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Pauline Blyweert, Nicolas Vincent, Jan Macutkevic, Vanessa Fierro, Alain Celzard. Tannin-based resins for 3D printing of porous carbon architectures. *ACS Sustainable Chemistry & Engineering*, 2022, 10 (23), pp.7702-7711. 10.1021/acssuschemeng.2c01686 . hal-04146303

**HAL Id: hal-04146303**

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Submitted on 29 Jun 2023

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# Tannin-based resins for 3D printing of porous carbon architectures

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17 KEYWORDS

18 Tannin, Porous carbon, Stereolithography, Additive manufacturing

19

20 ABSTRACT

21 Carbon structures, unlike metals or polymers, can hardly be directly implemented in additive  
22 manufacturing, and their sustainable nature is extremely limited. In this work, we demonstrate  
23 that porous carbon structures can be obtained by laser stereolithography of acrylate-tannin mixed  
24 resins, followed by a pyrolysis step. By adjusting the initial acrylate / tannin ratio in the resin, the  
25 density and volume shrinkage of the resultant carbon, and consequently the mechanical properties  
26 of the corresponding carbon-based architectures, could be modified. The moderate electrical  
27 conductivity of the structures, reaching about  $7 \text{ S.cm}^{-1}$ , and their broadband absorption in  
28 microwaves open up possibilities for electrochemical or electromagnetic applications. Thus, the  
29 possibility of obtaining complex free-standing structures with imperceptible warpage, low  
30 volume shrinkage, and adjustable density offers an opportunity to develop 3D-printed carbon  
31 materials with a significant proportion of bio-based precursors, which can be easily adapted for a  
32 large number of applications.

33

34 INTRODUCTION

35 Porous carbon materials, thanks to their excellent chemical stability and unique mechanical,  
36 electrochemical, thermal and electrical properties <sup>1,2</sup>, are used in many industrial processes such  
37 as heat management <sup>3</sup>, gas storage <sup>4</sup>, electrochemical energy storage and conversion <sup>5,6</sup>, among  
38 others. Given their central role, it would make sense to find a fast, inexpensive and accurate way

39 to produce tailored complex systems, not only to broaden the application range of these materials,  
40 but also to give them a more ecological character. This versatility can be achieved with 3D  
41 printing methods <sup>7</sup>, and especially by vat photopolymerisation, one of the most accurate  
42 technologies <sup>8,9</sup>. Nevertheless, since pure carbon cannot be melted, sintered or polymerised, this  
43 particular element is not directly applicable in additive manufacturing. Thus, most 3D-printed  
44 carbon materials are obtained by printing a carbon precursor, followed by a pyrolysis step.

45 Existing studies have reported the printing of porous carbon through stereolithography  
46 technology using commercial or custom resins, followed by a pyrolysis step. These approaches  
47 have allowed for the realisation of highly porous carbon materials with tailored pores in a  
48 reduced number of steps <sup>10-13</sup>. Nevertheless, in most cases, the printed resin had a low carbon  
49 yield <sup>14,15</sup> and underwent significant volume shrinkage (50 – 90%). Besides, the photocurable or  
50 thermosets resins <sup>16</sup> used in those approaches are all of petrochemical origin. To make 3D-printed  
51 porous carbons more sustainable, it is therefore interesting to use bio-based resins as carbon  
52 precursors. Unlike previous studies in which bio-based carbon precursors such as lignin, cellulose  
53 or monosaccharides have been used in Direct Ink Writing technology <sup>17-19</sup>, in this work we  
54 present an approach to print highly porous carbons with low shrinkage and warpage from bio-  
55 based photoresin using laser stereolithography.

56 This approach consists of adding a wood extract, condensed (mimosa) tannin, to the  
57 photocurable resin to build complex structures and then converting the latter into carbon through  
58 a pyrolysis step. Indeed, mimosa tannin is an abundant phenolic bioresource with a carbon yield  
59 on pyrolysis of about 47%, which has been widely studied over the years to synthesise a wide  
60 range of carbon structures <sup>20</sup>. Herein, we show for the first time the possibility of printing a  
61 tannin-based resin to ensure high carbon yield with low shrinkage upon carbonisation, and we

62 discuss some properties of these new materials based on rheological, structural and physical  
63 characterisation.

64

## 65 EXPERIMENTAL SECTION

### 66 **Materials**

67 Hexanediol diacrylate (HDDA, SR238), pentaerythritol tetraacrylate (PETA, SR295) and  
68 acrylate oligomer (CN154 CG) were kindly supplied by Sartomer (Arkema Group, France).  
69 Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) was supplied by Lambson (Arkema  
70 Group, England). Mimosa (*Acacia Mearnsii*) tannin extract, a light-brown powder containing 80-  
71 82% phenolic material based on flavonoid units, commercially available under the name Fintan  
72 OP, was kindly provided by SilvaChimica (St Michele Mondovi, Italy) and used as a bio-based  
73 carbon precursor. All products were used as received without further purification.

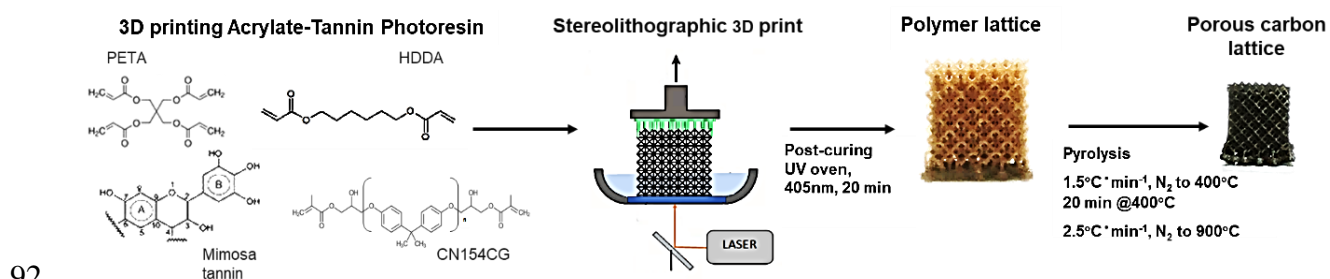
### 74 **Preparation of tannin-acrylate resins, 3D printing and pyrolysis**

75 A BAPO photoinitiator (content 0.30 wt.%) and the acrylates monomers (SR238, SR295 and  
76 CN154 CG), added in the proportions shown in Table S1, were mixed thoroughly at 50 °C for 20  
77 min to obtain a homogeneous resin. Then, a fixed amount of tannin was added and mixed by  
78 hand to the acrylate resin to obtain tannin-acrylate resin with a tannin content of 0, 10, 20, 25 or  
79 30 wt.%. The corresponding formulations and printed structures were named T-0, T-10, T-20, T-  
80 25 and T-30, respectively, and the derived carbons were called CT-0, CT-10, CT-20, CT-25 and  
81 CT-30, respectively.

82 A commercial desktop SLA ( $\lambda = 405$  nm, DWS J28, DWS, Italy) was employed to print 3D  
83 structures from tannin-acrylate resins. After the printing procedure, the structures were removed

84 from the build platform and rinsed twice in an isopropanol bath for 10 min to remove uncured  
85 resin. Afterwards, the products were post-cured in a UV oven ( $\lambda = 405 \text{ nm}$ ) for 20 min at room  
86 temperature.

87 The printed meshes were finally converted into carbon materials under pure nitrogen (flow  
88 rate  $100 \text{ mL}\cdot\text{min}^{-1}$ ) in a tubular furnace with a heating rate of  $1.5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  to  $400 \text{ }^\circ\text{C}$ , then a 20  
89 min step at  $400 \text{ }^\circ\text{C}$ , followed by a second ramp of  $2.5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  up to the final temperature of  
90  $900 \text{ }^\circ\text{C}$ , which was maintained for 1 hour (Figure 1). This particular temperature program was  
91 chosen to stabilise the architectures during thermal degradation.



93 Figure 1. Schematic illustration of the fabrication strategy for 3D-printed tannin-based carbon  
94 materials.

## 95 **Characterisation**

### 96 *Materials characterisation*

97 A Brookfield DVII+ PRO viscometer with cone-plate geometry (spindle CPE-51, gap 0.013  
98 mm) was used to measure the viscosity of the resins at room temperature.

99 The volume-based particle size distribution of the tannin powder was measured using a laser  
100 diffraction particle size analyser (Mastersizer 3000, Malvern), equipped with an automated dry  
101 powder dispersion unit (Aero S, Malvern). The powder was dried before measurements.

102 Thermogravimetric analysis (TGA) coupled with Differential Scanning Calorimetry (DSC)  
103 was performed using an STA 449 F3 Jupiter<sup>®</sup> apparatus (Netzsch) and provided access to the  
104 carbon yield (ratio of the weight of carbon after pyrolysis to the weight of the initial resin) and  
105 glass transition temperature of the different resins, respectively. Cured resin samples (~ 10mg)  
106 were tested from 30 to 800 °C with a heating rate of 10 °Cmin<sup>-1</sup> under argon flow. The argon  
107 flow was then replaced by air to deduce the ash content.

108 Elemental analysis (EA) of the resultant carbon materials was performed in an Elementar  
109 Vario EL Cube analyser.

#### 110 *Structure, porosity, and textural properties of carbon materials*

111 The linear shrinkage was calculated using Eq. (1), where the dimension can be height,  
112 thickness or length of the printed architectures. The data reported are the average values of at  
113 least 5 measurements on 3 samples obtained from each carbon type.

$$114 \quad \text{Shrinkage (\%)} = \frac{\text{Dimension before pyrolysis} - \text{Dimension after pyrolysis}}{\text{Dimension before pyrolysis}} \times 100 \quad (1)$$

115 Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were  
116 performed with a Zeiss GeminiSEM 360 microscope. Transmission Electron Microscopy (TEM)  
117 images were obtained using a JEM ARM 200F Cold FEG TEM/STEM operating at 200 kV,  
118 using spherical aberration (Cs) probe and image correctors. The samples were prepared by  
119 dispersing carbon powder in ethanol, after which a single drop of the suspension was deposited  
120 on a carbon-coated copper grid (200 mesh).

121 X-ray diffraction (XRD) was carried out using a Panalytical X'Pert Pro diffractometer in a  
122 Bragg-Brentano configuration in reflection with a Cu anode.

123 Raman spectra were recorded with a Horiba XploRa Raman apparatus equipped with a 50×  
124 long-range objective (wavelengths of 532 and 638 nm, filtered at 10% of their maximum energy).  
125 The spectra obtained at a wavelength of 638 nm were then fitted by the method described by  
126 Mallet-Ladeira et al.<sup>21</sup> using a double Lorentzian for the D band and an asymmetric mixed  
127 Gaussian-Lorentzian profile for the G band.

128 The bulk density ( $\rho_b$ , g cm<sup>-3</sup>) was calculated from the measured mass and volume of three  
129 samples of each carbon type obtained. The skeletal density ( $\rho_s$ , g cm<sup>-3</sup>) was determined by helium  
130 pycnometry using an Accupyc II 1340 (Micromeritics) automatic apparatus, averaging 30  
131 measurements. Samples were ground and dried before each measurement. The total porosity,  $\Phi$   
132 (dimensionless), was then calculated according to Eq. (2):

$$133 \quad \Phi = 1 - \frac{\rho_b}{\rho_s} \quad (2)$$

134 N<sub>2</sub> and H<sub>2</sub> adsorption experiments at -196°C were carried out with a Micromeritics 3-flex  
135 automatic adsorption apparatus. Samples (~ 1 g) were degassed under vacuum before analysis for  
136 at least 48h at 200 °C. The Brunauer-Emmett-Teller<sup>22,23</sup> (BET) method was applied to N<sub>2</sub>  
137 isotherms to obtain the BET area ( $A_{BET}$ ). Pore size distribution (PDS) and total surface area  
138 ( $S_{NLDFT}$ ) were calculated from the combination of N<sub>2</sub> and H<sub>2</sub> adsorption isotherms using a two-  
139 dimensional non-local density functional model (2D-NLDFT) available in SAIEUS software  
140 (Micromeritics<sup>24</sup>).

141 Mercury intrusion was performed using a Micromeritics AutoPore IV 9500 up to a pressure of  
142 414 MPa.



143 *Physical properties of carbon materials*

144 The electrical conductivity  $\sigma$  (S cm<sup>-1</sup>) was measured by the four-point method using a Keithley  
145 6430 source-measure unit on 3D-printed and then pyrolysed 2 mm × 2 mm × 15 mm  
146 parallelepipeds. The electrical conductivity was calculated according to:

$$147 \quad \sigma = \frac{2I}{(|V^+| + |V^-|)} \frac{L}{S} \quad (3)$$

148 where  $V^+$  and  $V^-$  are the voltage values (V) measured with the current  $I$  (A) flowing in one  
149 direction and then in the other, so as to correct the measurements for a slight thermoelectric effect  
150 that is always present.  $S$  (cm<sup>2</sup>) is the cross-sectional area and  $L$  (cm) is the distance between the  
151 two opposite sides on which the electrical contacts were placed. The electrical conductivity of the  
152 conductive skeleton,  $\sigma_s$ , was calculated with Eq. (4), which is a good approximation for rigid  
153 open-cell foams with node effects<sup>25,26</sup>. This equation was preferred to others corresponding to  
154 closed porosity, because polymeric precursors produce a significant amount of gases during  
155 pyrolysis and hence a totally open porosity, as already proved by the mercury intrusion  
156 experiments (see below):

$$157 \quad \sigma_s = \frac{3\sigma}{\left[ (1-\phi) + 2(1-\phi)^{\frac{3}{2}} \right]} \quad (4)$$

158 Microwave measurements in the 24-39 GHz (Ka-band) frequency range were carried out with  
159 an ELMIKA R2-408R scalar network analyser. The samples were placed directly in a 7.2 × 3.4  
160 mm cross-section waveguide, perpendicular to the wave propagation, and the modules of the  
161 amplitude of transmitted ( $S_{21}$ ) and reflected ( $S_{11}$ ) signals were measured. From these data, the  
162 (dimensionless) coefficients of reflection ( $R$ ), transmission ( $T$ ) and absorption ( $A$ ) were calculated  
163 according to Eq. (5):

$$\begin{aligned} 164 \quad R &= S_{11}^2 \\ 165 \quad T &= S_{21}^2 \\ 166 \quad A &= 1 - S_{11}^2 - S_{21}^2 \end{aligned} \quad (5)$$

167 Mechanical properties of the different 3D printed carbon were investigated by quasi-static  
168 compression using an Instron 5944 universal testing machine equipped with a 2 kN load cell. The  
169 compression tests were carried out in triplicate at a constant load rate of 2 mm·min<sup>-1</sup>.

170 More details of sample preparation and methods are given in the Supplementary Information.

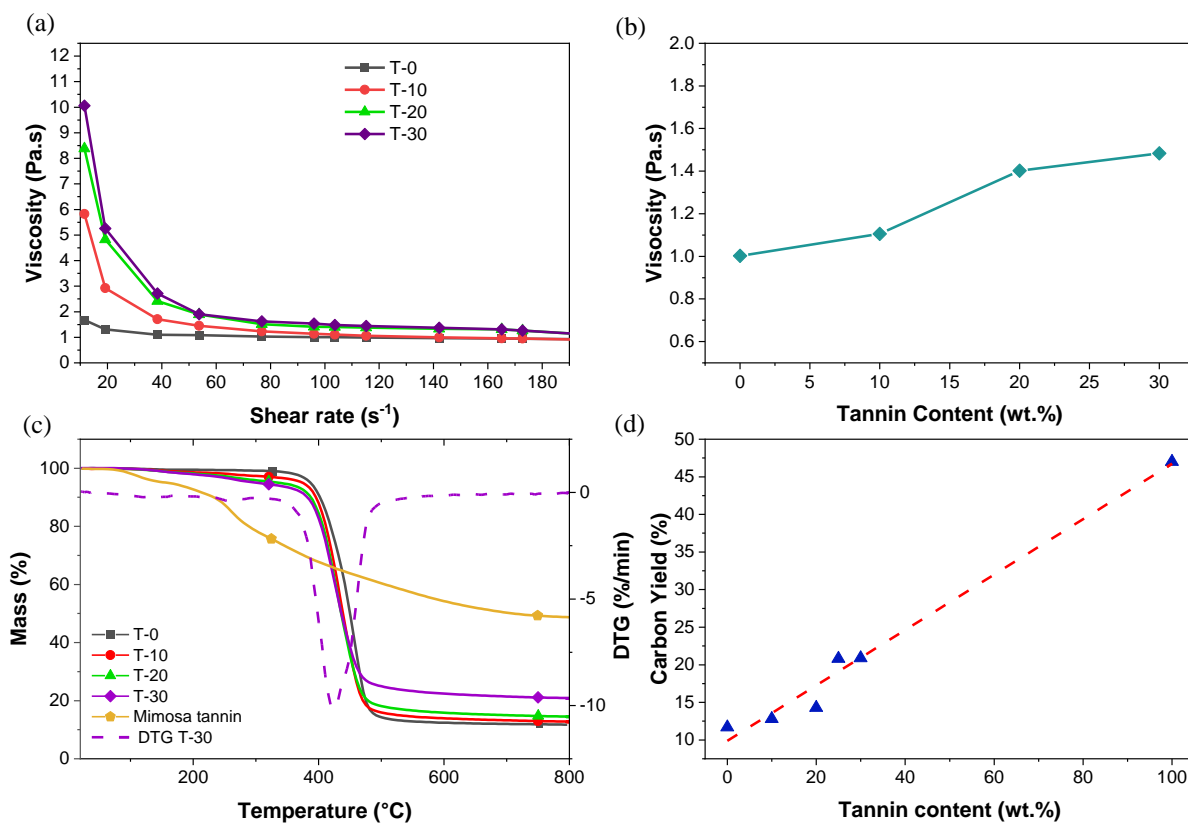
## 171 RESULTS AND DISCUSSION

### 172 **Rheological properties and thermal behaviour of the resins**

173 In stereolithography, the viscosity of the resin is a crucial parameter. In most cases, a viscosity  
174 of less than 3 Pa·s (at the printing temperature and a shear of about 100 s<sup>-1</sup>) is desired to promote  
175 recoating and self-levelling of the resin<sup>27,28</sup>. The viscosity of uncured acrylate-tannin resins with  
176 a tannin content between 10 and 30 wt.% was determined as a function of shear rate in a region  
177 of 10 to 200 s<sup>-1</sup> (Figure 2a). At higher tannin contents, the resultant resins were in the form of a  
178 paste that cannot be used in a stereolithography apparatus.

179 The unfilled resin (here referred to as T-0) showed Newtonian behaviour with a viscosity of  
180 about 1.0 Pa·s at a shear rate of 100 s<sup>-1</sup>. It turns out that Mimosa tannin is not soluble in the  
181 acrylate resin, and is therefore dispersed in it in the form of solid particles with an average  
182 diameter of 54.5 μm, according to measurements made with the Mastersizer (Figure S1). It is  
183 well established that, due to particle interactions, the viscosity of suspensions increases with the  
184 volume concentration of solids<sup>29</sup>. Thus, as expected, the viscosity increased with the tannin  
185 content (Figure 2b). For all filled resins, shear-thinning behaviour in the low-shear rate region  
186 (below 10 s<sup>-1</sup>) was observed, with viscosity decreasing to a steady state (tending towards 1.3 Pa·s)

187 at high shear rates. This observation, typical of highly particle-loaded suspensions, can be  
 188 explained by the variable interparticle and particle-fluid interactions under shear<sup>30-34</sup>. As the  
 189 shear stress increases, immobilised acrylate chains are indeed released, and the friction between  
 190 tannin particles decreases. Therefore, from a macroscopic point of view, the viscosity decreases  
 191 as seen in Figure 2a. Due to the initial viscosity of the acrylate resin, the suspension of tannin  
 192 particle remains stable during the printing processes (and even for weeks at room temperature),  
 193 which limits the heterogeneity of the final structure.



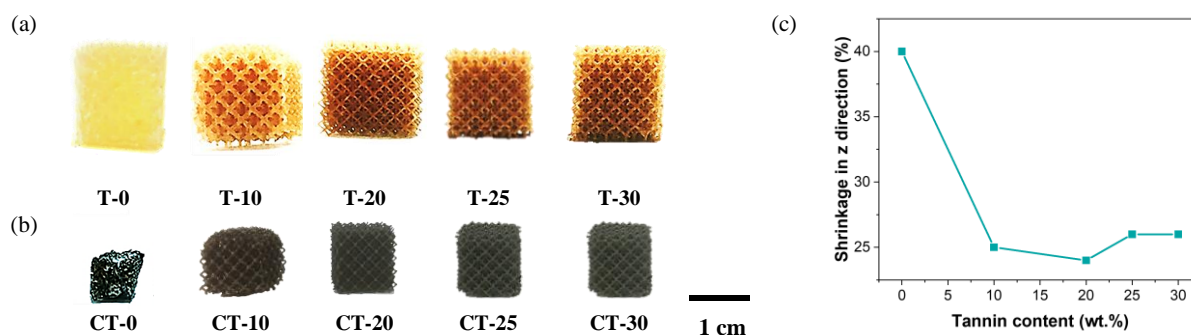
194  
 195 Figure 2. (a) Viscosity versus shear rate of acrylate resins containing different weight fractions of  
 196 tannin (from 0 wt.% in T-0 to 30 wt.% in T-30). (b) Viscosity of acrylate resin at a shear rate of  
 197 100 s<sup>-1</sup> as a function of tannin content. (c) TGA (mass loss) curves, under argon and up to 800 °C,  
 198 of the same acrylate resins as in (a); that of pure tannin is given for comparison, and the DTG

199 curve is provided as a guide for sample T-30 only, as the others DTG curves are similar. (d)  
200 Carbon yield at pyrolysis as a function of initial tannin content; the value corresponding to a resin  
201 with 25 wt.% tannin was also added.

202 The temperature behaviour of the acrylate-tannin resin was evaluated by TGA and the  
203 corresponding differential curves (DTG) (Figure 2c). The UV-cured acrylate resin without tannin  
204 started to lose weight at about 320 °C and degraded to char by 680 °C with a mass loss of about  
205 85%. This degradation corresponds to the depolymerisation of acrylates at high temperature as  
206 well as to the random radical scission of the free linear chains, leading to volatile chain fragments,  
207 including ethylene and methane, the quantitative yield of which depends on the stability of the  
208 radicals formed but also on side-chain reactions (side group elimination or rearrangement)<sup>35-37</sup>.  
209 In the presence of tannin, three regions of mass loss were clearly identified<sup>38</sup>. The first region is  
210 located between 30 and 170 °C, with a DTG peak around 132 °C, and corresponds to the  
211 evaporation of absorbed water and the formation of small volatile compounds (CO, CO<sub>2</sub>) released  
212 at the beginning of tannin degradation. The second region between 170 and 310 °C, with a DTG  
213 peak around 260 °C, is due to the degradation of tannin and acrylate resin. Finally, the  
214 decomposition of the rigid segments of the resin and the formation of carbon material occur  
215 between 310 and 680 °C. As expected, the addition of tannin significantly increased the final  
216 carbon yield at 800 °C, from 11.7 to 20.8 % for the samples with 0 wt.% and 30 wt.% of tannin,  
217 respectively. The carbon yield increased linearly with the weight fraction of tannin, as shown in  
218 Figure 2d, where the carbon yield of pure tannin (47 %) has been plotted. In addition, for all  
219 samples, the ash content remained below 0.5 wt.%.

## 220 Morphology and composition of printed carbon structures

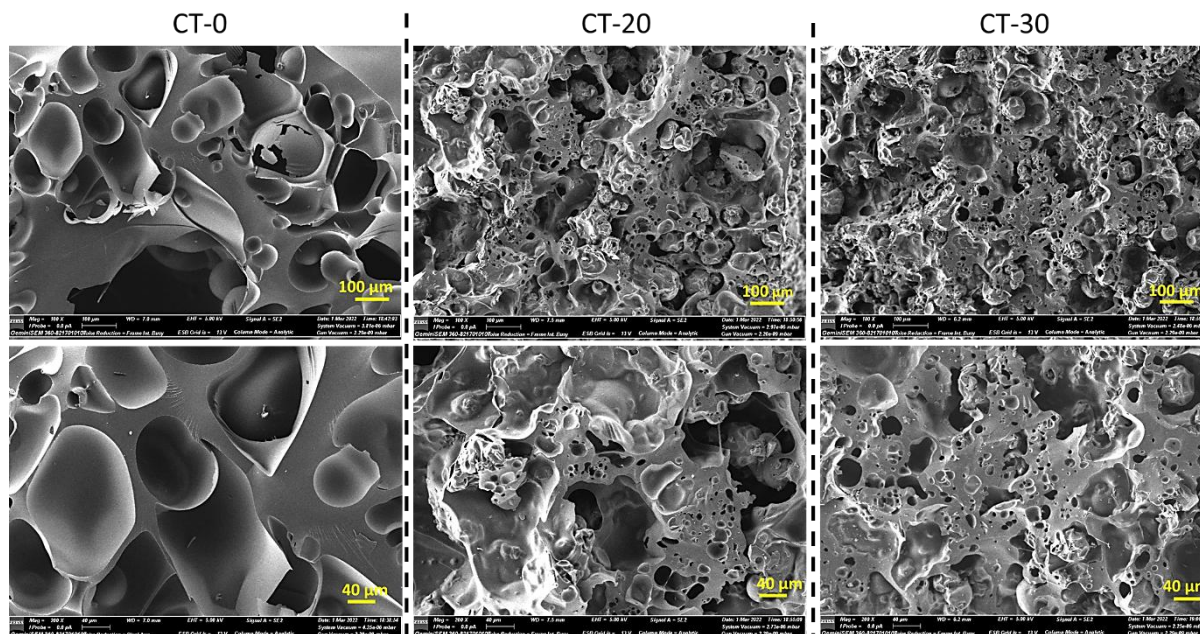
221 Tetraikaidecahedra meshes (Figure 3a, wall size of 200  $\mu\text{m}$ ) and solid cubes were printed from  
222 30  $\mu\text{m}$ -thick layers. After pyrolysis, the colour of the samples changed from light brown to bright  
223 black for the acrylate resin without tannin to matte black for the CT-30 structure (Figure 3b).



224  
225 Figure 3. 3D-printed structures: (a) before and (b) after pyrolysis, with various tannin contents  
226 increasing from left to right (formulations T-0, T-10, T-20, T-25 and T-30); (c) Linear shrinkage  
227 of the structures after pyrolysis in  $z$ -direction (printing direction) as a function of tannin content.

228 The addition of tannin to the formulation was found to have an effect on the structure  
229 shrinkage as evidenced in Table S2. The samples with tannin, regardless of their architecture,  
230 tended to shrink linearly by 25% in each direction, while the tannin-free structure shrank by 40%  
231 in the  $z$ -direction and by 30% in  $x$ - $y$  directions with warpage. The shrinkage phenomenon results  
232 from the evolution of volatile matters during carbonisation. During the pyrolysis process, the  
233 acrylate polymer matrix is progressively heated to temperatures above its glass transition  
234 temperature (found to be 126  $^{\circ}\text{C}$  by DSC measurement for the pristine resin, and reduced to  
235 115  $^{\circ}\text{C}$  for the T-25 resin due to polymer/particles interactions<sup>39,40</sup>, Figure S2) and enters a more  
236 flexible state subject to deformation. As the tannin degrades significantly less than the resin and  
237 loses much less weight, even at much higher temperatures (Figure 2c), it stabilises the structure  
238 during this plastic state and thus reduces warpage in different directions.

239 SEM images of carbon structures CT-0 and CT-30 are presented in Figure S3 and Figure 4.  
240 Rather smooth surfaces with a few craters allowing gases formed during the pyrolysis step to  
241 escape were observed on all structures (Figure S3). In contrast, SEM images after fracturing  
242 (Figure 4) revealed extensive internal porosity with many large oval bubbles in the CT-0  
243 structure, while narrower pores can be seen on the CT-30 carbon architecture. EDX results (not  
244 shown) evidenced similar carbon and oxygen composition for each sample.



245  
246 Figure 4. SEM images of a fractured area of CT-0, CT-20 and CT-30 samples of 3D-printed  
247 structures. Scale bars: 100 μm (top row), and 40 μm (bottom row).

248 Table S3 presents the bulk chemical composition of the different 3D-printed carbons. The  
249 nitrogen (N) content is very low and no sulphur (S) was detected, while oxygen (O) is present in  
250 significant amounts in the carbon structures. These measurements are in agreement with the  
251 composition of other carbons based on Mimosa tannin<sup>20,41</sup>, as no doping treatment was carried  
252 out on these materials. Given the usual uncertainties on this kind of analysis, it is difficult to

253 consider that the samples are really different in terms of composition, and we can assume that all  
254 of them have C, H, N, S and O contents of about 95, 1.3, 0.3, 0 and 3.5 wt.%, respectively. The  
255 differences between the samples do not show any clear trend, and can be attributed to  
256 inhomogeneities, despite the repetitions and calculated averages.

## 257 **Structural properties of printed carbon structures**

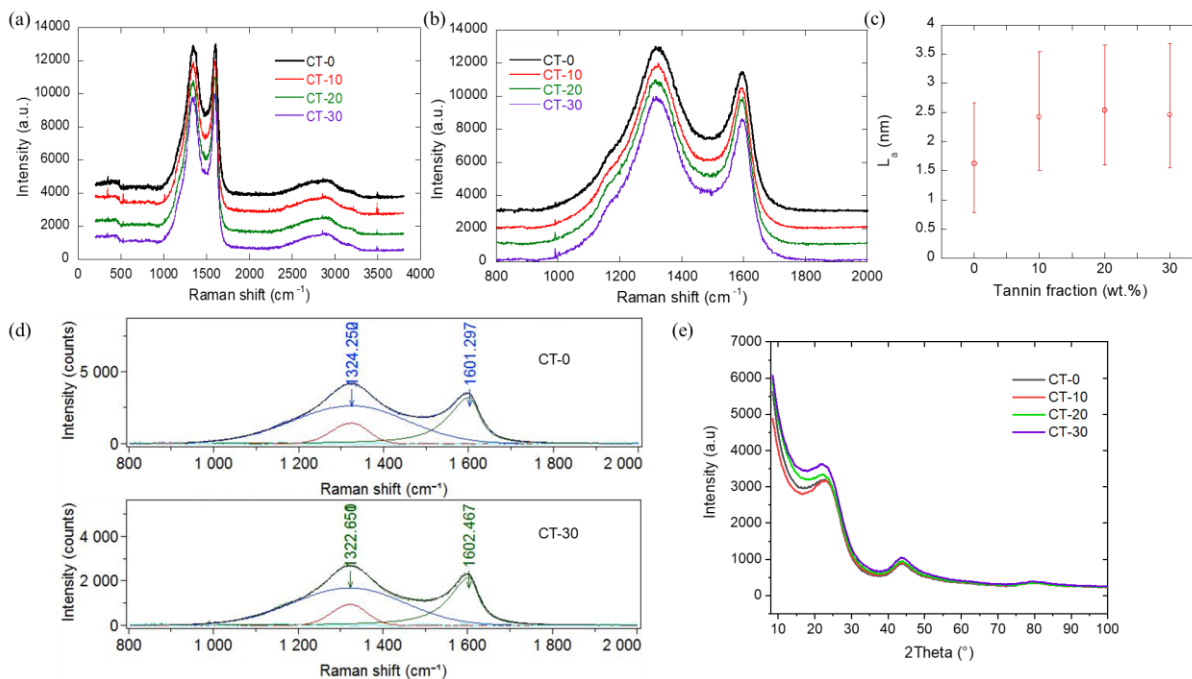
258 TEM observations were performed to investigate the nanostructure of the carbon materials  
259 (Figure S4). At high magnification, TEM evidenced a highly disordered structure in all samples,  
260 which was expected from a phenolic precursor in the absence of graphitisation catalyst<sup>20</sup>. High-  
261 resolution images and the presence of a well-defined halo seen by Fast Fourier Transform (FFT)  
262 also revealed the existence of very small lamellar domains dispersed in a highly disordered  
263 matrix.

264 Figure 5a shows the Raman spectra obtained at a wavelength of 532 nm, *i.e.*, with a green  
265 laser, which corresponds to the vast majority of carbon spectra reported in the literature. They are  
266 completely typical of highly disordered carbons, as expected from the precursors used<sup>20</sup>. Indeed,  
267 at first order, the D-band, whose maximum is around 1350 cm<sup>-1</sup>, is very broad with a shoulder  
268 around 1170 cm<sup>-1</sup>, and the G-band, centered around 1600 cm<sup>-1</sup>, is just a little less broad. The  
269 intensity ratio of the D/G bands is very close to 1, and at second order, the profile between 2200  
270 and 2700 cm<sup>-1</sup> is not structured. The spectra are very similar from one formulation to the other,  
271 especially when tannin is present. The carbon obtained with the formulation without tannin  
272 differs very slightly from the others by its somewhat shallower valley between the D and G bands.  
273 Moving from sample CT-0 to sample CT-30, the D/G intensity ratio increases very slightly, from  
274 1.01 to 1.04. Considering the very disordered and non-graphitizable character of these carbons,

275 this evolution corresponds to a slight increase in the size of the coherent domains, measured  
276 through the  $L_{a,Raman}$  parameter.

277 Figure 5b shows the first-order spectra, now obtained with the 638 nm laser, *i.e.*, with a red  
278 laser, at the wavelength of which equation (S2) applies. As expected, the D band has moved to  
279 lower Raman shifts, around  $1320\text{ cm}^{-1}$ , while the G band has remained fixed. The D/G intensity  
280 ratios also increased, but the trend remained the same, with values increasing from 1.13 to 1.16  
281 for samples CT-0 and CT-30, respectively. Figure 5d shows the fit of these two extreme samples  
282 by the method described in <sup>21</sup>. The fits provided the half-widths at half maximum of the G band,  
283 which decreased from  $59.5\text{ cm}^{-1}$  for CT-0 to  $55.2\text{ cm}^{-1}$  for CT-30, with which the values of  $L_{a,Raman}$   
284 could be calculated from Eq (S2). The corresponding values and their uncertainties are  
285 given in Figure 5c. On average,  $L_{a,Raman}$  thus increases from 1.6 to 2.5 nm, and the three  
286 formulations containing tannin gives values very close to each other. Such small values definitely  
287 confirm that these carbons are highly disordered and not graphitizable.





288

289 Figure 5. Raman spectra and XRD patterns of 3D-printed carbon structures for various initial  
 290 acrylate / tannin ratios: (a) Full spectra obtained at a wavelength of 532 nm; (b) First-order  
 291 spectra obtained at a wavelength of 638 nm. In (a) and (b), the spectra have been shifted with  
 292 respect to each other along the intensity axis (whose units are arbitrary) to better distinguish them;  
 293 (c) Changes of  $L_{a, Raman}$  with the tannin content in the formulation; (d) Fits of the spectra shown in  
 294 (b) according to the method detailed in <sup>21</sup>; (e) XRD patterns.

295 The XRD patterns are shown in Figure 5e. As expected, the XRD profile was nearly the same  
 296 for all samples, with the  $002$  reflection appearing as a broad band with a maximum at Bragg  
 297 angle  $2\theta$  of  $20-24^\circ$ . The presence of such a broad reflection confirmed the existence of crystalline  
 298 carbon nano-domains in a highly disordered carbon matrix, as expected from the observation in  
 299 the high-magnification TEM images. Bands  $10\lambda$  ( $2\theta = 44^\circ$ ) and  $11\lambda$  ( $2\theta = 80^\circ$ ) appeared as broad  
 300 and low-intensity reflections, which is indeed typical of disordered carbon. This is further  
 301 confirmed by the corresponding values of  $L_{a, XRD}$ , calculated from Eq. (S1), which are extremely

302 low, around 2 nm for all samples. These values are in agreement with those calculated above by  
303 Raman spectrometry. Finally, the high intensities observed at low angles indicate the presence of  
304 microporosity.

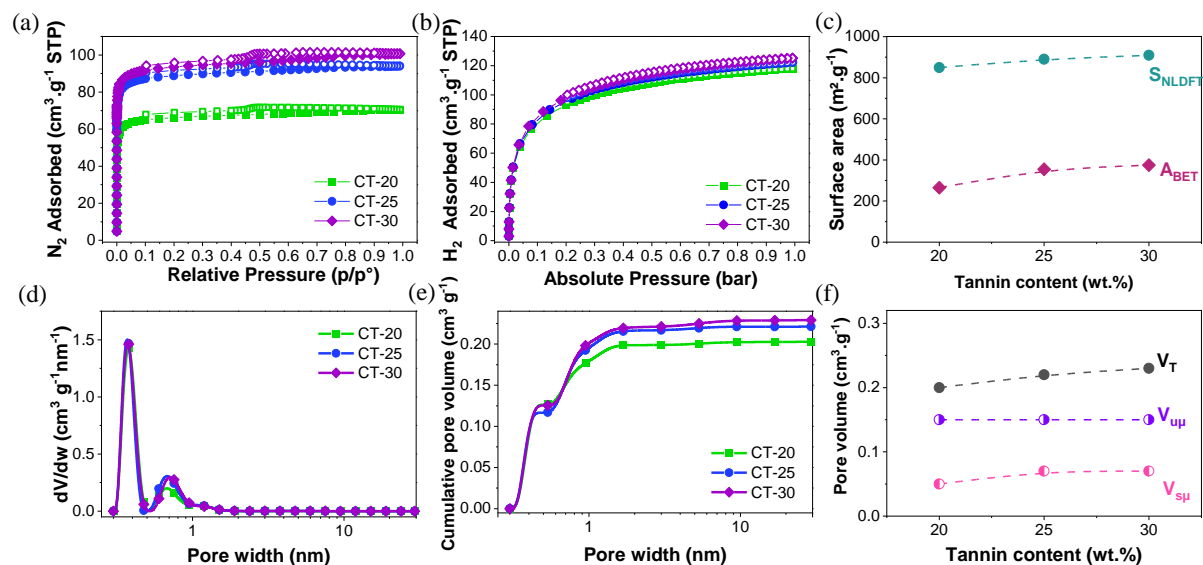
### 305 **Textural properties of printed carbon structures**

306 The bulk density of the 3D-printed structures after carbonisation depends on the acrylate /  
307 tannin ratio (Table S4). The carbonaceous material obtained from the pure acrylate resin was  
308 denser ( $0.442 \text{ g cm}^{-3}$ ) than its counterparts derived from tannin-acrylate mixed resins, with bulk  
309 density values ranging from  $0.305$  to  $0.408 \text{ g cm}^{-3}$  when the tannin content in the formulation  
310 increased from 10 to 30 wt.%. This difference can be explained by the significant linear  
311 shrinkage observed with sample CT-0 (40 % in the  $z$ -direction), compared to the other samples  
312 with an average shrinkage of 25 % (in the  $z$ -direction) (see again Table S2). In contrast, the  
313 carbon skeletal densities remained the same, within the standard deviation, for tannin content  
314 between 0 and 30%, with an average value of  $1.80 \text{ g cm}^{-3}$ . The high total porosity, ranging from  
315 76 to 83 %, is mainly due to the depolymerisation of acrylates and the gas released during  
316 transformation of tannin upon pyrolysis.

317 The influence of tannin content on the pore structure after pyrolysis, was studied. Figure 6  
318 shows the  $\text{N}_2$  and  $\text{H}_2$  adsorption-desorption isotherms, from which the textural properties of CT-  
319 20, CT-25 and CT-30 were calculated. The outgassing of samples CT-0 and CT-10 was too long,  
320 which indicates extremely narrow porosity preventing any correct adsorption measurement. We  
321 therefore report results for only 3 of the 5 carbon structures, which are given in Table S4. Figure  
322 6a shows type Ia nitrogen adsorption-desorption isotherms, characteristic of microporous  
323 materials with predominantly narrow (width less than  $\sim 1 \text{ nm}$ ) micropores, following the IUPAC

324 classification<sup>23</sup>. All three isotherms exhibited a low-pressure hysteresis that it is due to slow  
325 desorption in these very narrow pores. The amount of nitrogen and hydrogen adsorbed increased  
326 with the amount of tannin added, although the largest increase was observed for CT-25 when  
327 compared with CT-20, and slight differences were found between CT-25 and CT-30. Therefore,  
328 the textural properties increased with the amount of tannin added, and thus  $A_{BET}$  varied from 265  
329 to  $375 \text{ m}^2 \cdot \text{g}^{-1}$  while  $S_{NLDFT}$  varied from 850 to  $910 \text{ m}^2 \cdot \text{g}^{-1}$  (Figure 6c). These large differences  
330 between  $A_{BET}$  and  $S_{NLDFT}$  are due: first, to the fact that the BET method underestimates the surface  
331 area when a significant portion of the pores are smaller than 0.7 nm in diameter; secondly, to the  
332 fact  $S_{NLDFT}$  was calculated using  $\text{N}_2$  and  $\text{H}_2$  adsorption isotherms together, and the diameter of the  
333  $\text{H}_2$  molecule is about 0.3 nm while that of  $\text{N}_2$  is about 0.35 nm. Therefore,  $\text{H}_2$  has access to  
334 porous surface that  $\text{N}_2$  cannot penetrate. The corresponding isotherms are presented in Figure 6b.

335 Figure 6d shows that the three materials had very similar PSDs, the main difference being a  
336 slight increase in pores around 0.7 nm when increasing the percentage of tannin from 20 to 25%.  
337 Figure 6e shows the corresponding cumulative pore volumes. The total pore volumes,  $V_T$ , were  
338 relatively low, between  $0.20$  and  $0.23 \text{ cm}^3 \text{ g}^{-1}$  (see Figure 6f), and mostly composed of  
339 micropores. Only CT-30 had a few mesopores (pore diameter between 2 and 50 nm) but in  
340 almost negligible amount,  $0.01 \text{ cm}^3 \text{ g}^{-1}$  (thus not shown in Table S4). Most of the micropores, 75%  
341 for CT-20 and 65% for CT-30, were in the ultramicropore range, and their average diameter was  
342  $0.58 \pm 0.2 \text{ nm}$ . The latter means that only  $\text{H}_2$  molecules are able to form a bilayer inside pores  
343 with a diameter of about 0.6 nm, and thus provides insight into the large difference between  $A_{BET}$   
344 and  $S_{NLDFT}$ . The fraction of micropores where the  $\text{H}_2$  bilayer cannot be formed, corresponding to  
345 diameters smaller than 0.5 nm, is still remarkable and varies from 65 to 59% for CT-20 and CT-  
346 30, respectively.



347  
 348 Figure 6. (a) Nitrogen; and (b) hydrogen adsorption (full symbols) – desorption (empty symbols)  
 349 isotherms; (c) BET area and NLDFT surface area of the printed carbons as a function of initial  
 350 tannin content; (d) pore size distributions; (e) cumulative pore volumes calculated by the 2D-  
 351 NLDFT model; and (f) pore volumes as a function of initial tannin content.

352 Raw and differential mercury intrusion curves plotted as a function of pressure and pore  
 353 diameter, respectively, are presented in Figure S5. Analysis of meso/macropores structure by  
 354 mercury porosimetry confirmed that most of the pore volume can be attributed to large pores with  
 355 a distribution centred on a diameter of about 10  $\mu m$ , as observed in the SEM images. All pore  
 356 size distribution (PSDs) were very broad and rather multimodal, with pore diameters covering  
 357 three orders of magnitude. The addition of tannin to the initial resin was found to shift the median  
 358 pore diameter (calculated with Eq. S3) to lower values as the density increased, from 14  $\mu m$  for  
 359 CT-0 to 5  $\mu m$  for CT-30.

360 The average pore diameters were significantly higher than those reported for other 3D-printed  
 361 carbon monoliths prepared by stereolithography in the presence of porogens, followed by

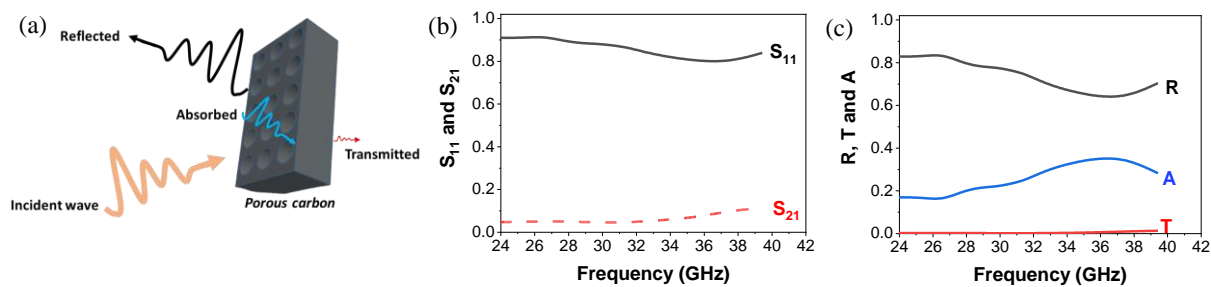
362 oxidation and pyrolysis steps, which exhibited typical pore diameters ( $d_{90}$ ) between 30 and 70 nm  
363 (but not including pores larger than 10  $\mu\text{m}$  in diameter)<sup>12</sup>. However, they were similar to those of  
364 pyrolytic carbon electrodes derived from SLA technology with pore diameters of about 10  $\mu\text{m}$ <sup>11</sup>  
365 and to those of tannin-derived monoliths prepared by emulsion templating, with values between 1  
366 and 10  $\mu\text{m}$ <sup>42,43</sup>. This is an important result because, unlike the latter materials, no particular  
367 synthesis strategy was used here to obtain pores of these dimensions in such large numbers. This  
368 result also indicates that this porosity is both wide and connected, and that it is therefore easy to  
369 develop, by classical activation processes, the micro- and mesoporosity observed above by gas  
370 adsorption. It should therefore be possible to obtain monolithic, architecturally structured  
371 activated carbons, useful for example as highly permeable, rigid and easy-to-handle catalyst  
372 supports, unlike granular or powdered carbons.

### 373 **Physical properties of printed carbon structures**

374 The electrical conductivity of a carbon structure may vary greatly as a function of texture,  
375 which in turn is a function of precursor and heat treatment temperature, and also somewhat as a  
376 function of the relative density of the material. Since the skeletal density and porosity of the  
377 different 3D-printed carbons are similar (see again Table S4), their electrical conductivity was  
378 assumed to remain of the same order of magnitude. Indeed, Table S5 shows values between 6.05  
379 and 7.1  $\text{S cm}^{-1}$  for the different formulations. Similarly, the solid electrical conductivity, *i.e.*, the  
380 electrical conductivity excluding the sample porosity, calculated using Eq. (4), was found to be  
381 between 43 and 59  $\text{S}\cdot\text{cm}^{-1}$ . This narrow range of values is reasonable considering the  
382 approximations made to obtain Eq. (4) on the one hand, and is moreover typical of glassy carbon  
383 on the other hand, for which values of 11  $\text{S}\cdot\text{cm}^{-1}$ <sup>44</sup> to 70  $\text{S}\cdot\text{cm}^{-1}$ <sup>45</sup> have been reported.

384 These relatively modest conductivity values are of great interest, as 3D-printed carbonaceous  
 385 architectures with low to medium conductivity struts have recently been shown to produce  
 386 broadband photonic crystals in the GHz range, while higher conductivities combined with the  
 387 same architectures result in higher absorption coefficients, but in an incomparably narrower  
 388 frequency range<sup>46</sup>. To prove this, printed CT-25 parallelepipeds with final dimensions of  $7.1 \times$   
 389  $3.3 \times 2$  mm were analysed in the Ka band.

390 In the whole range of frequencies studied, the EM response is strongly dominated by the  
 391 reflection, whose coefficient varies typically between 0.7 and 0.8. As a result, the absorption  
 392 coefficient varies between roughly 0.2 and 0.3, and the transmission is almost zero (Figure 7).  
 393 Analysis of the data collected yielded the shielding effectiveness,  $SE = -20 \log(S_{21})$ , and it can be  
 394 concluded that the studied material provide a shielding level in the range of 20 to 22 dB.  
 395 Although it is not very high, it is indeed a broadband absorption, which can be interesting to build  
 396 photonic crystals and thus brings new perspectives to these porous biosourced carbons.



397  
 398 Figure 7. Electromagnetic properties of the CT-25 structure: (a) schematic of the EM response; (b)  
 399 frequency dependence of the  $S$  parameters ; (c) corresponding behaviour of the reflection,  
 400 transmission and absorption coefficients.

401 The strain-stress compression curves of 3D-printed carbon cubic samples are given in Figure  
 402 S6a-S6e. The compressive strength was defined as the highest stress at the first peak, the slope of

403 which was used to determine the Young's modulus. Following this first peak, the stress decreased  
404 sharply, indicating a brittle failure of the material. The repetition of this phenomenon throughout  
405 the compression of the samples led to serrated stress-strain characteristics explained by the  
406 propagation of cracks in the carbon matrix. This behaviour then gave way to a progressive  
407 densification of the material, as indicated by the increase in stress at strains above 35 %.

408 As expected, due to its denser structure obtained after pyrolysis (see again Table S4), the  
409 sample printed with tannin-free acrylate resin showed relatively high compressive strength at  
410 break (2.9 MPa) and high Young's modulus (156 MPa). These values decreased significantly to  
411 1.4 MPa and 83 MPa, respectively, with the addition of 10 wt.% of tannin in the resin. This can  
412 be explained by the decrease in density of the structures due to the low volume shrinkage  
413 observed in the presence of tannin (Table S2). Then, due to this density gain, the mechanical  
414 properties of the 3D-printed carbons increased with the increase of tannin content from 10 wt.%  
415 to 30 wt.% to reach values close to those of the sample without tannin (CT-0), see Figure S6f and  
416 Table S6. Because of the reduction in porosity with tannin loading from 10 to 30 wt.%, the  
417 materials became more brittle, as indicated by the reduction in strain at break with values  
418 decreasing from 7.0 to 2.8% (Table S6). In this printed system, tannin, being a bio-based carbon  
419 precursor, helped to maintain the structure after pyrolysis and increase the material yield, but  
420 only really appeared as a reinforcement at high loading. Under these conditions, at 30 wt.% of  
421 tannin, mechanical properties are about equivalent to those of the carbonised pristine acrylate  
422 resin, but with a significantly better yield and with a non-negligible share of renewable and  
423 ecological material. Generally speaking, these mechanical properties are higher than those  
424 obtained for carbon manufactured by stereolithography with a similar density<sup>12</sup>.

425

## 426 CONCLUSION

427 The present paper demonstrated for the first time an effective strategy to develop 3D-printed  
428 carbon materials from bio-based resins using stereolithography (SLA). A new resin formulation  
429 based on an acrylate-tannin suspension was developed to meet the viscosity requirements for  
430 SLA printing. Indeed, despite its simple preparation and interesting mechanical properties, the  
431 shrinkage and warpage of the carbon structure derived from the pure acrylate resin remained  
432 significant and the carbon yield upon pyrolysis was low. Thus, the addition of tannin to the  
433 formulation allowed porous structures to be printed with an encouraging carbon yield close to  
434 20 %. At a loading above 20 wt.%, tannin significantly reduced the warpage and volume  
435 shrinkage of the resulting carbon structures by about 35 %.

436 Increasing amounts of tannin were found to increase the bulk density of the structures while  
437 the skeletal density remained the same, leading to a high total porosity of about 80%. However,  
438 the non-graphitizable and very disordered carbon structures exhibited low surface area and wide  
439 pore size distribution, demonstrating the presence of a limited amount of very narrow pores  
440 together with very large pores with a median diameter ranging from 5 to 10  $\mu\text{m}$ . These  
441 characteristics demonstrate the possibility of preparing architected activated carbons, for  
442 instance for catalytic applications, as the pre-existing porosity can be further developed by  
443 conventional activation methods.

444 These carbon architectures also showed correct electrical conductivities in the range of 6-7 S  
445  $\text{cm}^{-1}$ , varying with the textural properties, with a solid electrical conductivity between 43 and 59  
446  $\text{S}\cdot\text{cm}^{-1}$ , quite typical of glassy carbon. These properties open the way to the preparation of more  
447 sustainable 3D-printed devices for electrochemical applications, in which glassy carbon is widely  
448 used, but also for electromagnetic applications, for which moderate conductivities might be



449 preferable if broadband absorption is required. Finally, the new 3D-printed carbon structures  
450 presented here exhibited high mechanical properties with elastic-brittle behaviour. Nevertheless,  
451 in this system, tannin as a carbon precursor really appeared as a reinforcement only at high  
452 loading (> 25 wt.%).

453 The possibility of obtaining complex architectures with a non-negligible share of renewable  
454 and bio-based material, with good carbon yield and little shrinkage to tailor their properties,  
455 makes our approach promising for a broad range of applications. Thus, more detailed studies of  
456 such 3D carbon architectures will be carried out in the near future.

#### 457 ASSOCIATED CONTENT

458 **Supporting information:** Additional experimental details and results including data and figures  
459 related to elemental analysis, porous texture, mechanical properties, particle size distribution of  
460 mimosa tannin, and SEM and TEM images of two different 3D-printed carbons.

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##### 465 **Funding Sources**

466 This study was partially funded by ERDF [TALiSMAN project (2019-000214)]. This research  
467 received funding from Campus France and Lithuanian Science Council through the joint program  
468 PHC Gilibert #46414VC “Hybrid gels for electromagnetic applications”. It was also sponsored  
469 by the NATO Science for Peace and Security Program [Grant G5697 CERTAIN “Globular  
470 carbon-based structures and metamaterials for enhanced electromagnetic protection”].

471 ACKNOWLEDGMENT

472 P.B. acknowledges the French Ministry of Higher Education and the Grand-Est region for her  
473 PhD grant, resulting in the work presented herein. We thank Sartomer France and Elkem Silicone  
474 France for providing us materials. We also acknowledge the help from Christine Gendarme,  
475 François Montaigne and Jaafar Ghanbaja for SEM and TEM, Ghouti Medjahdi for X-ray  
476 diffraction, Rafael Luan Canavesi for gas adsorption, Alexander Zharov for electromagnetic  
477 properties and Philippe Gadonneix for technical assistance in the laboratory.

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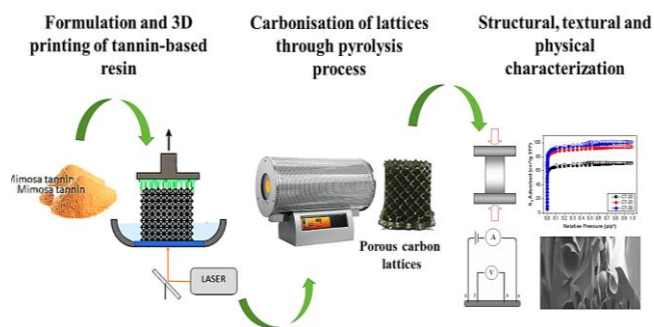
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626 GRAPHICAL ABSTRACT

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631 SYNOPSIS

632 Highly porous, conductive and mechanically resistant 3D-printed bio-based carbon were  
633 produced from tannin precursors through stereolithography.

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