Biophenolic compounds from chestnut as flame retardant in epoxy resin

Laurent Ferry, Valeriia Karaseva, Clément Lacoste, Anne Bergeret, Helene Fulcrand

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L. Ferry*[a], V. Karaseva[a,b], C. Lacoste[a], A. Bergeret[a], H. Fulcrand[c]

[a] *C2MA, IMT Mines d'Alès, Université de montpellier, 6 Avenue de Clavières, 30319 Alès France cedex*
[b] *INRA, UMR1083 Sciences Pour l'Œnologie, 2 Place Pierre Viala, 34060 Montpellier, France*
[c] *INRA, UMR1208 IATE, 2 Place Pierre Viala, 34060 Montpellier, France*

Main Message. Chestnut tannins can be used to develop biobased flame retardants

Key words. Biobased flame retardant, tannin, ellagic acid, gallic acid, boration

Abstract

Over the last twenty years, reflections on sustainable development in the polymer chemistry has led to the development of biobased materials. These reflections included also polymer additives and especially flame retardants (FR) as one of the main families among them [1]. Seeking green solutions for flame retardancy has motivated the exploration of different components of biomass (carbohydrate, phenolic, protein, lipid fractions) as bricks for new additives [2]. Biosourced phenolic compounds have been highlighted to be of primary interest due their ability to promote charring when burning. Hence many works have been dedicated to lignin, the most abundant natural aromatic polymer. This compound can be used as such or after chemical modification especially with phosphorous moieties. Other less complex aromatic compounds have also been assessed. In a previous study, we developed a series of reactive or additive flame retardants based on phloroglucinol, a benzenetriol that can be prepared from compounds from fruit trees. Some of these FR were highlighted to be particularly effective in epoxy resins generating a highly intumescent behavior [3], [4]. Tannins are another class of polyphenolic compounds found in numerous plants that can be of interest for fireproofing applications. The literature on this topic is not very abundant and mainly focused on condensed tannins (i.e. based on flavanoid subunits). Mimosa tannins were used with hexamine as hardener for the impregnation of wood [5]. Time-to-ignition was significantly increased when using these tannins in synergy with boric acid or phosphoric acid. Tannins from yam were also studied by Yang et al. as flame retardant for silk textiles [6]. A condensed phase action was evidenced leading to an increase of LOI above 27%.

The aim of this work was to investigate the potential of polyphenolic compounds extracted from chestnut wood as flame retardants for epoxy resins. One major motivation for choosing chestnut as bioresource was to develop new economic activities in Cévennes which is a region near Alès registered on the UNESCO list of world heritage sites. Indeed chestnut is an abundant tree species in Cévennes forest but its exploitation is declining. Chestnut is particularly rich in hydrolyzable tannins and therefore the target was to use tannin extracts for flame retardancy. Hydrolysable tannins are mainly based on enzymatically oxidized gallic acid moieties, namely hexahydroxydiphenoyl (HHDP) and nonahydroxytriphenoyl (NHTP) moieties connected to a central polyol or osidic core by esters and C-glycosidic bonds. After tannin hydrolysis, gallic and ellagic acid can be obtained. Therefore, a first part of the work was dedicated to the study of these compounds and their boron-derivatives as fire retardant in an epoxy resin. In a second part, different tannin-containing extracts were prepared and incorporated in the same resin in order to investigate their influence on the fire behavior.

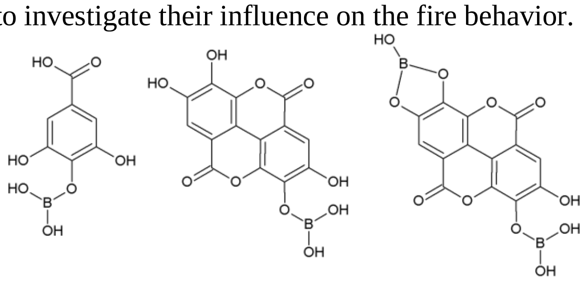

Figure 1: Examples of GA and EA boron derivatives

Pure gallic acid (GA) and ellagic acid (EA) were borated using boric acid in a basic solution (pH=9) at 50°C under vigorous stirring. After freeze-drying the solution, the synthesized products were characterized by MS and ^{11}B NMR techniques. These analyses confirmed the boration reaction. Two borated GA derivatives (GAD) and three borated EA derivatives (EAD) were identified. Examples of the derivatives are given in Figure 1.

Thermal behavior and flammability properties of the natural phenols and their derivatives were studied by TGA and PCFC. It was shown that EA is intrinsically more stable than GA and gives a higher residue and consequently has a lower effective heat of combustion. After boration, the thermal stability of both biophenols was increased as well as their high temperature residue that reached circa 50% at 900°C.

Pure and boron-modified gallic and ellagic acids were incorporated into a DGEBA/IPDA epoxy resin at a 10 wt% loading. It was shown by DSC that the incorporation of biophenols interferes to some extent with the crosslinking reaction and thus a decrease of the glass transition temperature of the resin was observed. It was more pronounced in presence of the boron-modified products.

TGA revealed an increase of the char yield at high temperature whatever the additives used. The most important effect was obtained with GAD. Correspondingly a decrease of heat release rate (HRR) was evidenced by PCFC. The cone calorimeter tests indicated that the peak of HRR is significantly reduced in the presence of phenolic compounds (Figure 2). This was attributed to the promotion of a char layer at the sample surface during combustion.

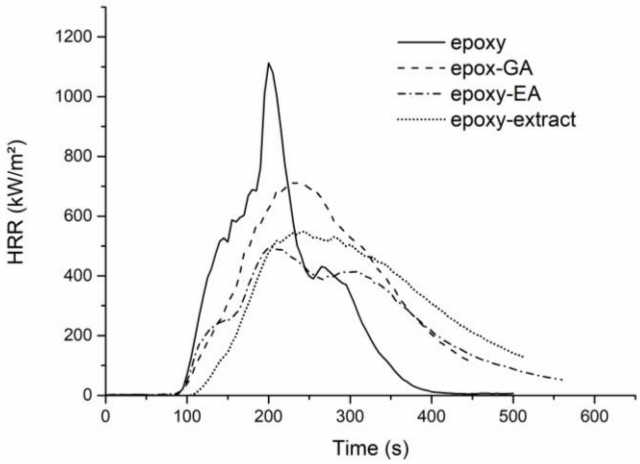

Figure 2: HRR curves of epoxy containing biophenols

In a second part of the work, tannin-containing extracts were prepared from chesnut sawdust using different solvents. The analyses of the resulting extracts indicated that they contain mainly tannins (castalagin and vescalagin) and saccharides. Depending on the solvents (or couple of solvents) the ratio tannin/saccharide may significantly vary. The characterization of thermal properties of extracts indicated that relatively high char residues are obtained (circa 35 wt% at 700°C). This value may slightly vary with the extract composition. A much remarkable effect of tannin/saccharide ratio was highlighted when characterizing the extracts by PCFC with the total heat release (THR) varying in the ratio one to three. Finally extracts were incorporated into the DGEBA/IPDA epoxy resin and the thermal and fire properties were assessed. Promising results were obtained with these relatively raw products offering interesting prospects for low cost and ecofriendly FR.

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