TANNIN-BASED SELF-BLOWING BIOMASS FOAM BY HUMIS SUBSTITUTING FORMALDEHYDE

Xinyi Chen[1], Antonio Pizzi[1*], Emmanuel Fredon[1], Christine Gerardin[2]
[1] LERMAB, University of Lorraine, 27 rue Philippe Seguin, BP 1041, 88051 Epinal, France
[2] LERMAB, University of Lorraine, Boulevard does aiguillettes, 54000 Nancy, France)

Abstract: Ambient temperature self-blowing tannin-furanic foam has been prepared by substituting a great part, even a majority of furfuryl alcohol with humins, a poly-furanic material derived from the acid treatment at high temperature of fructose. This foam was observed by scanning electron spectrometry (SEM) which shown different cell structure while the foaming process under a different temperature. The incorporation of humins resulted in enhanced mechanical property and increased bulk density. The thermal conductivity was measured and showed a lower value than other materials for green building. Furthermore, this bio-furanic foam exhibited outstanding fire resistance while undergoing combustion. This result was supported by a higher limiting oxygen index (LOI) value. Therefore, this green foam has a great potential for building energy saving, heat preservation, and fire safety as well.
Key words: Tannin-based foam; Self-blowing; Humins; Flame retardancy

Introduction

Tannin-based foam have been reported many years and attracted by serval researchers. But, the toxic crosslinker formaldehyde was the necessary chemical in the traditional formulation. Therefore, how to prepare a bio-based tannin foam without formaldehyde utilization is a hot-field in tannin-based foam researching.

Materials and Methods

Materials: Mimosa tannin (Acacia mearnsii, De Wild) bark extract and furfuryl alcohol (FA) were supplied by Silva Chimica (St. Michele Mondovi, Italy). Poly-furanic humins were laboratory prepared by the acid treatment of fructose at the Dept. of Chemistry, Université de la Cote d'Azur, Nice. *p*-Toluene sulfonic acid (p-TSA) was obtained from Sigma Aldrich (St. Louis, MO, USA).

Tannin foam preparation: The bio-sourced foams were prepared by the following steps. 15 g tannin extract powder was mixed with 5 g furfuryl alcohol thoroughly. After that, about 5.9 g of dark humins powder was added into the above mixture, stirred, and mixed well. Then, 1.5 g deionized water was added into the mixture and stirred intensely for 10 s. A mixture solution contains 6.0 g p-TSA and 1.5 g DE was put into the mixture and then keep stirring about 20 s to obtain a homogenous slurry. For the foaming under room condition, after 60-120 s, a soft, black tannin-based foam was obtained and then put it into oven at 80℃ for aging 24 h. Another group was that the mixture slurry was obtained and put into oven under 80℃ immediately for quick initiate the foaming process and then aging for 24 h.

Foam characterization: The apparent densities of the foams prepared were checked according to the ASTM D1622-03 standard. The foam morphology was observed by scanning electron microscopy (SEM, Hitachi TM-3000, Milexia, Paris, France) under the acceleration voltage of 15 kV. The compression strengths were carried out by using the universal testing machine (Instron 3300, Elancourt France). Thermal conductivity experiments were performed under ambient conditions by using a YBF-2 apparatus (Dahua Ltd., Hangzhou). Limiting oxygen index (LOI) measurements of samples were conducted based on the China National Standards

GB/T 2406.2-2009 utilizing XWR-2046 oxygen index apparatus (Yilu Instrument Co., LTD, Changzhou, China).

RESULTS AND DISCUSSION

The fabrication process of bio-sourced tannin-based foam with a high biomass content derived from natural lignocellulosic biomass-derived products is schematically illustrated in Figure 1. This formulation avoided the application of toxic formaldehyde, which improved the manufacturing safety and environmental-friendly nature than the traditional tannin-based foam. There are severs simultaneous reactions occurring, and they contribute to the expansion of the foams and to their stability of crosslinking. The furfuryl alcohol self-condensation exotherm accelerated the evaporation of the blowing agent, resulting in a volume expansion of the resultant foam. Tannin not only links to the furfuryl alcohol, but also reacts with the aldehyde groups of the humins (it probably structure is shown in Figure 2). Thus, the three-dimensional structure of the foams was obtained and maintained also by the additional cross-linking engendered by the interaction between tannin and humins.

The apparent density of tannin-based foams was shown in Table 1. Compared with reference tannin-formaldehyde foam [1,2], the tannin-humins have a higher bulk density. This is attributed that the high viscosity of humins and a well reaction crosslinking between tannin and it. However, the foaming process could be impeded by the high viscosity of the foaming mixture. Thus, the higher density can be obtained in this formulation.

Other, the foaming temperature have a significant effect on foam density and cell structure (Figure 3). The foam has a higher density under room condition while a lower density has been obtained by put the foaming mixture into oven under 80°C. This is due to the oven provided more foaming energy. The reason for this difference density is main attributed to the more vigorous evaporation of blowing agent and water at 80°C expanding more volume of foaming buck.

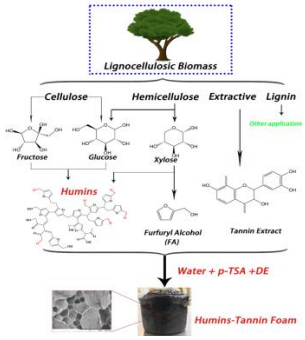

Figure 1. Schematic illustration of the fabrication of tannin-based bio-sourced foam.

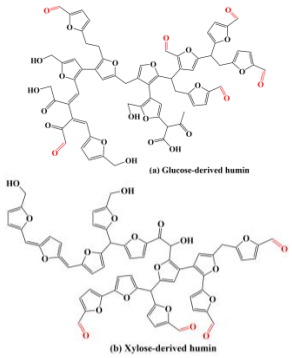

Figure 2. The probably structure of humins

The two tannin-humins were expanded and hardened one at ambient temperature (23°C, Figure 3 (a) and (b)) and the other at 80°C (Figure 3 (c) and (d)) to see how preparation temperature influenced the morphology of the finished foams. The differences observed by scanning electron microscopy (SEM) were indeed quite major as can be seen in Figure 3. The foam prepared at ambient temperature presented a closed cells structure while the one prepared at 80°C clearly presented an interconnected cells structure, with several open pores and cell walls breaks. The reason for this difference is due to the more vigorous evaporation of water at 80°C breaking weaker cell wall sites in the structure. This does not occur at ambient temperature. This means that a foam of this type prepared at ambient temperature, once stabilized, is more suitable for thermal isolation applications, while when prepared at 80°C it more suitable for acoustic insulation [3].

Table 1 Some parameters of tannin-humins foams

Samples	Density (g/cm^3)	Compressive strength (KN)	Thermal conductivity (W/mK)	LOI (%)
Ref. sample	0.08-0.12	0.08-0.25	0.044	Around 29
23℃	0.24	1.58	0.057	37.58
80℃	0.20	1.38	0.061	35.84

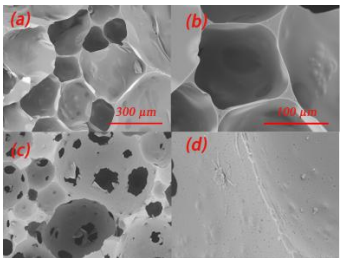

Figure 3. The morphological characteristics of tannin-humins foams. (a) and (b) is the foam obtained under 23℃; (c) and (d) is the foam obtained under 80℃

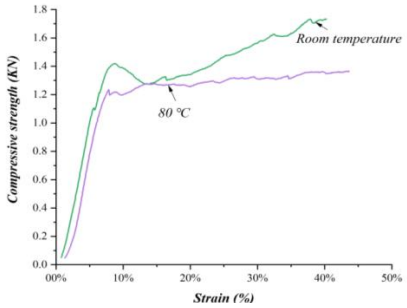

Figure 4. The compression curves of tannin-humins foams

These SEM observations explains the results of compression strength observed in Figure 4 and derives from the results shown in Table 1. Thus, in Figure 4 the curves of stress strain of the two kinds of foams indicate higher compression strength as a function of strain for both the foam with the low and higher foaming temperature. This observation infers that, if moderately higher foaming/curing temperatures are used, humins would most likely participate to a greater measure to the strength of the cell walls, but would also most likely present a predominant interconnected cells structure. Even though the foams obtained under 80°C has a higher compression strength but still lower than the foam got from room condition. Certainly, the one of reason is that such higher strength value is contributed to their high bulk density. In addition, the pores on the cell wall destroyed the structural integrity of the cell wall so that decreased their capacity of load. Another, the small number of cell structure in a unit area because of it has a bigger cell structure which resulting in a lower load capacity in the unit area. Therefore, the compression curve of foam obtained under 80°C exhibited a lower value than the other one.

The thermal conductivity of the tannin-humins foams were evaluated by the hot plate method and the results are shown in Table 1. These two kinds of samples are displayed a similar thermal conductivity, nearly 0.060 W/m·K, higher than from other studies of tannin-furanic-formaldehyde foams [4]. This result probably is attributed to changes in foams density, in general, the higher density will have a higher thermal conductivity [5,6]. The foaming temperature has a great influence on the thermal conductivity. But this result is related to the cell structure of foams formed by different temperatures. Clearly, foam obtained under room temperature has a smaller value because of its closed cell-structure. Therefore, as abovementioned, this all closed-cell wall foam can be applied to insulation thermal materials for building. However, such low thermal conductivity value still excellently lower than other kinds of insulation materials for green building.

The flame resistance of the tannin-humins foams was evaluated by measuring the limiting oxygen index (LOI) and the results are shown in Table 1. As expected, the LOI of a tannin-

humins foams, i.e., the research sample in this work, is around 36%, indicating it is a flame-retardant material [4]. The foam sample obtained under room temperature had higher LOI values, is 37.58%. This effect can be ascribed to the closed-cell morphology structure of it. SEM images (Figure 3) show that closed-cell structures with many "pores" are in the control sample obtained under 80℃. The air can then circulate in the foam interior through these opened pores, thereby providing a more suitable environment for combustion [4]. Conversely, the tannin-humins foam obtained under room temperature relatively closed-cell structures block the air exchange between the inside and outside of the foam cells, acting as a flame retardant.

CONCLUSIONS AND OUTLOOK

A green, high biomass, ecofriendly and flame retardant tannin-humins foam was prepared and evaluated in this research. The main results are exhibited as following:

(1) One with high biomass content tannin-humins foams was reported. And the manufacturing temperature has a strong influence on the structure of tannin foams.

(2) A well crosslinking reaction condition between tannin and humins which yielding a closed foam structure under room temperature.

(3) This kind of foam has an improved mechanical property, such as the compression strength can reach as high as >1 MPa.

(4) A lower thermal conductivity has obtained which was about 0.060 W/m·K. This value lower than the most of building applied thermal insulation materials. Most importantly, this kind of foam has an excellently fire resistance.

This kind of foam obtained from high biomass content formulation, and it is a potential route for forestry and biorefinery waste valorization. Such sustainable tannin-humins biomass foam has thus a great potential for industrial application and green building thermal insulation.

ACKNOWLEDGMENTS

This work was supported by Scholarship from China Scholarship Council (CSC). The LERMAB is supported by a grant of the French Agence Nationale de la Recherche (ANR) as part of the laboratory of excellence (LABEX) ARBRE.

References

[1] Tondi, G.; Zhao, W.; Pizzi, A.; Du, G.; Fierro, V.; Celzard, A. Tannin-based rigid foams: A survey of chemical and physical properties. Bioresource Technol. 2009, 100, 5162-5169.

[2] Lacoste, C.; Pizzi, A.; Basso, M.C.; Laborie, M.-P.; Celzard, A. Pinus pinaster tannin/furanic foams: Part 2: Physical properties, Ind. Crops Prod. 2014, 61, 531-536.

[3] Lacoste, C.; Basso, M.C.; Pizzi, A.; Celzard, A.; Ella Bang, E.; Gallon, N.; Charrier, B. Pine (P.pinaster) and quebracho (Schinopsis lorentzii) tannin based foams as green acoustic absorbers. Ind. Crops Prod. 2015, 67, 70-73.

[4] Wu, X.; Yan, W. ; Zhou, Y. ; et al. Thermal, morphological, and mechanical characteristics of sustainable tannin bio-based foams reinforced with wood cellulosic fibers[J]. Ind. Crops Prod. 2020, 158: 113029.

[5] Pizzi, A. Tannin-based biofoams-A review. J. Renew. Mater. 2019, 7, 474-489.

[6] Tondi, G.; Pizzi, A. Tannin based rigid foams: characterisation and modification. Ind. Crops Prod. 2009, 29, 1-2, 356-363.