, here pine tannin, is used. Since 1994 efforts have been made to obtain pine tannin-based rigid foams without much success. Recently, however, pine tannins was formulated into equally effective tannin/furanic rigid, environment friendly and, fire resistant foams (Basso et al., 2011). This article relates how this was done, the type of foams obtained and their characteristics.

2. Experimental

2.1. Pine tannins

Commercial tannin extracts from Pine (*Pinus radiata*) bark, supplied by Diteco, Ltda, Coronel, Chile, were used to prepare rigid tannin/furanic foams. Pine tannin procyanidins have flavonoid units oligomers with a high number average degree of polymerisation of between 6 and 7 and they are linked C4 to C8. Profisetinidin and prorobinetinidin tannins instead, such as mimosa tannins, have a number average degree of polymerisation of 4–5 and are mainly linked C4 to C6 (Pizzi and Mittal, 2003).

2.2. Formulation and preparation

Three kinds of foams were prepared: (A) pine tannin foams without formaldehyde; (B) pine tannin foams with formaldehyde; (C) mimosa tannin foams with formaldehyde, this latter as controls. The formulation of each foam is given in Table 1.

Firstly a liquid mixture is prepared and mechanically stirred for 10 s. The liquid mixture is composed of furfuryl alcohol, polyethylene glycol (PEG) 400 ((A), (B) foams) + water ((C) foams) + formaldehyde (37% water solution) ((B), (C) foams), and the blowing agent in order to disperse uniformly this latter. Then the tannins in powder form were added to the mixture and rigorously stirred for 90 s. Finally the catalyst, namely para-toluene-4-sulfonic acid (pTSA) (as a 65% water solution) was added and mixed in for 20 s. The resin got foamed within a few minutes and was allowed to dry for 24 h before samples were cut off its core. The formulations used are shown in Table 1.

Table 1
Formulations of organic foams.

Compound	Pine	Pine + formaldehyde	Mimosa + formaldehyde
Tannins (g)	30	30	30
Furfuryl alcohol (g)	35	19	10.5
Formaldehyde (g)	–	7.4	7.4
Water	–	–	6
PEG 400	3	4.5	–
Blowing agent (g) (DE or P)[a]	DE = 0.1–3	DE = 2–6 P = 3–6.5	P = 4–6
pTSA (g)	11	11	11

[a] DE, diethyl ether; P, pentane.

2.2.1. Blowing agent

Diethyl ether (DE) has already been used as blowing agent because of its low boiling point (34.6 °C) and the mixture has total solubility in it. Another low boiling point (36.1 °C) chemical, pentane, but in which the mixture is only slightly soluble, was tested. To study all effects of pentane was not the main purpose of this work and will be developed in details later.

2.3. Characterisation of foams

2.3.1. Thermal conductivity

Foams samples were put in an oven at 50 °C for 48 h in order to dry the residual gas in the foam, which may alter the measures. Moreover, the test was conducted under a stable humidity environment. For one measurement, two samples of 3 cm × 3 cm × 1.5 cm were prepared and the sensor was put between those two samples. The thermal conductivity analyser used was Hot Disk TPS 2600 with the 5501–6.403 mm sensor and the power used was 10 mW. The temperature in the laboratory was 18 °C.

2.3.2. Stress–strain compression

Stress–strain curves were recorded with an Instron 4467 universal testing machine equipped with 30 kN head, and using a load rate of 2.0 mm min^{-1}. Samples of dimensions 30 mm × 30 mm × 15 mm were tested in the growing direction of the foam (also called *z*-direction, on the opposite of *xy*-direction parallel with the growing direction of the foam).

Fig. 2 shows a schematic example of compression stress–strain curve for cellular solid, such as elastomeric foam. Different phases can be noticed: first a linear elasticity phase at low stresses, followed by a collapse plateau and finally densification. The initial slope in the linear elastic region is Young's modulus of the foam. In the case of open cells foams, this phase behaviour is caused by cell wall bending (Gibson and Ashby, 1997).

There is a strain maximum after this first phase, sometimes followed by a slight decrease before reaching the plateau region. If the plateau is clearly visible, then the stress average value is

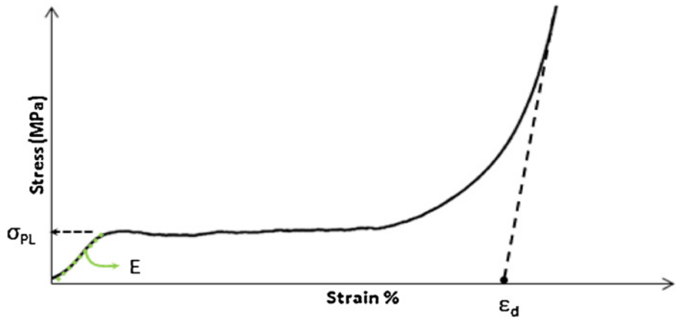

Fig. 2. Schematic example of stress–strain curve of compression in the growing direction of the foam (*z*-axis) for pine tannin-based foams with formaldehyde (density = 0.065 g cm^{-3}).

considered to be the compression strength. If instead the curve keeps rising and no stable plateau exists, in such cases the compressive strength is taken at 20% strain.

The last phase is the densification of the foam. All the cell walls have then collapsed and there is no more gas, the solid foam constituent being the only one remaining. The slope of the stress–strain curve suddenly increases. The densification strain is defined as the intersection point between the horizontal strain axis and the extension of the linear densification end-part of the curve (Fig. 2).

This method has already been used to determine organic foams compression characteristics (Celzard et al., 2010).

3. Results and discussion

3.1. Pine foams development

Pine tannins have a very high reactivity with formaldehyde under acid condition. This is the reason why it has been difficult to find the correct condition window to use these tannins to prepare foams. The reactivity of each type of tannin can be characterised by its gel time. At pH 7 and with 5% of paraformaldehyde hardener added pine tannin extract gels in 30 s at 100 °C while mimosa tannin extract gels in approximately 3 min and quebracho tannin extract gels in approximately 4 min (Meikleham and Pizzi, 1994).

Moreover, the curing rate of pine tannin/formaldehyde systems starts already increasing around 25 °C, while for mimosa (or quebracho) tannins, it starts at 35 °C (Tondi and Pizzi, 2009). Thus, the difficulty with pine tannin is to let the mixture foam and harden simultaneously, that is to gel and to harden at the same time that the solvent boils off. The curing reaction should not begin before a sufficiently high temperature is reached to let the solvent play its role of blowing agent.

To overcome this effect, polyethylene glycol has been introduced in the formulation. Its role is double: (1) It decreases the extent of the exotherm hence avoiding the formation of big bubbles inside the foam final structure. (2) It helps in reducing the agglomeration of tannin of the mixture, consequently improving the structural homogeneity of the final foam.

Finally, pine tannin-based foams require a significantly higher proportion of furfuryl alcohol to obtain a mixture not too viscous and a homogeneous distribution of the tannin.

Fig. 3 shows the temperature variation measured within the foaming mixture. Pine tannin-based foam with formaldehyde started to grow after 2 min of catalyst addition and the maximum temperature it reached was 73.9 °C. Conversely, pine tannin-based foam without formaldehyde started to grow after 10 min and reached 98.4 °C. Formaldehyde accelerates the reaction because of the reactivity of the formaldehyde with pine tannins (Pizzi and Mittal, 2003; Tondi and Pizzi, 2009).

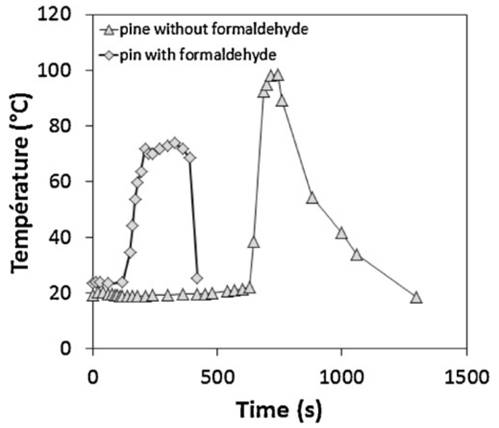

Fig. 3. Temperature as a function of time within a pine tannin-based foam mixture during foaming (DE = 3 g).

3.2. Thermal conductivity

Mimosa tannin rigid foams are good insulation materials and can be used for example as core between wood panels for interior or exterior applications (Tondi et al., 2008, 2009; Zhou et al., in press). Results of thermal conductivity measurement show that pine tannin-based foams are even better (Fig. 4). At density of 0.031 g cm^{-3}, the thermal conductivity reaches 0.033 W/m/K, 0.034 W/m/K (extrapolated) and 0.037 W/m/K for pine tannin foams without formaldehyde, and respectively for pine tannin and mimosa tannin foams with formaldehyde.

3.3. Mechanical tests

3.3.1. Stress–strain characteristics

Different densities have been tested and the full stress–strain curves of some foam samples are shown in Fig. 5. All samples with closed densities present similar behaviours so they are not all presented in Fig. 4 to allow for more clarity.

The stress–strain curves of foams without formaldehyde have typical behaviour of elastomeric cellular solids. From Fig. 5 it is interesting to note that these types of foams are softer and have significantly low mechanical resistance. During the first elastic region, they present similar straight lines, independent from the density, and Young's modulus is around 0.23 MPa. The plateau stress region is not well defined because of the positive slope. In order to

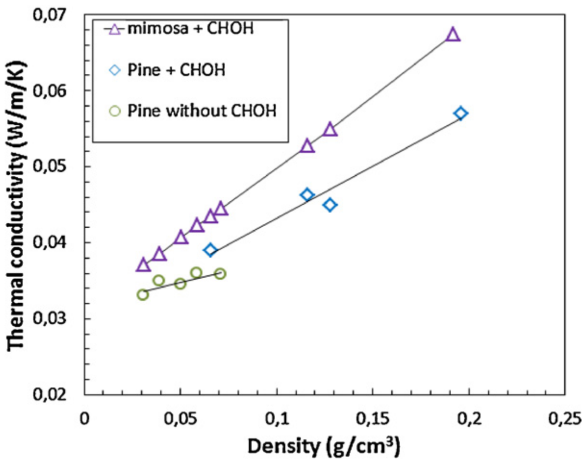

Fig. 4. Thermal conductivity as a function of foam density for pine tannin foams with and without formaldehyde and mimosa tannin foams with formaldehyde (control).

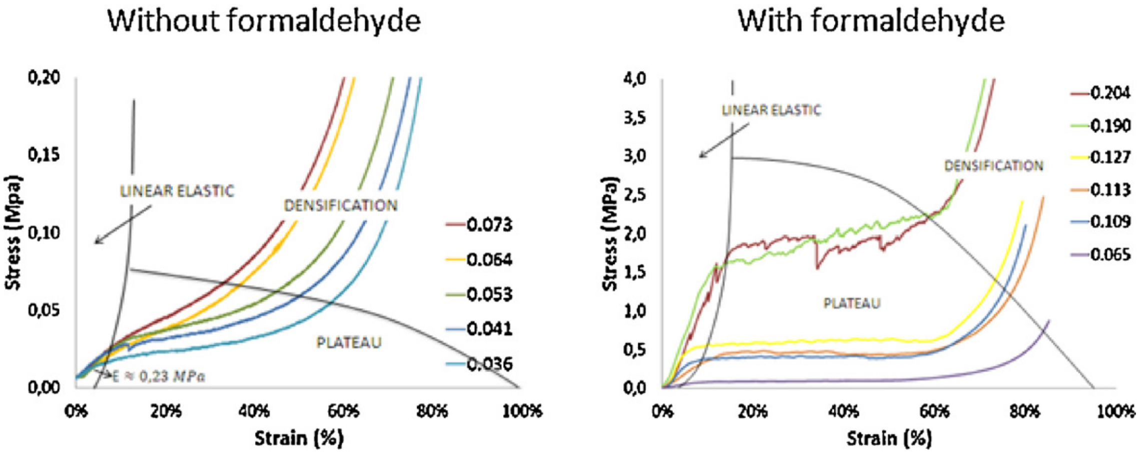

Fig. 5. Stress–strain curves of pine tannin-based foams (a) with formaldehyde, and (b) without formaldehyde (blowing agent = DE). Foam densities in g cm^{-3} are listed in the figure.

compare samples as rigorously as possible, the compressive strength was taken at 20% strain. For foams prepared with formaldehyde, the mechanical parameters are well defined and detailed in next part. All results are reported in Table 2.

3.3.2. Foams with formaldehyde

3.3.2.1. Young's modulus. Several micromechanical and phenomenological models are described by a power law, the dependence between the density and the elastic modulus, such as:

$$E \propto E_0 \cdot d^n \tag{1}$$

where E_0 is the elastic modulus of the solid from which the cellular material is made, d is the apparent density and n is an exponent depending on the failure mode.

Fig. 6 shows log(E) as a function log(d). The result is a straight line; the slope of which corresponds to the exponent n. This result confirms the validity of Eq. (1). This type of result has already been observed for, natural or carbonised foams (Celzard et al., 2010; Zhao et al., 2010a,b). Exactly the same behaviour is observed for both blowing agents: diethyl ether and pentane. The straight line corresponds to the data with diethyl ether and pentane, the slope value is 3.05, i.e. the double than for mimosa, the slope of which is 1.56.

3.3.2.2. Compression strength. According to extensive, analytical, numerical and experimental works (Ashby and Gibson, 1997; Celzard et al., 2010), the compression strength of foams is related to the density by the power law:

$$\sigma_{pl} \propto \sigma_{pl,s} \cdot d^a \tag{2}$$

where σ_{pl} is the yield strength of the solid and a is the exponent associated to the structure and its deformation mechanics.

The trend of log(σ_{pl}) as a function of log(d) is shown in Fig. 7. The compression strength of pine tannin-based foams made with pentane or DE shows the same behaviour. The straight line corresponds to the pine tannin-based foams with DE and pentane, with a slope of 2.63 instead of 2.10 for mimosa foams.

Table 2 gives Young's moduli and compression strengths of pine and mimosa foams. The data for pine foams are experimental results whereas mimosas are deduced from the fit. Pine tannin-based foams without formaldehyde have an elastic modulus of 0.23 MPa in average and no trend is observed in relationship with the density. This might be because of the weakness of the material. This latter can be seen with the compressive strength, which is very low: 0.028–0.058 MPa for 0.035 and 0.07 g cm^{-3} respectively.

When formaldehyde is added, the foams become stronger, but at low densities their mechanical properties get worse than

Table 2
Comparison of mechanical properties from rigid foams having similar densities.

Density (g cm^{-3})	Pine without formaldehyde	Pine with formaldehyde	Mimosa foam[a]	Phenolic foams[b]
Elastic modulus				
0.035	0.18	–	1.91	
0.04	0.31	–	2.47	
0.05	0.29	0.41	3.79	
0.06	0.17	0.97	5.38	
0.07	0.21	1.49	6.69	
0.11	–	7.16	12.25	
0.14	–	20.4	16.42	
0.19	–	26	23.37	
Compression strength				
0.035	0.028	–	0.11	
0.04	0.034	–	0.14	
0.05	0.041	0.06	0.20	0.76
0.06	0.042	0.09	0.27	
0.07	0.058	0.12	0.33	
0.11	–	0.045	0.59	
0.14	–	1.03	0.78	2.17
0.19	–	1.75	1.10	

[a] Celzard et al. (2010).
[b] Shen and Nutt (2003) and Auad et al. (2007).

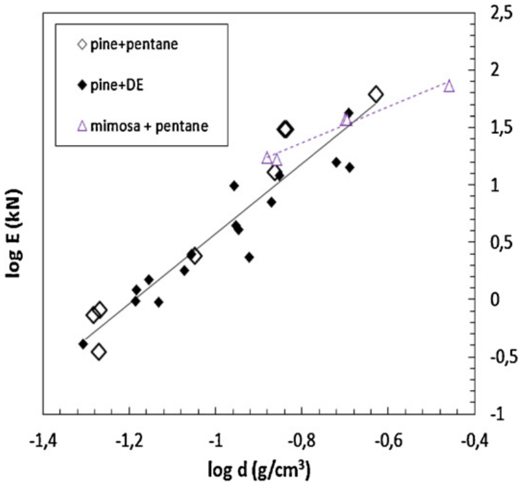

Fig. 6. Modulus of elasticity (MOE) as a function of density. The graph is plotted for mimosa and pine tannin foams using either pentane or diethyl ether as blowing agent.

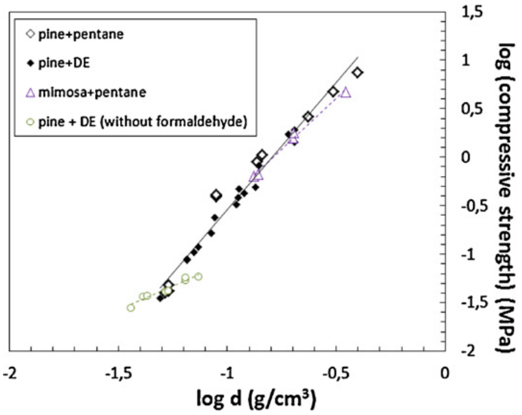

Fig. 7. Compression strength as a function of density for pine and mimosa tannin foams (blowing agent either DE or pentane).

those of mimosa tannin-based foams. However, at higher densities, pine foams have better mechanical properties than mimosa foams. It can be deduced from these results that pine tannin-based foams present higher values of Young's modulus and compression strength than mimosa tannin-based foams for relative density from 0.14 g cm^{-3} upward.

3.3.2.3. Densification. The stress–strain characteristic ends with the region of densification. The densification rate is taken as the intersection point of the strain axis and the densification straight line (Fig. 2). Densification rate also depends on the density of the foam and this relationship is described by the power law:

$$\varepsilon_d = d^x \tag{3}$$

where ε_d is the densification rate and d is the density. Fig. 8 gives the densification rate of pine tannin foams as a straight line fitting both the case with DE and with pentane as blowing agents, with a slope of −0.19. For mimosa tannin foams, the densification rate slope is −0.17; thus both the two tannins foams are similar on this aspect.

3.3.2.4. Absorbed energy. The energy absorbed by the foam under compression is defined as the area under the stress–strain curve up to the densification rate, and can be expressed as follows:

$$U = \int_0^{\varepsilon_d} \sigma(\varepsilon) d\varepsilon \tag{4}$$

It can be approximated by $U \approx \sigma_{pl}\varepsilon_d$, where $\boldsymbol{\sigma_{pl}}$ and $\boldsymbol{\varepsilon_d}$ are respectively the compressive strength and the densification rate defined above. Considering Eqs. (2) and (3), absorbed energy should also follow a power law:

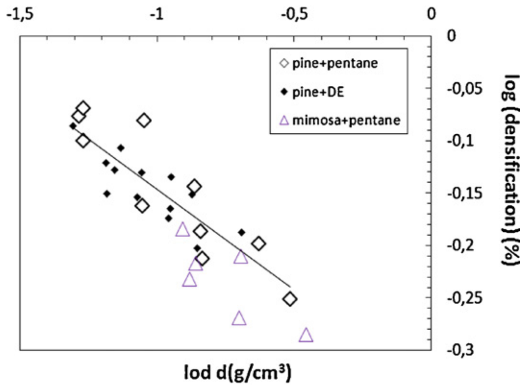

Fig. 8. Densification as a function of foam density for pine and mimosa tannin foams with formaldehyde and using DE and pentane as blowing agents.

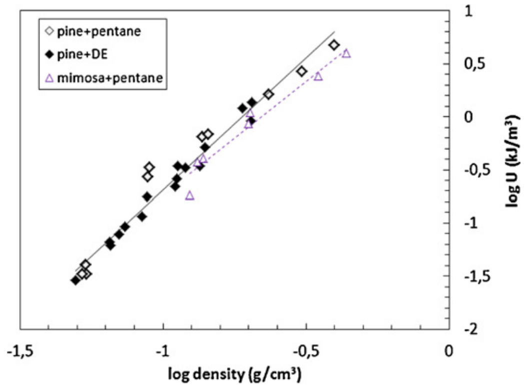

Fig. 9. Energy absorbed under compression by tannin foams as a function of foam density.

Table 3
Exponent values of Young's modulus, compressive strength, densification and absorbed energy of tannin foams with formaldehyde tested along the *z*-direction.

Exponent	Pine foams without formaldehyde	Pine foams with formaldehyde	Mimosa foams (DE or pentane)	Mimosa foams (DE)[a]
n	–	3.05	1.56	1.93
x	1.12	2.63	1.88	1.65
a	−0.08	−0.19	−0.17	−0.41
y	0.98	2.49	1.94	≈1

[a] Celzard et al. (2010).

$$U \propto d^y \quad (y = a + x) \tag{5}$$

Fig. 9 shows a linear dependence on foam density of the energy absorbed by tannin foam under compression, which confirms Eq. (5). Once again, no difference between pine foams prepared with DE or pentane is observed. Under compression, at parity of density, the energy absorbed by mimosa tannin foams is close to those of pine tannin foams. The slope of absorbed energy as a function of log(d) for pine and mimosa tannin foams is 2.49 and 1.94 respectively.

3.3.3. Foams without formaldehyde

Whatever the density, the elastic first stress is almost the same as shown in Fig. 5. As no clear trend is defined the average value of Young's modulus is reported as $E = 0.023$ MPa. Conversely, results of compressive strength (Fig. 7), densification and consequently the absorbed energy fit Eqs. (2), (3) and (5) (not shown). Their exponents are given in Table 3.

3.3.4. Mechanical parameters of pine tannin-based foams

The mechanical parameters are in relationship with the relative density with power laws as seen in Eqs. (1), (2), (3) and (5). Exponents of these equations are reported in Table 3. This study confirms the fact that changing the blowing agent does not change the mechanical properties of foams. For this latter reason, exponents are taken from slopes of the straight lines of pine foams made with DE and pentane.

4. Conclusion

For the first time rigid foams with pine tannins have been prepared and tested. Because of the high reactivity of pine tannins, the formulation of organic foam has been modified.

At very low densities, mimosa foams are more resistant than pine foams. Mimosa foams with formaldehyde have indeed a higher

Young's modulus below 0.10 g cm^{-3} and a higher compressive strength below 0.14 g cm^{-3} than pine foams. It also appears that pine foams without formaldehyde are very fragile material, with an $E = 0.21$ MPa and $\sigma_{pl} = 0.058$ MPa at 0.07 g cm^{-3}.

However, pine rigid foams are better insulation material with a thermal conductivity of 0.033 W/m/K for pine foam without formaldehyde, 0.034 W/m/K for pine foam with formaldehyde and 0.037 W/m/K for mimosa foam with formaldehyde at the density of 0.031 g cm^{-3}.

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