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Self-Extinguishing Epoxy Nanocomposites Containing Industrial Biowastes as Sustainable Flame-Retardant Additives [†]

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Abstract: Polymers are essential in modern life, but their large-scale production from non-renewable sources contributes to raw material depletion and environmental pollution. The shift from a linear to a circular economy aims to address these issues by promoting sustainable practices. Recent research focuses on incorporating natural fillers and biowastes to improve flame retardancy and reduce resource depletion. This work demonstrates the suitability of humic acids, biochar derived from both spent coffee grounds and the hydrothermal liquefaction of sludge, for use as flame-retardant additives in epoxy resins. The results are discussed in relation to the composition and preparation procedure of the composite materials. Particularly, the modification of epoxy chains with a proper coupling agent guarantees the uniform distribution of the waste throughout the polymer matrix.

Keywords: flame retardancy; wastes reuse; spent coffee grounds; humic acids; municipal sludges; biochar; sol–gel; epoxy resins

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1. Introduction

Polymers play a fundamental role in our daily lives, improving their quality. Due to their excellent properties, these materials are widely used in many industrial sectors where high-performance applications are demanded [1]. It should be noted that the large-scale production of polymers from non-renewable sources is one of the main causes of raw material scarcity and environmental pollution. The improper treatment and recycling of such materials is causing irreversible damage to both human health and the environment. To overcome these drawbacks, governments and the scientific community are encouraging the transition from a linear economy model to a circular one and the development of more sustainable approaches for synthesizing new functional polymer-based materials [2]. Due to their excellent physico-chemical properties, flame-retarded epoxy resins are broadly employed in many industrial sectors such as electronics, automotive, and aerospace [3,4].

To provide epoxy resins with good flame-retardant properties, such species as halogen- or phosphorus-based compounds are usually added to the polymer matrix. Halogen flame retardants (HFRs) are highly effective in improving the fire behavior of epoxy composites; however, during the combustion process, their decomposition produces toxic compounds. For this reason, recently, some regulations have banned most HFRs not only because of their toxicity but also the concerns linked to the effective recycling of polymeric wastes containing such species [5]. Phosphorus-based flame retardants (P-FRs), such as ammonium polyphosphate and phytic acid, are a safer alternative to HFRs, as they do not produce harmful gases during burning. However, compared to HFRs, the flame-retardant effect of P-FRs is lower as it requires larger quantities to achieve the same results. To foster the development of more sustainable and safe recyclable epoxy-based materials, the use of natural fillers together with P-FRs [6,7] and functional biowastes [8] as synergists or main flame retardants has recently been promoted. The combined use of bioderived additives (e.g., industrial biowastes) and P-FRs allows for employing a lower amount of phosphorus needed to achieve good fire performance and self-extinguishing capability, i.e., the best flammability rating. This reduces the depletion of phosphorus, hence contributing to the preservation of this important resource. On the other side, the possible reuse of industrial biowastes as flame-retardant additives in polymer matrices represents an added value in the context of desirable valorization of end-of-life products.

This work aims to show the valuable reuse of three different types of biowastes: (i) humic acid, (ii) biochar obtained from spent coffee grounds, and (iii) biochar derived from the hydrothermal liquefaction (HTL) of municipal sludge as flame retardants, together with P-FRs and other additives, in epoxy systems. Particularly, the effectiveness of their use in designing self-extinguishing epoxy-based nanocomposites was demonstrated. To obtain composite materials with optimal mechanical, fire, and thermal properties, it is essential to achieve a homogeneous dispersion of waste-derived fillers within the polymer matrix. Waste materials are generally polar, while the polymer matrix is nonpolar. Thus, a well-designed interface between them is crucial for enhancing the filler dispersion. Silane-modified epoxy systems, in which the polymeric chain has partially been functionalized with silanes through a sol–gel method, exhibit more alike interfaces between the polymer matrix and the biowaste, hence facilitating their dispersion throughout the polymer network. Hybrid silicon-containing epoxy moieties were synthesized through sol–gel routes using (3-aminopropyl)-triethoxysilane (AP) as a coupling agent. The silanized polymeric species (AP-epoxy molecules) allow for the formation of polar moieties that can promote a more uniform distribution of the waste-derived fillers in the epoxy matrix [9].

2. Flame-Retardant Hybrid Silicon-Epoxy Resins Containing Humic Acid

In this section, the main outcomes related to the exploitation of humic acids (HAs) as a flame-retardant filler for the preparation of hybrid AP-functionalized epoxy composites with improved thermal, mechanical, and fire performances are reported [10].

HAs are obtained from both animal and vegetable biomass degradation [11]; they consist of a complex structure formed by aromatic or aliphatic units and thus present amphiphilic behavior. The acidic character of HAs promotes the dehydration of the polymer matrix during the combustion process with consequent char formation; therefore, HAs have a great potential to act like flame-retardant additives in epoxy systems [12]. To achieve a uniform distribution of these additives throughout the epoxy matrix, bisphenol A diglycidyl ether (DGEBA) was modified with AP via a sol–gel route to obtain silicon-epoxy moieties (AP-epoxy molecules) [10], which interacted with polar and nonpolar species, allowing for the achievement of a fine dispersion of HAs in the epoxy matrix [13]. The epoxy system was cured using a cycloaliphatic amine, namely isophorone diamine (IDA).

In addition to HAs, urea (UR) and ammonium polyphosphate (APP) were added to the AP-modified epoxy matrix. In particular, the degradation of both UR and APP leads to the release of N_2 during the combustion, diluting the gas phase and thus reducing the flammability. On the other side, the decomposition of APP produces acid phosphorous compounds. These latter, together with HA, are responsible for the dehydration of the polymer matrix generating a char, which, in the presence of non-flammable nitrogen, becomes intumescent (Figure 1a). The synergistic flame-retardant effect exerted by the fillers, mainly in the condensed phase, resulted in self-extinguishing nanocomposites (V-0 rating in UL-94 test), even in the presence of very low content of phosphorus (i.e., 1 wt.%). The chemical composition of the different prepared samples and their UL-94 classification are reported in Table 1.

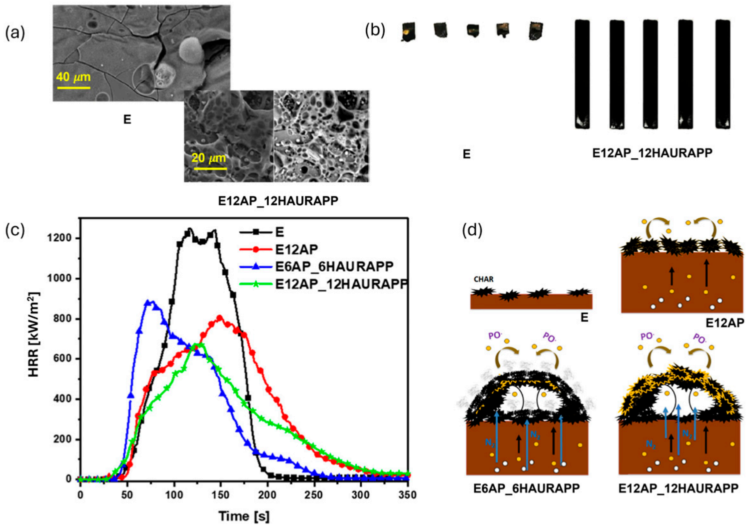

Figure 1. (**a**) SEM images of the residual char obtained after the CC test of E and E12AP_12HAURAPP, (**b**) residues after UL-94 vertical spread tests of E and E12AP_12HAURAPP, (**c**) heat release rate curves, and (**d**) flame retardant mechanism of epoxy nanocomposite containing humic acids (reprinted with permission from [10]). Copyright (2021) American Chemical Society.

Table 1. Chemical composition of epoxy nanocomposites containing HA, APP, UR, and AP. The amount of IDA is 20.6 wt.% for each formulation. The last column reports the classifications of samples resulting from the UL-94 vertical burning tests.

Sample	E (wt.%)	HA (wt.%)	AP (wt.%)	UR (wt.%)	APP (wt.%)	P (wt.%)	Si (wt.%)	UL-94
E	79.4							NC *
E12AP	79.4		12				1.4	NC *
E6AP_6HAURAPP	79.4	3	3	2	2	0.6	0.4	NC *
E12AP_12HAURAPP	79.4	6	6	4	4	1.1	0.6	V-0

* NC = non-classifiable.

Thermal and microscopy analysis revealed that the incorporation of HAs enhances the overall thermal stability of the epoxy system, also promoting the formation of a very stable char that limits heat diffusion during combustion. This char exhibits a thermal shielding effect in the condensed phase, slowing down the further decomposition of the underlying polymer. As mentioned above, UL-94 vertical spread tests were performed on the prepared composites: the formulation containing HA (6 wt.%), UR (4 wt.%), and APP (6 wt.%) gave a V-0 classification without any dripping phenomena (see Table 1 and Figure 1b). The fire behavior of epoxy nanocomposites was evaluated by performing cone calorimetry tests: the results show that the use of HA, UR, and APP causes a huge decrease (52%) in the peak of heat release rate (pHRR) (Figure 1c) and a significant increase in both the time to flash over and residual char. The combined use of HA, UR, and APP is responsible for the formation of P–N–O–Si–O–P polymeric substructures, boosting the insulation effect provided by the intumescent char (Figure 1d) [10].

3. Flame-Retardant Hybrid Silicon-Epoxy Resins Containing Coffee Biochar

The food industries produce a large amount of waste, of which spent coffee grounds (SCGs) are the most available, with an estimated yearly production of 6 million tons [14]. The surface of SCGs is characterized by the presence of many functional groups (e.g., hydroxyls), allowing for properly tailoring their properties and making them suitable for composite applications. The pyrolysis of SCGs at high temperatures (500–800 °C) accounts for the obtainment of a coffee biochar (CB) characterized by high porosity and excellent thermal stability, which shows high dispersibility in epoxy resins [15]. These features suggest using CB as a functional additive and flame-retardant for the manufacturing of epoxy-based nanocomposites, which are prepared through a sol–gel methodology according to a waste-to-wealth approach [16].

To improve the dispersion of CB in the polymer matrix, DGEBA resin was modified to obtain hybrid silanized moieties made of AP coupled with epoxy chains. In particular, the hybrid network allows for the creation of tailored interfaces between the filler and the polymer matrix. The primary amino groups of AP can open the oxirane rings of DGEBA and generate hybrid moieties able to interact with the polar species present on the surface of CB particles [17,18], facilitating the dispersion of the biowaste throughout the nonpolar epoxy network. The AP-modified epoxy resin was filled by other additives, namely a ternary oxide (SiO_2-TiO_2-MgO) and APP as a phosphorus source, both working synergistically with the CB to improve the flame-retardant properties of the final composites. The chemical composition and sol–gel synthesis of the ternary Si-Ti-Mg oxide were designed to improve the thermal stability and fire retardancy of the epoxy resin. Indeed, the presence of silica-based structures in Si-Ti-Mg oxide enables the production of a ceramic protective char, capable of limiting the heat exchange and oxygen diffusion during the combustion [19]; the titanium oxide moieties act as char promoters thanks to their acidic character [20]; the magnesium oxide and hydroxide species exert an endothermic effect and release nonflammable water vapor, diluting the gas phase [21–23]. Table 2 presents the chemical compositions of the prepared nanocomposites cured with a cycloaliphatic amine, IDA.

Table 2. Chemical composition of epoxy nanocomposites containing coffee biochar, APP, and Si-Ti-Mg oxide. The amount of IDA is 20.6 wt.% for each formulation. The last column reports the classifications of samples resulting from the UL-94 vertical burning tests.

Sample	E (wt.%)	CB (wt.%)	AP (wt.%)	Si-Ti-Mg (wt.%)	APP (wt.%)	P (wt.%)	UL-94
E	79.4	-	-	-	-	-	NC *
ESi	79.4	-	7	-	-	-	NC *
ESiC	79.4	20	7	-	-	-	NC *
ESiTAC0.5P	79.4	10	7	7	1.5	0.5	V1
ESiTAC1P	79.4	20	7	14	3	1	V-0

* NC = non-classifiable.

Field emission scanning electron microscopy (FESEM) images along the fracture sections of nanocomposites were collected to evaluate the morphological and structural modifications caused by the incorporation of CB, APP, and the ternary Si-Ti-Mg oxide into the hybrid epoxy matrix (Figure 2a). The silanized epoxy network enabled a homogenous distribution of CB particles, while the formation of a continuous and protective char was evident from the FESEM analysis performed on the carbonaceous residues after UL-94 vertical flame spread tests (Figure 2b). More specifically, the combustion of the pristine system gives a char with holes and cracks, while the samples containing CB lead to the formation of residual chars showing a compact and coherent structure, mainly due to the high graphitization degree and thermal stability of the bio-derived filler.

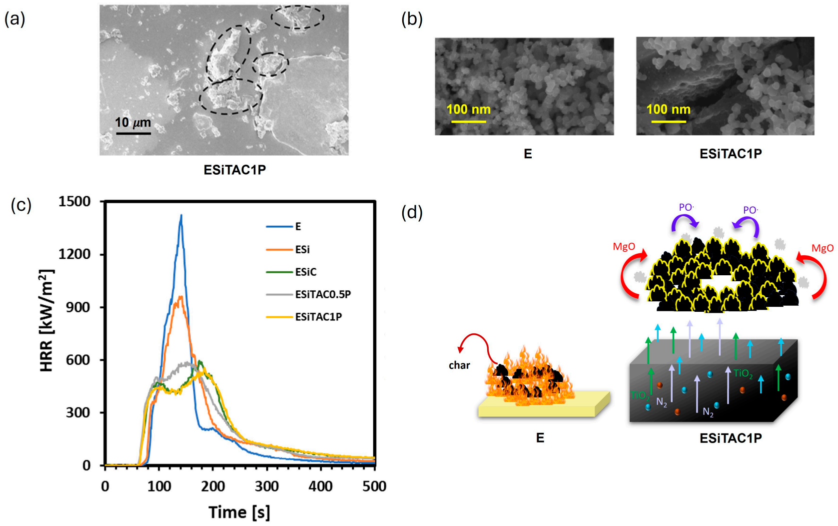

Figure 2. (**a**) FESEM captures of the cross-section of ESiTAC1P, (**b**) FESEM images of the residual char obtained after UL-94 test of E and ESiTAC1P, (**c**) heat release rate curves, and (**d**) flame-retardant mechanism of epoxy nanocomposites containing coffee biochar (reprinted with permission from [16]). Copyright (2024) Elsevier B.V.

To evaluate the flame-retardant performance of CB and its effect on fire, thermal, and mechanical properties of the epoxy nanocomposites, pyrolysis flow combustion calorimetry (PCFC) tests were also conducted. The PCFC results showed that the incorporation of CB into the epoxy matrix significantly enhances the fire performance of the composites: for example, the ESiC formulation filled by 20 wt.% CB exhibits a pHRR 65% lower than that of the unmodified resin (see Figure 2c). Figure 2d depicts the proposed flame-retardant mechanism. The combined use of CB with APP and Si-Ti-Mg oxide significantly improves the flame retardancy of epoxy resin, enabling the formation of a graphitized char containing N–P–O–Si substructures. This char acts as a thermal shield and oxygen barrier in the condensed phase during the decomposition of the epoxy matrix.

The flammability of samples was investigated through UL-94 vertical flame spread tests (Table 2). The hybrid epoxy systems containing CB, APP, and Si-Ti-Mg oxide with a low amount of phosphorus (1 wt.%) achieve a UL-94 V-0 classification, indicating very low flammability and no dripping behavior. The mechanical properties were evaluated by three-point flexural tests. The presence of additives in the hybrid epoxy composites causes the stiffening of the final composites, owing to the presence of hydrogen bonds established between the functional groups of fillers and the crosslinked epoxy resin. Indeed, the ESiTAC1P sample exhibits a higher flexural modulus ((3.71 ± 0.09) GPa) than the pristine resin ((3.23 ± 0.47) GPa).

4. Future Outlooks: Biochar Obtained from the Hydrothermal Liquefaction of Municipal Sludge

Hydrothermal liquefaction (HTL) is a thermochemical process through which wet biomass, including sludges from wastewater treatment plants, is converted into liquid biofuels with a higher energy density with respect to the feedstock. The solid residue obtained from HTL, known as biochar or hydrochar, is often discarded as waste, despite it containing an organic fraction and other elements depending on its origin, such as phosphorus, aluminum, calcium, iron, and magnesium [24]. As the percentage of biochar produced by HTL typically ranges from 17 to 45%, it is crucial to valorize this by-product to enhance the economic and environmental sustainability of the HTL process. Biochar derived from specific feedstocks is appropriate for energy production through combustion. However, biochar from sewage sludge has high ash content, including significant amounts of alkaline metals [25], with an associated modest higher heating value and other disadvantages, such as slag formation, fouling, and corrosion [26].

HTL-derived biochar, unlike that produced by high-temperature pyrolysis, has a higher concentration of oxygen-containing functional groups (i.e., hydroxyls) on its surface and supramolecular carbon architectures similar to those found in humic acids or nitrogen-based materials (e.g., melamine) [27]. Such chemical features could foster physical interactions with epoxy matrices and promote carbonization processes, forming an effective thermal shield during exposure to a flame [28]. Hence, HTL-derived biochar is a promising candidate as a natural flame-retardant additive for epoxy resins. Recent studies have demonstrated that the use of biochar in epoxy materials enhances the mechanical properties of the polymer matrix [29]; conversely, the use of biochar as an effective flame-retardant in polymer systems remains an underexplored area. It has been reported that the addition of 30 wt.% biochar and 40 wt.% magnesium hydroxide during the extrusion of high-density polyethylene increased the limiting oxygen index (LOI) from 23.9 to 31.9% while maintaining good mechanical properties such as flexural strength [30]. Furthermore, the functionalization of cotton fabrics with phytic acid and 8 wt.% biochar afforded a self-extinguishing material in UL-94 flame spread tests [31]. Despite these promising results, the development of flame-retardant epoxy systems containing biochar derived from HTL and their thermal and fire behavior remains limited. An in-depth study of these aspects, along with the synthesis of new materials with the above-mentioned properties, could promote the design of polymer composites with low flammability, excellent mechanical performance, and high sustainability.

The HTL-derived biochar samples analyzed in this work as flame-retardant additives were derived from the hydrothermal treatment applied to municipal sewage sludge [32]. To assess their effect on the thermal and fire behavior of epoxy resins, biochar samples produced in different operating conditions (time and temperature) were thoroughly characterized and then added into a DGEBA matrix and cured with IDA. The resulting epoxy composites containing 10 wt.% of biochar showed improved thermal resistance and nearly unchanged glass transition temperature (≈95 °C). To support the possible flame-retardant action in the condensed phase exerted by the biochar, the combination with other additives is under investigation, particularly urea, ammonium polyphosphate (APP), and non-woven fibers rich in silica nanoparticles obtained through an electrospinning process (Figure 3). Preliminary data about the flammability and fire performances of the composites suggest that synergism among these additives may confer self-extinguishing capabilities (a V0 rating in the UL-94 test). Based on the outcomes related to the flexural tests, the use of the above-mentioned products causes a slightly detrimental effect on the mechanical performance of the epoxy resin. This research may open new prospects for transforming the peculiar by-products of sludge exploitation processes into valuable functional materials.

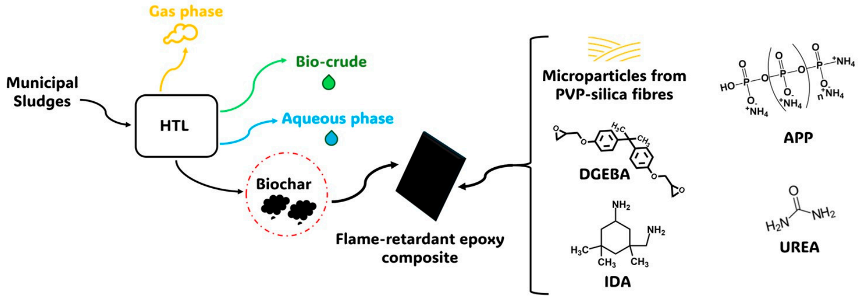

Figure 3. Scheme of flame-retardant epoxy composites containing biochar derived from HTL process.

5. Conclusions

The inappropriate management of polymeric materials at the end of their life is causing several problems to both human and environmental health. As a result, there is an increasing need to develop effective waste-to-wealth strategies to enhance the sustainability and safety of these materials. This work summarized the main outcomes referred to three different studies dealing with the reuse of some biowastes (humic acid, spent coffee ground biochar, and hydrothermal liquefaction-derived biochar) as flame retardants in epoxy resin. In particular, it was demonstrated that the combined use of nitrogen- and phosphorous-based compounds, together with an industrial biowaste, allows for the manufacturing of self-extinguishing epoxy nanocomposites, even with very low P loading (1 wt.%). Moreover, the generation of silicon-modified hybrid epoxy via sol–gel routes enables a good dispersion of the waste-derived additives into the polymer, making possible the effective preparation of epoxy systems with boosted thermal and fire responses. The proposed strategies can be of inspiration to develop new polymer-based materials with improved overall performances and more sustainable features that are suitable for different industrial sectors.

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Conflicts of Interest: The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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