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

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5 Immacolata Mazzuoccolo^{a,#}, Immacolata Climaco^{a,#}, Jessica Passaro^b, Francesca Di Lauro^{a,f}, Daniele
6 Battezzore^d, Milijana Jovic^e, Pietro Russo^b, Giulio Malucelli^d, Sabyasachi Gaan^e, Antonio Aronne^a,
7 Fabio Montagnaro^{c,f}, Marco Balsamo^c, Claudio Imparato^{a,*}, Aurelio Bifulco^{a,*}

8

9 ^aDepartment of Chemical, Materials and Production Engineering, University of Naples Federico II, 80125
10 Naples, Italy

11 ^bInstitute for Polymers, Composites and Biomaterials, National Council of Research, 80078 Pozzuoli, Italy

12 ^cDepartment of Chemical Sciences, University of Naples Federico II, Complesso Universitario di Monte
13 Sant'Angelo, 80126 Naples, Italy

14 ^dDepartment of Applied Science and Technology, Politecnico di Torino, 15121 Alessandria, Italy

15 ^eAdvanced Fibers Laboratory, Swiss Federal Laboratories for Materials Science and Technology (Empa), 9014
16 St. Gallen, Switzerland

17 ^fInstitute of Sciences and Technologies for Sustainable Energy and Mobility, National Research Council,
18 80125 Naples, Italy

19

20 * Corresponding authors: claudio.imparato@unina.it (C.I.); aurelio.bifulco@unina.it (A.B.)

21

22 # I.M. and I.C. contributed equally to this work.

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)₂ 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⁻¹) 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 SiO₂ 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.

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).

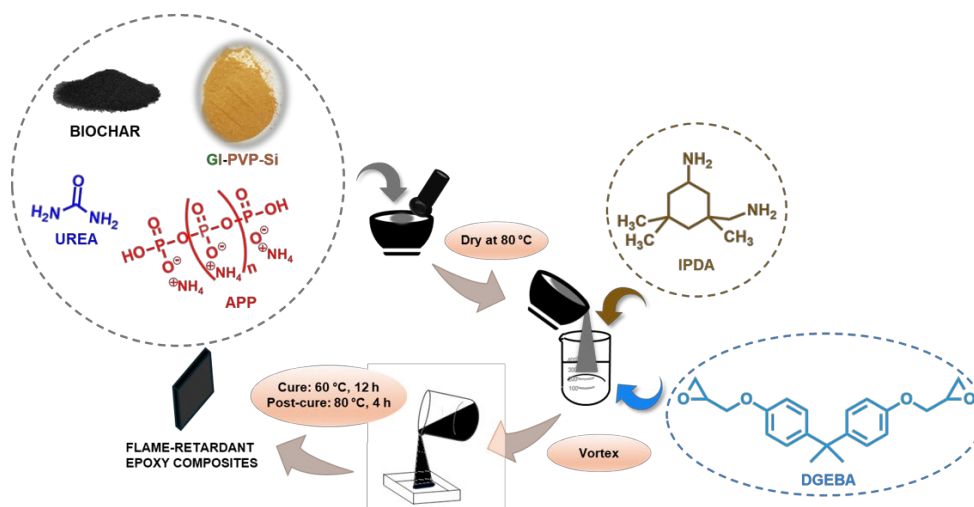
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Table 1. Composition of the fully characterized epoxy-based samples. The mass percentages are referred to (DGEBA+IPDA) basis.

Sample	DGEBA (wt.%)	IPDA (wt.%)	Ch_300-30 (wt.%)	APP (wt.%)	UREA (wt.%)	GI-PVP-Si (wt.%)	P ^a (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 ^a 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 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 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 μL 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 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 μm . 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 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, MJ/m^2), heat release rate (HRR, kW/m^2), peak
295 of the heat release rate (pHRR, kW/m^2), total smoke release (TSR, m^2/m^2), and specific extinction
296 area (SEA, m^2/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.

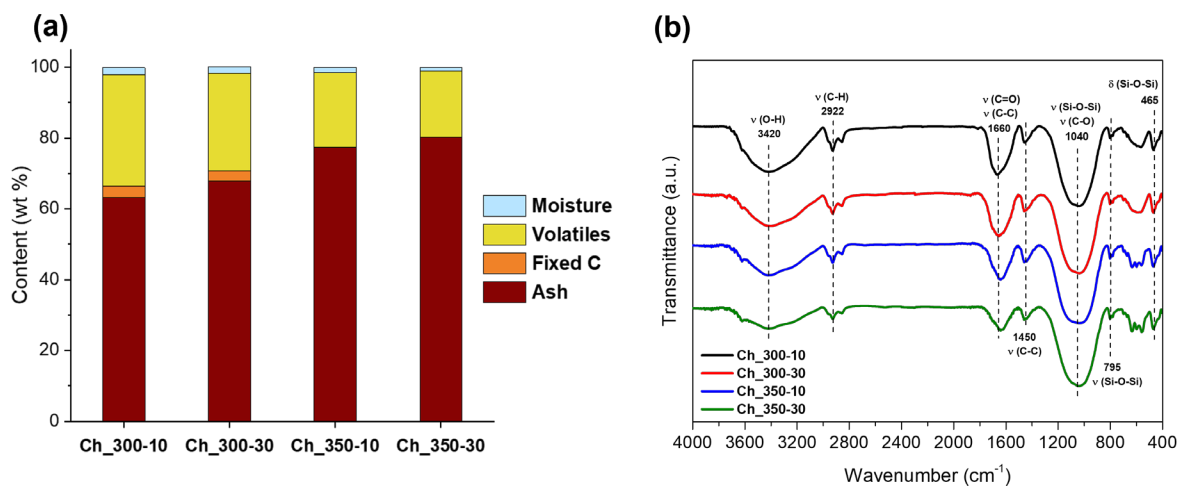
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301 **3. Results and discussion**

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⁻¹, aliphatic C–H stretching bands at about 2922 cm⁻¹, a rather wide band around 1660
 326 cm⁻¹, likely due to the overlap of C=O stretching and aryl C–C stretching (seen as a shoulder at about
 327 1600 cm⁻¹), a band commonly assigned to aromatic ring vibrations at 1450 cm⁻¹, a broad and intense
 328 band around 1040 cm⁻¹, 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 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 π -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 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 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 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.

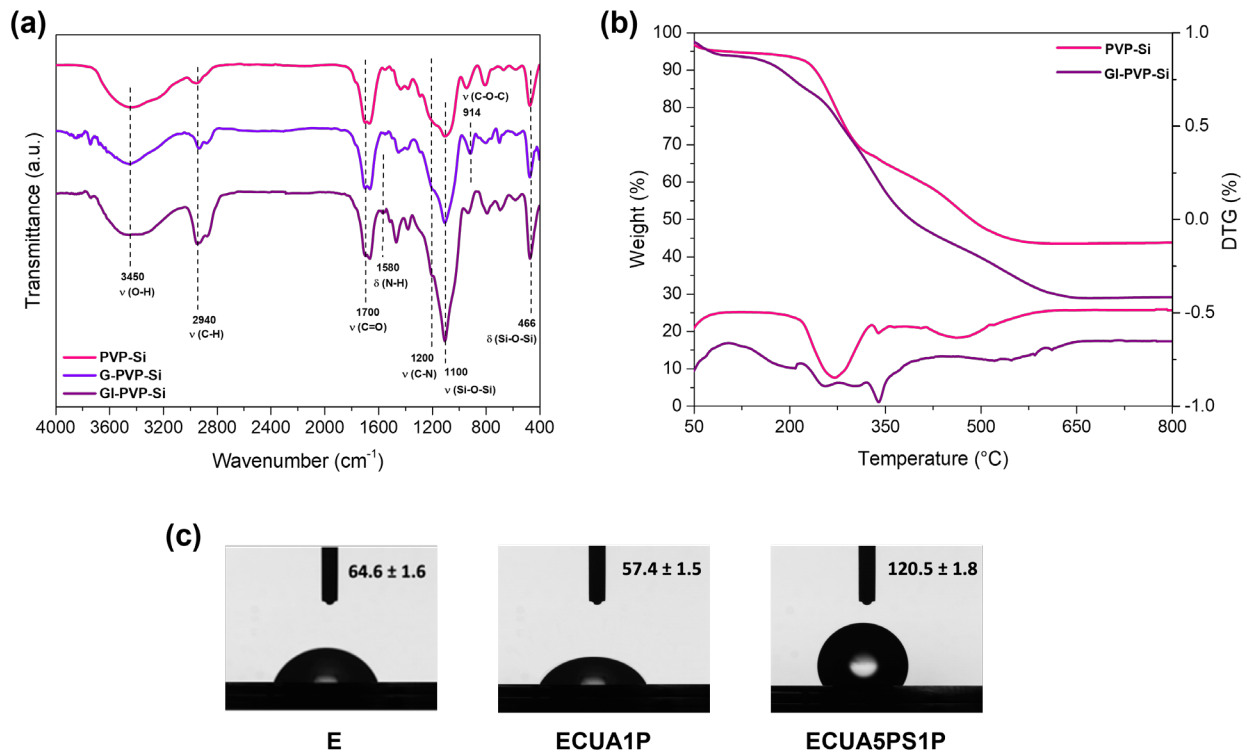
418

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 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 cm^{-1} , and the asymmetric band related to Si–O–Si stretching, around 1100 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 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 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 (θ) 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 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 (θ) 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].

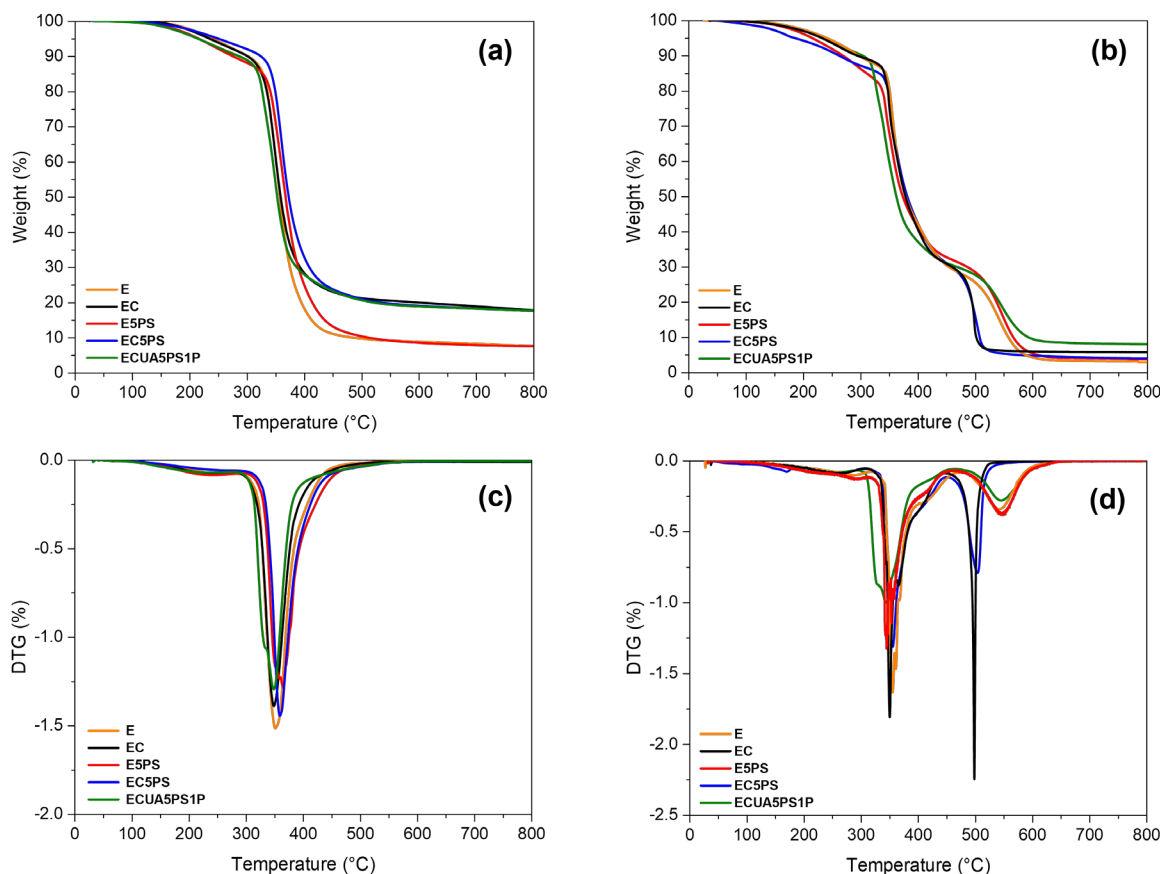
514 The addition of the biochar into EUA5PS1P sample allows for obtaining a formulation that exhibits
515 no dripping V0 rating (Table S6 and Table 2), even at a very low P loading (i.e., 1 wt.%), due to a
516 synergistic condensed phase action of the waste-derived material with the other additives during 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 O₂/N₂ 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_{5%}
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_{5%} 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

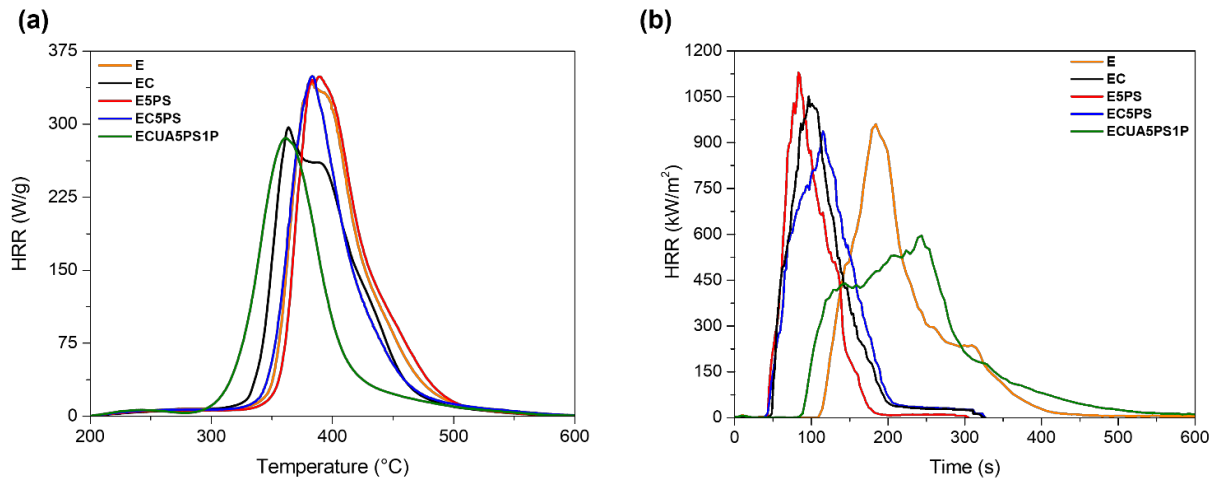
578 whiskers produces a huge amount of refractory silica nanoparticles, which promote the generation of
579 a stable aromatic char able to prevent the diffusion of flammable gases and oxygen from the
580 surroundings into the material, and act as effective thermal shield and barrier [67,68].

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.

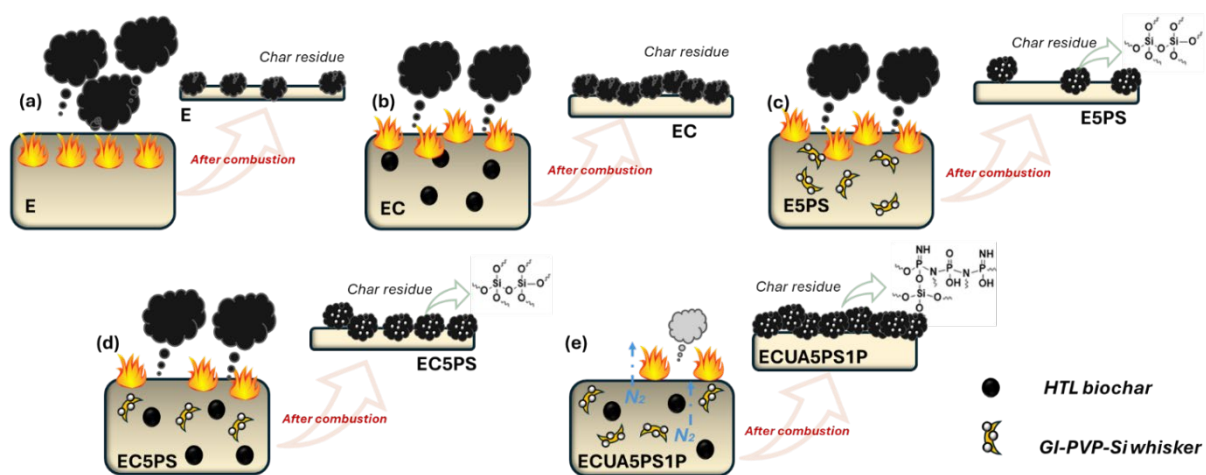
Sample	TTI (s)	THR (MJ/m ²)	ΔTHR (%)	pHRR (kW/m ²)	ΔpHRR (%)	Residue (wt.%)	TSR (m ² /m ²)	ΔTSR (%)	UL-94/dripping
E	109 ± 2	106 ± 9	-	961 ± 101	-	3 ± 0.1	3432 ± 33	-	NC/yes
EC	45 ± 1	82 ± 1	-23	1051 ± 95	+9	8 ± 0.1	3789 ± 17	+10	NC/no
E5PS	42 ± 15	71 ± 13	-33	1131 ± 97	+17	6 ± 0.2	3043 ± 96	-11	NC/no
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

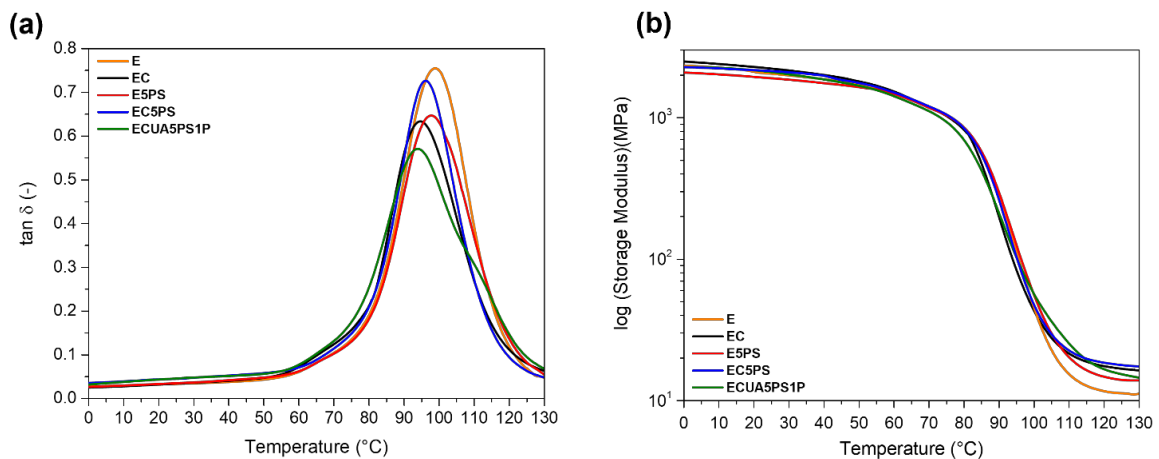
656 during the combustion (Figure 7a). The addition of biochar into the epoxy matrix (EC) causes the
657 formation of a jagged continuous char (Figure S9), limiting heat and mass transfer thanks to its
658 tortuous morphology (Figure 7b). Compared to the one generated from E, the residual char obtained
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 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 (PO^{\bullet} or 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 Mazzuocolo:** 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
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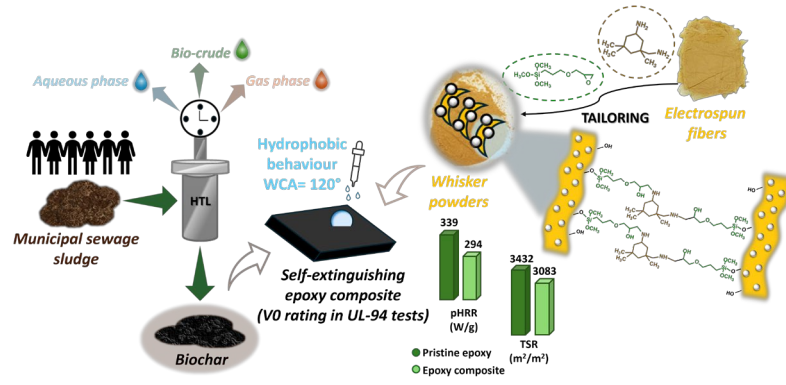
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Graphical abstract



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