Alkaline Tannin Rigid Foams

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ABSTRACT: Condensed flavonoid tannin foams were obtained under alkaline conditions. This entailed the elimination of furfuryl alcohol from these formulations, as under alkaline conditions, foam preparation could not rely on the heat generated by the self-condensation of furfuryl alcohol, which occurs only under strongly acidic conditions. The approach used to formulate the alkaline foam was: (i) the total elimination of furfuryl alcohol from the formulation, (ii) coupled with the use of an aldehyde hardener different from formaldehyde (for environmental reasons) and (iii) the application of moderate heat to allow foaming. These were not tannin/furanic foams as their acid-curing counterparts, but tannin only foams. The open cell foams were evaluated for bulk density, compressive strength, thermal conductivity and fire resistance. Their characteristics were similar to the acid-curing tannin/furanic foams.

KEYWORDS: Tannin foams, absence furanics, alkaline foams

1 INTRODUCTION

Polyflavonoid tannin-furanic rigid foams have been developed and tested for a number of different applications [1–4]. They are biosourced materials with excellent performance under a number of different conditions [5–13]. The formulation of appropriate combinations of materials to achieve the properties wanted for particular applications is a difficult undertaking and a number of different formulations have been developed in the last few years. Thus, formulations more environmentally acceptable such as those without formaldehyde [14] or formaldehyde and blowing agent [15], as well as formulations based on different flavonoid tannin types [12, 13], have been developed.

All these foam formulations, however, rely on the acid-catalyzed exothermal self-condensation reaction of furfuryl alcohol to provide blowing of the mixture to form the foam itself. They are all, then,

without exception, tannin/furanic foams. The catalyst of all these foams is invariably a strong acid such as para-toluene sulphonic acid; hence the foams themselves are strongly acidic due to the strong acid catalyst used. Such a strong acidity was necessary due to the need to generate the heat necessary for the blowing agent to foam the mixture, heat generated by the self-condensation reaction of furfuryl alcohol. Some self-neutralisation systems originating from other tannin technologies [16] have been successfully tested. However, the fact remains that at some important stage of the process the mix is strongly acidic and that acid can still be released in service. Such strong acidity, either permanent or transitory (as in self-neutralisation) can be rather damaging in some applications where the loose acid might seep through and damage materials with which the foam is in contact.

Thus, the need arose to develop formulations capable of curing under alkaline conditions and which

allowed the final foam to remain alkaline during its service life. This is no easy task as furfuryl alcohol does not give any exothermal self-condensation under alkaline conditions [17]. In the absence of the heat generated by the acid self-condensation of the furfuryl alcohol, the preparation of alkaline foams cannot be based on the same approach. Thus, previous formulations relying on this technology cannot be adapted to alkaline conditions. This limitation led to the investigation of a new approach to obtain tannin foams under alkaline conditions.

This approach has led to tannin only foams rather than tannin/furanic foams, as has been the case up to now for the acid-catalyzed variety.

2 EXPERIMENTAL

Commercial mildly sulphited quebracho (*Schinopsis lorentzii* and *Schinopsis balansae*) tannin (Tupan UP) ex Silva Chimica (San Michele Mondovi, Italy) was used for the preparation of all foams. The foams were prepared according to the mixture of components shown in Table 1. Five specimens for each case were prepared and the results of the tests are the average of the results obtained with the five specimens for each foam block prepared.

The foams were prepared by adding to the 50% solution of glutaraldehyde, the ethyleneglycol and the surfactant. Added to this blend under continuous mechanical stirring were the quebracho tannin spray-dried powder and the hexamethylenetetramine (hexamine) water solution. Then the pentane (blowing agent) and the 33% NaOH water solution used as catalyst were added. The mixture was strongly stirred after the addition of each reagent to ensure homogenisation. Finally, the mixture was placed in a water bath at a constant temperature for 20 minutes to allow foam formation. After this the foams, but not yet the cured specimens, were placed overnight in an oven to ensure curing. Three types of foams were prepared, namely at 50°C, 70°C and 85°C (Table 1).

Blocks of foam with dimensions of $3 \times 3 \times 1.5$ cm were weighed to obtain the bulk density. The cellular morphologies of the foams were obtained by scanning electron microscope (SEM Hitachi TM-3.000). Thermal conductivity of the foam samples with dimensions of $3 \times 3 \times 1.5$ cm was measured by the transient plane source method (Hot Disk TPS 2500) at room temperature. The mechanical resistance to compression was investigated with an Instron 4206 universal testing machine at a load rate of 2.0 mm min^{-1}. Flame resistance was tested by exposure to a flame at 1200°C. No significant differences in results were noticed within the specimens coming from the 5-repetition foams prepared for each case.

Table 1 Formulations and results for an alkaline-curing tannin foam.

Formulation	50°	70°	85°
Quebracho tannin (flavonoid) (g)	30	30	30
Ethylene glycol (g)	1	1	1
Glutaraldehyde 50% water solution (g)	24	24	24
Hexamethylenetetramine 30% water solution (g)	1	1	1
Pentane (g)	4.5	4.5	4.5
Surfactant (polyalkylsiloxane/polyalkylene copolymer) (g)	0.5	0.5	0.5
NaOH 33% water solution (g)	10	10	10
Oven blowing temperature (°C)	50	70	85
Oven curing temperature (°C)	50	70	85
Foam density (g/cm^3)	0.113	0.073	0.056
Thermal conductivity (W/mK)	0.067	0.050	0.050
Flame propagation rate (mm/s)	none*	none*	none*

*Instantaneous self-extinction

3 RESULTS AND DISCUSSION

The approach investigated in this paper to prepare alkaline tannin foams was based on the total elimination of furfuryl alcohol from the formulation, coupled with the use of a non-volatile aldehyde hardener different from formaldehyde (for environmental reasons) and the application of moderate heat to allow foaming. This approach has led to tannin foams without any furfuryl alcohol, thus to tannin only foams rather than the tannin/furanic types characteristic of the acid-catalyzed type.

The formulation is shown in Table 1. It relies on the use of glutaraldehyde as hardener of the tannin in the absence of furfuryl alcohol. Such a formulation needs heating because lacking the heat generated by the acid-catalyzed furfuryl alcohol self-condensation that is characteristic of the acid foams approach, there is no heat at all self-generated in the formulation, and thus it needs heat for both foam expansion and its cure.

The results are shown in Table 1. The thermal conductivity of the alkaline foam formulation is good, but slightly worse than that obtainable for acid-curing foams. Self-extinction when exposed to a flame is instantaneous once the flame is removed from the sample, as for the equivalent acid-curing foams [18]. The foaming and curing temperature can affect the final characteristics of such foams. Thus, at 70°C the best results of density and thermal conductivity are obtained (Table 1). At a lower temperature the density is higher and the thermal conductivity is worse without any advantages in mechanical performance for the higher density, indicating a lower level of crosslinking. At a higher foaming and curing temperature foaming is too quick: again mechanical resistance is lower due to early immobilisation of the network [19, 20], the cells appearance is not regular and there are no advantages as regards thermal conductivity.

Figure 1 shows the cell structure configuration of this foam formulation, with evident anisotropy in the direction of foam growth. Individual non-interconnected pores or cells separate from one to another, and membranes between cells, also called cell walls, may be observed. Figure 2 shows the stress/strain curves obtained from compression tests of foams based on this formulation, indicating that the structure is fundamentally rigid. As for tannin/furanic foams, the stress-strain curves always show three distinct regions: linear elastic, collapse and densification [21]. The alkaline-cured formulation foam behaved as typical elastic fragile cellular solids. Mechanical strength at 20% deformation is about 0.14 MPa.

Alkaline-catalysed foams solve the problem that acid-catalysed foams have; when very acid foams are in contact with lignocellulosic materials extensive
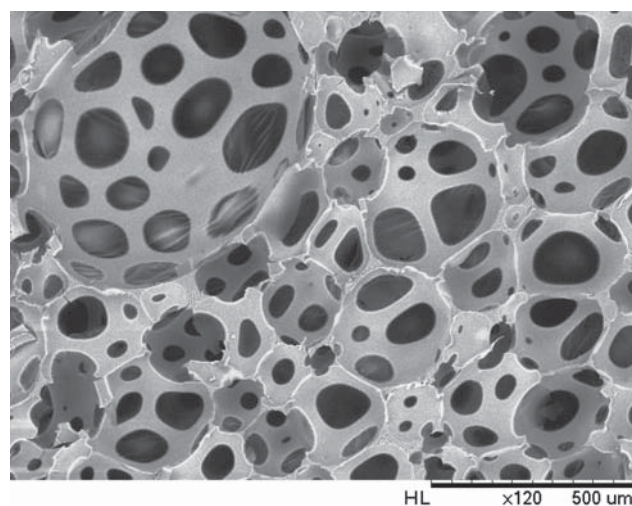

Figure 1 Scanning electron microscope image of alkaline-cured tannin foam prepared and hardened at 70°C.
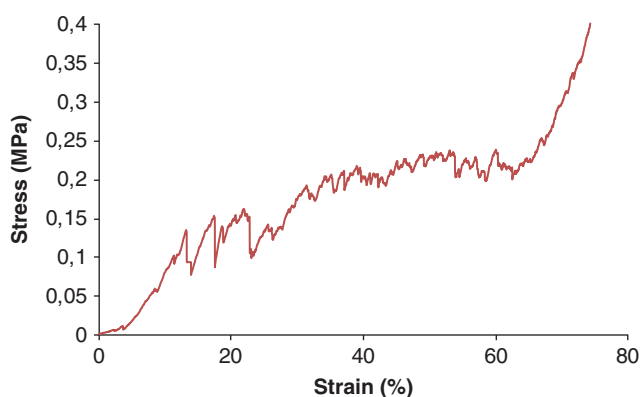

Figure 2 Stress vs strain diagram for compression of 70°C alkaline-cured tannin foam.

hydrolysis of cellulose and hemicelluloses ensues. This means that strongly acidic foams cannot be used as insulation in prolonged contact with wood panels or wood structures due to the weakening of the wood interface with the foam due to extensive hydrolysis of wood carbohydrate. The development of alkaline foams was then necessary for application to wood and wood products.

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