Innovative approach to the development of conductive hybrid composites for Selective Laser Sintering

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Abstract

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

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

1. Introduction

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

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

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

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

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

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

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

2. Experimental

2.1 Preparation and characterization of composite powders

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

- Polyamide 12 powder reinforced with 20 wt.% short carbon fibres (AdSint® PA12 CF) with density of 1,06 g/cm^3, used to provide both the polymer matrix and the carbon fibres.
- Polyamide 12 powder (AdSint® PA12) with median size of 38 µm and density of 0,99 g/cm^3, used to decrease the carbon fibres content.
- Graphite powders (crystalline, mesh size –300 mesh, purity level of 99%), used as second filler to produce hybrid composites.

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

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

$$\sigma = \frac{L}{RS} \tag{1}$$

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

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

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

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

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

$$\Phi = \frac{\rho_{bulk}}{\rho} \tag{2}$$

$$HR = \frac{\rho_{tap}}{\rho_{bulk}} \tag{3}$$

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

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

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

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

2.2 Selective Laser Sintering

The selected hybrid composites were processed by using Sharebot SnowWhite SLS machine (Sharebot S.r.l., Nibionno, Italy) equipped with continuous wave CO_2 laser. Commercial PA12 and 20 wt.% carbon fibres reinforced PA12 (PA12/CF) powders were also processed for mechanical and electrical properties comparison. The process parameters, summarized in Table 2, were optimized in order to maximize part density using a series of trails and errors builds specifically designed on the basis of the evaluation of the Stable Sintering Region (SSR) and the Energy to Melt Ratio (EMR) analysis, whose details are reported elsewhere [29].

Flat dog-bone samples complying ISO 527-2 standard (geometry 1BA) and coupons (10x10x3 mm^3 in size) were produced to evaluate the mechanical properties, the electrical conductivity and the microstructure of the composites. The specimens were built-up in the XY plane (i.e. the building plane) with a cross-directional scanning strategy (0/90°).

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

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

$$P_{pyc} = \frac{\rho_{sample}}{\rho_{powders}} x100 \quad (4)$$

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

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

3. Results and discussions

3.1 Hybrid composites powders

3.1.1 Electrical properties

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

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

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

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

3.1.2 Morphological and physical properties

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

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

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

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

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

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

3.1.3 Thermal properties

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

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

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

3.2 SLS printed parts

3.2.1 Microstructure and mechanical properties

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

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

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

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

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

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

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

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

3.2.1 Electrical properties

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

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

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

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

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

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

4. Conclusions

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

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

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

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

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

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

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The data that support the findings of this study are available from the corresponding author upon request.

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Figure captions

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

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

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

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

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

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

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

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

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

Tables

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

Table 2. Optimized process parameters for the production of PA12, PA12/CF and hybrid composite 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

Table 3. True density, packing factor, Hausner ratio and Hall flowability index of PA12, PA12/CF and 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

[a] Classification according to [47]

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

Material	$T_{m\ onset}$ (°C)	T_m (°C)	$T_{c\ onset}$ (°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

Table 5. Mechanical properties and porosity of PA12, PA12/CF and hybrid composite parts. The porosity 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

Table 6. In-plane electrical conductivity of PA12, PA12/CF and hybrid composite parts 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	$5.55 \cdot 10^{-2}$	$1.27 \cdot 10^{-2}$

[a] Resistance values outside the multimeter range (>120 MΩ)