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Impact of the formulation of biosourced phenolic foams on their fire properties

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Abstract

The fire retardance properties of rigid, biosourced phenolic foams derived from tannins, which are novel, environment-friendly thermal insulators, are essential before the latter can be applied to the building sector. In this work, tannin-based foams prepared from new formulations and using different foaming methods were investigated by thermo-gravimetric analysis (TGA), cone calorimetry, and pyrolysis combustion flow calorimeter (PCFC). It was found that the flammability strongly depends on the formulation, so that tannin foams perform very differently depending on the presence of surfactant and plasticiser and, more importantly, on their initial water content. Moreover, a good correlation was observed between TGA and PCFC results. Nevertheless, due to their highly resistant phenolic, crosslinked, polymer network, all materials released a quite low amount of hydrocarbon fuel during thermal decomposition, leading to low heat release rates and high ignition times, and thus providing very good fire retardance properties. Based on the above, the foam presenting the highest fire retardance was identified, confirming our conclusions about the role of the ingredients in the formulation.

Keywords: Tannin; Rigid foams; Flammability; Heat release rate; Pyrolysis combustion flow calorimeter

1. Introduction

The massive use of polymers in our everyday life is driven by their remarkable combination of properties, especially low density, specific mechanical resistance, and ease of processing. It is therefore not surprising that fire retardance and related properties such as emission of smoke or dripping of inflamed particles became very critical parameters to be considered in applications such as transportation, packaging or thermal and acoustic insulation, amongst others. Consequently, improving the fire retardant behaviour of those materials is a major challenge for extending their use to other applications.

Some of the most used commercial products for thermal and acoustic insulation are polyurethane or polystyrene foams. However, the latter are well-known for their relatively high flammability, most often accompanied by the production of heavy smoke, and suspected to release toxic gases during combustion [1,2]. Poor fire resistances and high flammability are also generally characteristic of natural and biodegradable products [3]. However, the fire properties of the first formulation of bio-based foams derived from tannin, here referred to as “standard” tannin foams, were studied some years ago [4], and those materials proved to present excellent fire retardance.

Tannins are secondary metabolites of most plants. Especially, trees such as Acacia (*Acacia mearnsii*) and Quebracho (*Shinopsis sp*) present a high content of such condensed (flavonoid) tannins. The latter are non-toxic, natural, phenolic molecules, presently available at the industrial scale for various applications including leatherwork, chemical and food industries, etc. They have the advantage of being reactive, leading to high-quality thermoset resins, from which adhesives, gels or foams, for instance, can be prepared with an excellent reproducibility, a rare quality for a natural raw material [5,6].

Our initial results thus turned tannin foams into very interesting materials since, in addition to their renewable, cost-effective, and environment-friendly properties, they exhibit much better fire retardance than most commercial materials for thermal insulation. Although tannin foams seem to have very attractive properties, they need to be investigated more in-depth from the point of view of fire properties, because almost no additional research has been carried out on this topic after the work on “standard tannin-based foams” [4] was published. Only a few more tests with similar results were indeed carried out with formaldehyde-free tannin foams [7]. However, many other formulations with new ingredients and / or new foaming methods have been developed recently, which might induce some changes in their fire properties.

Moreover, the flammability of a material is not a straightforwardly determined property. Inflammation can be due to thermal energy from an external heat source (radiation, convection or conduction), to a chemical process occurring inside the material (fermentation, oxidation, etc.) or to the exothermicity of the initiation of a combustion reaction [8]. The amount of energy required to initiate combustion generally depends on the physical and chemical characteristics of the material. Thus, the exhaustive study of the most relevant parameters influencing the fire retardance behaviour of tannin-based foams is of paramount importance for being able to control and to improve their properties.

The flammability of foams, i.e., their ability to burn or to ignite, causing fire or combustion, can be defined by the different parameters explained hereafter. The single most important variable in the definition of fire growth is the Heat Release Rate (HRR), i.e., the amount of heat generated by the burning material, expressed by unit of area and by unit of time. The HRR tends to occur in a positive-feedback way: heat makes more heat [9]. It controls the growth of a fire and, therefore, the production of undesirable effects of fire such as toxic gases, smoke and other types of fire hazards. Since the probability of such effects increases with the HRR, the latter represents the best variable to assess the hazard of a fire.

The ignition time is also one of the most important variables in the characterisation of the flammability of a material. It is defined as the time at which a continuous flame is supported on the material surface [10]. Thus, it is always recommended to control ignition sources and to use materials poorly prone to ignition, whenever possible. Indeed, neither HRR nor any other consequences of fire will come into play as long as there is no ignition.

On the other hand, the peak HRR and the total amount of released heat, as well as the composition of the gas phase, are interesting parameters that are worth investigating too. The peak HRR occurs over a very short period of time and often shortly after ignition, and is usually a good indicator of the maximum flammability of a material. The average HR is the total heat released averaged over the combustion period, and is considered as the most reliable measurement of the heat contribution to a sustained fire. Finally, as already mentioned above, it is also very important to evaluate the toxicity of the gases released during combustion, as gases cause the greatest health hazard [10].

The present work, dealing with fire reaction of original formulations of tannin-based foams, has been carried out by combining the aforementioned measurement techniques. First, the flammability of the main types of tannin-based foams has been studied and compared with that of other materials that are currently on the market of thermal insulation. Then, the influence of the formulation on the fire properties of the foams has been analysed. For that purpose, foams with some modifications either in their composition or in the foaming procedure have been studied in order to observe the corresponding effects on their flammability. Especially, it is the first time that the effects of surfactant, plasticiser, and water on the fire properties of biosourced materials for thermal insulation are investigated simultaneously, sorted out, and explained. Finally, for completing the study, thermo-oxidative and pyrolytic decomposition of two foams prepared by completely different ways was carried out, and the degradation products of these foams have been analysed and identified. Crossing the results from the various, aforementioned techniques, thereby allowed robust conclusions about the role of the ingredients on the fire properties of these new materials.

2. Experimental

2.1. Materials

Raw mimosa bark extract and two raw quebracho extracts, known as FINTAN OP®, FINTAN T® and FINTAN Q® on the market, respectively, and kindly supplied by the company Silva Team (San Michele Mondovi, Italy), were used as the main components to prepare the foams. The second most important ingredient was furfuryl alcohol, purchased from Sigma Aldrich. Other additives, depending on the formulations, were: polyethylene glycol (PEG) with molecular weight 400, supplied by Sigma Aldrich, various non-ionic surfactants also supplied by Sigma Aldrich with commercial names Tween 80®, Pluronic PE 7400®, Triton X-100® and Cremophor ELP®, and a foaming agent mainly composed of alkyl glycols and modified fatty acid soaps, SM2101-1, supplied by Condat (Chasse-sur-Rhone, France). Hexamethylenetetramine (hexamine), supplied by Merck, and formaldehyde (37 wt.% in water, stabilised by 10–15 wt.% of methanol), supplied by Roth, were used as crosslinkers, and 65% water solutions of either para-toluenesulphonic acid (pTSA) or phenolsulphonic acid, supplied by Merck and Capital Resin Corporation (Columbus, OH, USA), respectively, were used as catalysts. Finally, diethyl ether supplied by Sigma Aldrich was the blowing agent employed in the self-blowing formulations. All compounds were used as such, without further purification, and dissolved in lab-made bi-distilled water whenever required.

2.2. Foams preparation

Eleven different tannin-based foams were prepared and analysed in the present study. They are a representative selection of most of the types of tannin-based foams that presently exist. They were carefully selected in order to be able to analyse the effect of the contents of surfactant, plasticiser, furfuryl alcohol and crosslinker, as well as the effect of the way of foaming, temperature of curing, and type of tannin (mimosa, quebracho Fintan T$^{®}$ or quebracho Fintan Q$^{®}$), on the fire properties of the foams. Therefore, foams with very different compositions and features were developed, see Fig. 1.

Fig. 1. General view of all tannin-based foam samples studied in this work.

“Standard” tannin foams were prepared using two different kinds of tannin, mimosa (sample called STD-M), and quebracho Fintan T$^{®}$ (sample STD-Q), following the specific methodology described elsewhere [11]. In brief, a homogeneous blend of tannin (base of the resin), furfuryl alcohol (hardener and co-monomer), water (solvent), formaldehyde (crosslinker) and diethyl ether (blowing agent) presents a self-foaming behaviour as soon as an acid catalyst is poured and mixed with it. The acid-catalysed exothermic autocondensation of furfuryl alcohol and the polycondensation of tannin with furfuryl alcohol indeed induce a substantial increase of temperature, leading to the boiling of the foaming agent and hence to the expansion of the material. At the same time, hardening occurs, thus stabilising the as-obtained foam. Self-condensation of tannin and crosslinking of tannin with formaldehyde present in the formulation also contribute to stabilisation and curing. Such standard preparation with mimosa was also slightly modified by adding a plasticiser (sample PEG-M), as well as different kinds of surfactant (samples Pluro-M and Triton-M), to the initial tannin-based blend; those formulations were adapted from a recent work [12]. The details about the corresponding polymer chemistry have been given elsewhere [13 and refs. therein].

On the other hand, standard-like, formaldehyde-free tannin foams were also prepared from two kinds of tannin, mimosa (sample called SF-M) and quebracho Fintan T (sample SF-Q), according to the method detailed elsewhere [14]. Briefly, the absence of formaldehyde in those formulations was made possible by a corresponding increase of the amount of furfuryl alcohol. As a consequence, and in order to control the very exothermic polymerisation, the related amount of (acid) catalyst was decreased. Some formaldehyde-free foams containing a little amount of surfactant for improving the foaming process and containing various proportions of furfuryl alcohol were also developed (samples P21-Q and P24-Q).

Finally, other foams were also produced by using different methods of foaming and curing. Firstly, a “meringue” foam (sample called Meringue-M) was prepared by polymerisation at 85ºC of a stable liquid foam obtained by mechanical whipping of a liquid formulation containing surfactants, according to a method detailed elsewhere [15]. Herein, neither blowing agent was present nor self-foaming occurred: the cells of the foams were only produced by air incorporated into the viscous resin by frothing. Due to the absence of furfuryl alcohol, hardening in an oven was necessary. The corresponding polymer chemistry was detailed in the latter paper as well as in older ones [13,16,17]. Secondly, a new method based on the mechanical foaming of a formulation implying auto-polymerisation of tannin with furfuryl alcohol on the one hand, and self-condensation of furfuryl alcohol on the other hand [18], was also used (sample NM-Q’). Thus, this method is based as before on frothing of a liquid formulation, but the latter contained acid and furfuryl alcohol so that, even if no chemical foaming occurred, crosslinking took place at room temperature. More details about the chemistry of this system can be found in [19].

The detailed compositions of the foams prepared for carrying out this study are gathered in Table 1. All those materials present a cellular, open, porosity, whose morphology was thoroughly described and analysed in former papers from the authors in terms of cell size, connectivity, total pore volume, etc. These results include photographs and studies of electron microscopy, mercury porosimetry, micro-computed tomography, and even a technique of diffusion of light, see [15,20–22].

Table 1. Formulation of the different types of foams.

	Chemical foaming + auto-polymerisation									**Mechanical foaming + reaction at 85°C**	**Mechanical foaming + auto-polymerisation**
	Mimosa					**Quebracho Fintan T**				**Mimosa**	**Quebracho Fintan Q**
	STD-M	**PEG-M**	**Triton-M**	**Pluro-M**	**SF-M**	**STD-Q**	**SF-Q**	**P21-Q**	**P24-Q**	**Meringue-M**	**NM-Q’**
Tannin (g)	30	30	30	30	30	30	30	30	30	30	30
Furfuryl alcohol (g)	10.5	10.5	10.5	10.5	21	10.5	21	21	24	-	24
Water (g)	6	6	6	6	6	6	6	6	6	45	40
Formaldehyde (37% in water) (g)	7.4	7.4	7.4	7.4	-	7.4	-	-	-	-	-
Plasticiser (g)	-	8	8	8	-	-	-	-	-	-	2.2
Diethyl ether (g)	6	6	6	5	3	3	3	3	3	-	-
Surfactant (g)	-	-	0.6[A]	0.6[B]	-	-	-	3[C]	3[C]	4.5[D]	9.56[E]
pTSA (65% in water) (g)	11	11	11	11	11	11	11	11	11	1.68*	-
Hexamine (g)	-	-	-	-	-	-	-	-	-	2.18	-
Phenolsulphonic acid (65% in water) (g)	-	-	-	-	-	-	-	-	-	-	26.5
Bulk density (g·cm^{-3})	**0.039**	**0.055**	**0.057**	**0.044**	**0.028**	**0.060**	**0.038**	**0.065**	**0.048**	**0.065**	**0.081**

Surfactant: [A] Triton X-100; [B] Pluronic PE 7400; [C] Cremophor ELP; [D] Tween80; [E] Cremophor ELP (4 g) + Foaming agent SM2101-l (5.56 g)

Plasticiser: PEG 400, i.e., polyethylene glycol with molecular weight 400 g mol^{-1}

Catalyst: para-toluenesulphonic acid (pTSA). * solid pTSA, i.e., not in solution

2.3. Foams properties

The main fire parameters: flammability, ignition time, peak HRR and total amount of released heat, were measured for the tannin-based foams by three complementary flammability testing techniques: mass loss cone calorimetry (MLC), pyrolysis combustion flow calorimetry (PCFC), whereas the analysis of the gas phase was carried out by thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy (TGA-FTIR). At this point of the paper, it is very important to stress that our former studies clearly showed that fire properties of tannin-based foams are independent of porosity and cell sizes: only the nature of the material has an impact, and no significant differences were indeed observed for foams having bulk densities varying by a factor of 4 [4]. In the present materials, the cell morphology was quite homogeneous within a set of samples (see again Fig. 1), the cell size was in a narrower range than in our former study [4], and the bulk density was only different by a factor 2 between two extreme formulations (see again Table 1).

2.3.1. Mass Loss Cone Calorimetry (MLC)

An FTT Mass Loss Cone Calorimeter (referred to MLC below, from Fire Testing Technology Ltd, UK) was used to carry out measurements on samples following the procedure defined in the ASTM E-906 standard. The equipment operated in this study was identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90). However, unlike in the latter standard, a thermopile in the chimney was used to obtain the heat release rate (HRR) rather than employing the oxygen consumption principle. Each foam of dimensions 100 × 100 × 20 mm was horizontally installed in a sample holder, itself placed on a load cell for measuring the weight loss during the experiment. For that purpose, the samples were wrapped in aluminium foil but leaving the upper surface exposed to the heater, and placed on a ceramic backing board at a distance of

25 mm from the cone base. A conical radiant electrical heater uniformly irradiated the sample from above with a heat flux of 50 kW·m^{-2}, representing a flashover situation of fire. The combustion was triggered by an electric spark. The combustion gases that were produced passed through the heating cone and were captured by means of an exhaust duct system. Fig. S1 of the Electronic Supplementary Information illustrates in detail the experimental set-up of the MLC.

The quantity of heat released per unit of time and surface area, the HRR (kW·m^{-2}), was therefore measured. Besides, the time to ignition and the fire growth rate (FIGRA) index were calculated too. The latter is defined as the maximum value of HRR divided by elapsed time, and is a good estimation of the spread (rate) and the size of a fire. All those parameters enable to qualitatively establish the capability of a fuel to spread a flame. The data were computed using a software developed at UMET laboratory. The experiments were repeated 3 times, and the results presented in the following are averages.

2.3.2. Pyrolysis combustion flow calorimetry (PCFC)

The combustibility of the gas phase was evaluated with a pyrolysis combustion flow calorimeter (PCFC) developed by Lyon [23]. The tests were performed according to the ASTM D-7309-07 standard which mimics the burning of a polymer in a normal fire situation. The PCFC device used in this work was supplied by Fire Testing Technology Ltd (UK), and is schematically represented in Fig. S2 of the Electronic Supplementary Information. The samples, typically weighing from 10 to 20 mg, were heated under nitrogen flow at a constant rate of 1ºC·s^{-1} up to 750ºC. The gases generated during such heating were forwarded to a tube furnace by the flow of nitrogen, used as carrier, where a total combustion of those gases took place. The combustor temperature was fixed at 900ºC, and the inlet of oxygen/nitrogen flow was 20/80 cm^{3}·min^{-1}. Combustion products that exited the combustor were removed by the scrubbers, and the nitrogen and the residual oxygen passed through the flowmeter and the oxygen analyser. The deconvolution of the oxygen consumption signal was performed numerically during the test, and the various parameters (see below) were calculated.

The main parameters obtained from the PCFC that are associated with flammability and hazard in case of fire have been calculated for all tannin foams. The specific heat release rate HRR ($W \cdot g^{-1}$) at a given sample heating rate ($K \cdot s^{-1}$) was calculated from oxygen consumption. Furthermore, the heat release capacity HRC ($J \cdot g^{-1} \cdot K^{-1}$) corresponds to the peak of heat release rate (pHRR) measured in PCFC divided by the heating rate [23]. This value does not depend on the heating rate, and is an intrinsic characteristic of the material.

Interesting parameters were extracted from these measurements: maximum (peak) specific heat release rate (pHRR, $W \cdot g^{-1}$) at a given heating rate, heat release capacity (HRC, $J \cdot g^{-1} \cdot K^{-1}$), total amount of heat release (HR, $kJ \cdot g^{-1}$) and temperature at maximum pyrolysis rate (T_{max}, ºC). Each sample was tested in duplicate, and the reproducibility of the data in PCFC was very high, since less than 2% of deviation between two analyses (for both pHRR and HRC) was obtained.

2.3.3. Thermogravimetric analysis coupled with Fourier-Transform Infrared Spectroscopy (TGA-FTIR)

The weight loss characteristics and the composition of the corresponding released gas were investigated for two different tannin foams formulations by Thermogravimetric Analysis (TGA) coupled with Fourier-Transform Infrared Spectrometry (FTIR), using a TA Instrument (USA) TGA Q5000IR and a ThermoFisher Scientific (USA) Nicolet iS10 spectrometer. The temperature was increased from 30ºC to 800ºC at a heating rate of $10ºC \cdot min^{-1}$ after a preliminary stabilisation of 30 min at 30ºC. The experiments were carried out either under air or under nitrogen flow. Gases evolved during the TGA experiments were detected continuously by the FTIR device (only under air flow). The spectra were recorded every 10 seconds with the OMNIC® software in a spectral range of 4000-650 cm^{-1} with a 4 cm^{-1} resolution. The temperature of the transfer line between the TGA and the FTIR instrument was set to 225ºC to avoid condensation of the evolved gases.

3. Results and discussion

3.1. MLC studies

Meringue-type tannin foams were characterised according to the ISO5660 standard, using the cone calorimetry technique. With the latter, ignition delay times, HRR, FIGRA index and critical heat flux for ignition could be determined. The study of the flammability of meringue tannin foams is very important, not only because it is one of the most recent formulations and foaming methods developed so far, but it is also very different from the other tannin-based foams. The meringue formulations indeed contrast with the other ones by several aspects such as the absence of furfuryl alcohol, the presence of surfactant, the large amount of water, a different crosslinker, and a different heat source for polymerisation (see again Table 1). All those modifications were expected to have a strong influence on the fire properties of this kind of material.

The evolution of HRR of the meringue foams (Meringue-M) submitted to a radiant heat flux of 50 $\text{kW}\cdot\text{m}^{-2}$ is presented in Fig. 2 as a function of time. The flammability of standard tannin foams (type STD-M) and formaldehyde-free foams (type SF-M) was also measured in the same conditions as reported elsewhere ([4] and [7], respectively): those results are also shown in Fig. 2 for comparison. Discussing former results obtained with standard formulations is important here since, in addition to providing valuable insight of tannin foams, it also allows comparing with the data of materials obtained here with a different preparation method: meringue foams.

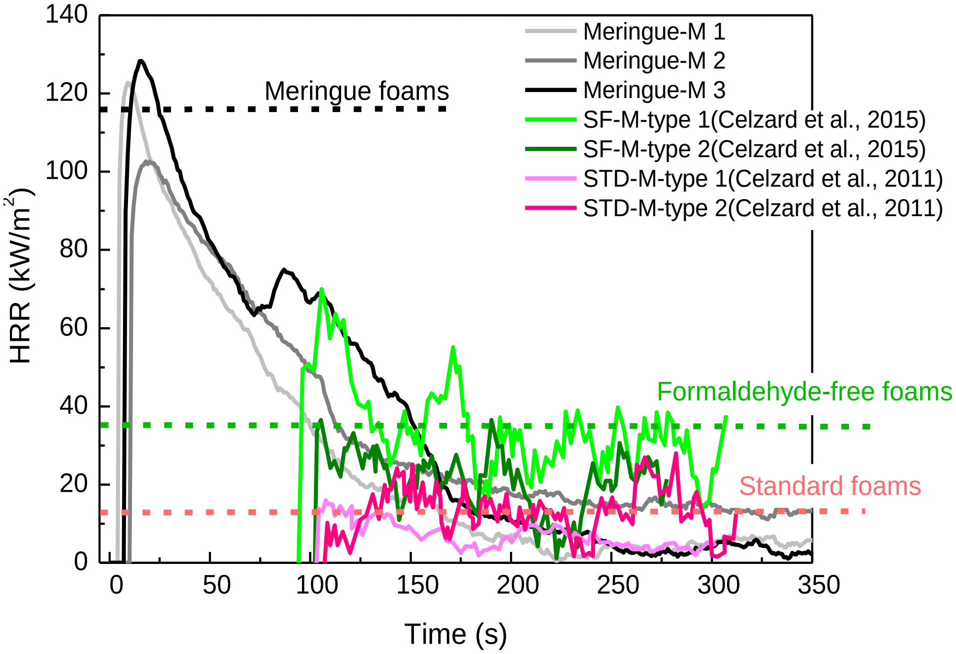


Fig. 2. HRR of tannin-based foams submitted to a radiant heat flux of 50 kW·m^{-2}.

In a former work [4], standard foams with different densities were tested under different external heat fluxes (35, 50 and 60 kW·m^{-2}). The peak heat release rates (pHRR) of those foams under a heat flux of 50 kW·m^{-2} were not higher than 12 kW·m^{-2}, on average, and the time to ignition was around 100 s (see again Fig. 2), which led to the conclusion that such foams present outstanding fire retardance. Furthermore, the tests under different external heat fluxes (not shown here) proved that the peak HRR always remained the same, suggesting that the gases released and the contribution of the material to the fire were similar regardless to the external heat flux, i.e., to the different fire scenarios. This is a sign of robustness of the materials' performances. Finally, it was also shown that their flammability was not altered by the density of the foam, despite highly porous, lightweight, foams might have *a priori* appeared to have a faster flame propagation rate and a higher thermal degradation as observed for PU foams, for instance [2]. On the other hand, the pHRRs of formaldehyde-free foams under a heat flux of 50 kW·m^{-2}, analysed in [7], were around 35 kW·m^{-2}, and the average time to ignition was 90 s. Thus, the fire retardance was slightly lower than that of standard tannin foams but still remained excellent (see again Fig. 2).

Herein, meringue-M foams were analysed by cone calorimetry in the same conditions as for the aforementioned tannin-based foams. They presented one order of magnitude higher pHRR, 120 kW·m^{-2}, and their ignition time was ten times shorter, 9 s, than the standard tannin foams (Fig. 2). These foams showed a very high initial peak at around 20 s, and then the HRR dropped down to a value rather similar to that found for other tannin foams previously studied (Fig. 2). That initial peak corresponds to the important flame that is observed in the photos taken during the cone calorimetry test (Fig. 3). After 100 s, and without additional application of heat, the flame disappeared completely, and the HRR decreased to a value as low as about 2 kW·m^{-2}.

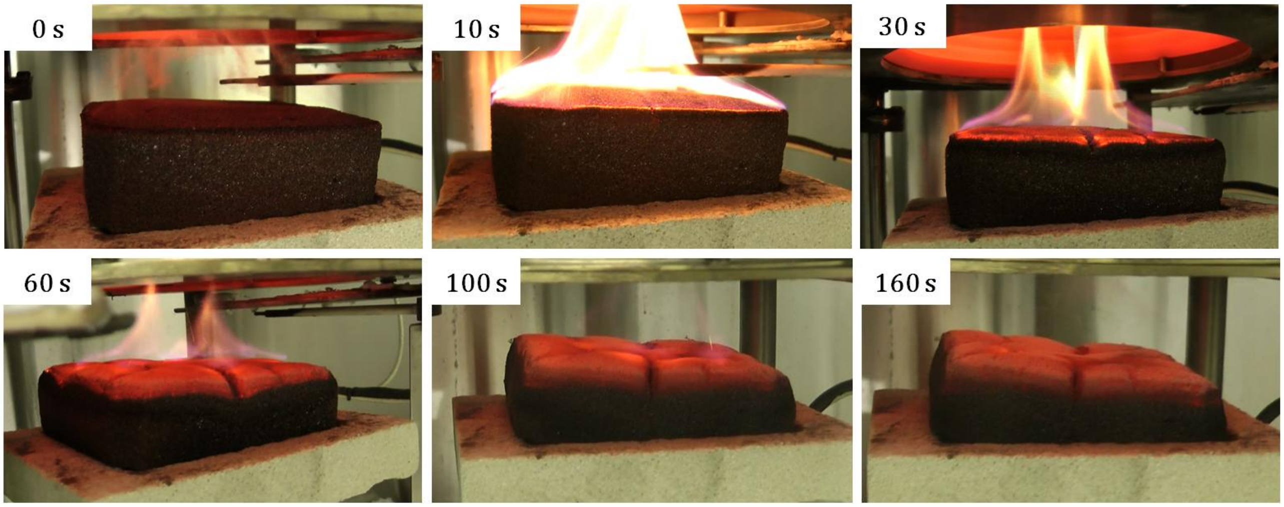


Fig. 3. Meringue-M foam during cone calorimetry test as a function of time.

Such large initial HRR values for meringue foams might be due to the presence of surfactant that can be released and cause flames, hardly seen with the standard and formaldehyde-free formulations, which are surfactant-free. They might also be due to the large amount of water contained in these formulations causing, when released, the fragmentation of the materials and hence a dramatic decrease of their fire properties (see next subsection). A similar effect with these two parameters, surfactant and water content, was also observed elsewhere for polyurethane foams [24]. The surfactant content had a negative impact, decreasing all fire properties of the polyurethane foams, and an increase of water proportion produced an increase in the intensity of the first peak of HRR and in the production of smoke. The latter effect was also seen with meringue foams at the beginning of the test. Those points will be deeply analysed and developed further in the next section, supported by the results from PCFC.

One may also assume that the reason of the decrease of fire retardance of the meringue foam could be due to the weaker polymer network formed with hexamine as crosslinker, compared to that formed by polymerisation of furfuryl alcohol and tannin. However, such possibility is not that obvious. In fact, in the two previous studies about fire properties of tannin foams [4,7], it was observed that eliminating the formaldehyde weakened the polymer structure and slightly lessened the fire properties, but the induction time was not significantly changed. Thus, if only the polymer structure was involved, the decrease of fire retardance would be affected in all its different aspects, which was not the case here.

In general, the critical heat flux for ignition of all tannin foams was quite high since no ignition was detected under a heat flux of 25 $kW \cdot m^{-2}$ in any of the foams tested, including meringue foams whose ignition time was not very high. Materials with such ignition characteristics are normally expected to propagate a flame very slowly or to self-extinguish unless a very strong external heat flux is applied [25]. Most polymers and natural materials, with the exception of those being highly retardant, exhibit a critical heat flux which is much lower than that of tannin-based foams [26–28]. The huge amount of radiant heat that is required for maintaining the combustion with respect to the resultant HRR explains the marked self-extinguishing character of tannin foams.

Maximum heat released rate (pHRR), ignition time and FIGRA index of tannin foams are gathered in Table 2, together with those of other interesting materials having the same potential applications. The aim here was to compare and to rank tannin-based foams within the thermal insulation market as a function of their fire properties. The materials selected for the comparison are phenolic foams, which present a polymeric structure rather similar to that of tannin foams, epoxy foams, polyurethane and expanded polystyrene foams, which are their main competitors on the market, and some natural and organic materials for thermal insulation.

Table 2. Fire parameters of tannin foams and other thermal insulation materials obtained by cone calorimetry under heat flux of 50 kW·m^{-2} unless otherwise stated.

	pHRR (kW·m^{-2})	Ignition time (s)	FIGRA (W·s^{-1})
Standard foam (STD-M-type) [4]	12	100	1.2
Formaldehyde-free foam (SF-M-type) **[7]**	35	95	3.2
Meringue foam (Meringue-M)	117	9	130
Pure epoxy foam [29]	314	2	1570
Pure phenolic foam [29]	106	6	177
Polyurethane foam [30]	550	4	1375
Expanded polystyrene foam [25]	256	9	284
Insulating non-woven hemp fibres [27]	284	3	710
Insulating agro-materials from flax short fibres (35 kW·m^{-2}) [31]	126	11	115

The results gathered in Table 2 show that tannin foams are the materials definitely presenting the highest ignition times and the lowest heat release rates of this list of materials. As expected, phenolic foams have similar properties to tannin foams, and especially to meringue foams. The insulating agro-materials seem to have similar properties but the corresponding tests, described in the literature from which the results were taken, were performed at lower heat flow (see the relevant line in Table 2). In contrast, epoxy and polyurethane foams ignite instantly and also release a high amount of heat. Thus, tannin-based rigid foams have, in general, better fire retardance properties than other cellular materials of similar density and applications. Very difficult ignition and very low heat release rate are the main features of those materials.

3.2. Pyrolysis combustion flow calorimetry (PCFC) studies

Eleven tannin-based foams were tested with the PCFC device, used to evaluate their flammability characteristics. It is indeed a useful instrument to examine the combustibility of the gases released during the decomposition of the material, and it offers a valuable insight into the effect that some components of its formulation may have on the flammability.

At 1 $K \cdot s^{-1}$, the HRC is equal to the pHRR in the case of a single-step decomposition as in the case of Meringue-M foam (Fig. 4(a) and Table 3). In the case of a multistep decomposition, Lyon et al. [32] proposed to use the sum of the HRC of each peak after deconvolution [33,34]. On the other hand, the total heat release (Total HR, $kJ \cdot g^{-1}$) is the specific heat release rate HRR integrated over the entire duration of the experiment. The heat release temperature (T_{max}, ºC) is the sample temperature at pHRR. All those parameters obtained for the 11 tannin-based foams, and averaged over two samples of each type, are gathered in Table 3.

Table 3. PCFC results for tannin-based foams.

	HRC ($J \cdot g^{-1} \cdot K^{-1}$)	Peak HRR ($W \cdot g^{-1}$)	Total HR ($kJ \cdot g^{-1}$)	T_{max} (ºC)
STD-M	20.152	14.552	2.286	378.2
PEG-M	34.479	18.077	3.498	257.5
Triton-M	41.655	23.613	4.057	260.8
Pluro-M	40.272	22.138	4.148	255.9
SF-M	23.433	14.171	2.961	365.5
STD-Q	19.607	12.807	2.192	375.2
SF-Q	19.753	12.541	2.266	376.1
P21-Q	27.313	18.125	4.309	415.9
P24-Q	26.985	18.233	4.280	425.4
Meringue-M	51.178	49.578	6.001	376.4
NM-Q’	46.568	24.245	5.516	412.1

The dynamic flammability data derived from PCFC of all the foams are shown in Fig. 4(a), where the heat release rate (HRR) is presented as a function of temperature. The different shapes of the curves of HRR allowed roughly separating the foams into four main groups (see Fig. 4(b)), depending on their thermal degradation process, i.e., depending on the absolute amount of heat released and on the number of steps in their degradation. Three groups correspond, as expected, to the three existing types of foaming: (i) chemical foaming + auto-polymerisation; (ii) mechanical foaming + polymerisation at 85ºC; and (iii) mechanical foaming + auto-polymerisation. A last additional group could also be defined for a special situation where the foams contained additives such as plasticiser and/or surfactant.

In general, the initial peak for those foams whose decomposition is divided in two steps is due to the presence of plasticiser and surfactants in the formulation, and the second peak, or the single one in the case of single-step degradation, is due to the decomposition of the polymeric structure of the foam. Such assignment is consistent since most polymers and organic materials such as lignin, cellulose, etc. degrade between 350-450ºC [35–37]. Moreover, the plasticiser and the surfactants are thermally unstable and usually decompose above around ∼180ºC, having an detrimental effect on the fire retardance of the materials containing them [26]. Fig. 4(b) shows the attribution of those peaks.

The peak centred on around 400ºC is indeed the main difference between foams obtained from different foaming methods. Such peak, related to polymeric structure, is the highest for the foams made by mechanical foaming + polymerisation at 85ºC (Meringue-M), followed by foams made by mechanical foaming + auto-polymerisation (NM-Q') and, finally, is the lowest for foams made by chemical foaming + auto-polymerisation (STD-type). This order was also observed in the heat release capacity of the foams (Table 3).

The amount of water present in the formulation (see again Table 1) follows exactly the same trend of the heat released, i.e., the higher the amount of water, the higher the heat release capacity. This finding leads to the conclusion that a higher percentage of water in the initial formulation of the foams might lead to a polymeric structure that is much easier to degrade. Some authors have already reported similar behaviour on the failure of their materials submitted to fire [24,38]. Especially interesting is the work carried out by Feih et al. [38] in which phenolic composites under fire evidenced a high influence of their water content. It was proved that the vaporisation of water within the phenolic matrix caused explosive delamination and cracking of the thermoset polymer network, increasing the degradation of the material. This is probably what occurs in some tannin foams during fire tests, for which the high water content in the polyphenolic structure results in high internal pressures generated by vaporisation that favours the degradation of the foams. This effect increases with the amount of water present in the foams, in agreement with the results of cone calorimetry showing that Meringue-M had lower fire retardance properties than STD-M.

Analysing Meringue-M more in-depth, it can be observed that this foam did not present an initial peak around 180ºC, despite having a significant amount of surfactant in its formulation. Two assumptions can account for this finding: (i) either the curing of the foam at 85ºC has already removed the surfactant, or (ii) the surfactant was incorporated into the polymer network, which made its release more difficult unlike what happens when polymerisation by self-generated heat takes place and when the surfactant is not part of the structure, and thus degrades easily. The first assumption might be due to the time spent at 85°C (24 h) in a ventilated oven for polymerising the foam; in such conditions, the vapour pressure of Tween80 should not be negligible, and a significant part of the surfactant can evaporate from the surface of the cells. The second assumption is related to the embedding of the surfactant within the thermoset polymer network but also to a possible reaction of the surfactant with tannin through its polyether chains. The corresponding mechanism was indeed recently evidenced by NMR and MALDI-ToF studies carried out with ethylene glycol, bearing the same kind of moieties, see [39]: ethylene glycol was proved to be grafted on tannin in the presence of para-toluenesulphonic acid at 85°C. These conditions are thus extremely similar to those encountered here, so that the same reaction is expected to occur. Anyway, these possibilities eliminate the surfactant as the cause of the worsening of fire properties of Meringue foams, and corroborate the explanation of the amount of water as the leading factor.

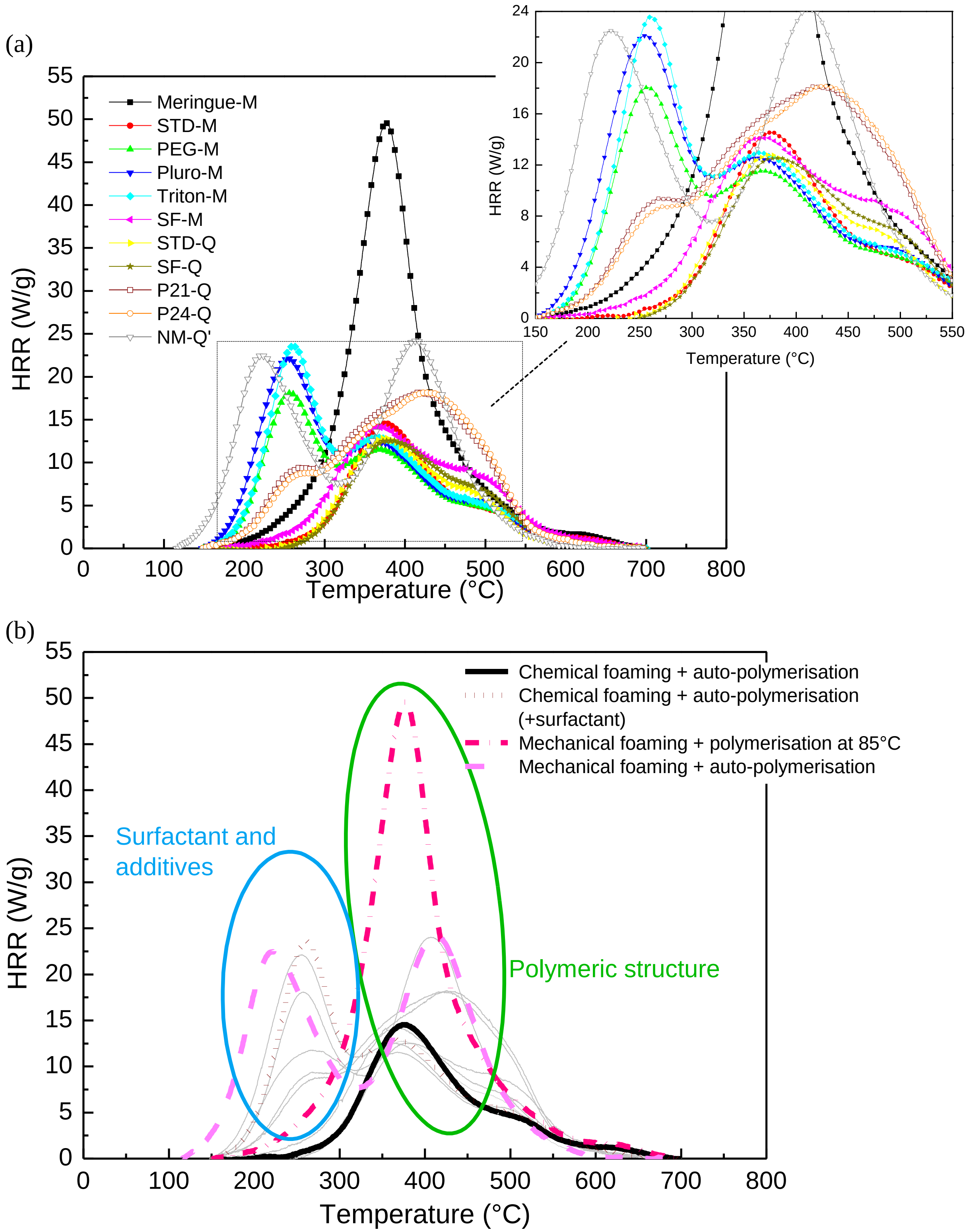


Fig. 4. Heat release rate curves measured by PCFC at 1 K·s^{-1} for several tannin-based foams: (a) investigated foams; (b) corresponding, major kinds of thermal degradation process and assignment of the degradation peaks.

As for NM-Q’, obtained by mechanical foaming + auto-polymerisation, this material also showed a totally consistent behaviour with what was described above. It indeed exhibited two peaks, an initial one due to the high amount of surfactant and foaming agent used in its preparation, and a second one related to the degradation of the polymeric structure. The second HRR peak was in-between those of STD and Meringue foams, since the initial water content was also in-between. It may be objected here that this foam was prepared with a different source of tannin, which might influence in some way the HRR. However, it should not have any impact here since it will be demonstrated below that the effect of the nature of the tannin on the fire properties of the resultant foams is not very significant.

Tannin-based foams analysed by PCFC were prepared conscientiously in order to be able to detect the effect of some parameters such as: presence of surfactant and plasticiser, amount of furfuryl alcohol, type of tannin, etc., on their fire properties. Thus, tannin foams with exactly the same formulation but differing by the type of tannin, mimosa or quebracho, were analysed (see Fig. 5). The results show that the foams based on quebracho tannin present a slightly lower heat release capacity (Table 3) and, therefore, quebracho slightly improves the behaviour of the corresponding foams under fire. However, in general, the foams showed very similar flammability which is really interesting from the manufacturing point of view, as it means that foams can be prepared from a considerably more available resource, the supply of mimosa tannin being limited. Fig. 5 also shows the effect of the elimination of formaldehyde from the formulation of “standard” formulations. Upon eliminating the formaldehyde (SF formulations), the total heat release and the heat release capacity of the foams slightly increased, more remarkably for materials based on mimosa tannin than for those based on quebracho (Table 3). Such increase is consistent with the one found from cone calorimetry results and, as pointed out in the previous subsection, it is probably due to the weaker polymer network that formed in the absence of formaldehyde.

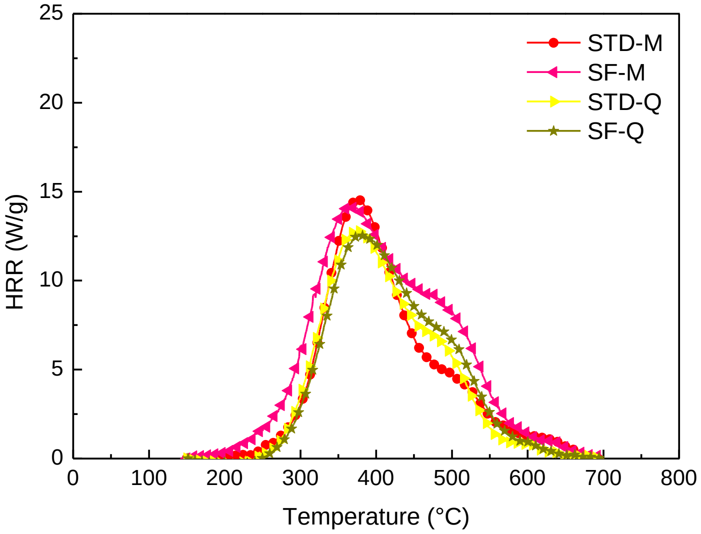


Fig. 5. Effect of the type of tannin and of the elimination of formaldehyde on the flammability of tannin foams.

On the other hand, the effect of plasticiser on the flammability of the foams was studied by adding a little amount of plasticiser in the formulation of STD-M foam, everything else being constant. After that, the same procedure as before for analysing the effect of surfactant was carried out. Thus, it is shown in Fig. 6 that all the additives in the STD formulation altered significantly the thermal decomposition profile of the foam. Indeed, pristine STD foam primarily decomposed in one single step, but PEG-M, Pluro-M and Triton-M presented a multi-steps decomposition process. As seen in Fig. 6, the incorporation of PEG to the formulation led to an earlier decomposition of the foam. It indeed produced a high initial degradation peak at 250ºC due to the degradation and volatilisation of the plasticiser which was not present in STD-M. Such effect considerably increased with the additional incorporation of surfactant. Those components increased the HRC of the Standard foam from 20 to 34 $J \cdot g^{-1} \cdot K^{-1}$ with the addition of PEG and up to 40 J·g^{-1}·K^{-1} with the addition of PEG plus surfactant. In the latter case, the flammability of the foam with surfactant was thus two times higher than that of the original formulation. A similar effect was observed for polyurethane foams wherein adding more surfactant decreased the fire properties [24].

The effect of the amount of furfuryl alcohol on the flammability of tannin foams was also analysed by testing two foams with different amounts of furfuryl alcohol: P21-Q and P24-Q. The results obtained were very similar (see Table 3), suggesting that increasing the proportion of furfuryl alcohol had a minor impact, or that the difference of furfuryl alcohol content in these two formulations was not significant enough to produce a clear change of fire properties. Those foams were also prepared with a little amount of surfactant which was revealed by a shoulder around 250ºC (see again Fig. 4(a)).

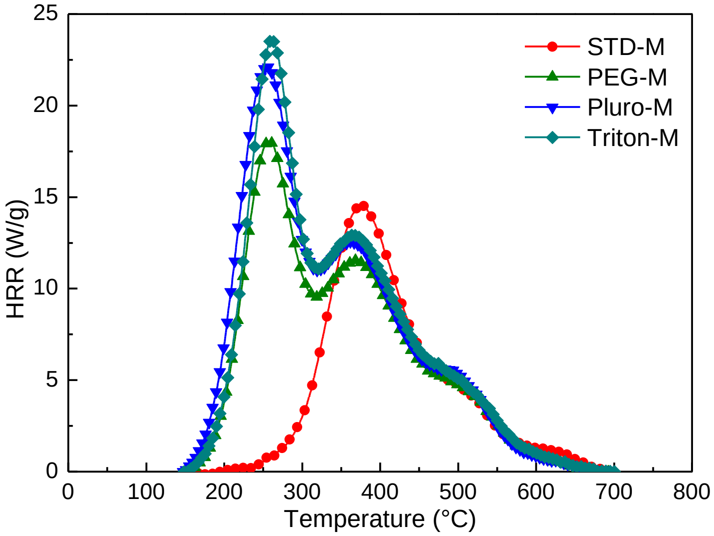


Fig. 6. Effect of the addition of plasticiser and surfactant on the flammability of tannin foams.

In summary, the flammability of tannin-based foams strongly depends on the chemicals used in their formulation. Most of the components and additives used for changing the features of the foams were found to have a non-negligible influence on the fire properties of the materials.

As a general remark, the results of PCFC do not entirely agree with those of MLC, due to different sample sizes (e.g. thermally thin vs. thermally thick behaviour of the sample) and test conditions. Moreover, unlike in the cone calorimeter experiments, the solid phase reactions and the gas phase combustion reactions are separated in PCFC. However, the PCFC tests complement very well the cone calorimetry experiments, and the results are consistent and follow the same trends [40]. Moreover, although it is a recent technique, some studies already applied this technique to insulation materials [40–42]. Some of the latter are of natural origin, such as rice husk + starch, barley straw + starch or barley straw + alginate with total HR of 6.5, 7.1 and 6.2 $kJ\cdot g^{-1}$, respectively, or are synthetic such as polystyrene and polyurethane foams with total HR of 38.7 and 13.5 $kJ\cdot g^{-1}$, respectively [42]. If the total HR of such insulation materials is compared to that of tannin foams (see again Table 3), then tannin foams definitely have superior fire properties. The same conclusion can be obtained from cone calorimetry.

3.3. Thermogravimetric analyses coupled with Fourier-Transform Infrared Spectroscopy (TGA-FTIR)

Thermo-oxidative and pyrolytic decomposition of two very different tannin-based foams, STD-M and Meringue-M were carried out, and the results are shown and compared in Fig. 7. According to those curves presented under two atmospheres, flowing air or nitrogen, two main phases of thermal decomposition can be identified, also typically observed for lignocellulosic materials such as natural fibres, lignin, etc. [31,37]. The first stage, until 350ºC, was independent of the atmosphere since it was the same in air and in nitrogen. On the other hand, the second stage of decomposition occurred only in air, in a temperature range of 350-550ºC, which indicates the predominance of oxidative decomposition. Thus, the point of fastest degradation was shifted to higher temperatures under oxidative conditions. The maxima of weight loss rate were reached for both samples at around 300ºC under pyrolytic conditions, and at around 450ºC under oxidative conditions.

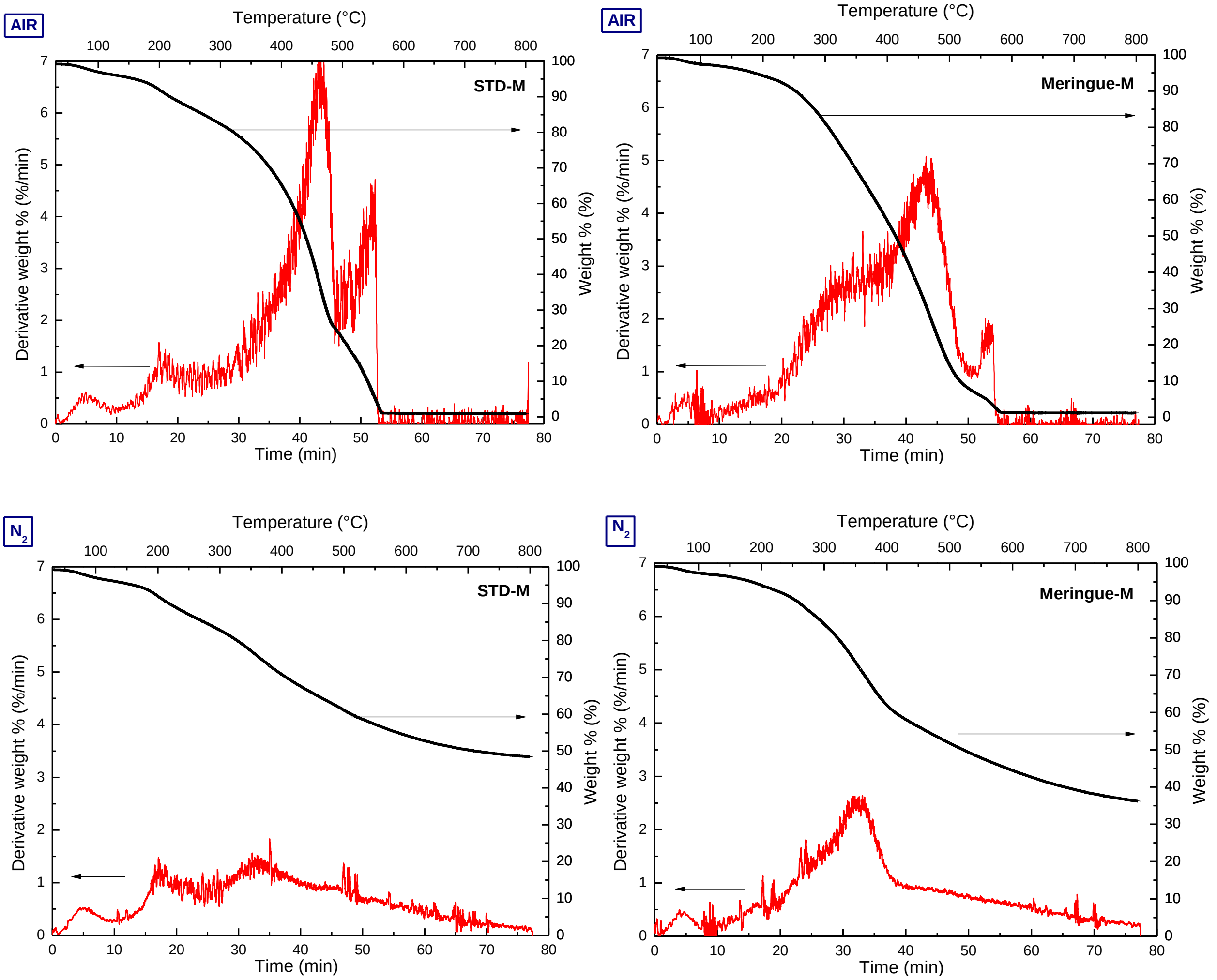


Fig. 7. TGA of tannin-based foams, STD-M (left) and Meringue-M (right), under air (top) and N_2 (bottom) atmospheres (heating rate: 10ºC·min^{-1}).

The decomposition steps shown by the differentials in Fig. 7 were more marked and separated in STD-M than in Meringue-M, whose decomposition was more continuous. This is possibly due to the more complex structure of the polymer network of STD-M, since its formulation was based on more components (tannin, furfuryl alcohol and formaldehyde) than that of Meringue-M (tannin with hexamine as crosslinker). It was also observed that under oxidative degradation, both tannin foams were completely degraded and no residue was left at 600ºC, while under pyrolysis conditions, 48 wt. % of residue remained from STD-M but slightly less, 37 wt. %, in the case of Meringue-M.

The major factor limiting the rate of heat release in a material burning in the PCFC is the thermal decomposition of the polymer, which releases volatile fuels that feed the flame [33,37,43]. A good way to check such assumption is to compare PCFC and TGA (under N_2) methods, since both were performed at constant heating rate and under inert gas. Fig. 8 shows the corresponding comparison for STD-M and Meringue-M foams and, in general, the results of TGA indeed correlate very well with those of PCFC. The temperature at the maximum heat release rate was only slightly shifted to higher temperatures because of the higher heating rate in the PCFC ($1ºC\cdot s^{-1}$ for PCFC versus $10ºC\cdot min^{-1}$ for TGA) [33]. But the shapes of the curves were quite similar, showing approximatively a single-step thermal decomposition with both methods. The correspondence of the curves was really good for the Meringue-M foam. STD-M, however, presented a secondary peak of weight loss between 180ºC and 250ºC, but no combustion was noticed in the PCFC at that temperature although some products were released. This means that the decomposition products between 180ºC and 250ºC were not combustible in those conditions. This observation suggests that dehydration and decarboxylation were the main reactions occurring at the beginning of the heating (release of water and carbon dioxide), in good agreement with what was observed in other phenolic materials such as lignin [37].

The good correlation between weight loss in inert atmosphere and heat release rate proves that the main factor controlling the HRR of tannin-based foams is their thermal decomposition, as already anticipated above. The higher weight loss of Meringue-M indeed produced a higher heat release rate than for STD-M. Such a good qualitative correlation between weight loss and heat released by the material makes TGA a useful technique to understand thermal degradation pathways [43]. Even though PCFC delivers more information about the heat release rate, which is the accepted characterisation tool for fire risks, TGA also provides interesting data.

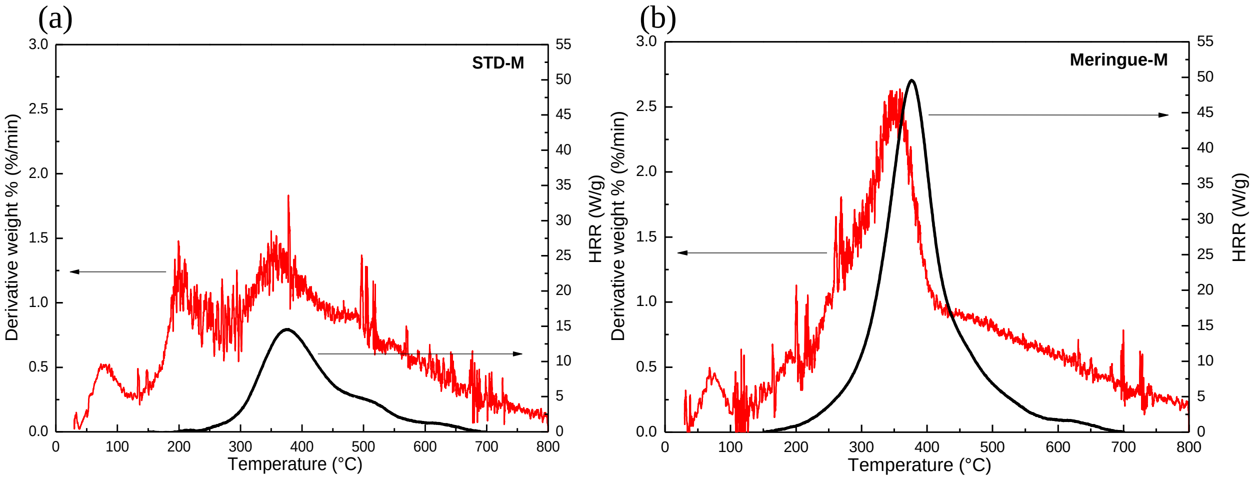
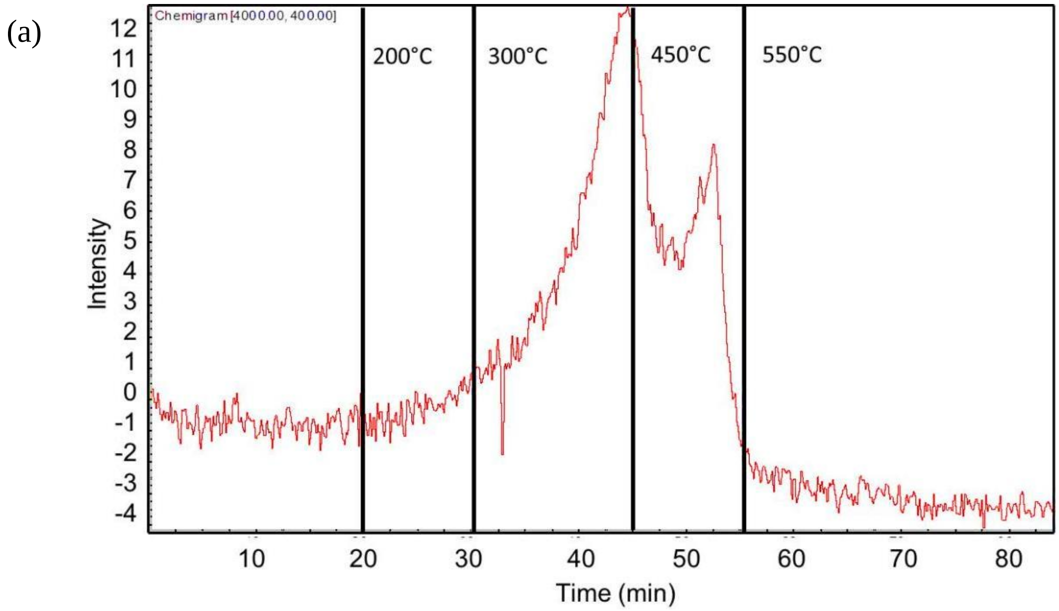


Fig. 8. Comparison between heat release rate and weight loss rate monitored with PCFC (right axis) and TGA (left axis), respectively, for: (a) STD-M, and (b) Meringue-M foams.

The identification of the gases released during the thermooxidative decomposition of tannin-based foams was also done using TGA-FTIR. With the FTIR device used in this study, quantification was not possible but the profiles were normalised by the Gram–Schmidt orthogonalisation method, making possible the comparison of the different peaks. This kind of study can give a valuable idea of the gases that might be released in a real fire, although one should be aware that the gases released in a true fire test are not exactly the same as those obtained by simply heating the same sample at 10ºC·min^{-1} in an air flow. The conditions of a real combustion (uncontrolled temperature, self-generated heat, propagation of a flame, etc.) can indeed never be the same as in the present test, and it is likely that the emitted gases do not present exactly the same compositions. However, such test can provide interesting information about the possible molecules to be found in the gases emitted during tannin foam combustion. STD-M and Meringue-M were studied by this method too.

The results corresponding to STD-M and Meringue-M foams are given in Fig. 9 and 10, respectively. In both figures, the graph (a) represents the intensity of gas signal recorded by FTIR during all the experience time; vertical lines have been drawn to mark the temperatures at which the infrared signal has been studied more in-depth. The graph (b) shows the FTIR spectra at the temperatures mentioned in (a) with the same scale, but shifted along an arbitrary intensity scale for better observing and identifying each peak.

Firstly, it can be observed that the intensity of the emitted gases collected by the infrared analyser in Fig. 9(a) and 10(a) coincides consistently with the weight loss rate recorded by TGA under air atmosphere (see again Fig. 7).



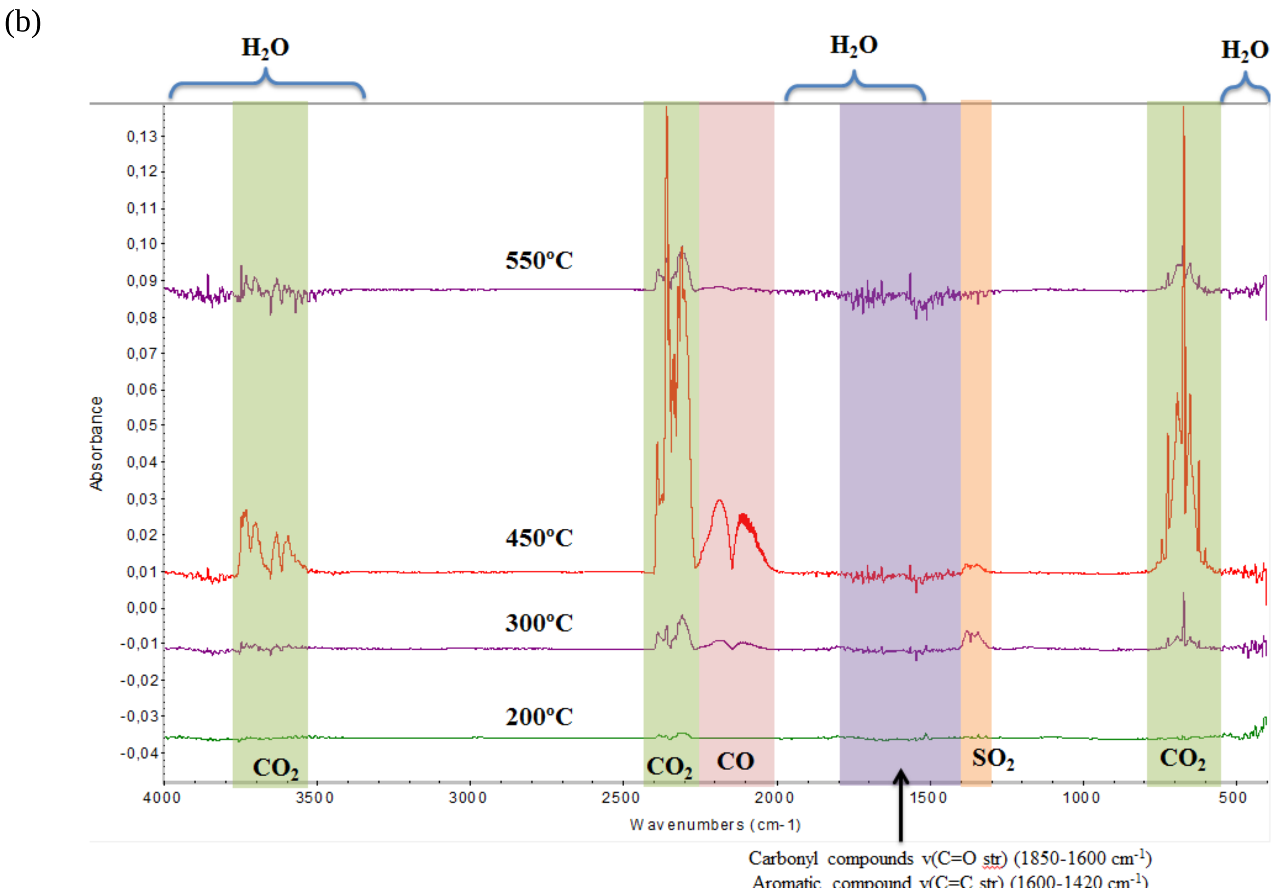


Fig. 9. Results obtained from the TGA-FTIR analysis of STD-M foam.

Fig. 9(b) shows mainly CO$_2$ peaks due to the combustion of the organic foam. At the point where the combustion was the fastest, i.e., corresponding to the highest weight loss rate, the appearance of two CO peaks indicates that the combustion was slightly incomplete. A very small signal can also be observed in the 1800-1400 cm^{-1} range due to the release of some carbonyl and aromatic components. This finding is not so significant, however, since the presence of water vapour was also detected in the same range of wavenumbers. The emitted gases also contained SO$_2$, which is attributed to the high amount of para-toluenesulphonic acid used as catalyst in the STD formulation (Table 1).

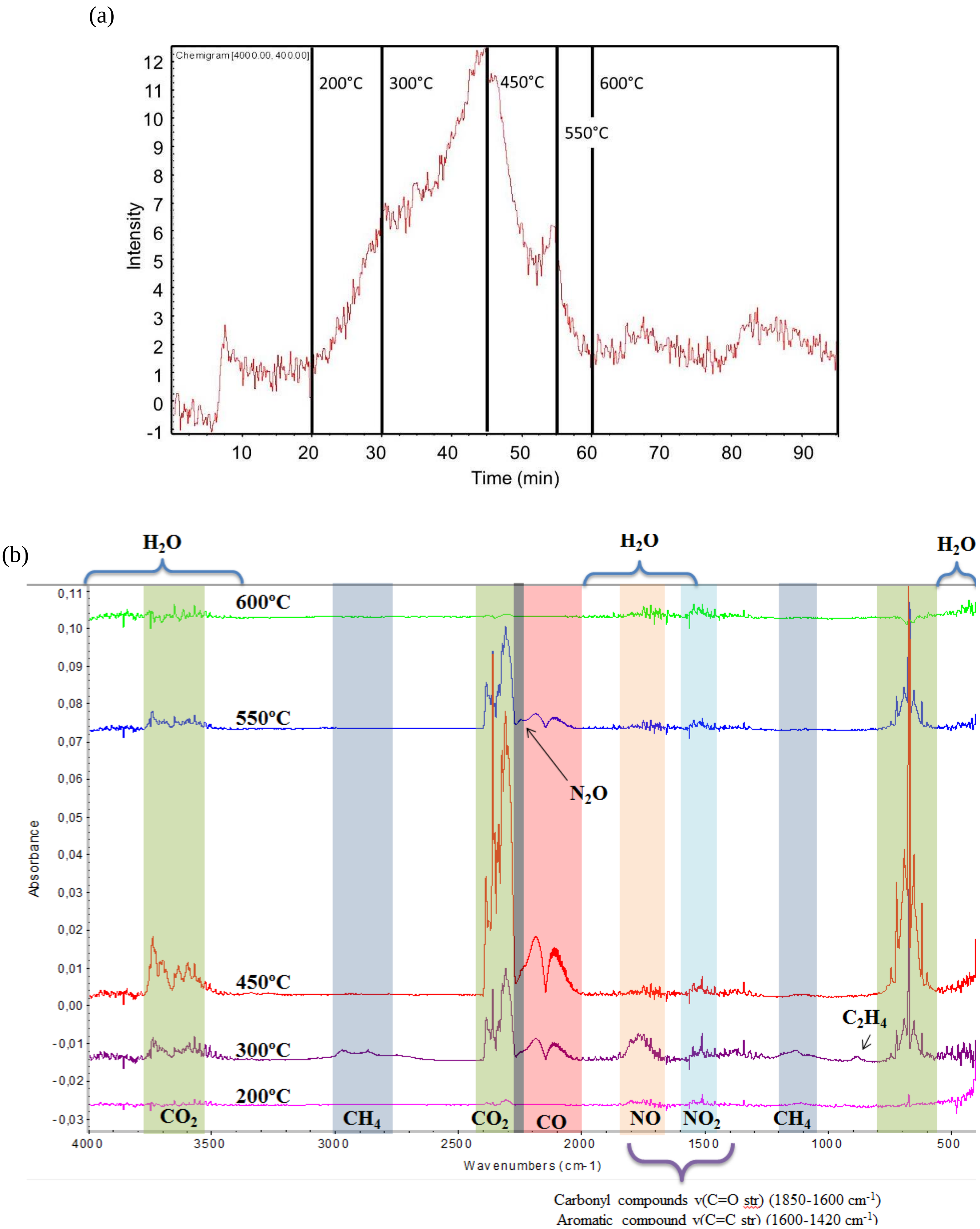


Fig. 10. Same as Fig. 9, but for Meringue-M foam.

As for Meringue-M foam (Fig. 10(b)), the FTIR spectra show more incomplete combustion than for STD-M. This is suggested by the presence of compounds such as methane and ethylene in the gases released, especially at low temperatures, and by the increase of the CO peak areas. CO, methane and ethylene peaks were not perfectly synchronised because CO still appeared at high temperatures while the other two gases practically disappeared at 450°C. Also worth noticing in the spectra of Meringue-M foam is the appearance of NO_x compounds such as NO_2 and NO. These nitrogen-based molecules are associated with the use of hexamine as crosslinker, which increased the concentration of nitrogen in the foam. Finally, the peak of SO_2 observed in the STD-M spectra did not appear here because the quantity of acid used in this case was very low.

4. Conclusion

The good fire retardance of tannin-based foams is mainly due to the aromatic composition of the matrix that forms a resistant crosslinked polymer network with low weight loss during the thermal decomposition process. As a result, a little amount of hydrocarbon fuel is provided by the foams to drive the combustion process, thus producing high ignition time and low heat release. This was evidenced by the good correlation between the weight loss observed by TGA in inert atmosphere and the heat released rate derived from PCFC experiments.

On the other hand, it was observed that the flammability of tannin-based foams strongly depends on the formulation, but not that much on the structure of the foams. The density and the porosity are therefore quantities that need to be controlled during foam processing but that are not really critical with respect to the flammability of tannin foams. However, most of the components and additives used for changing the features of those foams have a significant influence on their fire properties. Actually, it was observed that different tannin foams could perform very differently in fire scenarios, depending on the presence of surfactant and plasticiser and, more importantly, on the initial water content in their formulation. The water content is really important since the vaporisation of water weakens the polymer structure, facilitating the thermal degradation of the foam. Thus, reducing the water content in the formulation may improve the performances of tannin-based foams submitted to fire. Furthermore, foams prepared from the same formulation but with different types of tannin showed a very similar flammability. This is very interesting from the point of view of the industrial manufacturing of such kind of material, as it suggests that other sources of condensed tannins can be used for the same application.

From the above, the most basic "standard-type" formulation of tannin-based foams, i.e., made by chemical foaming + auto-polymerisation in the absence of plasticiser and surfactant, was confirmed to be the one presenting the best fire properties, having simultaneously the lowest HRR and the highest ignition time. Our analyses allowed explaining that such excellent features are due to the fact that this foam combines a low amount of water, no volatile additives, and formaldehyde for a better crosslinking. As a result, the polymer network is strong, and gases produced by heating are both emitted in very low amount and are poorly flammable.

Generally speaking, all formulations of tannin-based organic rigid foams were found to exhibit excellent fire retardance. The corresponding results were compared to those of the main insulating materials presently commercialised such as polystyrene, polyurethane and phenolic foams, confirming that thermal insulation based on tannin foams presents a far better behaviour in case of fire. Their low flammability associated with other remarkable properties such as low specific weight, low thermal conductivity, biosourced nature, etc., definitely makes tannin-based foams superior polymeric materials.

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