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1 **Innovative approach to the development of conductive hybrid composites**
2 **for Selective Laser Sintering.**

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10
11 **Abstract**

12 Selective Laser Sintering (SLS) was used to manufacture electrically conductive polymer composites
13 made of polyamide 12 reinforced with carbon fibres and graphite (PA12/CF/GP). Since material design is
14 critical in developing conductive polymer composites, an innovative experimental technique is proposed
15 to preliminary evaluate the electrical behaviour of the powders before SLS processing and select the most
16 performing hybrid compositions. The properties of starting powders and the microstructure, mechanical
17 and electrical behaviour of PA12/CF/GP composites were studied. Results reveal that the addition of
18 graphite lowers the flowability and mechanical properties of the composites compared to the carbon
19 fibres reinforced counterparts. Hybrid composites display great enhancements in the electrical
20 conductivity with respect to the neat PA12 up to anti-static and conductive range; however, no synergistic
21 effect between the two fillers was observed.

22
23 **Keywords:** A. Carbon fibres; A. Hybrid; B. Electrical properties; E. 3-D printing

24
25 **1. Introduction**

26 Selective Laser Sintering (SLS) of polymeric composite materials has attracted intensive research interest
27 thanks to the combination of the advantages of Additive Manufacturing (AM) techniques and the unique
28 mechanical and functional properties of composite materials [1]. Moreover, since the material choice for
29 SLS has mainly been restricted to polyamide 12 (PA12), as the most broadly used engineering polymer,

30 great efforts have been applied to improve the properties of PA12 parts using functional reinforcements
31 [2] or through infiltration with epoxy resin [3].

32 Among carbon fillers, carbon fibres (CF) and graphite platelets (GP) are frequently preferred to
33 nanofillers to minimize the cost of the material and to avoid agglomeration during the mixing process due
34 to the strong Van der Waals attraction between nanoparticles. Carbon fiber reinforced polyamide 12 is in
35 fact the most widely used composite powder within the SLS community, due to its excellent combination
36 of structural and functional properties. An increase in mechanical properties with respect to pure PA12 is
37 consistently reported [4–6]. Graphite has also been employed as filler in mechanically mixed powders to
38 enhance the mechanical and functional properties of the polymers produced by SLS. However, only a few
39 studies have been carried out on these composites. Wang et al. [7] reported that the addition of graphite
40 platelets improved the mechanical properties of Poly Ether Ether Ketone (PEEK) composites produced
41 through High Temperature Laser Sintering (HT-LS). However, graphite greatly reduced the flowability of
42 the PEEK powders, leading to not uniform powder deposition during the layer spreading. Consequently,
43 an increase of porosity and pore size with increasing graphite loading was observed. Guo et al. [8] found
44 that the size of the graphite platelets greatly influence the electrical conductivity of SLS-fabricated
45 bipolar plates as larger flakes improve the electrical behaviour of the composites to a greater extent than
46 powdered graphite [9,10].

47 Hybrid polymer composites have attracted increasing attention in recent years since the addition of
48 different fillers to polymers can provide a synergistic effect resulting in great improvement of mechanical
49 properties, thermal and electrical conductivity [11–14]. Although the enhancement of composite
50 performances is not always achieved [15,16], it is generally recognized that the synergistic effect on the
51 electrical conductivity comes from the formation of percolative network structures within the polymer
52 due to the presence of two conducting fillers with different aspect ratios and geometrical morphology
53 [11]. Improvement of electrical conductivity was observed in polyethylene with carbon fibres and
54 graphite platelets [17] as well as in polymer composites containing a combination of nano and micro
55 fillers such as carbon black (CB) and CF [18,19] or multiwalled CNTs and CF [20]. Interestingly,
56 Zambrzycki et al. [21] found that CNTs and CB are particularly effective in increasing the electrical
57 conductivity of hybrid epoxy composites reinforced with carbon fibres, while GNPs seem to play a
58 detrimental role due to a poorer dispersion within the polymer matrix.

59 Moreover, although recent research advances suggests that the mechanical and electrical behaviour of
60 hybrid composites considerably depend on the ratio between the amounts of the two types of fillers, a
61 generally accepted theory has not been reached [11,12]. Therefore, hybrid composites should be tailored
62 for each application.

63 However, the strategy commonly used for testing new materials by SLS firstly involves the processing
64 of composites by varying the starting powder composition in term of both filler nature and amount, and
65 then the characterization of obtained samples to investigate the effect of carbon-based reinforcements.
66 This approach is costly and time-consuming slowing down the development and optimization of new
67 composite systems [22–26]. For these reasons, designing a method to preliminary assess the electrical
68 conductivity of the polymer composites before physical processing of the powders in the SLS machine
69 entails great interest.

70 In the present work a new approach involving the measurement of electrical conductivity of raw
71 powders is proposed to evaluate “a priori” their electrical properties and percolation behaviour at varying
72 fillers nature and content. This can trigger the development of conductive hybrid composites powders for
73 SLS. Moreover, the research aimed to exploit the possible synergistic effect of different carbon
74 microfillers on the electrical conductivity of the sintered samples. Different combinations of carbon fibres
75 and graphite were investigated as fillers because they greatly differ in morphology and aspect ratio,
76 resembling at micro-scale CNTs and GNPs respectively. PA12 powders were used as matrix to exploit
77 their unique advantages in terms of SLS processing. These polyamide 12/carbon fiber/graphite
78 composites (PA12/CF/GP) also offer the possibility to reduce material cost by replacing the rather
79 expensive carbon fibres with a cheaper filler without modifying the mechanical mixing process used for
80 powders production.

81 **2. Experimental**

82 **2.1 Preparation and characterization of composite powders**

83 The hybrid composite powders were produced starting from two commercial SLS powders, purchased
84 from ADVANC3D Materials® GmbH (Hamburg, Germany), and natural graphite powders purchased
85 from Alfa Aesar (Haverhill, MA, USA). The properties, according to the datasheet provided by the
86 producers, and the function of the raw powders are reported in the following:

- 87 • Polyamide 12 powder reinforced with 20 wt.% short carbon fibres (AdSint® PA12 CF) with density
88 of 1,06 g/cm³, used to provide both the polymer matrix and the carbon fibres.
- 89 • Polyamide 12 powder (AdSint® PA12) with median size of 38 µm and density of 0,99 g/cm³, used to
90 decrease the carbon fibres content.
- 91 • Graphite powders (crystalline, mesh size –300 mesh, purity level of 99%), used as second filler to
92 produce hybrid composites.

93 Samples of 20 g each were obtained by mechanical mixing the raw materials in different relative
94 amount by using a TURBULA® mixer (WAB-GROUP®, Muttenz, Switzerland) for 3 hours. Binary
95 composites reinforced with a single filler (from 0 to 20 wt.% of carbon fibres or graphite) and ternary
96 hybrid composites with different concentrations of both fillers, as summarized in Table 1, were processed.

97 The electrical conductivity of the powders was evaluated by using the measurement set-up derived
98 from Giorcelli et al. [27]. The instrument sketched in Figure 1 was constituted by two aligned copper
99 cylinders with a diameter of 30mm; around 3 g of composite powders were inserted in the inner chamber
100 (with a thickness of few millimetres) created between the copper cylinders using a hollow plastic
101 container. The electrical resistance of powdered materials was evaluated at increasing pressure (up to
102 1500 bars) through a digital multimeter (Keysight 34401A, Keysight Technologies, CA, USA). Insulating
103 plastic square weighing dishes were placed between the conductive cylinders and the load surfaces of the
104 hydraulic press to ensure that the electrical signal moved across the powders. The stabilized value of
105 electrical resistance and the distance between copper electrodes were recorded at zero pressure and at 150
106 bar in order to compact the powders. The electrical conductivity was calculated using Ohm's law reported
107 in equation (1)

$$\sigma = \frac{L}{RS} \quad (1)$$

108 where L is the distance between copper electrodes, R is the resistance of the composite powders and S is
109 the surface area of the electrodes. R was calculated subtracting from the measured data the resistance of
110 the system without any material samples.

111 Hybrid composite powders that showed the best electrical properties were selected to be processed by
112 SLS and the production was scaled up to 600 g using the same TURBULA® mixer.

113 The morphology of the powders and the dispersion and distribution of the fillers were characterized
114 by using a field emission scanning electron microscope (FESEM Zeiss MERLIN, Carl Zeiss Microscopy

115 GmbH, Jena, Germany) with an accelerating beam voltage at 3–5 kV. The particle size distribution of the
116 composite powders was assessed examining several 500x micrographs through image analysis using
117 Image J[®] software. Carbon fibres length distribution was evaluated before and after the mixing process to
118 reveal potential fiber breakage. 300 particles were measured from 20 different images to assess the
119 particle size distribution of polyamide powders, graphite particles and carbon fibers respectively. The
120 crystalline phase of graphite powders and PA12/CF/GP composite was evaluated by X-ray diffraction
121 analysis through a Panalytical PW3040/60 X'Pert PRO diffractometer (Cu-K α radiation, $\lambda = 1.5418 \text{ \AA}$).
122 The 2θ angular range in recording was 10° – 60° with a step size of 0.013° .

123 The bulk and flow behaviour of the unfilled PA12 and the composite powders was investigated
124 through tap density and Hall flow tests. The apparent and tapped density, determined using a simplified
125 procedure based on ASTM D7481 and reported elsewhere [28], were used to evaluate the packing factor
126 (Φ) and the Hausner ratio (HR), using the equation (2) and (3) respectively

$$\Phi = \frac{\rho_{\text{bulk}}}{\rho} \quad (2)$$

$$\text{HR} = \frac{\rho_{\text{tap}}}{\rho_{\text{bulk}}} \quad (3)$$

127 where ρ_{bulk} and ρ_{tap} are the apparent and tapped density respectively, and ρ is the true density of the
128 powders, determined by using a gas pycnometry (UltraPyc 5000, Anton Paar Italia S.r.l, Rivoli, Torino,
129 Italia) according to ASTM B923-20 standard. The flowability was assessed using the Hall Flowmeter
130 funnel according to ASTM B213–17 standard.

131 The melting and crystallization behaviour of the powders was analysed by using Differential Scanning
132 Calorimetry (DSC). Experiments were carried out in inert atmosphere (nitrogen flow, 30 mL/min) with a
133 heating-cooling cycle between 100°C and 230°C with a rate of $10^\circ\text{C}/\text{min}$ by using a PerkinElmer Pyris
134 1 equipment (PerkinElmer Inc., Waltham, MA, USA). A temperature modulated step-scan DSC program
135 was used to evaluate the specific heat capacity of the powders according to ASTM E1269–11 standard.
136 The powders were analysed alternating dynamic (heating rate of $10^\circ\text{C}/\text{min}$) and isothermal segments (1
137 min) with a 5°C step from 80°C to 240°C .

138 Thermal Gravimetric Analysis (TGA) tests were performed by using a Mettler-Toledo TGA/SDTA
139 851e instrument (Mettler Toledo, Columbus, OH, USA) to evaluate the thermal stability of the powders.

140 The samples were heated from 25 °C to 800 °C with a rate of 10 °C/min in inert atmosphere (argon flow,
141 50 mL/min),

142 **2.2 Selective Laser Sintering**

143 The selected hybrid composites were processed by using Sharebot SnowWhite SLS machine
144 (Sharebot S.r.l., Nibionno, Italy) equipped with continuous wave CO₂ laser. Commercial PA12 and 20
145 wt.% carbon fibres reinforced PA12 (PA12/CF) powders were also processed for mechanical and
146 electrical properties comparison. The process parameters, summarized in Table 2, were optimized in
147 order to maximize part density using a series of trials and errors builds specifically designed on the basis
148 of the evaluation of the Stable Sintering Region (SSR) and the Energy to Melt Ratio (EMR) analysis,
149 whose details are reported elsewhere [29].

150 Flat dog-bone samples complying ISO 527-2 standard (geometry 1BA) and coupons (10x10x3 mm³ in
151 size) were produced to evaluate the mechanical properties, the electrical conductivity and the
152 microstructure of the composites. The specimens were built-up in the XY plane (i.e. the building plane)
153 with a cross-directional scanning strategy (0/90°).

154 The mechanical properties of the composites were evaluated by using a MTS Criterion Model 43 testing
155 system (MTS Systems S.r.l., Italy). Tensile tests were performed on four SLS-printed samples for each
156 composition with a strain rate of 1 mm/min and a 25 mm length extensometer for strain measurements.

157 The surface fracture of tensile specimens and the interfacial bonding between polymer matrix and
158 fillers particulate were analysed by using a FESEM Zeiss MERLIN microscope. In order to evaluate the
159 orientation and distribution of fillers in the polymer matrix, optical microscope (Leica DMI 5000 M,
160 Leica Microsystems GmbH, Wetzlar, Germany) was used. Y-Z and X-Y samples cross sections were
161 mounted in acrylic resin and properly polished using standard metallographic preparation (SiC grinding
162 papers up to 4000 grid and napped cloth for diamond paste polishing up to 1 µm). The porosity of the
163 sintered parts was evaluated by analysis of optical micrographs and gas pycnometer. In the former
164 method, high-resolution images of entire Y-Z cross section of the samples were constructed by stitching
165 40 individual optical micrographs (magnification 100x). These images were analysed through Image J®
166 software to measure the voids content and their distribution in the cross section. The obtained values were
167 then compared to the porosity determined by using helium gas pycnometer (P_{pyc}) according to equation
168 (4):

169
$$P_{\text{pyc}} = \frac{\rho_{\text{sample}}}{\rho_{\text{powders}}} \times 100 \quad (4)$$

170 where ρ_{sample} is the printed parts density and ρ is the true density of the powders (determined as
171 reported in section 2.1). The bulk density of the sintered coupons was measured by gas pycnometry
172 according to MPIF 63 standard.

173 The electrical conductivity of the sintered coupons in the X and Y direction was measured through a
174 Keysight 34401A digital multimeter (full scale of 120 M Ω) with the 2-point probe method according to
175 ASTM D4496-13 standard. The surface of the samples was properly grounded and painted with a silver
176 conductive paint to improve measurement consistency.

177 **3. Results and discussions**

178 **3.1 Hybrid composites powders**

179 **3.1.1 Electrical properties**

180 The electrical properties of binary and ternary composite powders were assessed with the instrument
181 sketched in Figure 1. Since SLS is a pressureless manufacturing technique, the electrical behaviour of the
182 powders at zero and low applied pressure (150 bar) is of great interest. The percolation curves of binary
183 and ternary hybrid composite systems are depicted in Figure 2. The measured values of resistance at 0 bar
184 (Figure 2a) describe the electrical behaviour of the powders deposited without applying any pressure (it
185 resembles the condition of the powder bed in SLS machine). Carbon fibres reinforced composites show
186 the highest electrical conductivities, while graphite ones maintain an insulating behaviour even at high
187 filler content. The hybrid composites display intermediate electrical properties with a percolation
188 threshold that lies between 15 wt.% and 20 wt.% of reinforcements.

189 The conductivity values obtained at low pressure (Figure 2b) can provide some insights on the
190 electrical properties of the composites after powders consolidation. It can be seen that the percolation
191 threshold of the powders decreases during compression to 10 wt.% or less at 150bar. This behaviour
192 could be ascribed to the decrease of voids among filler particles and the flattening of polymer powders
193 due to compressive forces. Therefore, denser conductive networks of carbon fillers forms inside the
194 powders leading to the improvement of their electrical properties. At this pressure (150 bar), the electrical
195 conductivity of the hybrid composites approaches the value obtained for carbon fibres/polyamide binary
196 systems with high filler content, showing the best performances at 20 wt.% of fillers loading. However,

197 the measured values are probably overestimated since during the SLS process the powders are distributed
198 on the building chamber by roller or blade systems and will not be compacted.

199 The electrical behaviour at 0 bar appears to be highly significant for SLS processing conditions. In
200 fact, unlike other manufacturing technologies of polymer parts, during the SLS process the consolidation
201 of powders is achieved only by laser irradiation and melt diffusion with extremely weak flow. As a result,
202 the original dispersion and distribution state of the fillers particles is preserved. Therefore, the percolation
203 behaviour and the electrical properties of raw powders are expected to be similar to those of the sintered
204 parts. Based on this consideration, hybrid composites containing 5 wt.% of carbon fibres and 15 wt.% of
205 graphite (PA12/5CF/15GP) and 10 wt.% of carbon fibres and 10 wt.% of graphite (PA12/10CF/10GP)
206 were selected as candidate material to produce conductive parts by SLS.

207 **3.1.2 Morphological and physical properties**

208 Figure 3a-c shows the different morphology and surface structure of the powders used to prepare the
209 hybrid composites as revealed by FESEM microscopy. Their particle size distribution, obtained from
210 image analysis, are reported in Figure 4a. Polyamide 12 powders show a cauliflower-like morphology and
211 nearly regular shape as a result of the anionic ring opening polymerization production process (Figure
212 3a). A slightly wavy surface structure with some grooves is also visible. The powders display a particle
213 size distribution between 30 μm and 60 μm (Figure 4a), which is the preferable range for SLS processing
214 [30]. Chopped carbon fibres with a diameter of about 7 μm and a wide length distribution (Figure 4c)
215 were used as filler in PA12/CF composite. The surface of the fibres is clean and reveals parallel grooves
216 along their longitudinal direction, as shown in Figure 3b. Graphite powders consist of low-aspect ratio
217 platelets with surface area and shape that varies from elongated to small and rather spherical particles
218 (Figure 3c). The width of the graphite platelets was evaluated by image analysis: a narrow particle size
219 distribution with mean width of 24 μm was recorded (Figure 4b). These morphological characteristics are
220 significant to minimize the negative effect of graphite platelets on the packing and flowability behaviour
221 of the composite powders. In fact, graphite powders seems to be more effective than high aspect ratio
222 flakes at granting continuous and homogeneous powder layers during powder bed recoating. However,
223 the improvement of the electrical conductivity of the resulting composites is generally lower [9].

224 Figure 3d-f displays the morphology of the mechanically mixed composite powders. PA12 particles
225 retain their size, cauliflower-like shape and surface structure (Figure 3d). This indicate that mechanical

226 mixing does not compromise the morphological characteristics of the polymeric powders, which are
227 favourable for SLS processing. In fact, Turbula shaker mixers are not equipped with mixing tools, thus
228 avoiding the application of high shear stresses that can damage the PA12 powders. Therefore, the packing
229 efficiency, flowability and effectiveness of sintering between adjacent polymer particles are preserved.
230 The powders exhibit a rather homogeneous distribution of fillers with no obvious agglomeration observed
231 in FESEM images (Figure 3d and e). At higher magnification it can be seen that the grooves in PA12
232 particles surface are partially coated by small graphite platelets with sizes near 1 μm (Figure 3f). These
233 particles could enhance the laser absorption of the powders and help transfer the heat to the polymer
234 particles, as revealed by detailed study of the absorbance of graphite reinforced polycarbonate and PEEK
235 composites [7,31].

236 In addition, it is worth noting that carbon fibres and graphite are not significantly broken or exfoliated
237 during the mixing process (Figure 3d and e). The comparison between the length distribution of carbon
238 fibres before and after the mixing step, graphically depicted in Figure 4c, largely confirms the FESEM
239 analysis. However, a slight difference in the length distribution of carbon fibers was recorded (Figure 4c).
240 This can be attributed to the rupture of a of fibers with a starting length greater than 100 μm as a result of
241 the low shear stresses induced by the 3D motion (i.e. rotation, translation and inversion) of the mixing
242 system. In the same way, XRD analysis was used to investigate the possible exfoliation of the graphite
243 particles during the mixing step (Figure 4d). The position of (002) and (004) graphite peaks in the
244 PA12/CF/GP composite pattern are not shifted with respect to that observed in the pure graphite. These
245 results reveal that the basal spacing of the graphite sheets is unchanged (3.37 \AA), thus confirming that the
246 mixing process does not affect the crystalline structure or exfoliate the graphite platelets [32].

247 The packing and flowability behaviour of the powders were investigated by using Hall flow and tap
248 density tests (Table 3). A correlation between these results and those obtained from morphological and
249 granulometric analysis can be evidenced. Unfilled PA12 powders show an almost free flowing behaviour.
250 In fact, it is well-known that particles with nearly spherical shape and regular size could be homogeneously
251 spread on the part bed of the SLS building chamber by the recoating system [30]. The high aspect ratio
252 and large length distribution of chopped carbon fibres significantly affect the flowability of the powders,
253 as highlighted by a 10% increase in Hausner ratio and the failure of Hall flow test. This effect is more
254 pronounced in hybrid composite powders since polymer particles and carbon fillers highly differ in terms

255 of shape, morphology and particle size distribution (Figures 3 and 4). Therefore, the packing efficiency
256 decreases due to hindering of physical contact between polymer particles caused by graphite platelets and
257 carbon fibres. This poorer powder flowability reduce powder bed density and surface quality, thus
258 negatively affecting the effectiveness of the sintering process.

259 **3.1.3 Thermal properties**

260 Figure 5 shows the DSC curves of unfilled PA12, PA12/CF and hybrid composite powders. Sharp and
261 well defined melting (Figure 5a) and crystallization (Figure 5b) peaks, in addition to a wide temperature
262 interval between the onset of melting ($T_{m\ onset}$) and crystallization ($T_{c\ onset}$) events can be observed. This
263 interval, referred as “sintering window”, is usually adopted as guideline to define the powder bed
264 temperature for semicrystalline polymers. A large sintering window is favorable in order to delay
265 crystallization as long as possible, thus preventing out-of-plane warping of the part [1,30].

266 A small shift to higher temperatures of the crystallization event appears in hybrid composites (Figure
267 5b). In fact, the addition of graphite generally affects the crystallization behaviour of polymers leading to
268 the reduction of the supercooling degree at increasing filler content. This behavior is ascribed to the fact
269 that graphite acts as nucleating agent in polymer composites, as frequently reported in the literature [33–
270 35]. In fact, graphite platelets prevent the mobility of polymer chains due to the interaction with the
271 repeating units and increase the number of heterogeneous nucleation sites, that ultimately results in a low
272 energy barrier for crystal nucleation [34]. However, the reduction of the “sintering window” extent is
273 small and it is not regarded as relevant for SLS processing. The data obtained from DSC curves are
274 summarized in Table 4.

275 Figure 6 illustrates the TGA curves of unfilled PA12, PA12/CF and hybrid composite powders. It can
276 be seen that the powders show a similar behaviour with a single-step degradation process occurring at
277 temperatures above 400°C. As expected, the char residue is higher for composites powder with respect to
278 unfilled PA. DSC and TGA results reveal that the addition of graphite does not significantly influence the
279 thermal properties of the powders. Therefore, the authors suggest that the processing conditions, namely
280 powder bed temperature and laser exposure parameters, are similar between the composite materials
281 under investigation.

282 **3.2 SLS printed parts**

283 **3.2.1 Microstructure and mechanical properties**

284 The mechanical properties of PA12 parts, PA12/CF and hybrid composites are summarized in Table
285 5. The addition of carbon fibers improves the mechanical properties of neat PA12. In particular, the
286 elastic modulus is more than doubled and the tensile strength is enhanced by 19%. However, the overall
287 mechanical properties dramatically decrease when 10 wt.% and 15 wt.% of CF are replaced by graphite.
288 The elastic modulus of the hybrid composites decreases as graphite particles exhibit lower stiffness than
289 carbon fibres, but it remains higher compared to unfilled PA12 parts (Table 5). The tensile strength and
290 elongation at break of PA12/5CF/15G sintered parts are reduced by 40% and 46% respectively in
291 PA12/5CF/15GP composite with respect to PA12/CF. A similar drop in mechanical properties was
292 observed by Panda [36], that reported a reduction of strength by 23% and failure strain by 48% when 10
293 wt.% of particulate graphite was added to glass fiber/PEEK composites. However, it should be noted that
294 the addition of graphite produces lower tensile strength parts (over 20%) with respect to neat PA12. A
295 comparable reduction of strength was reported by Athreya et al. [26] for 4wt.% carbon black reinforced
296 PA12 powders processed by SLS due to filler agglomeration.

297 The poor flowability of the powders does not seem to significantly affect the microstructure of the
298 hybrid composites, as revealed by the low content of porosity within the sintered parts (Table 5). This
299 unexpected result could be explained by the fact that the negative effect of the poor flowing behaviour of
300 the powders is probably counterbalanced by the increased laser absorption that promotes the fusion and
301 coalescence of the polymer particles [7,31]. The trend of porosity values obtained by image analysis and
302 gas pycnometry was in good agreement (Table 5): PA12 samples show the lowest porosity degree, while
303 the addition of carbon-based filler increases the porosity values. Hybrid composites containing both
304 carbon fibers and graphite show a slightly higher porosity when compared to samples reinforced with
305 carbon fibers only. It can be seen that the results obtained by image analysis are lower with respect to
306 experimental values determined by gas pycnometry. The former are slightly underestimated due to
307 polishing defects (i.e., small pores can be smeared and ignored) and inherent section-bias errors (i.e.,
308 analysis of a 2D cross section instead of volumetric information) [37].

309 FESEM micrographs of the tensile fractured surfaces of PA12/10CF/10GP parts are shown in Figure 7.
310 The images reveal that the poor mechanical properties of hybrid composites parts can be attributed to the
311 addition of graphite in the polymer matrix and the weak interfacial bonding at graphite-polymer interface.
312 In fact, the low magnification image in Figure 7a displays that an almost-fully dense part has been

313 obtained by laser sintering. Although few pores induced by fibres pullout can be observed in the fractured
314 surface, a strong interfacial bonding between fibres and polymer matrix has been developed (Figure 7b
315 and c). The fiber surface is coarse and mostly coated by polymer, leading to the formation of a ductile
316 interphase revealed by the plastic deformation of the polymer at the fiber-matrix interface (Figure 7c). On
317 the contrary, the interfacial interaction between graphite platelets and polyamide matrix is insufficient and
318 “fragile” debonding around the filler particles is observed (Figure 7e and f). It can be assumed that
319 graphite platelets act as point of stress concentration, inducing non-uniform stress distribution in the
320 material with subsequent filler-matrix debonding and formation of sites for crack nucleation and potential
321 composite failure [36,38]. Thus, the poor affinity between unmodified graphite particles and PA12
322 matrix, which limits the ability of the interface to transfer stresses, explain the increased brittle behavior
323 of the hybrid composites [39].

324 The high amount of graphite in the hybrid composites (from 10 wt.% to 15 wt.%) plays a key role in
325 the reduction of tensile strength and ductility as well. The study carried out by Wang et al. [7] on
326 PEEK/graphite composites produced through HT-LS showed a significant drop of mechanical properties
327 in composites with 7.5 wt.% graphite due to a considerable increment of porosity and pore size within the
328 parts. Yasmin et al. [32], Karevan et al. [40] and Alshammari et al. [33] described similar effects on
329 graphite/polymer composites with thermoplastic and thermoset matrices, indicating that the
330 agglomeration of filler particles negatively affects the tensile strength and elongation at break. In the
331 present study, the sintered parts show low porosity content, as revealed by optical microscopy images of
332 polished cross sections of PA12/5CF/15GP parts (Figure 8a and b). However, some agglomeration of
333 graphite platelets due to Van der Waals attraction between particles can be observed at higher
334 magnification (Figure 8b and c). The hindering effect induced on the polymeric chains by graphite
335 agglomerates further limits the plastic deformation of the polyamide matrix, resulting in decreased
336 strength and strain at failure [41].

337 In conclusion, the following factors are proposed to be responsible for the overall reduction of
338 mechanical performances in hybrid composites:

- 339 • Partial substitution of high strength carbon fibres with graphite.
- 340 • Poor interfacial interaction between graphite platelets and polymer matrix. This leads to particle-
341 matrix debonding, thus significantly reducing the stress transfer at the filler-matrix interface [36].

- 342 • Agglomeration of graphite particles that acts to some extent as stress concentration sites and hinders
343 the deformation of polymer chains before failure [38].

344 **3.2.1 Electrical properties**

345 The in-plane electrical conductivity values of PA12, PA12/CF and hybrid composites parts are
346 reported in Table 6. The electrical conductivity of the laser sintered PA12/CF/GP composites achieves
347 values between 10^{-2} and 10^{-3} S/m, which are several orders of magnitude higher compared to the unfilled
348 PA12 (10^{-9} S/m). This reveals that the percolation threshold effectively occurs below the 20 wt.% of total
349 fillers loading, thus revealing a good agreement between the electrical properties of the raw powders and
350 the SLS parts. Moreover, the electrical conductivity of the different compositions exhibits the same trend
351 ($\sigma_{\text{PA12CF}} > \sigma_{\text{PA12/10CF/10GP}} > \sigma_{\text{PA12/5CF/15GP}}$) (Table 6 and Figure 2a). In fact, the addition of graphite to
352 partially replace carbon fibres does not improve the electrical properties compared to the PA12/CF
353 powders and SLS parts and no synergistic effects between the fillers is thereby observed. This behaviour
354 could be ascribed to the low surface area of graphite powders and the resulting high interfacial resistance
355 between adjacent platelets, that hinders an effective electrical charge transport. Moreover, the creation of
356 conductive networks is more difficult since the formation of point-to-point contact between filler particles
357 in the composite is less frequent when graphite powders with low aspect ratio are used instead of larger
358 flakes [8,9]. Therefore, a lower improvement in the electrical characteristics occurs at increasing graphite
359 content (Table 6). This observation is in good agreement with the “bridge double percolation model”
360 proposed by Thongruang et al. [17] to explain the electrical properties of hybrid CF/graphite/polyethylene
361 (PE) films. The authors reported that the conductivities of PE composites containing 5 wt.% of CF and
362 different amount of graphite are lower compared to those of the parts with 15 wt.% of CF and graphite.
363 This can be ascribed to the role of carbon fibers that span across insulating regions and bridge the
364 graphite particles, thus promoting the formation of continuous conductive pathway.

365 Interestingly, the electrical conductivity is different along x and y direction: this anisotropic behaviour
366 is attributed to the preferential orientation of carbon fibres along the x axis, induced by the recoater
367 movement during the spreading of a new layer of powders. The physical mechanism involved in fibres
368 orientation during SLS building process has already been described elsewhere [42] and this study
369 confirmed it. In fact, optical micrographs of polished X-Y cross sections of PA12/10CF/10GP samples in
370 Figure 8d indicate that most of the carbon fibres, particularly those with length comparable to layer

371 height, are hit by the recoater and tend to align in the x direction. By contrast, graphite platelets maintain
372 a random orientation within the polymer matrix, as their size is significantly lower than layer height.

373 Although the slight decrease of the electrical conductivity, PA12/5CF/15GP and PA12/10/CF/10GP
374 parts produced by SLS meet the industrial requirements of anti-static and conductive polymer composites
375 respectively [43]. Therefore, these composites provide a low-cost alternative to the carbon fibres
376 counterparts to manufacture non-structural components in the automotive and aerospace industries.

377 Similar electrical conductivities values has been reported for SLS-processed PA12 composites
378 reinforced with other carbon fillers, such as carbon black (CB) [26,44,45], carbon nanotubes (CNTs) [43]
379 and graphene (GNP) [23] (Figure 9). However, the percolation thresholds are significantly lower due to
380 the fillers size (i.e. nanoscale) and the used powders preparation technique (i.e., ball milling or solution-
381 based methods). In fact, nanofillers are coated onto the surface of PA12 particles, thus promoting the
382 formation of segregated conductive structures among powder boundaries [23,26,43–45]. Nevertheless, it
383 should be noted that nanofillers are expensive compared to CF and graphite and the powder preparation
384 methods employed are not as easily scalable as mechanical mixing to high-volume manufacturing
385 environments.

386 The SLS hybrid composites parts exhibit similar electrical behaviour compared with graphite
387 reinforced polymer micro-composites produced by SLS [46] and compression moulding [11], resin
388 casting [11] and calendaring [12] (Figure 9). In fact, unlike these processes, the pressure and shear flow
389 during laser sintering is extremely weak. Consequently, the initial dispersion and distribution of graphite
390 particles are likely not altered, thus promoting the formation of conductive network structures at lower
391 filler content (Figure 9). Therefore, the powder-based additive manufacturing technique used offers a
392 reliable alternative to replace traditional technologies in the production of electrically conductive spare
393 parts or components with complex geometries without the fabrication of moulds.

394 **4. Conclusions**

395 The development and optimization of hybrid PA12/CF/GP composites from powders to laser sintered
396 parts were carried out in this work. Several compositions were prepared with various amount of carbon
397 fibres and graphite. A new approach involving the preliminary evaluation of the electrical properties of
398 powdered polymer composites was proposed. This technique provides information on percolation

399 phenomena of powders at atmospheric pressure, and it can be useful to preliminary assess the most
400 promising SLS materials before physical testing in the SLS machine.

401 The hybrid composite powders exhibit highly heterogeneous morphology and size distribution due to
402 the addition of both carbon fibres and graphite particulates. This results in a poor flowing behaviour, as
403 revealed by the Hausner ratio and Hall flowability index. However, mechanical mixing has proved to be
404 appropriate to uniformly disperse the fillers without affecting powders morphology. The calorimetric
405 analysis shows that the hybrid composites exhibit a slightly smaller sintering window compared to the
406 unfilled PA12 as graphite promotes the crystallization of the polymer matrix.

407 The mechanical properties of laser sintered PA12/CF/GP samples greatly decreases compared with the
408 binary PA12/CF counterparts due to graphite addition. Although the laser effectively sintered the powders
409 (an average porosity between 3% and 1.5% was observed), the poor interfacial bonding at graphite-matrix
410 interface and the agglomeration of graphite platelets throughout the structure is believed to be responsible
411 for the drop in tensile properties.

412 Although no synergistic effect between the two types of fillers has been observed, the hybrid
413 composites show electrically conductive behaviour. However, the conductivity values remain slightly
414 lower compared with PA12/CF counterparts since graphite powders are less effective than fibres for
415 improving the electrical properties. The investigation also demonstrates that the in-plane electrical
416 properties show anisotropic behaviour due to the preferential orientation of carbon fibres along the
417 recoater movement direction.

418 The developed PA12/CF/GP composites produced by an easy scalable mixing process, could offer a
419 low-cost alternative to carbon fibres counterparts to fabricate electrically conductive components through
420 SLS. Therefore, the proposed approach is a promising and simple method for an intelligent development
421 and qualification of conductive composites powders for SLS. In fact, only a few grams of material are
422 necessary to perform the test. However, the results highlight the key role of filler morphology and
423 characteristics in powders development. Future research work should focus on the investigation of the
424 influence of these factors on flowability, mechanical and electrical properties of the sintered parts.

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573 **Figure captions**

574

575 **Figure 1.** Schematic illustration of the measurement set-up used for testing the conductivity of binary and
576 ternary hybrid composite powders.

577 **Figure 2.** Effect of fillers content on the electrical conductivity of binary and ternary composites powders
578 at a pressure of (a) 0 bar and (b) 150 bar

579 **Figure 3.** FESEM images of (a) PA12 particles, (b) carbon fiber surface at high magnification, (c)
580 graphite powders and (d, f, e) PA12/5CF/15GP composites. The white arrows in (f) indicate the small
581 graphite platelets placed in the grooves of PA12 particles.

582 **Figure 4.** Particle size distribution of PA12/CF/GP composites constituents: (a) polymer particles size,
583 (b) graphite platelets width and (c) carbon fiber length before and after mixing; (d) XRD patterns of raw
584 graphite and PA12/CF/GP composite.

585 **Figure 5.** DSC (a) melting curves and (b) recrystallization curves of PA12, PA12/CF and hybrid
586 composites powders (heating/cooling rate of 10°C/min)

587 **Figure 6.** TGA curves of PA12, PA12/CF and hybrid polymer composites powders. Inset: weight loss
588 derivative curves that reveal the temperatures at maximum weight loss rate (T_{max})

589 **Figure 7.** FESEM micrographs of the fractured surface of PA12/10CF/10GP parts: (a) morphology of the
590 fracture surface at low magnification; (b,c) carbon fiber-matrix interface; (d) weak region rich in graphite
591 platelets (indicated by white arrows) and (e,f) graphite-matrix interface at different magnification.

592 **Figure 8.** Optical micrographs of Y-Z cross sections of PA12/5CF/15GP samples showing (a,b) the
593 dispersion and distribution of carbon fillers and (c) higher magnification image of graphite agglomerates
594 within the polymer matrix; (d) optical micrographs of X-Y cross sections of PA12/10CF/10GP.

595 **Figure 9.** Comparison of the electrical conductivities of polymer composite reinforced with different
596 carbon fillers processed by SLS and graphite reinforced polymer composites produced by other
597 manufacturing processes (CM=compression moulding, IM=injection moulding, RC=resin casting,
598 C=calendaring).

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600

601

602 **Tables**

603

604 **Table 1.** Binary and ternary composite powders for electrical conductivity characterization

Composition	Carbon fiber CF (wt.%)	Graphite powder GP (wt.%)
PA12 + CF	5	–
	10	–
	15	–
	20	–
PA12 + GP	–	5
	–	10
	–	15
	–	20
PA12 / 5% CF + GP	5	5
	5	10
	5	15
PA12 / 10% CF + GP	10	5
	10	10

605

606

607 **Table 2.** Optimized process parameters for the production of PA12, PA12/CF and hybrid composite
 608 samples for tensile and electrical properties characterization.

Material	T _{bed} (°C)	Laser power (W)	Scan speed (mm/s)	Layer height (µm)	Energy density (J/mm ³)	EMR
PA12	170	5.6	2400	100	0.233	3.8
PA12/CF	170	5.6	2400	100	0.233	5.0
PA12/5CF/15GP	170	6.3	2400	120	0.219	5.1
PA12/10CF/10GP	170	6.3	2400	120	0.219	4.9

609

610

611 **Table 3.** True density, packing factor, Hausner ratio and Hall flowability index of PA12, PA12/CF and
 612 hybrid composite powders.

Parameter	PA12	PA12/CF	PA12/5CF/15GP	PA12/10CF/10GP
True density ρ (g/cm ³)	0.94 ± 0.05	1.08 ± 0.01	1.07 ± 0.01	1.08 ± 0.02
Packing factor ϕ	0.522	0.408	0.397	0.401
Hausner ratio HR	1.16 (good) ^a	1.28 (fair) ^a	1.40 (passable) ^a	1.37 (passable) ^a
Hall Flow Rate (s/20cm ³)	3.85	fail	fail	fail

613 ^aClassification according to [47]

614

615

616 **Table 4.** Thermal transition temperatures and sintering window (ΔT) of PA12, PA12/CF and hybrid
 617 composite powders obtained from DSC experiments

Material	$T_{m \text{ onset}}$ (°C)	T_m (°C)	$T_{c \text{ onset}}$ (°C)	T_c (°C)	ΔT (°C)
PA12	174.6	182.2	153.2	150.3	21.4
PA12/CF	174.7	182.3	153.9	151.2	20.8
PA12/5CF/15GP	174.8	181.7	156.7	153.6	18.2
PA12/10CF/10GP	174.8	181.2	156.6	153.6	18.3

618

619

620 **Table 5.** Mechanical properties and porosity of PA12, PA12/CF and hybrid composite parts. The porosity
 621 was calculated using microscopy (P_{mic}) and gas pycnometry (P_{pyc})

Material	Elastic modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Porosity P_{mic} (%)	Porosity P_{pyc} (%)
PA12/5CF/15GP	2.1 ± 0.6	31.1 ± 1.0	2.6 ± 0.1	1.5	2.6
PA12/10CF/10GP	2.6 ± 0.6	34.0 ± 1.9	2.4 ± 0.5	2.1	3.0
PA12/CF	3.7 ± 0.1	50.3 ± 2.5	4.9 ± 0.3	1.0	2.4
PA12	1.5 ± 0.1	42.1 ± 1.1	15.8 ± 2.1	1.2	2.2

622

623

624

Table 6. In-plane electrical conductivity of PA12, PA12/CF and hybrid composite parts

625

along x and y direction

Material	σ_x (S/m)	σ_y (S/m)
PA12 ^a	$< 10^{-9}$	$< 10^{-9}$
PA12/5CF/15GP	$1.37 \cdot 10^{-3}$	$3.06 \cdot 10^{-4}$
PA12/10CF/10GP	$1.62 \cdot 10^{-2}$	$6.01 \cdot 10^{-3}$
PA12/CF	$5.55 \cdot 10^{-2}$	$1.27 \cdot 10^{-2}$

626

^aResistance values outside the multimeter range ($>120 \text{ M}\Omega$)

627