

Self-extinguishing and hydrophobic epoxy composites containing hydrothermal liquefaction-derived biochar and whisker-like particles based on tailored PVP-coated silica

*Original*

Self-extinguishing and hydrophobic epoxy composites containing hydrothermal liquefaction-derived biochar and whisker-like particles based on tailored PVP-coated silica fibers / Mazzuoccolo, Immacolata; Climaco, Immacolata; Passaro, Jessica; Di Lauro, Francesca; Battegazzore, Daniele; Jovic, Milijana; Russo, Pietro; Malucelli, Giulio; Gaan, Sabyasachi; Aronne, Antonio; Montagnaro, Fabio; Balsamo, Marco; Imparato, Claudio; Bifulco, Aurelio. - In: SUSTAINABLE MATERIALS AND TECHNOLOGIES. - ISSN 2214-9937. - ELETTRONICO. - 47:(2026), pp. 1-15.

[10.1016/j.susmat.2026.e01900]

*Availability:*

This version is available at: 11583/3007208 since: 2026-02-06T10:18:54Z

*Publisher:*

Elsevier

*Published*

DOI:10.1016/j.susmat.2026.e01900

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4

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21

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23

24 **Abstract**

25

26 The hydrothermal liquefaction (HTL) of waste biomass produces bio-oil along with solid, aqueous,  
27 and gaseous co-products. The utilization of solid residue (biochar) is a crucial step in achieving the  
28 sustainability and circularity of the entire HTL process. Here, we propose the valorization of biochar  
29 derived from HTL of municipal sewage sludge as a functional additive for epoxy resins to enhance  
30 their flame retardancy. Biochar samples from HTL, obtained under different operative conditions,  
31 were characterized and incorporated into an epoxy resin cured with a cycloaliphatic amine. Biochar  
32 was used in combination with whisker-like particles, made of silica coated with electrospun  
33 poly(vinylpyrrolidone) (PVP) and functionalized to enhance compatibility with the polymer matrix.  
34 The synergy of these fillers with ammonium polyphosphate and urea enabled the preparation of no-  
35 drip self-extinguishing composites (V0 rating at UL-94 vertical flame spread tests), showing excellent  
36 fire performance, as assessed by cone calorimetry and pyrolysis combustion flow calorimetry, with a  
37 limited effect on the viscoelastic behavior and some impact on the flexural properties. Notably, a  
38 strong flame retardant action in the condensed phase, with a slight effect in the gas phase, was  
39 responsible for the formation of a ceramic continuous char, which decreased the peak of the heat  
40 release rate (~36%) as well as the total smoke release (~10%) during the burning process. Besides,  
41 the tailored whisker-like particles were able to migrate at the surface of composites, providing water  
42 contact angles of ~120°, suggesting a potential use of the designed materials as water-proof protective  
43 coatings or components for multifunctional infrastructures.

44

45 **Keywords:** Epoxy resin, municipal sewage sludge, hydrothermal liquefaction, biochar, flame  
46 retardancy, combustion behaviour.

47

48

49 **Highlights**

50

51 • Biochar from hydrothermal liquefaction was valorized as filler in epoxy systems.

52

53 • Biochar enabled the reduction of total smoke release (~10%) and peak heat release rate (~36%).

54

55 • Functionalized silica-based whisker-like microparticles were incorporated in the epoxy.

56

57 • The composites containing 10 wt.% of biochar and 1 wt.% of P loading achieved self-extinction.

58

59 • The composites showed hydrophobic surface and a limited mechanical response.

60

61

## 62 **1. Introduction**

63 In recent years, human activities have been responsible for growing environmental impacts in terms  
64 of depletion of natural resources and increased waste production [1]. Hence, a transition from a linear  
65 economic model toward a more sustainable circular approach, considering waste as a resource in the  
66 design of new products, opens opportunities for technological development [2] supported by  
67 governmental policies, such as the European Next Generation EU program [3]. In the manufacturing  
68 of polymer-based products, the use of additives is crucial to fulfill functional and mechanical  
69 performance requirements. However, such compounds mostly derive from nonrenewable sources and  
70 can pose ecological concerns in the use and recycling of polymeric materials, mainly due to the  
71 release of toxic species [4,5]. Among thermosetting polymers, epoxy resins are used to develop a  
72 large array of high-performance products, including laminates, panels, adhesive layers, tubes/pipes,  
73 which must usually comply with severe fire safety standards and regulations [6,7]. Polymeric  
74 coatings, often based on epoxy resins, with high adhesion and chemical resistance toward salts and  
75 solvents, can ensure protection against water (or water vapor) to building materials, like concrete or  
76 wood. Such coatings, employed for roofing, flooring, and waterproofing of tanks and pipes, are  
77 typically subject to fire testing (e.g., EU: ENV 1187:2002; US: ASTM E648, E84) [8], and thus  
78 require flame retardant additives [9].

79 In this field, it is crucial to replace harmful halogen-based flame retardants. Phosphorus- and nitrogen-  
80 containing additives (e.g., ammonium polyphosphate (APP), phytic acid, urea, and melamine),  
81 inorganic particles (e.g., silica, metal hydroxides), and biomass-derived materials (e.g., chitosan,  
82 lignin, spent coffee grounds) have been investigated as greener alternatives [10,11]. Recently,  
83 nano/micro-structures prepared from electrospun fibers have revealed their potential in the  
84 manufacturing of polymeric materials with improved fire behavior, due to their specific morphology,  
85 superior active surfaces, and low-cost synthesis [12,13]. For instance, nanofibers based on  
86 poly(vinylpyrrolidone) (PVP), a biocompatible polymer, easily obtained by electrospinning for  
87 biomedical or environmental systems [14,15], can incorporate silica nanoparticles and undergo  
88 thermal treatment to counter their water solubility and flammability [16–18]. Thus, materials derived  
89 from silica-filled fibers could be interesting candidates in the scope of flame retardancy.

90 Turning to biomass-derived and biowaste materials, their use as renewable components of polymer-  
91 based systems represents a promising approach toward improved sustainability and circularity  
92 [19,20]. On the other hand, sizeable amount of these compounds must often be incorporated into the  
93 epoxy matrix to achieve satisfying fire performances. As an example, Vahabi et al. modified spent  
94 coffee grounds with dimethyl phosphite to obtain a functional filler for a bisphenol A diglycidyl ether  
95 (DGEBA) resin, finding that 30 wt.% of this additive was needed to lower the flammability and

96 reduce the peak of heat release rate by 40%, compared to the virgin sample [21]. In this context,  
97 growing attention is raised by biochar, the solid product resulting from the thermochemical  
98 conversion of biomasses (e.g., wastes deriving from agriculture and food industry or municipal  
99 sludge) [19]. Biochar has great significance for carbon sequestration, contributing to carbon neutrality  
100 and greenhouse effect mitigation, and has been applied as a soil conditioner to reduce the need for  
101 fertilizers and pesticides in agricultural production [22–24]. It can also be employed as an additive  
102 for plastics and molding materials, owing to its highly carbon-enriched skeleton, porous  
103 supramolecular surface structure, and oxygen-containing functional groups [25]. The effect of the  
104 addition of biochar particles with different morphologies on the mechanical and electrical properties  
105 of epoxy resin was extensively studied by Bartoli, Giorcelli, and coworkers [26–28]. The composition  
106 and architecture of biochar allow it to establish good physical interactions with the polymer matrix,  
107 and to promote the charring process and the formation of an effective thermal shield during the  
108 polymer degradation upon exposure to heat or fire [29,30]. Particularly, the combined use of APP  
109 and biochar has been found to significantly enhance the flame retardant performance of polymers,  
110 offering a sustainable and cost-effective solution in reducing fire risks [31,32]. This is due to the  
111 intumescent and char-promoting properties of APP, joint with the ability of biochar in forming a  
112 robust char layer, strengthening the thermal stability of the residue. Their synergistic action also slows  
113 down fire propagation and helps reduce the flammability and smoke production of polymeric  
114 composites [33,34]. Recently, the introduction of 20 wt.% biochar into a modified epoxy matrix along  
115 with a Si-Ti-Mg mixed oxide and APP allowed to obtain thermally stable self-extinguishing  
116 composites, with a strongly reduced heat release rate and a decrease (~11%) in the total smoke  
117 production [33].

118 Notwithstanding these promising results, the exploitation of biochar as a flame retardant has been  
119 poorly investigated to date. Other examples include the incorporation of 30 wt.% biochar and 40 wt.%  
120 Mg(OH)<sub>2</sub> into high-density polyethylene, which increased the limiting oxygen index (LOI) from  
121 23.9% to 31.9% while keeping good flexural strength [25], and the preparation of an all-bio-sourced  
122 waterborne system comprising phytic acid and biochar to improve the fire behavior of cotton fabrics,  
123 providing self-extinction in UL-94 flame spread tests with a limited dry add-on (8 wt.%) [35].

124 When planning the use of biochar as an additive, it should be considered that its chemical and  
125 structural features vary widely according to the starting material and the production process. Biochar  
126 is a typical co-product of hydrothermal liquefaction (HTL), a thermochemical depolymerization  
127 process carried out to convert wet biomass into biocrude oil as target product and other chemicals at  
128 moderate temperature (typically 200–400 °C) and high pressure (10–25 MPa) [22,36], avoiding the  
129 energy-intensive drying step associated to conventional combustion and gasification. The HTL of

130 civil and industrial sludges, generated during wastewater purification treatments, produces a solid  
131 biochar, water soluble compounds, and non-condensable gas, in addition to the target biocrude [37].  
132 The average yield of solid residue from HTL processes is around 45%, depending on the feedstock:  
133 hence, its valorization is an important goal to improve the sustainability and circularity of this  
134 technology [38]. Compared to biochar produced by high-temperature pyrolysis, the one derived from  
135 HTL generally shows structural differences [39]: the latter tends to have more abundant oxygen-  
136 containing functional groups [40], which make its organic fraction similar to humic acids obtained  
137 by the biological and chemical degradation of vegetable and animal biomasses [41,42], and a larger  
138 inorganic content. The oxygenated species and the inorganic fraction may increase surface acidity,  
139 favouring the dehydration of polymer matrix, and contribute to a flame retardant action in the  
140 condensed phase, resulting in a robust final carbonaceous residue. Despite these suitable features of  
141 HTL biochar, its potential in improving the thermal and fire behavior of thermosets is still unexplored.  
142 The HTL of different sludges for the production of bio-oil is being actively investigated [43–45].  
143 With the aim of developing an integrated biorefinery process with optimized exploitation of mass and  
144 energy and minimized waste generation, we are proposing the reuse of the resulting biochar as filler  
145 in epoxy-based materials. In this work, we report a comprehensive characterization of the composites  
146 obtained by incorporating biochar into an epoxy resin, also combined with whisker-like particles  
147 derived from electrospun PVP-silica fibers and widely available flame retardants (urea and APP).  
148 The optimal composition provided very low flammability (V0 rating in UL-94 flame spread tests),  
149 neatly enhanced fire performances, measured by cone calorimetry, and good thermal resistance, with  
150 a limited impact on mechanical behavior.

151 This study represents the first report on the valorization of biochar from HTL as functional additive  
152 in a polymeric material. The results reveal how the characteristics of different biochar samples  
153 influence their effect and how the synergy with other additives boosts the properties of the final  
154 composites. This approach appears as a viable waste reutilization pathway, conferring added value to  
155 the residue of a waste transformation process.

156

## 157 **2. Materials and methods**

### 158 **2.1. Materials**

159 The biochar used in this study derives from the hydrothermal liquefaction process of municipal  
160 sewage sludge deriving from a wastewater treatment plant located in Milan (Italy), tested in a  
161 previous experimental campaign [43–45]. Previous proximate and ultimate analysis indicated that the  
162 sludge has moisture, volatile matter, fixed carbon and ash contents of 12.1, 57.4%, 21.1% and 9.3%,

163 respectively, and the elemental composition on a dry basis is 34.6% (C), 4.9% (H), 5.9% (N), and  
164 0.8% (S).

165 Poly(vinylpyrrolidone) (PVP, 1,300,000 g mol<sup>-1</sup>) and tetraethyl orthosilicate (TEOS, 98%),  
166 purchased from Sigma-Aldrich (St. Louis, USA), were the starting materials for the synthesis of PVP-  
167 silica fiber blankets, which will be named PVP-Si. Their functionalization was performed using (3-  
168 glycidyloxypropyl)trimethoxysilane (GPTMS, 98%) as a coupling agent, purchased from Sigma-  
169 Aldrich (St. Louis, USA), and isophorone diamine (IPDA), a cycloaliphatic diamine hardener,  
170 provided by Mates S.r.l. (Milan, Italy). The composite materials were prepared employing an epoxy  
171 system (SX10) from Mates S.r.l. (Milan, Italy), composed of Bisphenol A diglycidyl ether (DGEBA)  
172 and IPDA. Urea and ammonium polyphosphate (APP), acquired from Sigma-Aldrich (St. Louis,  
173 USA), were used as flame retardant additives.

174

## 175 **2.2. Production of biochar by hydrothermal liquefaction**

176 A detailed description of the experimental apparatus and protocol used for biochar production is  
177 reported in [43]. Briefly, it consists in a 500 mL Hastelloy C-276 batch stirred reactor (Parr  
178 Instruments, series PA 4575A) equipped with a digital pressure transducer coupled with a needle  
179 valve for pressure measurement and control, and a heating system combining cylindrical blocks and  
180 a band heater. HTL experimental tests were carried out at 200 bar for slurries containing 10 wt.%  
181 sludge in the aqueous phase. The HTL operating conditions for the production of biochar were the  
182 ones that in a previous work determined the best yield of the target biocrude: set point temperatures  
183 of 300 °C and 350 °C, with isothermal holding times of 10 min and 30 min at each temperature [43].  
184 After the HTL test, the liquid and solid phases were recovered from the vessel with a spatula, and 30  
185 g of dichloromethane (DCM) were added to maximise the products recovery. The resulting slurry  
186 was filtered on a Büchner under vacuum. After filtration, focusing on biochar recovery, the solid  
187 phase was subjected to Soxhlet extraction to recover the biocrude from the solid pores, using about  
188 150 g of DCM as extracting solvent. At the end of this operation, the solid residue was oven-dried at  
189 105 °C for 24 h. The biochar samples were named Ch\_X-Y, where X is the set temperature for the  
190 isothermal stage (300 or 350 °C) and Y is the isothermal time at the set temperature (10 or 30 min).

191

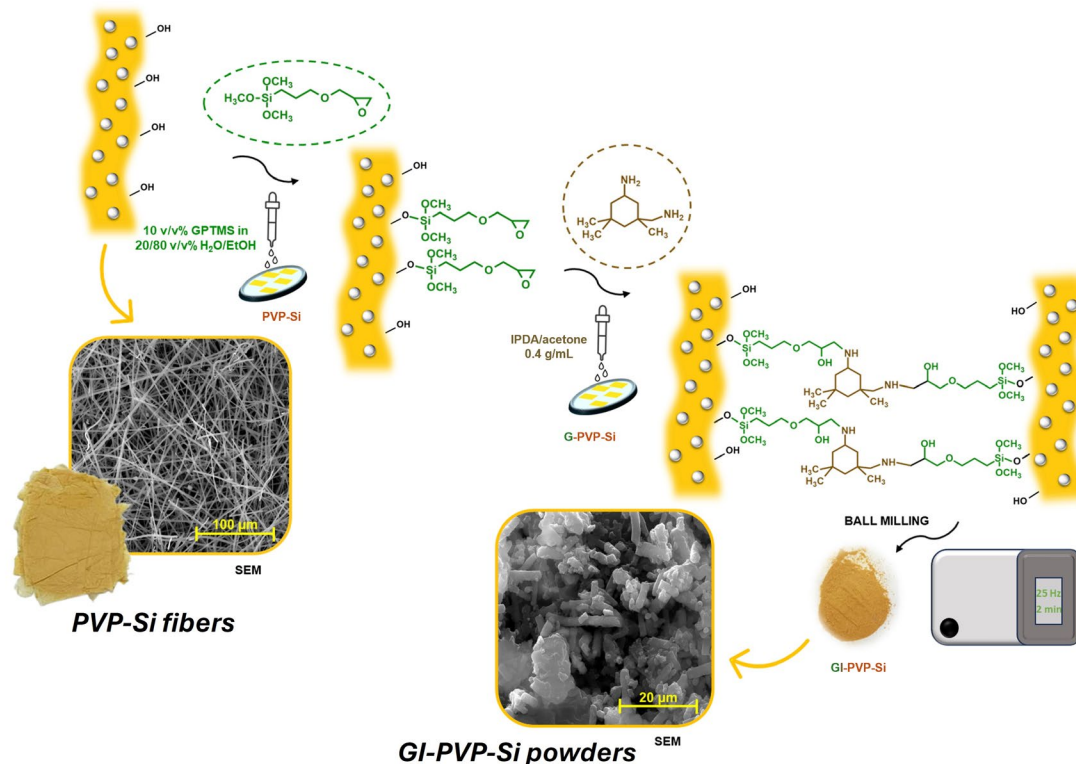
## 192 **2.3. Preparation of functionalized PVP-silica particles**

193 PVP-Si blankets were fabricated using the electrospinning technique. The procedure was reported in  
194 a previous publication, and the main steps are briefly mentioned in the following [18]. Sol-gel method  
195 was employed to prepare SiO<sub>2</sub> nanoparticles starting from TEOS as a precursor. PVP was dispersed  
196 in an ethanol solution (20 wt.%) and mixed with a suspension (40 wt.%) of silica particles in ethanol.

197 The mixture was electrospun under a voltage of 30 kV by keeping the room temperature and humidity  
198 of  $(45 \pm 10)\%$  and ensuring a flow rate of 0.100 mL/min. The electrospun non-woven mats were dried  
199 at 80 °C for 60 min, then heat-treated from 150 to 200 °C, and finally maintained at 200 °C for 6 h to  
200 cross-link the fibers. The thermal treatment of PVP-Si blankets gives them resistance to humidity,  
201 while the sol-gel particles embedded into the fibers become exposed at the surface and able to be  
202 functionalized [18,46].

203 The PVP-Si fibers were further treated to enhance their compatibility with the epoxy resin and to  
204 make them easily dispersible in the polymer matrix. The procedure is schematized in Figure 1. A  
205 solution containing 10 v/v% GPTMS in a 20/80 v/v% water/ethanol mixture was added dropwise  
206 using a micropipette onto PVP-Si fragments (4 mL/1 g); the impregnated fibers were dried at 80 °C  
207 for 30 min in a ventilated oven, giving G-PVP-Si samples. Then, a 0.4 g/mL IPDA solution in acetone  
208 was added dropwise onto dried G-PVP-Si fibers, as described above. After drying at 80 °C for 12 h,  
209 a functionalized material, referred to as GI-PVP-Si, was obtained. GI-PVP-Si was finally ground in  
210 an agate mortar and by ball milling, with a Mixer Mill MM 400 (Retsch, Haan, Germany) for 2 min  
211 at 25 Hz, resulting in a fine powder. The morphology of initial PVP-Si fiber mats and GI-PVP-Si  
212 powders is shown in Figure 1.

213



214

215 **Figure 1.** Scheme of the preparation procedure of functionalized PVP-Si particles. Photographs and SEM  
216 images of PVP-Si fibers and GI-PVP-Si powders are also shown.

217

218 **2.4. Preparation of epoxy composites**

219 In a typical procedure, the selected biochar (see section 3.1), urea, APP, and GI-PVP-Si (see Table 1  
 220 and section 2.3) were mixed and ground in a mortar. The powder mixture was dried at 80 °C for 30  
 221 min and then incorporated into DGEBA resin. The system was stirred using a vortex to obtain a  
 222 uniform distribution of the additives in the polymer matrix. Finally, IPDA (26 wt.% with respect to  
 223 the DGEBA resin) was added into the system to start the curing process (60 °C/12 h and 80 °C/4 h)  
 224 in a silicone rubber mold. The whole synthesis procedure of epoxy composites is displayed in Figure  
 225 2, while the composition of all the prepared samples is listed in Table S1. In particular, the  
 226 composition of the fully characterized epoxy systems is reported in Table 1.

227 To give an example of the meaning of the samples' codes, ECUA5PS1P represents the epoxy (E)  
 228 formulation containing the biochar (C, 10 wt.%), urea (U, 2 wt.%), APP (A, 3 wt.%), GI-PVP-Si (PS,  
 229 5 wt.%), and 1 wt.% of P as APP, considering the nominal content of P in APP as ~30 wt.% (Table  
 230 1 and Table S1).

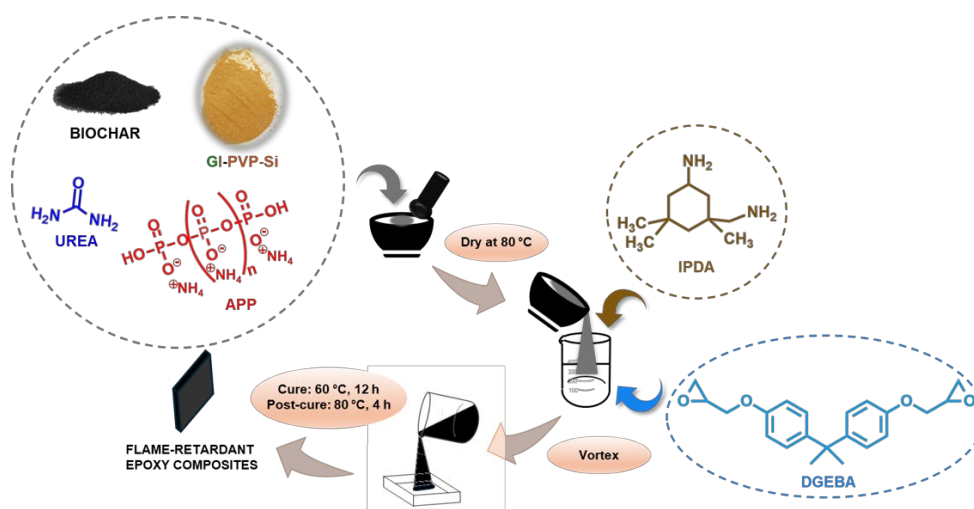
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232 **Table 1.** Composition of the fully characterized epoxy-based samples. The mass percentages are referred to  
 233 (DGEBA+IPDA) basis.

Sample	DGEBA (wt.%)	IPDA (wt.%)	Ch_300-30 (wt.%)	APP (wt.%)	UREA (wt.%)	GI-PVP-Si (wt.%)	P <sup>a</sup> (wt.%)
E	79.4	20.6	-	-	-	-	-
EC	79.4	20.6	10	-	-	-	-
E5PS	79.4	20.6	-	-	-	5	-
EC5PS	79.4	20.6	10	-	-	5	-
ECUA5PS1P	79.4	20.6	10	3	2	5	1

234 <sup>a</sup> nominal content of phosphorus

235



236

237

238

239

**Figure 2.** Synthesis procedure of epoxy composites.

## 2.5. Characterization techniques

240 The chemical composition of the four biochar samples produced by HTL was investigated by Fourier  
241 Transform InfraRed spectroscopy, ultimate and proximate analysis.

242 **Fourier Transform InfraRed (FTIR)** spectra were collected using a Nicolet 5700  
243 (ThermoScientific, Waltham, MA, USA) with a DTGS KBr detector in the range from 400 to 4000  
244  $\text{cm}^{-1}$ . The IR transmittance spectra of powders mixed in KBr pellets were collected as the sum of 32  
245 scans with a resolution of  $2 \text{ cm}^{-1}$ .

246 **Proximate analysis** was carried out by reference to UNI 9903/ASTM D5142 standards and using a  
247 TGA701 LECO thermobalance to evaluate moisture, volatile matter, fixed carbon and ash in the  
248 biochar.

249 **Ultimate analysis** was obtained by means of a LECO CHN628 analyzer and according to ASTM  
250 reference standard D5373 to determine C, H, and N contents in the biochar; the S percentage in the  
251 solid samples was evaluated via an elementary LECO SC-144DR analyzer and using as reference  
252 standard the UNI 7584.

253 Ch\_300-30 was also investigated by **scanning electron microscopy (SEM)** equipped with an  
254 **energy-dispersive X-ray (EDX)** detector (FEI Quanta 200 FEG SEM equipped with an Oxford Inca  
255 Energy System 250 and an Inca-X-act LN2-free analytical silicon drift detector). SEM investigations  
256 were performed using a FEI Quanta 200 FEG SEM (Thermo Fisher Scientific Inc., USA) operating  
257 in high vacuum conditions ( $\sim 10^{-5}$  mbar). The measurements were conducted using a secondary  
258 electron detector, applying an accelerating voltage from 10 to 30 kV.

259 PVP-Si and GI-PVP-Si were analysed by FTIR spectroscopy and SEM-EDX analysis, using the  
260 abovementioned instruments.

261 The wettability of pure resin and epoxy composites was evaluated using a Dataphysics OCA 30  
262 instrument. **Water contact angle (WCA)** measurements were performed at  $\sim 25 \text{ }^\circ\text{C}$ , placing water  
263 droplets with a volume of 6-9  $\mu\text{L}$  on the surface of thermosetting substrates [47].

264 The epoxy-based composites were analysed by FTIR spectroscopy, and their thermal properties were  
265 assessed by **differential scanning calorimetry (DSC)** and **thermogravimetric analysis (TGA)**.  
266 DSC measurements were carried out using a Mettler DSC 822/400 thermal analyzer (Mettler-Toledo,  
267 Columbus, OH, USA), applying a typical procedure consisting of three consecutive heating-cooling-  
268 heating stages, over the temperature range between  $20 \text{ }^\circ\text{C}$  and  $300 \text{ }^\circ\text{C}$ , with a thermal scanning rate  
269 of  $10 \text{ }^\circ\text{C}/\text{min}$ , under a nitrogen atmosphere (flow rate:  $50 \text{ mL}/\text{min}$ ). The glass transition temperature  
270 was identified at the inflection point of the second heating scan. TGA was carried out on the biochar  
271 samples and epoxy composites using a Mettler TGA/SDTA 851 instrument (Mettler-Toledo  
272 Columbus, OH, USA) under air and  $\text{N}_2$  atmospheres with a flow rate of  $50 \text{ mL}/\text{min}$  for both. Weight

273 loss profiles were recorded as a function of temperature by heating the samples from 25 °C to 800 °C  
274 at 10 °C/min.

275 The viscoelastic behavior of the materials was assessed through **dynamic mechanical analysis**  
276 **(DMA)** carried out using a DMA 850 (TA Instrument, USA) operating in dual cantilever mode to  
277 evaluate the storage ( $E'$ ), loss moduli, and  $\tan\delta$  vs. temperature of pristine resin and epoxy  
278 nanocomposites. All samples ( $60 \times 10 \times 3 \text{ mm}^3$ ) were characterized through a heating ramp from -30  
279 °C to 180 °C at 2 °C/min. A sinusoidal load was applied at a frequency of 1 Hz with an amplitude of  
280 10  $\mu\text{m}$ . Glass transition temperature was determined as the maximum of the peak of the  $\tan\delta$  curve.

281 **Three-point bending tests** were performed, according to ASTM D790, using an Instron 4505  
282 universal testing machine (Instron Corporation, Canton, MA, USA) to evaluate the flexural  
283 behaviour. The setup included a 1 kN load cell, a crosshead speed of 2 mm/min, and a span length of  
284 50 mm. The specimens measured  $120 \times 12 \times 3.4 \text{ mm}^3$  and the recorded results were averaged on at  
285 least five samples.

286 The **flammability** of all epoxy composites was assessed by UL-94 vertical flame spread tests (IEC  
287 60695-11-10; sample dimensions:  $13 \times 125 \times 3 \text{ mm}^3$ ).

288 **Limiting oxygen index (LOI)** tests were carried out by using a FIRE oxygen index apparatus  
289 according to the ASTM D2863 standard.

290 To evaluate the fire behavior of pristine resin and epoxy nanocomposites, a **cone calorimeter test**  
291 (Noselab ATS, Monza, Italy) was conducted applying an irradiative heat flux of  $35 \text{ kW/m}^2$  according  
292 to the ISO 5660 standard. Specimens measured  $10 \times 10 \times 0.3 \text{ cm}^3$  and were positioned horizontally  
293 on a supporting grid. The cone calorimetry tests were performed to obtain key parameters including  
294 the time to ignition (TTI, s), total heat release (THR,  $\text{MJ/m}^2$ ), heat release rate (HRR,  $\text{kW/m}^2$ ), peak  
295 of the heat release rate (pHRR,  $\text{kW/m}^2$ ), total smoke release (TSR,  $\text{m}^2/\text{m}^2$ ), and specific extinction  
296 area (SEA,  $\text{m}^2/\text{kg}$ ). Further, in accordance with ASTM D7309 standard, a **pyrolysis combustion flow**  
297 **calorimeter (PCFC)**, Fire Testing Technology Instrument, London, UK) was employed to evaluate  
298 the heat release capacity. The specimens (20-25 mg) were heated from 150 to 750 °C at 1 °C/s in the  
299 pyrolysis zone.

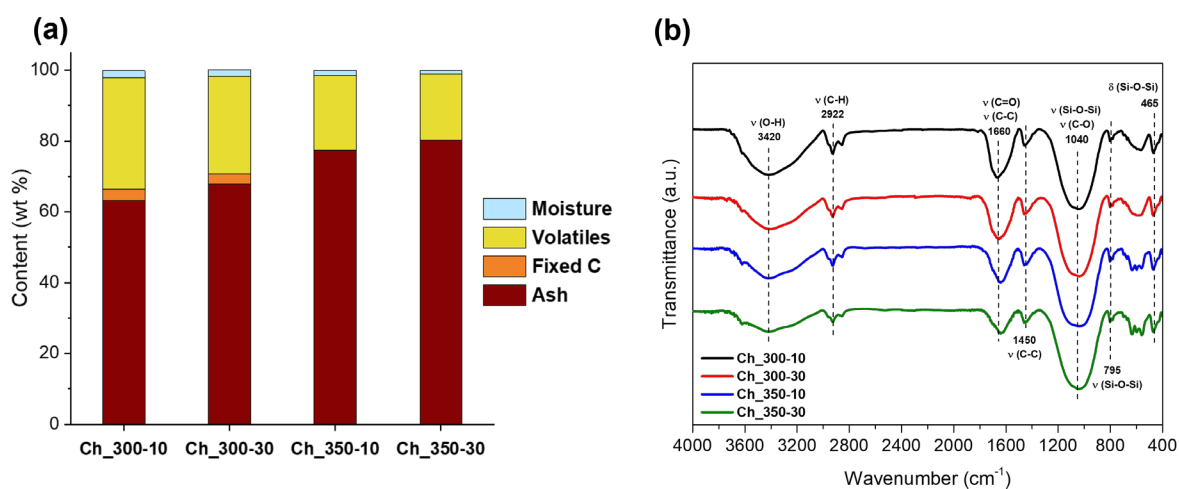
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### 301 **3. Results and discussion**

#### 302 **3.1. Characterization of biochar samples**

303 The four biochar samples produced by HTL under different conditions were thoroughly characterized  
304 in terms of composition, structure, and thermal stability to gain insight into their potential interactions  
305 with the polymer matrix and the resulting impact on its behavior. The results of ultimate and  
306 proximate analyses, reported in Table S2, indicate that increasing the temperature and time of the

307 HTL process leads, as expected, to a higher conversion of the organic matrix of the initial sludge. As  
 308 a result, the content of carbon, hydrogen, nitrogen, and volatiles is reduced in the solid residue, while  
 309 the ash content increases (Figure 3a). The large ash percentage (ranging from 63 to 80 wt.%) is  
 310 consistent with the previously reported inductively coupled plasma mass spectrometry (ICP-MS)  
 311 data, which revealed a considerable concentration of inorganic elements of the starting sludge  
 312 (especially Fe, P, Ca, Mg, Al) in the solid residues Ch\_300-30 and Ch\_350-10 [43]. The low moisture  
 313 content in all biochar samples (1-2 wt.%) makes a drying step before their use unnecessary.  
 314 Furthermore, with increasing process temperature and isothermal time at 350 °C, a growth in C/H  
 315 ratio is observed (Table S2), suggesting the presence of larger fractions of cyclic or aromatic  
 316 compounds, which are more thermally stable than linear chains. The introduction of a carbonaceous  
 317 filler with high aromatic content into a polymer matrix can positively affect the thermo-oxidative  
 318 stability of final composites, resulting in a larger amount of residual char after combustion [48,49].



319  
 320 **Figure 3.** Results of proximate analysis (a) and FTIR spectra (b) of the four biochar samples obtained in  
 321 different HTL operating conditions.  
 322

323 FTIR spectra (Figure 3b) give further information on the chemical structure of the biochar samples.  
 324 They display similar profiles, including the broad band associated with O–H bond stretching, centred  
 325 around 3420 cm<sup>-1</sup>, aliphatic C–H stretching bands at about 2922 cm<sup>-1</sup>, a rather wide band around 1660  
 326 cm<sup>-1</sup>, likely due to the overlap of C=O stretching and aryl C–C stretching (seen as a shoulder at about  
 327 1600 cm<sup>-1</sup>), a band commonly assigned to aromatic ring vibrations at 1450 cm<sup>-1</sup>, a broad and intense  
 328 band around 1040 cm<sup>-1</sup>, which could encompass the contribution of Si–O–Si and C–O stretching. The  
 329 signals at lower wavenumbers can be attributed to other Si–O vibrations, C–H bending in aromatic  
 330 and unsaturated structures, as well as vibrations of metal–oxygen bonds. Therefore, aliphatic and  
 331 aromatic units seem to coexist in the organic fraction. The relative intensities of the bands  
 332 corresponding to the organic groups, along with the O–H stretching one, tend to decrease with

333 increasing temperature and residence time, in agreement with the observations of ultimate analysis.  
334 On the other hand, it can be noted that the shoulder around  $3622\text{ cm}^{-1}$ , ascribed to the hydroxyl groups  
335 linked to the inorganic component, does not significantly decay with increasing temperature. A  
336 structure rich in surface hydroxyl groups may have a partially acidic character and favour the  
337 dehydration of the polymer matrix, thus acting as a char promoter.

338 TGA was performed in both nitrogen and air to evaluate the thermal and thermo-oxidative stability  
339 of the biochar samples, respectively (see Figure S1a-d). Figures S1a,b show a larger mass loss for  
340 biochar obtained at  $300\text{ }^{\circ}\text{C}$ , due to higher volatiles and moisture content (see the proximate analysis  
341 data, Table S2). The residues at  $800\text{ }^{\circ}\text{C}$  of samples Ch\_300-10 and Ch\_300-30 are about 10 wt.%  
342 lower than those of Ch\_350-10 and Ch\_350-30, as also shown in Table S3. In oxidative atmosphere  
343 (Figure S1b), Ch\_350-Y biochars present an almost identical profile to that recorded in pyrolysis,  
344 since they contain a lower concentration of volatiles and no fixed carbon. In contrast, Ch\_300-Y  
345 samples, with a higher carbonaceous content, show a larger mass loss around  $350\text{ }^{\circ}\text{C}$  due to the  
346 combustion of these components. Overall, the final residues confirm the significant inorganic fraction  
347 of HTL biochar, and the differences in the residual mass values recorded in air well agree with the  
348 composition variations between the samples.

349 Ch\_300-30 was chosen as the representative biochar for SEM-EDX analysis. Figure S2 shows a SEM  
350 micrograph that highlights the rough and apparently porous surface of a Ch\_300-30 particle. The  
351 surface composition of the sample (Table S4) reveals a carbon percentage approximately double with  
352 respect to the value obtained by ultimate analysis, suggesting that the carbonaceous fraction is more  
353 concentrated in the outer layers of the biochar particles than in the bulk. After C and O, the most  
354 abundant elements detected by EDX in Ch\_300-30 are Fe, P, Si, and Ca, in fair accordance with the  
355 abovementioned ICP-MS data [43].

356 The selected HTL biochar, obtained from a process conducted via an isothermal treatment at  $350\text{ }^{\circ}\text{C}$ ,  
357 shows a large fraction of thermally stable compounds with branched or conjugated structures (cyclic  
358 or aromatic), whose presence is supported by the high C/H ratio. Aromatic structures are intrinsically  
359 more thermally stable due to the resonance stabilization of their delocalized  $\pi$ -electron systems, which  
360 require higher energy input to undergo bond scission. Aromatic-rich carbonaceous fillers tend to  
361 promote the formation of a thermally stable char layer during heating, which acts as a physical barrier  
362 that limits heat flux, mass transport of volatile degradation products, and oxygen diffusion [50,51].  
363 Using HTL biochar as filler may increase the thermal stability of final epoxy composites, also giving  
364 a larger amount of residual mass after burning. Besides, thanks to their acidic characteristics, the  
365 hydroxyl groups detected on the biochar surface by spectroscopic analysis may boost the occurrence  
366 of char-forming phenomena along the decomposition of the polymer matrix. Finally, as also reported

367 in the literature, Fe, P, Si, and Ca species can catalyze the production of char in synergy with the  
368 other acidic moieties, accelerating dehydration reactions [52].

369 The design of materials containing HTL biochar derived from municipal sludge should take into  
370 account that the composition of the feedstock is subject to variations depending on the location and  
371 time of collection [38]. While the HTL operating conditions are expected to play a major role in  
372 determining the composition and surface features of the solid product, the possibility of some  
373 differences linked to the feedstock cannot be excluded.

374

### 375 **3.2. Screening of epoxy composites**

376 To examine the effect of the addition of biochar on the main characteristics of the epoxy resin, four  
377 composites were prepared by adding 10 wt.% of each biochar sample to the matrix. The FTIR spectra  
378 of these composites (named EC 300-10, EC 300-30, EC 350-10, and EC 350-30) are shown in Figure  
379 S3, along with that of the cured epoxy matrix (E), as a reference. The successful curing process of all  
380 materials is attested by the disappearance of the characteristic signals of the epoxy ring (at 970, 912  
381 and 870  $\text{cm}^{-1}$ ), which are visible in the spectrum of DGEBA (uncured resin, Figure S4), and by the  
382 intense O–H stretching band around 3400  $\text{cm}^{-1}$ , showing up as a result of the ring opening during the  
383 curing reaction. The IR spectra of the biochar-containing composites appear identical to that of E,  
384 indicating that the fillers do not cause any chemical modification of the polymer matrix. As the main  
385 vibrational bands of the biochar overlap with intense signals of the polymer chains, the only evidence  
386 of the presence of filler particles is the band at 466  $\text{cm}^{-1}$ , due to bending of Si–O–Si units.

387 The results of TGA carried out in nitrogen and air on bare epoxy resin and the four biochar-filled  
388 samples are shown in Figure S5a-d and summarized in Table S5. Comparing the  $T_{5\%}$  values, it can  
389 be seen that the decomposition in nitrogen tends to start at a lower temperature in the presence of  
390 biochar, possibly because the weak acidic character of the biochar favors the dehydration and charring  
391 of the matrix. On the other hand, in air, the resin containing Ch\_300-30 gives the highest  $T_{5\%}$  value,  
392 indicating a good thermo-oxidative stability in the initial decomposition stage. All profiles are  
393 characterized by a main decomposition step around 350 °C, which agrees well with the behavior of  
394 similar aliphatic epoxy systems described in the literature [53]. The composites show larger residual  
395 mass at 800 °C than the bare resin in both atmospheres, which is ascribed to the formation of a  
396 thermally resistant char that lowers the heat transfer coefficients, besides the contribution of the  
397 ceramic component of biochar. In pyrolytic conditions, the final residue of the composite embedding  
398 Ch\_300-30 is the highest (Table S5), indicating a considerably improved thermal stability, while in  
399 air, Ch\_350-10 provides the highest residual mass. The effectiveness of these two samples in  
400 enhancing the thermal behavior of the epoxy resin could be related to the balance between an

401 abundance of surface functional groups, which positively affect the interactions with the polymer  
402 matrix and may foster the charring, and a substantial inorganic fraction, which can provide both  
403 thermal shielding and char-promoting effects.

404 DSC analysis was performed on the epoxy-biochar composites and pristine resin to verify the curing  
405 and measure the glass transition temperature ( $T_g$ ). The absence of exothermic peaks associated with  
406 crosslinking reactions in the first heating ramp (see Figure S6a) indicates that the polymer network is  
407 completely cured, in agreement with the results from FTIR spectra. Figure S6b reports the DSC  
408 curves of the second heating ramp and the respective  $T_g$  values. The composites show  $T_g$  values close  
409 to that of the pristine resin (97 °C), suggesting that the addition of the biochar does not significantly  
410 alter the mobility of the polymer chains.

411 Based on the information gathered from the thermal analyses, Ch\_300-30 was selected among the  
412 biochar samples for further experimental study, as it appears to be the best candidate for improving  
413 the thermal and thermo-oxidative stability of the epoxy resin. In the following, the EC 300-30  
414 composite will be named “EC” for brevity, with “C” standing for the Ch\_300-30 biochar. A  
415 preliminary flammability test (UL-94 vertical burning test) was performed on EC, which, like the  
416 unfilled resin, resulted as non-classifiable. Therefore, the introduction of other additives into the  
417 matrix was investigated to suppress the flammability of the system.

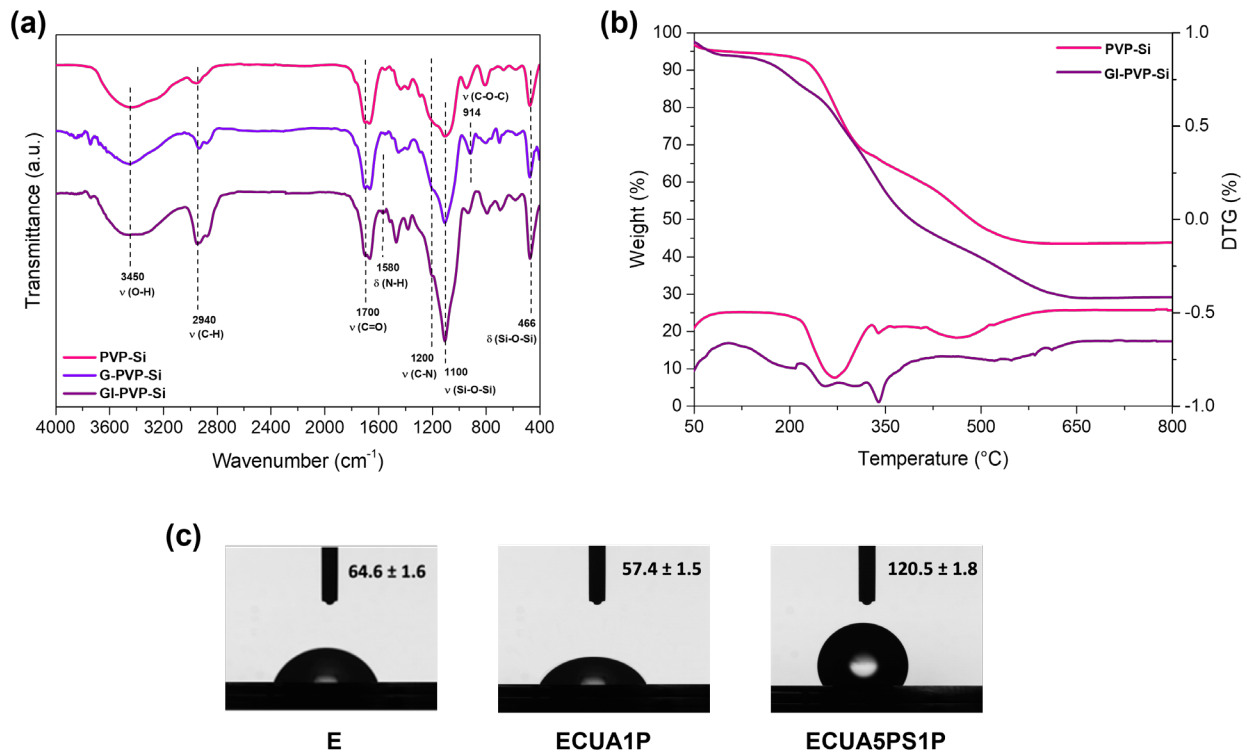
418

### 419 **3.3. Functionalization and characterization of PVP-silica filler**

420 Nonwoven mats of PVP-based electrospun fibers with a backbone of silica nanoparticles were  
421 previously shown to have multiple properties, namely low flammability, good sound absorption [18],  
422 and adsorption capacity toward organic dyes in water [54]. The excellent behavior of this material in  
423 vertical burning and smoke density tests was attributed to the high content of nanosized silica in the  
424 fibers. These results suggested the potential use of the hybrid fibers to prepare a filler that may reduce  
425 the flammability of epoxy resin in combination with HTL biochar.

426 To improve their dispersion and chemical affinity for the epoxy matrix, the PVP-Si fibers were  
427 functionalized first with GPTMS (G-PVP-Si) and then with the curing agent used for the resin, IPDA  
428 (GI-PVP-Si). The FTIR spectra of the samples before and after functionalization (Figure 4a) prove  
429 the successful linking of both molecules to the fibers. The spectrum of the PVP-Si fibers is  
430 characterized by a broad O–H stretching band (around 3446  $\text{cm}^{-1}$ ), due to the highly hydroxylated  
431 sol-gel-derived silica particles that fill the polymeric fibers, the stretching of the carbonyl group of  
432 PVP, at 1700  $\text{cm}^{-1}$ , and the asymmetric band related to Si–O–Si stretching, around 1100  $\text{cm}^{-1}$  [18].  
433 The condensation of GPTMS with the silanol groups of PVP-Si leads to an increase in intensity of  
434 the Si–O–Si stretching band, with respect to the C=O band, and to the appearance of the bands at 761

435 and 912  $\text{cm}^{-1}$  in G-PVP-Si, both related to the free epoxy rings of the silane. These latter decrease  
 436 after contact with IPDA, pointing to a ring-opening reaction by the amino groups. A contribution of  
 437 N–H stretching can also be seen in the GI-PVP-Si spectrum at about 3300  $\text{cm}^{-1}$ .  
 438



439  
 440 **Figure 4.** Characterization of PVP-Si filler: FTIR spectra of PVP-Si, G-PVP-Si, and GI-PVP-Si (a) and TGA  
 441 curves of PVP-Si and GI-PVP-Si recorded in air with the corresponding derivative TG curves (b). Water  
 442 contact angles ( $\theta$ ) of epoxy resin (E) and composite samples ECUA1P and ECUA5PS1P (c).  
 443

444 The effective functionalization is confirmed by comparing the TGA profiles of PVP-Si and GI-PVP-  
 445 Si (Figure 4b). The samples show a limited mass loss (5 wt.%) below 100  $^{\circ}\text{C}$ , due to the removal of  
 446 adsorbed water. The two mass loss steps of PVP-Si between 200 and 500  $^{\circ}\text{C}$  are associated with the  
 447 thermo-oxidative decomposition of PVP, along with the condensation and sintering of the silica  
 448 particles within the fibers [18]. The final residue of approximately 45 wt.% corresponds to the silica  
 449 content in the pristine material. The decomposition of GI-PVP-Si starts at a lower temperature (the  
 450  $T_{10\%}$  is 180  $^{\circ}\text{C}$  vs. 240  $^{\circ}\text{C}$  for PVP-Si), which can be attributed to the limited thermal stability of the  
 451 introduced organosilane chains, bonded with IPDA, and of residual methoxy groups of GPTMS [55];  
 452 it also stretches over a wider range, up to 600  $^{\circ}\text{C}$ . The difference in the thermal profile (also  
 453 highlighted by the derivative TG curves in Figure 4b) and overall mass loss (15 wt.% higher than that  
 454 of PVP-Si), related to the organic component of the sample, gives further evidence of the successful  
 455 linkage of GPTMS and IPDA on the surface of the electrospun fibers. The final  $\text{SiO}_2$  content in GI-  
 456 PVP-Si can be estimated as 30 wt.%.

457 The SEM images (Figure 1) of the original PVP-Si fibers and GI-PVP-Si powders obtained by milling  
458 after the functionalization show a clear change in morphology. The electrospun material is a network  
459 of long randomly oriented fibers, while the latter sample mainly consists of particles with a  
460 morphology that can be described as rods (some of them slightly bent) or whiskers. Their mean  
461 diameter is  $(1.8 \pm 0.6) \mu\text{m}$ , while their length varies in a relatively large range, with a mean of  $(7 \pm$   
462  $3) \mu\text{m}$ . Some heterogeneous particle aggregates can also be seen. The functionalization induced some  
463 segments of the fibers to crosslink, as sketched in Figure 1, and increased their rigidity, facilitating  
464 their reduction into small particles. Indeed, the PVP-Si mats are soft and porous and tend to be  
465 compressed rather than fragmented under ball milling, while dried GI-PVP-Si samples were easily  
466 turned into a powder. GI-PVP-Si samples have a better affinity to the cured epoxy resin, resulting  
467 from the bonding of IPDA, compared to the hydrophilic untreated fibers. Owing to the size reduction  
468 (high interfacial surface area) and chemical compatibilization, the dispersion of the silica-based filler  
469 in the epoxy matrix was significantly improved, as can be seen from pictures of composites obtained  
470 by adding either PVP-Si fibers or GI-PVP-Si powders (Figure S7).

471 The whisker-like particles maintain a partially acidic character due to the hydroxyl-rich silica  
472 structure, which can promote the dehydration and carbonization of the polymer matrix and the  
473 formation of a stable ceramic char residue during combustion [56]. It is worth noting that the proposed  
474 treatment could be applied either to PVP-Si composite blankets recovered after their use or to small  
475 scraps derived from the electrospinning process for the manufacturing of the fibrous material.

476

### 477 **3.4. Surface wettability of epoxy composites**

478 To evaluate the wettability of the epoxy formulations and the influence of additives on their surface  
479 characteristics, the static water contact angle ( $\theta$ ) was measured on representative samples. A surface  
480 can be categorized as hydrophilic ( $\theta < 90^\circ$ ) or hydrophobic ( $\theta > 90^\circ$ ), while extremely hydrophobic  
481 surfaces provide a water contact angle  $\geq 150^\circ$  [57]. As it is possible to observe in Figure 4c, the epoxy  
482 resin and ECUA1P composite (containing biochar, urea, and APP) have a hydrophilic surface. The  
483 incorporation of PVP-Si whiskers into ECUA5PS1P causes a large increase in the water contact  
484 angle, meaning a lower wettability for the composite surface. While APP, urea, and biochar have a  
485 hydrophilic chemical nature, PVP-Si whiskers show a more hydrophobic character, due to the  
486 functionalization with IPDA (Figure 1). However, the surface of these whiskers is not fully coated by  
487 IPDA (see section 3.3); therefore, they are still characterized by residual polar moieties (i.e., hydroxyl  
488 groups), possibly driving the migration of some silica-based microparticles at the interface with air  
489 [46]. The functionalization with IPDA provides the PVP-Si whiskers with hydrophobic features,  
490 while their inherent fibrous morphology is responsible for the formation of a slightly rougher surface

491 for ECUA5PS1P compared to that of E. Finally, the wettability of the composite surface seems to be  
492 affected by the exposure of the well-tailored whiskers, conferring both chemical and morphological  
493 contributions to the higher hydrophobicity of ECUA5PS1P, with respect to pristine resin and  
494 ECUA1P (Figure 4c) [58]. These hydrophobic features of ECUA5PS1P enable its potential  
495 application as waterproof membranes or protective coatings for building materials.

496

### 497 **3.5. Flammability, thermal and fire behavior of epoxy composites**

498 Epoxy composites were prepared using the selected biochar (Ch\_300-30, 10 wt.%) and the GI-PVP-  
499 Si whisker particles. UL-94 vertical burning tests were performed on pristine resin and the epoxy  
500 composites listed in Table S6 to investigate their flammability behavior. The unfilled epoxy system  
501 could not be classified because the specimen captured the flame after the first application of the  
502 Bunsen burner and burned completely, dripping as it burned. Similarly to E, it was not possible to  
503 classify the formulations containing only HTL-derived biochar or PVP-Si particles, though these  
504 latter did not drip during combustion. However, EC5PS shows lower flammability compared to E,  
505 EC, and E5PS, probably ascribed to the combined char-forming character of additives causing the  
506 formation of a carbonaceous material able to act as an effective barrier toward the release of  
507 flammable gases [33,49,59]. Then, small amounts of urea (2 wt.%) and APP (3 wt.%) were also added  
508 to the epoxy systems. Looking at EUA5PS1P, urea and APP promote a decrease in the  $t_1$  after-flame  
509 times (Table S6), due to the flame retardant action of these compounds during the early combustion  
510 stages and along the burning process. Particularly, the decomposition of APP generates acid  
511 phosphorus compounds promoting the dehydration of the polymer matrix and the consequent char  
512 formation, while the degradation of urea mainly produces nitrogen, exerting a dilution effect in the  
513 gas phase [60].

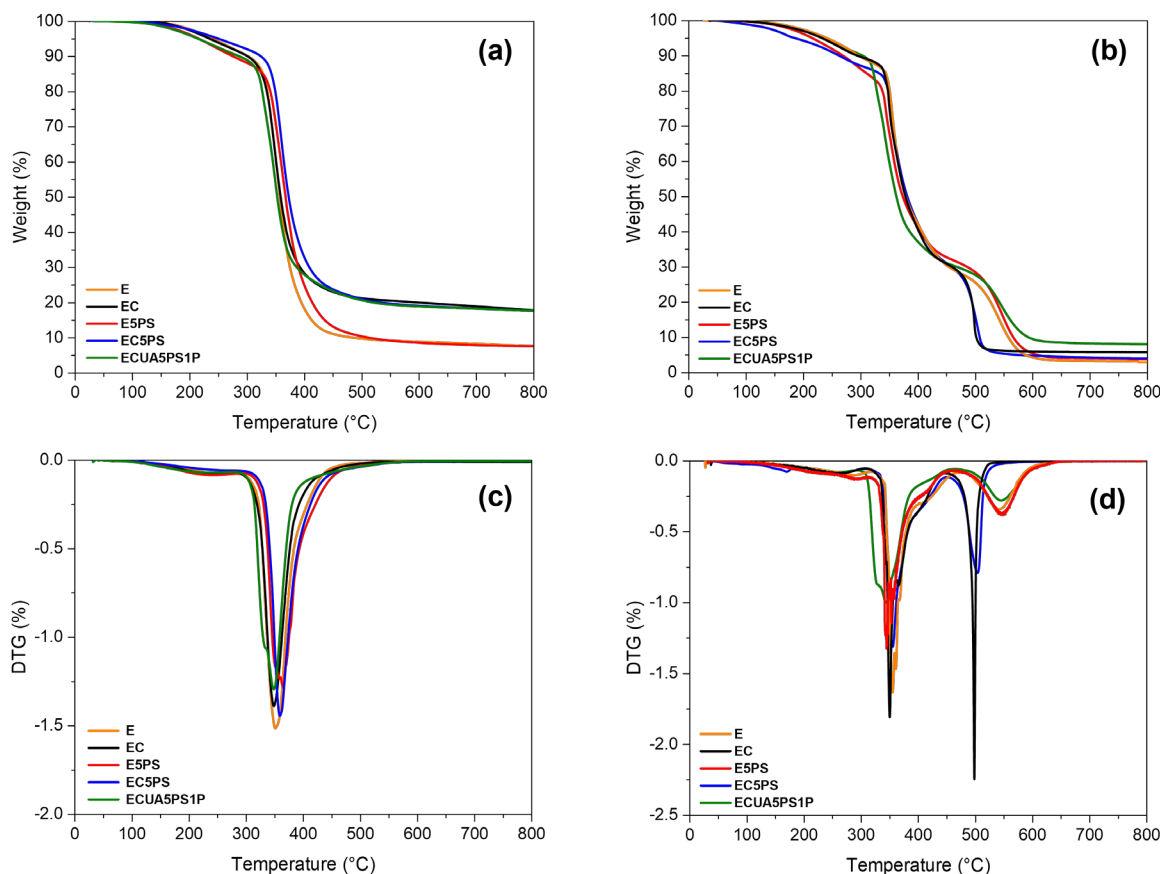
514 The addition of the biochar into EUA5PS1P sample allows for obtaining a formulation that exhibits  
515 no dripping V0 rating (Table S6 and Table 2), even at a very low P loading (i.e., 1 wt.%), due to a  
516 synergistic condensed phase action of the waste-derived material with the other additives during the  
517 combustion [61]. Concerning ECUA5PS1P, the use of biochar and a specific amount (i.e., 5 wt.%)  
518 of PVP-Si particles, together with urea and APP, is fundamental to significantly reduce the after-  
519 flame times along the whole test and give rise to a residual char with a coherent and continuous  
520 structure (Table S6). The flame retardant effectiveness of urea arises from its multifunctional role as  
521 a heat sink, gas-phase diluent, and char-forming synergist, particularly when used in combination  
522 with APP and carbonaceous fillers. It is reported that this synergistic behavior enhances flame  
523 retardancy without significantly compromising the processing or mechanical performance of the  
524 polymer composite [42,62].

525 Since the whiskers mainly consist of silica nanoparticles, their decomposition generates refractory  
526 material at the surface (see section 3.3), while their slightly acidic nature boosts the dehydration of  
527 the epoxy matrix to produce a large amount of ceramic char. Unlike the biochar obtained at higher  
528 temperature (350 °C), the one used for the preparation of ECUA5PS1P exhibits more hydroxylated  
529 surface and thus can promote the occurrence of charring processes. These flame retardant  
530 mechanisms, taking place during the combustion of the self-extinguishing sample (ECUA5PS1P),  
531 cause an increase in the melt viscosity of the burning system and the generation of a stable char, rich  
532 of silicon-based species (see section 3.5), acting as an oxygen barrier and thermal shield for the  
533 underlying polymer [63].

534 In view of the outcomes related to the flammability tests, only the thermal properties, mechanical  
535 response, and fire behavior of the self-extinguishing system and some other counterparts (E, EC,  
536 E5PS, and EC5PS) will be discussed to show the influence of each component on the performance of  
537 the final product. LOI measurements were carried out on the above-selected samples (E, EC, E5PS,  
538 EC5PS, and ECUA5PS1P) and ECUA3PS1P to evaluate the minimum percentage of oxygen needed  
539 to sustain the candle-like combustion after ignition in an O<sub>2</sub>/N<sub>2</sub> mixture. Table S7 shows that the right  
540 amount and concurrent presence of PVP-Si whiskers, biochar, urea, and APP effectively slow down  
541 the candle-like combustion. The highest value of LOI is observed for ECUA5PS1P, surpassing  
542 ECUA3PS1P, which could only achieve V1 rating in UL-94 vertical burning tests, thus confirming  
543 that a certain content of GI-PVP-Si is important for enhancing the flame retardant behavior. These  
544 results well agree with the outcomes of the UL-94 vertical flame spread tests.

545 The thermal decomposition profiles of pristine epoxy and epoxy composites are reported in Figures  
546 5a-d. All the samples exhibit the main decomposition step at ~350 °C. The presence of hydroxyls and  
547 other oxygen-containing functional groups on the surface of PVP-Si whiskers and HTL-derived  
548 biochar particles confers acidic characteristics. These chemical features favor the carbonization  
549 process through the dehydration of epoxy resin [64–66], resulting in an anticipated mass loss (see T<sub>5%</sub>  
550 in Table S8) for EC and E5PS compared to E. This effect is particularly evident in the case of EC, as  
551 the use of biochar particles also leads to an increase (10 wt.%) in the residual mass at 800 °C,  
552 compared to the counterpart resulting from the pyrolytic decomposition of the pristine system (Table  
553 S8). On the other hand, PVP-Si whiskers have a slightly weaker effect on the carbonization process  
554 because the PVP film covers the silica nanoparticles and their surface hydroxyl groups. [54].  
555 However, the pyrolysis of PVP-Si whiskers contributes forming an abundant ceramic char when the  
556 microstructures are employed in combination with biochar particles. Indeed, EC5PS shows very good  
557 thermal stability, as both its T<sub>5%</sub> and residual mass at 800 °C are higher than those of E (Table S8).  
558 The addition of APP and urea into EC5PS does not affect the residue but causes an anticipation of

559  $T_{5\%}$ , probably ascribed to their decomposition that releases acidic phosphorus compounds and non-  
560 flammable volatiles (i.e.,  $N_2$  and phosphorus species) [33,62].  
561



562  
563 **Figure 5.** TGA curves (a, b) and DTG curves (c, d) of pristine resin and epoxy composites recorded under  $N_2$   
564 (a, c) and air (b, d).  
565

566 Figures 5b,d show the thermogravimetric data collected in air. Looking at EC, the results confirm the  
567 char-forming behavior of the biochar particles, which allows for a higher (6 wt.%) residual mass  
568 compared to the one (3 wt.%) of E (Table S8). The presence of metal species in the waste-derived  
569 biochar additionally boosts the charring phenomena taking place during the combustion of  
570 composites containing such an additive [52]. The good thermo-oxidative stability of ECUA5PS1P  
571 rises from the combined use of APP, urea, PVP-Si whiskers, and biochar particles. The additives  
572 enable a significant increase in  $T_{max2}$ , which means that the heat exchange at the boundary phase  
573 between the gas phase and the polymer bulk is limited, and the highest residual mass is produced at  
574 800 °C (Table S8). This effect on the thermo-oxidative stability of ECUA5PS1P may be due not only  
575 to the char-forming character of the biochar particles and acidic phosphorus compounds, but also to  
576 other mechanisms taking place during the combustion, namely: (i) the decomposition of APP and  
577 urea in air forms nitrogen able to disrupt the diffusion of oxygen; (ii) the degradation of PVP-Si

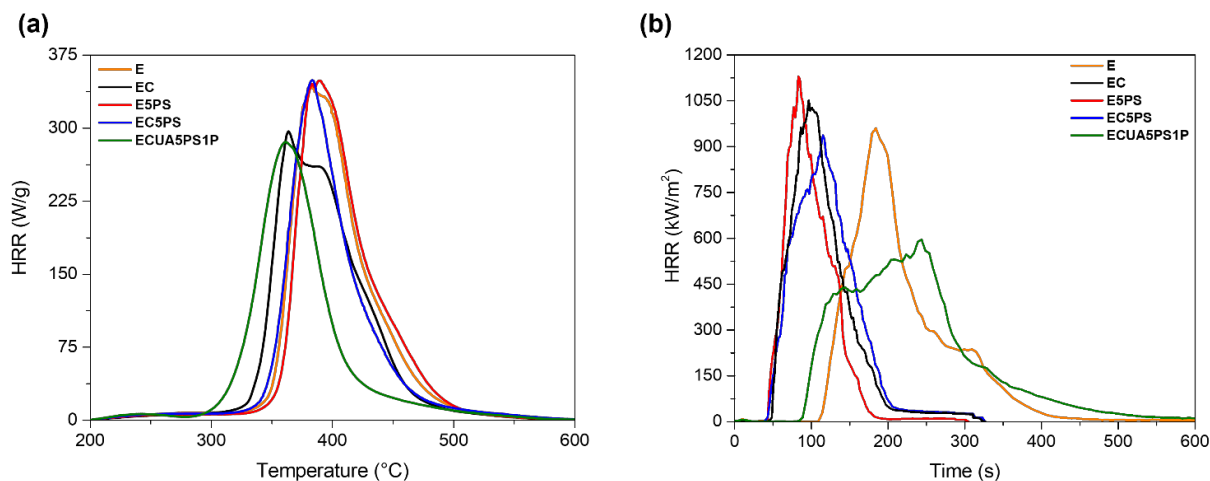
578 whiskers produces a huge amount of refractory silica nanoparticles, which promote the generation of  
579 a stable aromatic char able to prevent the diffusion of flammable gases and oxygen from the  
580 surroundings into the material, and act as effective thermal shield and barrier [67,68].

581 Figures S8a,b displays the DSC curves of the unfilled resin and epoxy composites. It is possible to  
582 observe that the first heating ramp does not show any presence of residual exothermic peak,  
583 confirming the completeness of the curing process for all the investigated samples in the adopted  
584 experimental conditions. These results agree with the outcomes of FTIR analyses. Overall, Figure  
585 S8b reveals that the glass transition temperatures of all systems are not significantly changed  
586 compared to that of the pure epoxy resin.

587 PCFC measurements prove that the inclusion of the HTL-derived biochar into the epoxy resin causes  
588 the most significant increase in the residual char (Table S9, Figure 6a). The biochar has a crucial role  
589 in the condensed phase; indeed, as mentioned above, it acts as a char-former, thanks to the hydroxyl  
590 groups present on its surface, and slows down the oxidative degradation of the polymer matrix [33].  
591 As attested by the significant decrease in pHRR (13%), HRC (13%), and THR values (19%)  
592 compared to the pristine resin (Table S9), PCFC tests performed on ECUA5PS1P highlight that the  
593 biochar, in synergy with GI-PVP-Si whisker particles, APP, and urea, limits the oxygen diffusion and  
594 thus affects the heat release parameters [69,70]. Finally, the highest residue recorded for  
595 ECUA5PS1P, together with the anticipation of the initial decomposition stage at a very low  
596 temperature, with respect to the unfilled systems as benchmark (Table S9, Figure 6a), clearly suggest  
597 a strong condensed phase action of all the additives.

598 Figure 6b and Table 2 show the results from the cone calorimetry tests. The data confirm the char-  
599 forming character and dehydrating effect exerted by the GI-PVP-Si whisker particles and biochar  
600 during the burning, as all the epoxy formulations containing both fillers, even alone, give lower TTI  
601 and higher residues with respect to the pristine resin. While the weak acidic nature of these fillers is  
602 mainly responsible for an anticipated ignition, the ceramic component of whisker particles and the  
603 high thermal stability of the biochar favour the formation of higher amounts of residual char, due to  
604 the thermal barrier action slowing down the heat exchange and the oxygen diffusion at the boundary  
605 phase (Table 2) [71,72].

606



607

608 **Figure 6.** HRR vs. time of pristine resin and epoxy composites measured by PCFC (a) and cone calorimetry  
 609 tests (b).

610

611 **Table 2.** Results obtained from cone calorimetry and UL-94 vertical burning tests for the investigated epoxy  
 612 systems.

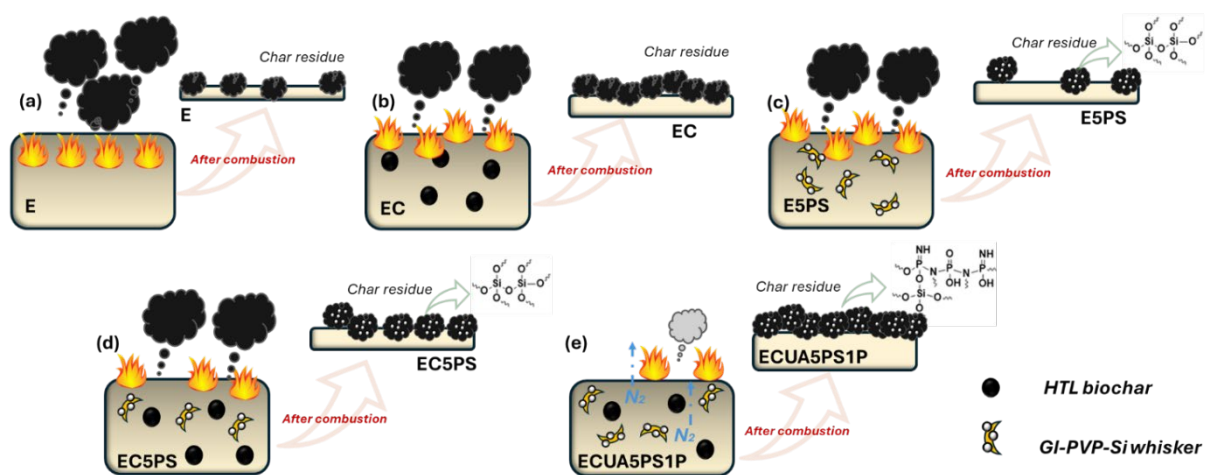
Sample	TTI (s)	THR (MJ/m <sup>2</sup> )	ΔTHR (%)	pHRR (kW/m <sup>2</sup> )	ΔpHRR (%)	Residue (wt.%)	TSR (m <sup>2</sup> /m <sup>2</sup> )	ΔTSR (%)	UL-94/dripping
E	109 ± 2	106 ± 9	-	961 ± 101	-	3 ± 0.1	3432 ± 33	-	NC/yes
EC	45 ± 1	82 ± 1	-23	1051 ± 95	+9	8 ± 0.1	3789 ± 17	+10	NC/no
E5PS	42 ± 15	71 ± 13	-33	1131 ± 97	+17	6 ± 0.2	3043 ± 96	-11	NC/no
EC5PS	42 ± 8	85 ± 1	-19	937 ± 141	-2	10 ± 1	3595 ± 27	+5	NC/no
ECUA5PS1P	80 ± 11	109 ± 7	+2	619 ± 61	-36	11 ± 1	3083 ± 56	-10	V0/no

613 **TTI** = Time To Ignition, **TTFO** = Time To Flame Out, **THR** = Total Heat Release, **HRR** = Heat Release  
 614 Rate, **pHRR** = peak Heat Release Rate, **TSR** = Total Smoke Release

615

616 Looking at Figure 6b, E5PS shows the sharpest curve with the highest pHRR, which is probably  
 617 ascribed to the non-charring and highly flammable PVP. The addition of the biochar into E5PS  
 618 mitigates such an effect on the heat release rate, limiting the heating diffusion along the epoxy matrix.  
 619 The incorporation of APP and urea into EC5PS results in a broadening of the heat release rate curve,  
 620 revealing a slower heat release over a longer timespan for ECUA5PS1P compared to the blank epoxy  
 621 (Figure 6b). The endothermic decomposition of APP and urea causes the release of phosphorus  
 622 radicals and nitrogen, resulting in higher TTI value for ECUA5PS1P than EC, E5PS, and EC5PS.  
 623 The phosphorus radicals poison the oxygen radicals in the flame (i.e., acting as radical scavengers),  
 624 while nitrogen dilutes the flammable volatiles in the gas phase [73]. Urea decomposes under heat  
 625 releasing nitrogen, which reduces the oxygen concentration in the atmosphere surrounding the  
 626 polymer bulk, thus decreasing the amount of species sustaining the flame. Moreover, nitrogen can  
 627 absorb part of the heat radiation, lowering the temperature of the gas phase and thus inhibiting the  
 628 production of flammable species by thermal feedback. The combination of nitrogen dilution and

629 reduced oxygen availability in the gas phase contributes to the self-extinguishing behavior of  
 630 ECUA5PS1P and the lowest value of pHRR, which is 36% lower than that of E (Table 2).  
 631 The decomposition of APP generates acidic phosphorus compounds, which enhance the charring of  
 632 the polymer matrix during combustion. This contributes to the condensed phase action of the GI-  
 633 PVP-Si whisker particles and the biochar, giving rise to the formation of a stable char able to adsorb  
 634 gases (e.g., phenol, cresol, carbon dioxide, naphthalene, anthracene, among others) and limit the  
 635 emission of volatile acid compounds. This may explain the lowest values of TSR and SEA collected  
 636 for ECUA5PS1P, which are up to 18% lower than those of E (Table 2 and Table S10). Finally, it is  
 637 worth mentioning that the presence of metallic species in the HTL-derived biochar (Table S2) may  
 638 catalyze the charring of the organic polymer matrix, well supporting the higher amounts of residual  
 639 char formed after the burning of EC, EC5PS, and ECUA5PS1P, with respect to the other formulations  
 640 (Table 2). In many applications of HTL-derived biochar (e.g., wastewater treatment), metallic  
 641 impurities can have a negative impact on the process and raise pollution concerns. In this case,  
 642 however, these impurities are a functional component. [74]. In view of the above results, a simplified  
 643 flame retardant mechanism is proposed (Figure 7), which illustrates the phenomena occurring along  
 644 the combustion of all the prepared formulations.



645  
 646 **Figure 7.** Proposed condensed phase mechanism of epoxy composites in oxygen atmosphere. (a) E, (b) EC,  
 647 (c) E5PS, (d) EC5PS, (e) ECUA5PS1P. The advanced stage of the decomposition of the polymer matrix is  
 648 illustrated in the dark yellow region. The chemical structures describe the polymeric substructures formed in  
 649 the respective carbonaceous residue surface.

650  
 651 To explore more deeply in the condensed phase, SEM-EDX measurements (Figure S9 and Table S11)  
 652 were performed on residual chars to highlight the differences in terms of chemical composition and  
 653 morphologies among the burned materials derived from the pristine system and its composites after  
 654 UL-94 vertical flame spread tests. Figure S9 shows that the residual char of E is characterized by  
 655 some small holes and thin cracks that facilitate the release of flammable volatiles to the gas phase

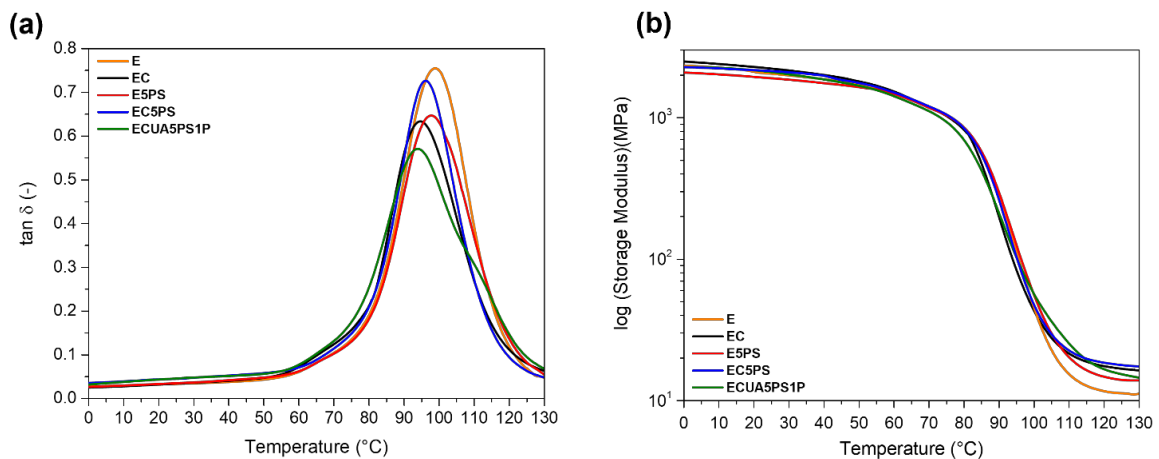
656 during the combustion (Figure 7a). The addition of biochar into the epoxy matrix (EC) causes the  
657 formation of a jagged continuous char (Figure S9), limiting heat and mass transfer thanks to its  
658 tortuous morphology (Figure 7b). Compared to the one generated from E, the residual char obtained  
659 from the combustion of E5PS appears more compact and coherent, although several holes are present.  
660 The compactness may be ascribed to the whisker particles giving rise to a ceramic char with silica  
661 substructures (Si–O–Si, Figure 7c, Table S11). On the other side, the presence of PVP in the matrix  
662 causes the generation of bubbles, made of flammable gases, which hinder the formation of a  
663 continuous char, well supporting the poor fire behavior of E5PS [17]. The incorporation of GI-PVP-  
664 Si whisker particles into EC (EC5PS) provides compactness to the char of EC, and thus the  
665 carbonaceous residue appears free of cracks and holes, confirming the crucial role of the HTL-derived  
666 biochar in the condensed phase, especially in synergy with the inorganic filler (Figures S9 and 7d).  
667 The combined use of whisker particles, biochar, APP, and urea accounts for the formation of a slightly  
668 intumescent and swollen multicellular char characterized by the presence of P–N–O–Si–O–P  
669 polymeric substructures (Figures S9 and 7e) on the surface, as confirmed by the high retentions of P  
670 and N (Table S11). The decomposition of urea releases  $\text{NH}_3$  that reacts with polyphosphoric acids to  
671 give P–N–O substructures (e.g., phosphorus oxynitride) [75], which can consequently condense with  
672 the silanol groups of Si–O–Si and P–O–Si polymeric species to generate a thermally stable residue  
673 [76]. This char works as an effective thermal shield and oxygen barrier at the boundary layer and is  
674 responsible for a delayed ignition (Table 2), compared to the other epoxy systems, and the excellent  
675 performances in the UL-94 (V0 class flammability without any dripping) and cone calorimetry tests.  
676 This strong condensed phase mechanism, in which the biochar plays a key role, may be enhanced by  
677 a slight gas phase action through active radical scavenging and dilution. Overall, each component  
678 exerts its crucial function into a clear synergistic chain enabling the construction of a dense, stable,  
679 intumescent ceramic-like char layer rich in P–N–O–Si hybrid structures, protecting the underlying  
680 polymer, and a side slight gas phase activity. PVP-Si whisker particles act as a silicon source and  
681 initial charring catalysts, while the biochar contributes giving carbon skeleton to the final thermally  
682 stable char and metal catalytic sites, promoting char-forming reactions. Simultaneously, the  
683 decomposition of APP generates: (i) polyphosphoric acids able to dehydrate the polymer matrix, (ii)  
684 ammonia as source of nitrogen (diluting the combustible volatiles in the gas phase) and former  
685 component for phosphorus oxynitrides, (ii) phosphorus radicals ( $\text{PO}^{\bullet}$  or  $\text{HPO}^{\bullet}$ ) working as inhibitors  
686 for oxygen radicals in the gas phase, as observed in previous research studies by gas evolved analysis  
687 [42,77]. Finally, as already stated above, urea synergizes the release of nitrogen and promotes  
688 physical crosslinking by forming, together with APP, a strong intersegmental hydrogen-bonded  
689 network with the epoxy resin.

690 Despite the use of an aliphatic amine as hardener (i.e., IPDA), the application of a well-designed  
691 strategy exploiting phosphorus flame retardants, nitrogen additives, and a waste-derived biochar can  
692 be a promising methodology to obtain sustainable self-extinguishing epoxy composites, even with  
693 only 1 wt.% of P in the polymer matrix. Considering the outcomes related to flammability and fire  
694 behavior, it appears clear that whisker-like particles based on tailored electrospun PVP-coated silica  
695 fibers represent the tip of the balance in the proposed flame retardant strategy. This innovative  
696 synergist, which can be easily obtained by electrospinning, without any issue linked to optimization  
697 of yield, and by using inexpensive PVP, is able to exert a strong charring effect, while providing a  
698 ceramic barrier during the burning.

### 699 **3.6. Dynamic-mechanical behavior and mechanical properties of epoxy composites**

700 DMA was performed to evaluate the viscoelastic response as a function of temperature of E and  
701 epoxy composites. The glass transition temperatures of the samples were taken from the maximum  
702 values of  $\tan \delta$  curves (Figure 8a). The blank epoxy shows a symmetric and narrow  $\tan \delta$  curve with  
703 the highest  $\tan \delta$  peak (at 99 °C), revealing that E can easily dissipate the application of a load by  
704 energy dissipation mechanisms (e.g., segmental motions) [78]. The incorporation of the HTL-derived  
705 biochar into the epoxy matrix (EC) leads to a material exhibiting an asymmetric and wider  $\tan \delta$  curve,  
706 due to a broad distribution of relaxation phenomena (Figure 8a) [33,64]. Biochar particles insert  
707 between polymer chains, shield intermolecular interactions, increase free volume, and unequivocally  
708 lower the  $T_g$ . The presence of such particles causes a plasticizing effect in the epoxy network, giving  
709 rise to a slight decrease (~4%) in the  $T_g$  and a material less able to dissipate energy. This effect on  
710 the viscoelastic behavior is also evident in E5PS, probably ascribed to the increase of filler-matrix  
711 interface defects [54]. Despite the hydroxyl groups on the surface of whiskers (see section 3.3 and  
712 Figure 4a), the compatibilization of these microstructures by IPDA makes it possible for their good  
713 dispersion throughout the polymer matrix, which explains the  $T_g$  of E5PS that is almost the same as  
714 E. The combined use of GI-PVP-Si and biochar (EC5PS) allows for the synthesis of a material giving  
715 a symmetric and narrow  $\tan \delta$  curve, with a  $T_g$  (96 °C) that is practically unvaried compared to E  
716 (Figure 8a). On the other side, the addition of urea and APP into EC5PS triggers again relaxation  
717 phenomena and the generation of two co-continuous phases with different chain mobilities in the  
718 polymer matrix. As reported in the literature, urea and APP can form a strong intersegmental  
719 hydrogen-bonded network with epoxy resin systems [42,79]. These intersegmental interactions,  
720 together with the establishment of hydrogen bonds between the oxygen-containing functional groups  
721 on the surface of both the biochar particles and the PVP-Si filler (see section 3.3) with the hydroxyls  
722 originated by the crosslinking process appear to lead to a second  $T_g$  (Figure 8a) [54], which is higher  
723 than that of E; thus, ECUA5PS1P displays a  $\tan \delta$  curve with a maximum located at 94 °C ( $T_{g1}$ ) and

724 a shoulder at 112 °C ( $T_{g2}$ ), as confirmed by the good curve fitting obtained with two overlapped peaks  
 725 (Figure S10). Hydrogen bonding, as a strong secondary interaction, typically acts as a physical  
 726 crosslink, restricting polymer chain segment mobility and thus tending to increase the  $T_g$  [80]. The  
 727 coexistence of these hydrogen-bond-rich, interfacial domains with the bulk matrix introduces  
 728 dynamic and structural heterogeneity within the composite, reflecting the presence of polymer  
 729 segments experiencing different degrees of mobility and constraint, which lead to the formation of  
 730 phases characterized by distinct relaxation dynamics compared to the bulk epoxy network [42,81].  
 731 Despite hydrogen bonding, the interface between the rigid biochar particles and the epoxy matrix may  
 732 be imperfect (e.g., interfacial voids, stress concentration). These defects can act as initiation sites for  
 733 early relaxation during thermomechanical scanning, manifesting as  $T_g$  peak broadening and a slight  
 734 peak temperature decrease. The introduction of free volume by the filler is another possibility;  
 735 irregularly shaped filler particles may disrupt the close packing of polymer chains, introducing extra  
 736 free volume at the interface, thereby facilitating chain segment relaxation.  
 737



738  
 739 **Figure 8.** Mechanical damping factor ( $\tan \delta$ ) (a) and storage moduli ( $E'$ ) (b) of pristine resin and epoxy  
 740 composites, collected as a function of temperature.

741  
 742 The hydrophilic character of PVP-Si particles (see section 3.3), composed of porous fibers embedded  
 743 with sol-gel silica nanoparticles full of hydroxyl groups in their backbone, disturbs the dipole-dipole  
 744 intra- and inter-macromolecular interactions between the epoxy chains: for this reason, E5PS shows  
 745 the lowest value of storage modulus ( $E'$ ) in the glassy state region (Figure 8b), compared to the  
 746 pristine system and the other composites [82,83]. Considering the other samples, the less hydrophilic  
 747 nature of biochar and the hindering action of additives cause a stiffening effect on the polymer  
 748 network, resulting in  $E'$  values that approach those of E. To conclude, the simultaneous use of PVP-  
 749 Si and biochar is crucial to obtain final composites with very low flammability as well as good  
 750 dynamic-mechanical behavior.

751 To shed light on the effect of the selected fillers on the mechanical properties of epoxy resin, the  
 752 flexural behavior of E, EC, E5PS, EC5PS, and ECUA5PS1P was evaluated (Table 3). The presence  
 753 of oxygen-containing functional groups on the surface of char particles negatively affects the flexural  
 754 response of EC, as it exhibits lower modulus ( $E_B$ ), fracture strength ( $\sigma_{u,B}$ ), and elongation at break  
 755 ( $\epsilon_{f,B}$ ) compared to the pristine resin. While the use of char particles alone is detrimental because of  
 756 their polar character, the incorporation of compatibilized PVP-Si whiskers alone (E5PS) in the epoxy  
 757 system leads to an improvement of the flexural modulus, with respect to EC and E (Table 3) [33,84].  
 758 This result may be ascribed to the good distribution of the microstructures in the epoxy matrix and  
 759 their interaction with the crosslinked polymer chains. However, the introduction of the other additives  
 760 into the resin (ECUA5PS1P) causes a decrease in the motion of the chain segments and consequently  
 761 the formation of topological constraints, which result in a stiffer network (Table 3), well supporting  
 762 the hinderance phenomena observed from DMA measurements [85,86]. In view of that, despite the  
 763 beneficial effect of the functionalized PVP-Si whiskers on the flexural modulus of epoxy resin,  
 764 ECUA5PS1P is characterized by lower  $E_B$ ,  $\sigma_{u,B}$ , and  $\epsilon_{f,B}$  values than E5PS. Thus, the self-  
 765 extinguishing material appears less ductile and more brittle.

766  
 767 **Table 3.** Flexural test results of pristine resin and epoxy composites for comparison.

Sample	Flexural Modulus (MPa)	Fracture strength (MPa)	Strain at break (%)
E	4345 ± 65	144 ± 8	3.9 ± 0.1
EC	4148 ± 26	33 ± 3	0.8 ± 0.3
E5PS	5251 ± 41	40 ± 5	0.7 ± 0.2
EC5PS	4550 ± 53	51 ± 3	1.1 ± 0.1
ECUA5PS1P	4540 ± 76	30 ± 4	0.7 ± 0.2

768  
 769 The decrease in toughness can be attributed to the combined effects of stiffening of the polymer  
 770 matrix, a restricted plastic deformation, and a stress concentration induced by the additives. The  
 771 incorporation of rigid fillers and flame retardant components (such as APP, biochar, and PVP-Si  
 772 whiskers) increases the elastic modulus of the epoxy matrix, which limits energy dissipation through  
 773 plastic deformation under applied stress. Indeed, ECUA5PS1P shows higher  $E_B$  compared to blank  
 774 epoxy, but lower  $\sigma_{u,B}$  and  $\epsilon_{f,B}$  values than pristine system (see Table 3). Also, imperfect filler-matrix  
 775 interfacial adhesion and particle agglomeration can introduce stress concentration sites, facilitating  
 776 crack initiation and accelerating crack propagation [87,88]. Moreover, the formation of hydrogen-  
 777 bonded or highly crosslinked interfacial regions reduces chain mobility, further suppressing  
 778 toughening mechanisms such as shear yielding. Collectively, these factors reduce the capability of

779 ECUA5PS1P in absorbing and dissipating mechanical energy, resulting in a significant decrease in  
780 toughness.

781 Overall, the above outcomes highlight the strong potential of the developed epoxy composites for  
782 multifunctional integration, as good performances of fire safety, moisture/water resistance, and  
783 mechanical behavior can be simultaneously satisfied. The achievement of V0 rating in UL-94 flame  
784 spread tests, combined with a highly hydrophobic surface (with water contact angle  $\sim 120^\circ$ ), and good  
785 thermomechanical properties, demonstrates that the synergistic incorporation of APP, urea, biochar,  
786 and PVP-Si whiskers enables functionalities that are often difficult to design within a single material  
787 system. Such a combination of properties makes these materials particularly attractive for applications  
788 requiring integrated fire resistance, environmental durability, and lightweight construction, including  
789 transportation interiors (e.g., rail, aerospace, and automotive components), electronic device  
790 encapsulation, housing exposed to thermal and humidity stresses, and protective or insulating  
791 components for energy storage and power management systems.

792

#### 793 **4. Conclusions**

794 This study presents a novel waste-to-wealth approach for valorizing the solid residue produced by  
795 HTL of sewage sludge, employing it as a functional additive in epoxy-based composites. The HTL-  
796 derived biochar, characterized by high inorganic content and a hydroxyl-rich surface, can effectively  
797 interact with the epoxy matrix. Among the four different biochar samples evaluated, one was  
798 identified as particularly suitable for flame retardant applications (biochar obtained at 300 °C and 30  
799 min), due to its ability to confer enhanced thermal stability to the resin, without adversely affecting  
800 its viscoelastic properties, even at a significant loading of 10 wt.%. However, the integration of other  
801 additives into the polymer matrix was needed to provide the composites with self-extinction. To this  
802 aim, PVP-coated silica fibers produced by electrospinning were reduced to powder and functionalized  
803 to obtain whisker-like microparticles that were uniformly dispersed in the epoxy resin. The  
804 combination of these tailored silica-based particles with biochar, along with small amounts of urea  
805 and APP, resulted in composites that attained a V0 rating in UL-94 vertical flame spread tests, even  
806 with only 1 wt.% of P loading. Compared to the pristine epoxy system, final composites showed a  
807 notable reduction in the peak of heat release rate and in the total smoke release,  $\sim 36\%$  and  $\sim 10\%$ ,  
808 respectively.

809 These enhanced flame retardant properties can be attributed to the effects among the additives during  
810 combustion. Thanks to their surface acidity, both biochar and PVP-coated silica fibers synergistically  
811 promote the dehydration of the polymer matrix and the formation of a continuous and stable ceramic-  
812 like char layer, effectively hindering the diffusion of heat, oxygen, and smoke. Simultaneously, urea

813 and APP provide a moderate gas phase effect through the release of nitrogen and phosphorus species,  
814 quenching oxygen radicals in the flame. Importantly, the resulting composites retain mechanical and  
815 thermal integrity, with glass transition temperature and flexural modulus remaining nearly unchanged  
816 with respect to the pristine resin. However, the presence of fillers negatively affects both the flexural  
817 strength and the strain at break of final composites. In addition, the incorporation of functionalized  
818 silica whiskers imparts surface hydrophobicity (with contact angles up to  $\sim 120^\circ$ ) to the material,  
819 suggesting potential use in multifunctional applications requiring both fire and water resistance. The  
820 proposed composite formulation may represent a promising platform for the design of next-  
821 generation multifunctional polymer materials tailored to demanding safety-critical applications.  
822 Overall, this work demonstrates the feasibility of a dual waste valorization pathway in which sewage  
823 sludge can be used as both a feedstock for biocrude production and a source of valuable solid co-  
824 products. The unique physicochemical properties of HTL-derived biochar offer new possibilities for  
825 the development of sustainable materials. Future research could investigate how different sewage  
826 sludge sources influence biochar functionality, as well as exploring additional applications such as  
827 environmental remediation through the removal of water contaminants. Defining utilization options  
828 for this solid product prevents its landfilling or incineration, enables medium-term carbon  
829 sequestration and improves resource cycling, with consequent environmental as well as economic  
830 benefits. It is envisaged that the integration of such model of co-product management in the HTL  
831 process would ultimately promote its implementation in biorefineries.

832

### 833 **CRedit authorship contribution statement**

834 **Immacolata Mazzuoccolo:** Investigation, Formal analysis, Visualization. **Immacolata Climaco:**  
835 Investigation, Formal analysis, Visualization. **Jessica Passaro:** Investigation, Formal analysis.  
836 **Francesca Di Lauro:** Investigation, Writing – original draft. **Daniele Battegazzorre:** Investigation.  
837 **Milijana Jovic:** Investigation. **Pietro Russo:** Validation, Supervision. **Giulio Malucelli:** Validation,  
838 Supervision, Writing – review & editing. **Sabyasachi Gaan:** Validation, Supervision, Writing –  
839 review & editing. **Antonio Aronne:** Validation, Supervision, Writing – review & editing. **Fabio**  
840 **Montagnaro:** Validation, Writing – review & editing. **Marco Balsamo:** Methodology, Supervision,  
841 Project administration, Funding acquisition, Writing – review & editing. **Claudio Imparato:** Formal  
842 analysis, Project administration, Conceptualization, Funding acquisition, Writing – original draft,  
843 Writing – review & editing. **Aurelio Bifulco:** Formal analysis, Methodology, Project administration,  
844 Conceptualization, Funding acquisition, Writing – original draft, Writing – review & editing.

845

846

847 **Declaration of competing interest**

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

850

851 **Funding Sources**

852 This research work was partially funded by the Project “Eco-sustainable Production of biofuels from  
853 the Conversion of sludges through hydrothermal liquefaction” (EPIC), Programma per il  
854 Finanziamento della Ricerca di Ateneo (FRA) 2022 of the University of Naples Federico II, and by  
855 the Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component  
856 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell’Università e della Ricerca  
857 (MUR); funded by the European Union – NextGenerationEU, Project code PE0000021, Project title  
858 “Network 4 Energy Sustainable Transition – NEST”.

859

860 **Acknowledgements**

861 The authors thank Maria Cristina Del Barone, in charge of LaMest (SEM and TEM laboratory) at  
862 Polymers Composites and Biomaterials Institute of National Research Council (IPCB-CNR,  
863 Pozzuoli, Naples), and Francesco Saverio Esposito (University of Naples Federico II) for the  
864 experimental support.

865

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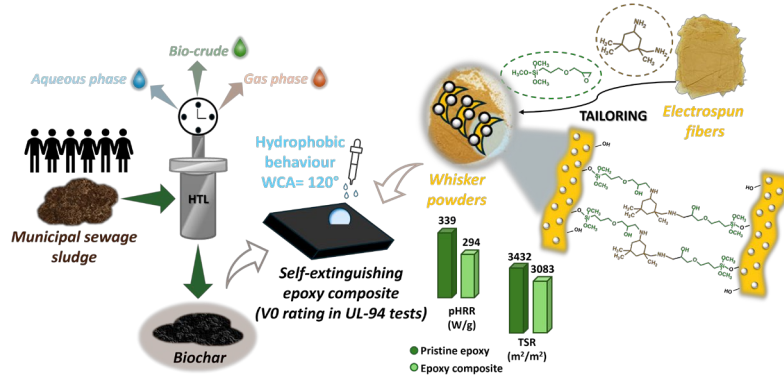
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### Graphical abstract



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