FORMALDEHYDE-FREE TANNIN-BASED FOAMS AND THEIR USE AS LIGHTWEIGHT PANELS

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100% natural tannin-based rigid foams were synthesized. Tannin-furfuryl alcohol networks were polymerized in an acid environment applying a temperature between 120° and 160°C. The process was developed in two ways: in a ventilated oven and in between the heated plates of a press. The foams produced showed a high homogeneity in both cases. By modifying the formulation in terms of type and amount of components it was possible to produce two kinds of foams: (1) light with density of approximately 50 Kg/m³, and (2) resistant having a density of approximately 180 Kg/m³. The compression resistance and the water absorption of these materials were evaluated. The results of these tests, in comparison with those of formaldehyde-reinforced tannin foams, indicated that these lightweight foams have lower mechanical strength but higher water affinity. The latter was also demonstrated with moisture uptake measurements. Particular attention was dedicated to the press-produced foams for their possible application as core-layer for lightweight composite panels.

Keywords: Tannin; Rigid foams; Lightweight; Board; press; Natural

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INTRODUCTION

Among the most innovative foams proposed in the last few years are the tannin-based rigid foams. These 95% natural new materials have already been studied in depth to assess their chemical and physical characteristics. It was observed that the tannin foams are hetero-polymers chemically constituted of randomly organized oligomeric tannin branches and hydroxymethylated furanic chains (Pizzi et al. 2008).

Various physical properties such as compression resistance and water absorption of the foam were analysed (Tondi and Pizzi 2009). The foams were found to be strongly dependent on their density. Highly-density foams of more than 100 Kg/m³ showed high mechanical resistance and poor water absorption, while the low-density foams (less than 50 Kg/m³) showed poor mechanical properties and significant water affinity. Fire and chemical resistance, permeability, and thermal conductivity were also monitored (Tondi et al. 2009a). These new materials demonstrated a broad inert behaviour and really low thermal conductivities (0.024 to 0.030 W/m K). Further characteristics of these foams were analysed to define intrinsic properties such as porosity, surface area, pore size distribution, and granulometry (Tondi et al. 2009b). Various applications for these materials were evaluated. The most promising applications exploited the low thermal

conductivity of the foam: insulation of buildings was considered and positive results were obtained (Tondi et al. 2009c).

Another factor concerning the applicability of these foams was the combination between the high water absorption of the foam and the high tendency of flavonoids to complex heavy-metals. Tannin foams were proposed as a heavy metal scavenger for copper/lead polluted water solutions (Tondi et al. 2008).

The results could be seen as encouraging for the majority of tests performed; however the scaling-up of these products was delayed due to the toxicity of the only synthetic component of the formulation: formaldehyde. This chemical, indeed, was classified in 1987 as a "probable human carcinogen" but in recent years its toxicity level was upgraded to "human carcinogen" (IARC, 2006). Since then the emissions of formaldehyde have been strongly decreased and its use in composite materials was strongly abated. Hence, this topic is probably the most sensitive in the wood composite panel market (Pizzi et al. 1994; Wang et al. 2008; Young and Kim 2005) and it creates impediments in the scaling up of the tannin foams.

Up to now, tannin-based rigid foams have always been produced at room tempera-ture with the important hardening contribution of formaldehyde. This paper presents an example of copolymerization between condensed flavonoids and furfuryl alcohol without formaldehyde activation in the foam production. Considering the lower reactivity of formaldehyde-free formulations, the hardening time of the resin was shortened, increasing the temperature of the blowing system. With this forethought it was possible to obtain innovative and more environmentally friendly formaldehyde-free foams.

EXPERIMENTAL

Materials

Mimosa (*Acacia mearnsii*, formerly *mollissima* de Wildt) tannin extract was provided by Silva Chimica (Italy). This light-brown powder consists of more than 90% flavonoids with a prevalence of resorcinolic units (Pizzi 1993). The other chemicals such as: Furfuryl alcohol (98%), 2-propanol (99%), diethyether (98%) and sulphuric acid (32%) were supplied by Carl Roth and Sigma-Aldrich.

Sample Preparation

Oven synthesized tannin foams

Tannin-based rigid foams were prepared as follows: furfuryl alcohol, water, and blowing agents were mixed with tannin extract in a 500 mL beaker. The blend was stirred until it was completely homogeneous. The acid catalyst was added to the beaker, and the whole viscous solution was poured in a preheated square (10x10x2.5 cm) wooden mold. The reaction was let run into a Binder M53 ventilated oven. According with previous experiences of tannin foam preparations, the process of foam expansion was completed after 10 minutes. In the first few minutes the foam blew and afterwards the resin hardened, stabilizing its inner network.

The amounts and the conditions applied for the production of each foam are reported in Table 1.

Hot press synthesized tannin foams

The foams were also prepared directly between press plates to simulate the process of lightweight panel production. A wooden mould for the foam used was similar to the one built for the oven test, whereby a covering panel was necessary to produce the final sandwich panel. Hence, three holes of 3.5 mm diameter were drilled in the upper part of two opposite lateral sides to allow the excess blowing agent to escape from the structure during the development of the foam. Pre-heating of the mould was necessary to enable the foam to evolve homogeneously. This operation was done laying the wooden box between the press plates (120°C) for 2 to 3 minutes.

The homogeneous mixture produced according to Table 1 (3^{rd} and 4^{th} row) was distributed in the box that was then exposed to the press plate for 10 minutes. A temperature of 120°C was applied, and the distance between plates was regulated to the final thickness of the sandwich board (3.3 cm). The foams produced were named "light" and "resistant" in accord with their main features.

Particular attention was paid to the blowing process during foam production. The slight excess of foam that was exuded from the holes ensured that the box was filled completely. The foam then acted as an adhesive, gluing itself to the top layer.

Tab. 1. Formulations of Tannin-based Rigid Foams Made in Oven and in Press

Sample	*Mimosa Tannin (g)*	*Furfuryl alcohol (g)*	*Water (g)*	*Blowing Agent (g)*	*Sulphuric acid (g)*	*Temperature (°C)*	***Density (Kg/m³)***
Light Oven	30	18.6	6	Diethyl ether 4	13	140	**43**
Resistant Oven	30	16	7	Propanol 7	10	160	**191**
Light Press	30	18.6	6	Diethyl ether 4	13	120	**50**
Resistant Press	30	10	7	Propanol 7	10	120	**180**

The density reported in the last column is an average value that considers at least six samples made with the same formulation.

Cutting and seasoning of the foams

The boxes with the blown black foam were cut out and made into 50 x 50 mm samples. The sponge-like material was left to age for 1 to 3 days at 20°C and 65% m.c. to allow the complete evaporation of the residual blowing agent trapped in the foam. The original partial elasticity of the foam disappeared because of the finalization of the polymerization process, with a consequent increase in the stiffness of the resin.

Testing Methods

Density

The bulk density (D) is the raw ratio between mass (M) and volume (V) of the whole foam without the external skin ($D = M / V$).

The density profiles of the foams were measured to evaluate the homogeneity from bottom to top of the foam for a length of approximately 20 mm. The density profile measurements were performed using an EWS Dense-lab X instrument.

Compression tests

Preliminary compression tests were performed using pieces cut into 50 x 50 x 20 mm. The tests were executed in a Zwick-Roll universal mechanical testing machine. 15 samples for each formulation were tested along the direction of growth of the foam applying a compression rate of 2 mm/min. The value of maximal mechanical resistance was evaluated at the moment in which the elastic behavior of the foam was compromised (collapse of the first layer of cells).

Water absorption test

Five samples of 50 x 50 x 20 mm of tannin foams were forcedly immersed in water, during which period the weight increase was monitored until the foam could be considered completely impregnated. The water uptake (*U*) was measured according to the following formula,

$$U = \frac{M2 - M1}{M1} \times 100 \quad (1)$$

where *M2* is the weight of the sample after dipping and shortly absorbing the excess surface water with blotting paper, and *M1* is the original weight of the dry foam. Each formulation was evaluated measuring five samples after 24 hours immersion time.

Moisture uptake

Two series of ten pieces, each constituted of 50 x 50 x 20 mm samples of tannin foams, were subjected to various moisture conditions. The weight of the foams was monitored every 24 hours until a stable value was obtained. The climate chamber was regulated at 20°C, and the moisture was varied at 15, 23.7, 40, 65, 80, and 95% of moisture content.

RESULTS AND DISCUSSIONS

Four formaldehyde-free formulations of tannin foams were placed into the oven and between the press-plates at high temperatures. The seemingly large number of ten to twelve panels for each formulation was prepared because lab-scale systems were not always reproducible: The fifty most homogenous samples, produced after cutting the boards to 50 x50 mm specimens, were selected to undergo the tests. The foams made were evaluated analysing their density, their homogeneity and their related properties such as compression resistance and behaviour towards water.

Formulation and Bulk Density

Foams with a density range from 25 Kg/m³ to 360 Kg/m³ were synthesized. Two examples of foams, with comparable density, were selected for each heating process

(Table 1) to show the versatility of these formulations. "Light" and "Resistant" foams had densities of around 50 and 180 Kg/m³ respectively.

The parameters used to generate such types of products were not exactly the same for the methods in the ventilated oven or in between the press plates. In the oven the heat was transmitted by hot air, while in the press most of the energy was transferred by direct contact. The latter method is more effective, and lower temperatures were required to obtain the same results. Conversely, the evaporation of the solvent was more accelerated in the ventilated oven, and an important loss of solvent occurred before the resin begins to harden. In particular for slow blowing systems this loss was significant and the formulation was adapted to maintain the correct equilibrium between the evaporation of blowing agent and hardening of the polymer. The production method for foams certainly affects the appearance of the final material. For example, after cutting out the skins, the foams from the press showed less emphasized cell anisotropy: the height and the width of the cells were more similar; consequently the oval shape of the cells was rounder.

The regulation of the density of the final foam was attained by modifying the type and the amount of blowing agents. A lower boiling point solvent easily allows low density formulations to be obtained, while higher boiling point solvents required more energy and started their evaporation later. At the right equilibrium between solvent evaporation and the hardening of the resin, the viscosity of the blowing blend played an important role. When the blowing blend was too viscous or too fluid, the distribution in the box was often inhomogeneous. As a consequence the derivate foam did not develop correctly and some defects could occur. When the viscosity of the blend was high, local phenomena were favoured and diversely blown foams were strongly liable to internal cracks and inhomogeneous local densities. In case of excessively fluid mixtures, the evaporation of the solvent occurred more violently, producing large volumes of the foam with empty cavities. For this reason, the ratio between solid and liquid components in the blowing solution was fixed at approximately 50% by weight.

Density Profiles and Homogeneity

The two most representative formulations (lightweight and resistant) are discussed for the two processing lines and compared with the formaldehyde-reinforced formulation. In Fig. 1 two sandwich panels produced in the press are shown with the light (1a) and the resistant (1b) formulation, respectively. In the two formulations the polymeric network appears homogeneous. In particular, the homogeneity of the light-foam was evaluated, and the density profile is reported in Fig. 2a.

This graphic confirms the homogeneity of the light-weight material, showing that the local density of the foam stays in a range of approx. 10 kg/m³. This fluctuation can be considered satisfactory for lab-made foam. The resistant foam (Fig. 1b) is also homogeneous but in this case the cells are larger and the walls are thicker. Unfortunately the instrument is extremely sensitive to high differences in local density. For this reason, it was not possible to achieve a correct measurement of the resistant foam: In this material the cells can also reach 10 mm in diameter, and the density profile device calculates the pores as zero. Hence, this device is not suitable for measuring the homogeneity of foams having pores with a diameter of more than 1.5 mm.

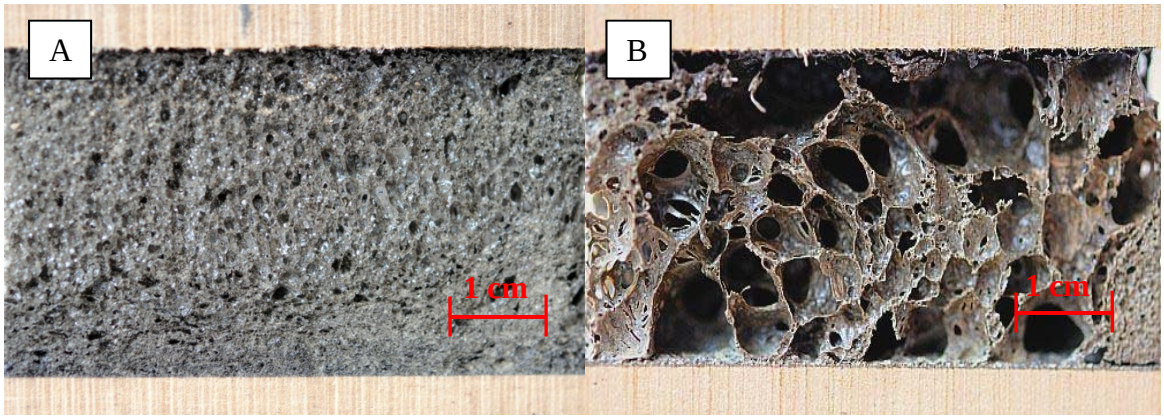

Fig. 1. Press-plate produced formaldehyde-free tannin-based rigid foams: A) Light-weight foam; B) Resistant foam.

Formaldehyde-reinforced formulations, reported in Fig. 2b, were also quite homogeneous, but the fluctuation in this case could also reach 20 Kg/m³. This result confirms that the formaldehyde-free tannin foam can be at least as homogenous as the homologous reinforced material.

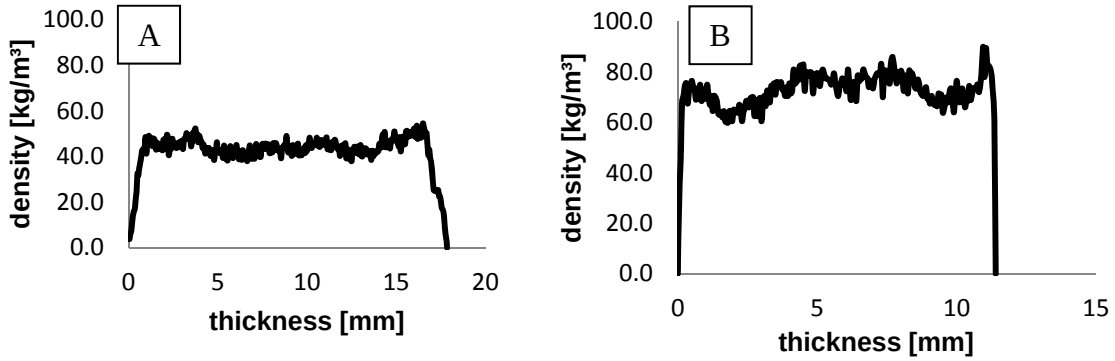

Fig. 2. Density profile measurements: a) light-weight foam; b) formaldehyde-reinforced foam

Mechanical Properties vs. Formaldehyde-Reinforced Tannin Foams

The compressive stress–strain curve of light (50 Kg/m³) oven-made foam is represented as an example for the behavior of the tannin foams (Fig. 3). This material shows a linear elastic region, followed by a stress-plateau region. At the end of the latter, the stress starts increasing again. Obviously, the slope of the initial, linear part of the curve is the Young's modulus; the stress reaches a peak value at the end of the elastic region and corresponds to the yield strength, or fracture stress. The maximum stress is sometimes followed by a decrease before the stress-plateau is reached. Cracks initiate at the peak stress value and the material tends to generate fragments as a result of these cracks.

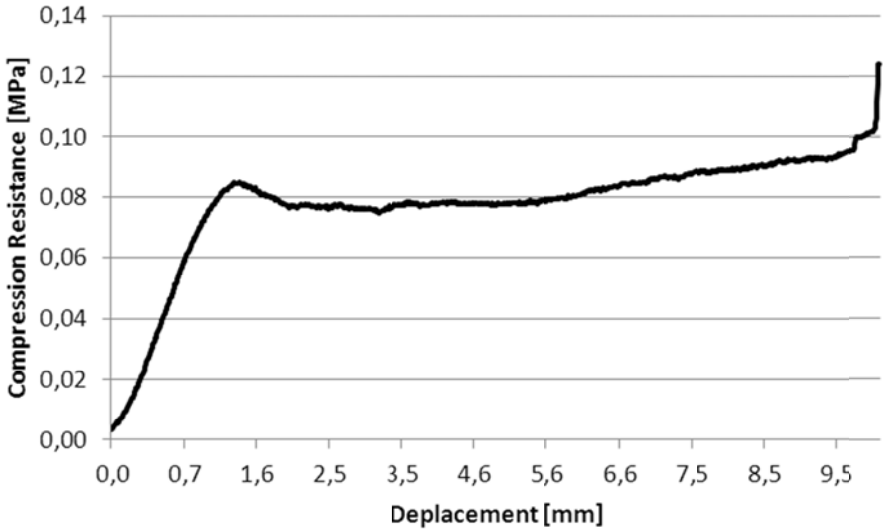

Fig. 3. Compression resistance behavior of a lightweight formaldehyde-free tannin-based foam

This behavior is typical for foamed structures, and it conforms perfectly to that of formaldehyde-reinforced tannin foams. In Fig. 4 the compression resistance values for the four completely natural foams are reported, together with the corresponding values for the formaldehyde-reinforced foams (Tondi and Pizzi 2009).

The foams without reinforcing agent were expected to be less resistant, and the results confirm this hypothesis. However, also in these foams, mechanical properties were proportional to density. The difference in mechanical properties can be directly related to the degree of crosslinking of the resin. Formaldehyde-reinforced tannin-furfuryl alcohol polymers are more likely to create crosslinking because the methylol groups of the activated (methylolated by formaldehyde) condensed tannins can more easily produce covalent bonds either with other flavonoid oligomers or with furfuryl alcohol.

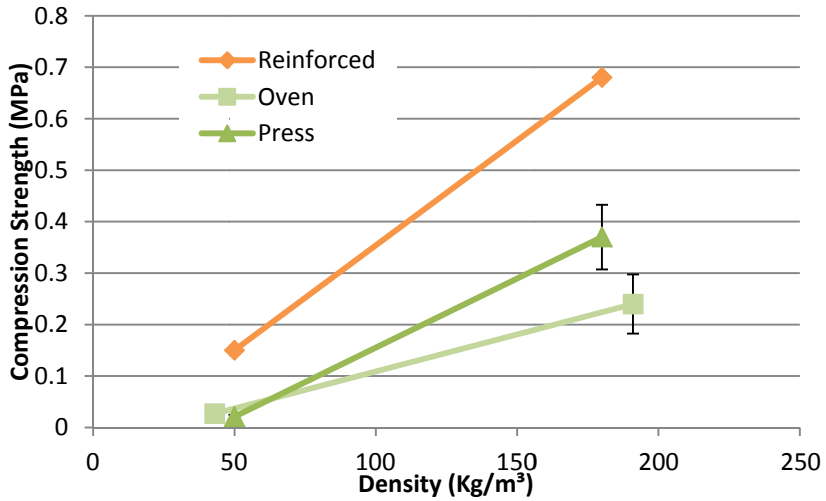

Fig. 4. Compression resistance of tannin-based rigid foams: Oven and press prepared formaldehyde-free foams compared with a formaldehyde-reinforced foam

Water Properties vs. Formaldehyde-Reinforced Tannin Foams

Forced water absorption tests showed that formaldehyde-free foams had high affinity to water (Fig. 5). The lightweight formulations, in particular, were able to take up approximately 35% more water than the corresponding formaldehyde-reinforced one. The same tendency was shown for higher densities foams. This phenomenon can be explained considering the difference of the polymers. The cells of the formaldehyde-reinforced foams have a smooth surface with a really poor amount of micro- and meso-pores (Tondi et al. 2009d, 2010). The formulations without formaldehyde seemed to be rougher, therefore enabling the water to penetrate the foam cells more easily.

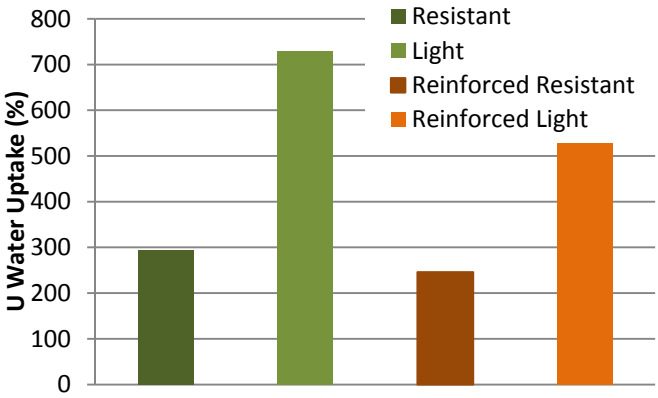

Fig. 5. Water absorption test after 24 hours of forced immersion for: Resistant and Light formaldehyde-free tannin foams compared with the homologous-density reinforced one

This higher water affinity of the formaldehyde-free tannin foams was confirmed by the behaviour of the material in different moisture conditions (Fig. 6). It can be observed that the increase in water in the network was similar for light, resistant and formaldehyde (HCHO) reinforced foams. Nevertheless some discrepancy exists.

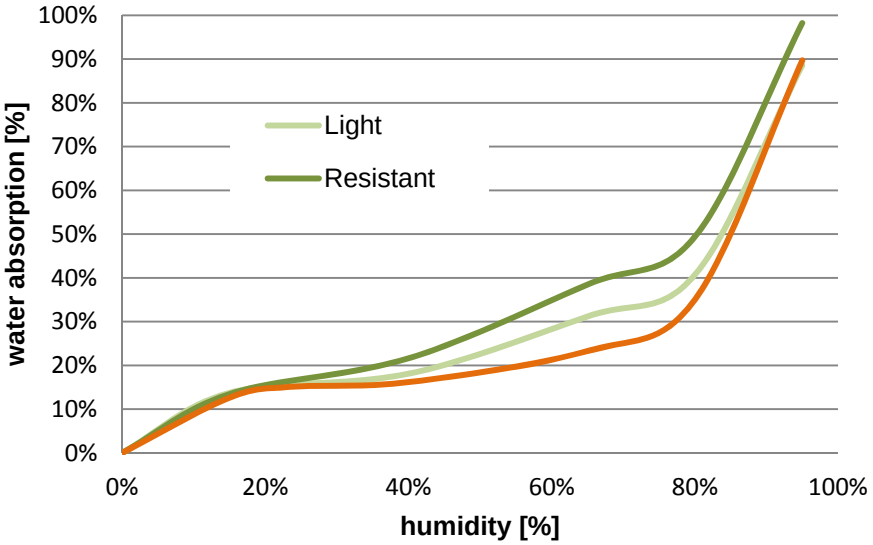

Fig. 6. Moisture absorption behavior at the temperature of 20°C of light and resistant formaldehyde-free tannin-based rigid foams compared with formaldehyde-reinforced one

In the case of formaldehyde-free foams, water uptake was more constant. It seems that water can be absorbed in a wider surface, and for this reason the slope of weight increase at the beginning of the curve had a higher gradient. When the moisture increased up to 80%, all the foams continued to absorb water proportionally, but in this case the molecules are probably arranged in secondary water layers.

Hypothesis of Chemical Cross-linking

It has been seen that tannin-based rigid foams are constituted by randomly arranged tannin oligomers connected to each other through formaldehyde and furanic rings (Pizzi et al.2008). Formaldehyde easily activates the position 6 and 8 of the A rings of the flavonoids, which thereby become more reactive for condensation reactions (Pizzi 1994).

Therefore, the formaldehyde-free formulations crosslink the tannin oligomers only through furanic rings. The positions 6 and 8 of the A ring of the flavonoid are less reactive, and then a smaller number of them will produce branches. As a consequence of this, the number of cross-links in the resin is smaller. Hence:

- the polymer requires a longer time to harden.
- the structure has lower mechanical properties.
- the structure should be more penetrable, and the water molecules can be more easily enclosed.

An hypothetical example of hetero-crosslinking is illustrated in Fig. 7.

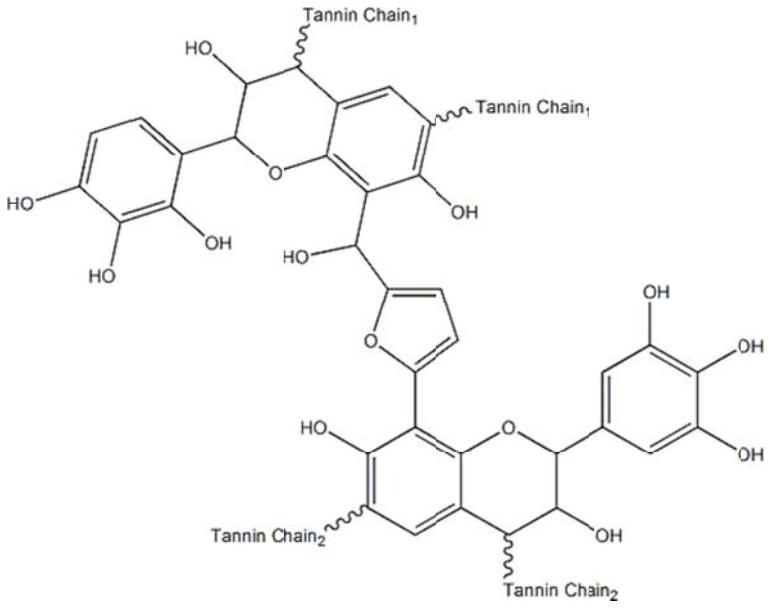

Fig. 7. Hypothesis of flavonoid-furanic crosslinking without methylolic activation

CONCLUSIONS

Tannin-based rigid foams can be produced without formaldehyde. Mimosa tannin and furfuryl alcohol can react with each other in the presence of acid catalysis and heat to produce a stable polymer suitable for foams. The foams made in this way are rather homogeneous, and they can be tailored with specific densities between 25 and 360 Kg/m³.

The production system presented is innovative: the ventilated oven and hot-press formats offer two suitable methods that can raise industry's interest in customised solutions. Hot-pressing, in particular, opens the door to potential developments of these foams as core layers for 100% natural lightweight sandwich panels (Kawasaki and Kawai 2006; Shey et al. 2006).

Mechanical properties of these natural foams are directly proportional to the density. Although the foams are weaker than the formaldehyde-reinforced ones, they are still suitable for structural applications. For instance, a 180 kg/m³ foam can support the weight of approx. 700 Kg on a surface of a size 8 foot (205 cm²).

The water affinity of these foams was proved to be even higher than the homologous formaldehyde-reinforced product. Thus, this material could be exploited as a water-holding product (e.g. floral sponge) due to its attribute of being able to take up more than 7 times its weight of water.

Further studies regarding the development of these products are being carried out, and higher-performance, customised formulations will be upgraded in the near future.

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