Research Article Adv. Mat. Lett. 2011, **2**(6), 378-382 ADVANCED MATERIALS *Letters*

www.vbripress.com, www.amlett.com, DOI: 10.5185/amlett.2011.4254

# Green, formaldehyde-free, foams for thermal insulation

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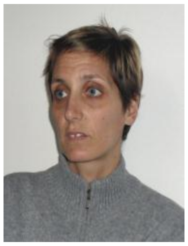
**Received: 16 April 2011, Revised: 22 July 2011 and Accepted: 26 July 2011**

## ABSTRACT

New, green and cheap rigid foams presenting outstanding performances for thermal insulation are described. Such ultra-lightweight cellular materials are mainly based on renewable chemicals: tannin and furfuryl alcohol, are very easy to produce and have thermal conductivity as low as 38 mW/m/K. Compared to previously reported tannin-based foams, these new materials are much “greener” and present improved resistance to compression and to water. Especially the formaldehyde, formerly used as cross-linking agent of tannins but known as a volatile and harmful chemical, could be successfully removed from the formulation. The as-obtained, 2nd generation, tannin-based foams are totally stable and have an expected interest for thermal insulation of buildings. Copyright © 2011 VBRI press.

**Keywords:** Rigid foam; formaldehyde; thermal conductivity; bulk density



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## Introduction

Organic foams have been suggested and used for long as insulating materials [**1**]. Low density, mechanical resistance, and narrow and closed porosity are the main criteria. However, infusibility, fire retardance, “green” origin, and low cost are highly sought after additional features. No presently commercialised foam is able to combine simultaneously all these benefits. For instance, expanded or extruded polystyrene and polyurethane foams are very sensitive to fires [**2, 3**], whereas phenolic foams are thermally resistant [**4-7**] but are more fragile and expensive [**8-12**]. Moreover, all these materials are synthetic and based on chemicals derived from the petrochemical industry. Lignophenolic foams [**13**] and tannin-resorcinol foams [**14-16**] are much greener but remain brittle and are still based on various amounts of non renewable compounds.

In the present communication, foams based on natural resources at the 90% level are presented for the first time. Their composition is mainly based on flavonoid tannins, being small polyphenolic molecules extracted from some tree species [**17**], and on furfuryl alcohol, a residue from the hydrolysis of the sugars from several agricultural crops [**18**]. The main present advance, compared to materials from the same authors already described in former works

[**19, 20**], is the complete absence of formaldehyde. The latter was indeed used so far as the cross-linking agent in the formulation, allowing a fast and strong hardening of the material after foaming. However, it is known for its volatility and for its toxicity. On 10 June 2011, the US National Toxicology Program has even described formaldehyde as "known to be a human carcinogen" [**21**]. The major obstacle that could be overcome here is producing more ecologic foams with even improved properties despite the lack of formaldehyde.

The interest for biosourced materials for various purposes is quickly increasing [**22-25**]. Moreover, biosourced materials are much more acceptable from the societal point of view than synthetic ones, especially for in-house applications. However, this statement is true provided that these new materials don't comprise potentially hazardous chemicals which might be slowly released in the atmosphere. This is the reason why new formaldehyde-free formulations were looked for and motivated the present work. After describing their preparation, characterizations in terms of structure, thermal conductivity and mechanical resistance are carried out. We show that such foams are both greener and present higher performances than previously reported tannin-based foams containing formaldehyde.

## Experimental

### *Foam preparation*

Formaldehyde-free tannin-based foams were prepared as follows. Furfuryl alcohol (16 to 22 g), water (6 g) and diethylether (blowing agent: 3 to 5 g) were first mixed together. Then, 30 g of tannin were progressively incorporated, strongly stirring the bulk during 15 s. Finally, p-toluenesulfonic acid (catalyst: 9 to 11 g) was added under stirring during 20 s, and the mixture was poured into a mould. After a several-minutes long induction period, after which heat was generated by the auto-polymerisation of furfuryl alcohol and its reaction with tannin under acid conditions, boiling of diethyl ether occurred and therefore foaming started. Due to a subtle balance between growing and hardening, the foams neither collapsed nor cracked. The same procedure was used for preparing one "standard" tannin-based foam according to the composition optimized in our past works [**14, 26, 27**]. All the compositions tested are reported in **Table 1**. Absence of formaldehyde in the new foams was compensated by higher amounts of furfuryl alcohol, which had an impact on the amounts of catalyst and blowing agent. Hardening, and hence stabilisation of the material after foaming, indeed strongly depends on temperature: the higher the temperature, the easier the hardening. Adding more furfuryl alcohol, polymerizing in the presence of acid, generated more heat, thus allowed decreasing the amount of catalyst in the formulation. Doing this, more blowing agent was thus needed for reaching the same low densities as in the absence of formaldehyde. However, these effects are not so significant, and different formulations could also be prepared and successfully foamed, except 2 samples (see below).

### *Foam characterization*

All the foams were cut into parallelepipeds and weighed in order to measure their bulk density. All were homogeneous and flawless, except samples F9-16 and F11-16 who did not rose, and were thus not characterized. Small sample pieces were metallised with gold and examined in a Hitachi S 520 scanning electron microscope. Thermal conductivity was measured by the transient plane source method (Hot Disk TPS 2500) at room temperature, and the resistance to compression was obtained with an Instron 4206 universal testing machine at a load rate of 2.0 mm min$^{-1}$.

**Table 1**. Composition of new foams, termed Fx-y, where x and y are the amounts of catalyst (p-TSA) and furfuryl alcohol (FA), respectively, compared to the standard (STD) composition. Fo and DEE stand for formaldehyde and diethylether, respectively.

| **Sample name** | **F9-16** | **F9-18** | **F9-20** | **F9-22** | **F11-16** | **F11-18** | **F11-20** | **F11-22** | **STD** |
|---|---|---|---|---|---|---|---|---|---|
| p-TSA (g) | 9 | 9 | 9 | 9 | 11 | 11 | 11 | 11 | 11 |
| FA (g) | 16 | 18 | 20 | 22 | 16 | 18 | 20 | 22 | 10.5 |
| Fo (g) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7.4 |
| (g) | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 3 |

## Results and discussion

### *Foam structure*

SEM pictures of formaldehyde-free foams are presented in **Fig. 1** and compared to the standard formulation with formaldehyde. Most cells are closed and separated from their neighbours by thin membranes. In some places, the membranes were crazed, especially at higher amounts of furfuryl alcohol. Adding more pTSA in the formulation led to smaller cells but the effect was low. In contrast, higher amounts of furfuryl alcohol had no clear impact on the average pore size but decreased significantly the bulk density, as seen in **Fig. 2**. Such an effect has been already observed in the past [**15**] but, in the present case, only a limited range of FA amounts (18 – 22 g) could be used, otherwise the foam was neither stable nor homogeneous.

The higher amount of furfuryl alcohol, compared to that of the standard formulation, produced a strongly exothermal reaction, allowing the rising of the foam. Because of this, less catalyst (9g instead of 11) could be used without noticeably changing the structure. Tannin absorbed part of the heat, making the foaming homogeneous and rather slow.

### *Foams properties*

Thermal conductivities of new foams are presented in **Fig. 3**, and compared to other values taken from the literature for phenolic (PF) [**11, 13**], lignophenolic (LPF) [**13**], polyurethane (PU) [**28, 29**], urea-formaldehyde-furfuryl alcohol (UFF) [**30**] and polyethylene (PE) [**31**] foams. Though the thermal conductivity is not so low as that of PU foams, the latter are highly sensitive to fires, and release highly toxic compounds when burnt [**2**]. In the present case, the outstanding fire retardance of foams based on tannin and furfuryl alcohol has already been demonstrated [**32**] and is fully maintained here. Moreover, tannin – furfuryl alcohol mixtures are presently commercialised as binder for consolidating foundry sands [**33**].

Compression curves have the typical shape expected for cellular solids, already observed with standard formulations comprising formaldehyde [**14, 16, 27**]. Stress-strain curves indeed presented three well identified regimes: linear elastic, plateau stress, and densification, as shown in **Fig. 4**. However, whereas standard tannin-based foams were brittle, formaldehyde-free materials are elastic and do not crack so easily. Their elastic modulus is also significantly lower. This is a significant improvement compared to the former formulation. Formaldehyde is known to immobilise easily tannin molecules during cross-linking, giving them an extremely low mobility. This feature leads to incomplete polymerization and to a brittle, vitreous polymer network [**34**]. Absence of formaldehyde consequently allowed a much higher flexibility of the polymer chains.

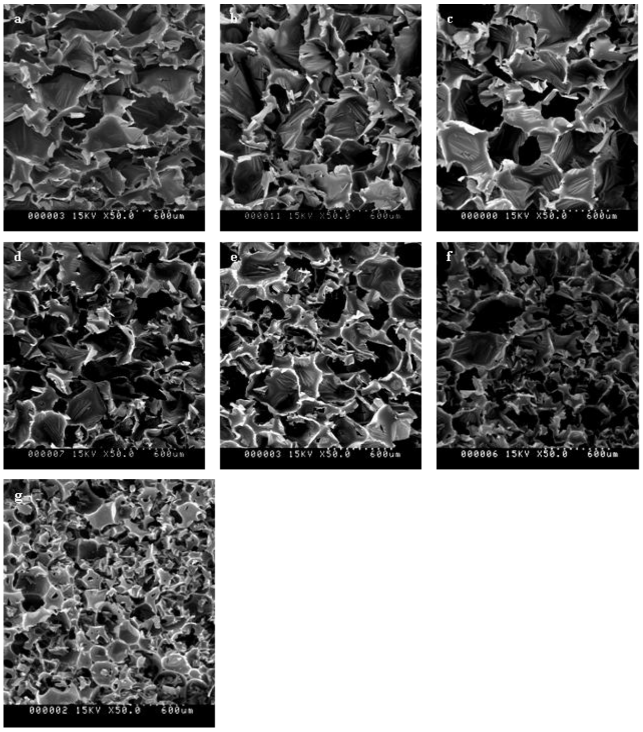

**Fig. 1**. SEM pictures (magnification 50 ×) of new foams (see Table 1) compared to the standard (STD) formulation. (a) F9-18; (b) F9-20; (c) F9-22; (d) F11-18; (e) F11-20; (f) F11-22; (g) STD.

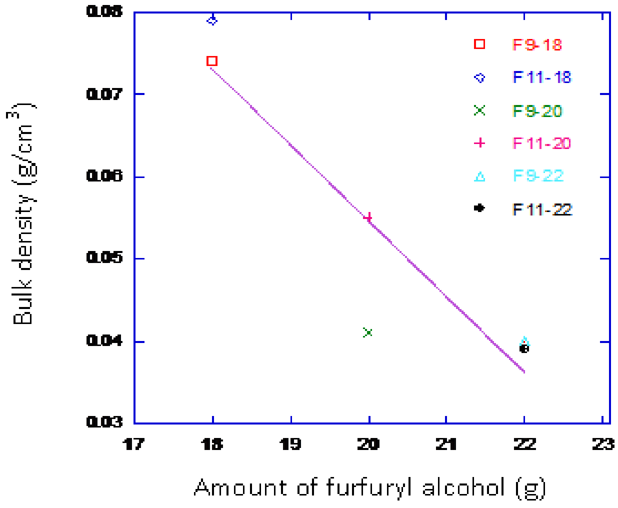

**Fig. 2**. Bulk densities of foams made from 30 g of tannins as a function of the additional amounts of furfuryl alcohol.

Foams are usually classified as stiff, partly stiff or flexible, according to their compression strength: > 0.08 MPa, 0.015 – 0.08 MPa, and < 0.015 MPa, respectively [**35**]. The new foams are mainly stiff, except the one having the lowest density, F11-22, which is really soft. Given that it is also the material having the lowest thermal conductivity, 0.038 W/m/K, F11-22 is the most interesting material of the series, combining lightness, insulating character, green origin, fire retardance and low cost.

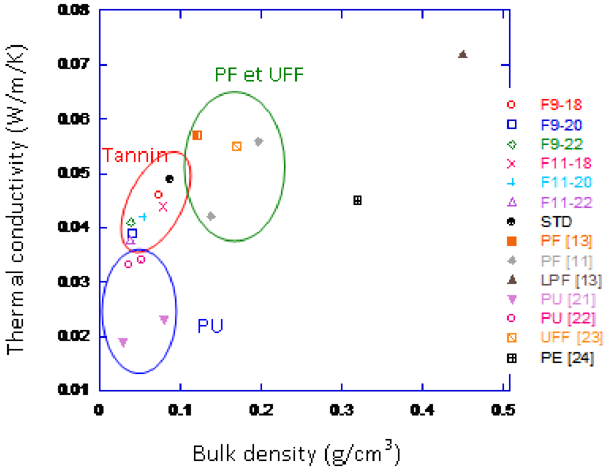

**Fig. 3.** Thermal conductivities of tannin-based foams as a function of their bulk densities. Several data from the literature were added for comparison (see text).

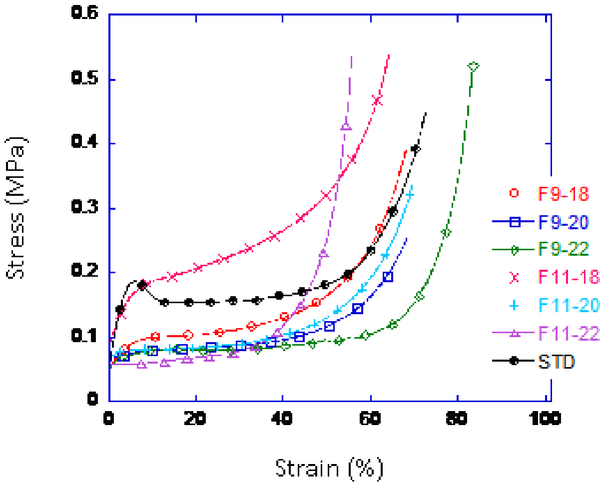

**Fig. 4.** Strain – stress characteristics of tannin-based foams submitted to compression.

Finally, though not yet investigated in detail, the new foams are considerably less hydrophilic than their formaldehyde-bearing counterparts. One water drop put onto the surface of the new materials require a very long time, between 5 and 10 min, for being slowly absorbed. Given the very low wettability, absorption probably occurs because of the porosity of the material, water gradually spreading onto itself. In contrast, water absorption of the former formulation was fast and significant, up to 7 times the initial weight of the dry foam [**16**]. Water absorption experiments are presently in progress, but much lower hydrophilicity was already clearly evidenced.

## Conclusion

We clearly showed the possibility of preparing "greener", formaldehyde-free, rigid foams for thermal insulation. The new materials have, compared to the first generation of tannin-based foams, lower density, lower thermal conductivity, and lower hydrophilicity but are also much less brittle due to a much higher flexibility. Such significantly improved characteristics could be obtained through the replacement of formaldehyde with furfuryl alcohol, a renewable chemical, and a higher amount of blowing agent.

## Acknowledgement

The authors gratefully acknowledge the financial support of the CPER 2007-2013 "Structuration du Pôle de Compétitivité Fibres Grand'Est" (Competitiveness Fibre Cluster), through local (Conseil Général des Vosges), regional (Région Lorraine), national (DRRT and FNADT) and European (FEDER) funds.

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