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Development of Polypropylene Composites through Extrusion-Based Additive Manufacturing: The Effect of Carbon-Based Fillers

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Highlights

- PP composites reinforced with carbonaceous fillers were developed using FDM
- Filaments of each material were processed, and a viable FDM process was optimized
- The effect of fillers was evaluated in terms of materials' thermo-physical properties
- The addition of fillers led to improvements of mechanical properties of FDM samples

Abstract

Extrusion-based Additive Manufacturing, also known as Fused Deposition Modeling (FDM), is the most widespread additive manufacturing technique for polymeric materials. However, only a limited number of materials are available to be processed through this technique. Polypropylene and its composites are extremely versatile materials which are employed in a wide range of applications, but their use in FDM has not been much investigated due to issues related to adhesion and warping. In this work, composites having polypropylene as matrix and different carbonaceous fillers, namely carbon nanotubes and carbon fibers, were developed using FDM. Filaments were produced and a viable FDM process was optimized. The materials were characterized in terms of their thermo-physical properties and the effect of the fillers on these properties was investigated. The addition of

carbon fibers led to a significant improvement of mechanical properties, and a more moderate increase was observed in the case of carbon nanotubes addition.

1. Introduction

Additive Manufacturing (AM), also known with the synonymous of 3D printing in non-technical contexts, is defined as a group of processes in which materials are joined to make parts from 3D model data, usually layer upon layer [1]. AM processes can employ polymeric, metal, and ceramic materials; these processes allow to obtain complex parts that could not be processed by conventional subtractive manufacturing technologies or would need several assembly steps [2].

Amongst AM processes of polymeric materials, material extrusion AM is by far the most widespread technology due to its flexibility and cost-effectiveness [3]. This technology, which is commonly known as Fused Deposition Modeling (FDM), is based on the extrusion of a thermoplastic filament; the polymer feeds a heated extruder, where it is softened and finally deposited by the nozzle on the build platform in a layer-by-layer way to form the desired part. At the beginning, FDM was mainly used as Rapid Prototyping (RP) technology; this was also due to the limited availability of materials, which at first included only few amorphous polymers such as poly-lactic acid (PLA) and acrylonitrile-butadiene-styrene (ABS). Nowadays, thanks to both the evolution of the technology and the increment of available materials, FDM is used in a wide variety of fields, and it enables to manufacture also ready-to-use components. Nevertheless, although the number of polymers available for FDM has seen a significant increase, there are still few materials which are tailored for 3D-printing through FDM.

A polymer which is widely processed using traditional technologies, but which has only recently started being used in FDM, is polypropylene (PP). PP, together with polyethylene (PE), is the most used polyolefin; thanks to its good properties, such as tensile strength, elastic modulus, and chemical resistance, it is widely used in many fields such as automotive, packaging, and warehouse [4]. There are also few scientific works related to the employment of PP using other AM techniques, such as melt electrospinning writing [5], powder bed fusion [6] and multi jet fusion [7]; nevertheless, most of the literature is focused on FDM process.

The first work that addressed PP as a valid candidate for FDM technology was made by Carneiro et al. [8], who studied FDM of neat PP and PP reinforced with glass fibers. In this study, mechanical properties were evaluated by considering the influence of different process parameters such as layer thickness, infill percentage, and layer orientation. Comparisons were made between neat and glass-filled PP, and also between FDM-made and compression molded samples. However, this study highlighted some criticisms of processing PP through FDM. One of these issues is related to the poor adhesion between PP and the materials typically used as substrate of the build platform (in particular, glass and blue tape). Carneiro [8] used a PP plate to ensure chemical compatibility with the filament; the plate was brushed to avoid welding between the platform and the printed part. The optimization of the adhesion between PP and the building platform was also examined in the study by Spoerk et al. [9], who found ultra-high-molecular-weight polyethylene (UHMW-PE) as the most promising platform material, as it would ensure good adhesion without having issues related to welding.

Another issue is related to the high tendency of shrinkage and warping of PP when printed, which is related to the high degree of crystallinity of PP and can cause the detachment between the part and the build platform. The solution which has been proposed in several works to counteract shrinkage and warping issues of PP is the development of PP composites reinforced with either inorganic or organic fillers. Literature works reported the development through FDM of PP composites reinforced with glass spheres [10][11], glass fibers [8][12], perlite [13], cellulose [14][15][16], talc [17], hydrocarbon resins [18]. Another approach which has been considered in other works is the formulation of blends between PP and other polymers [19][20][21].

In general, processing PP composites can lead to the development of new materials with improved mechanical performances and highly customizable functional properties, thanks to the addition of specific fillers. Amongst the different reinforcements, a special mention should be headed to carbon-based fillers, and in particular carbon fibers (CF) and carbon nanotubes (CNTs). Carbon fibers are amongst the most employed fillers in the realization of composites, as the fibers provide high stiffness and strength; besides, CF can improve also thermal and electrical properties [22]. Carbon nanotubes feature outstanding mechanical, thermal, and electronic properties, making CNT-composites ideal for a wide range of applications [23]. Furthermore, both fillers were employed in the

development of metal-free electronic circuits using laser writing in some works by our research group [24][25][26].

The interest of the scientific community towards FDM of composites reinforced with CF and CNTs has seen a significant increase over the last years [27]. Nevertheless, there are still few works regarding FDM of PP composites reinforced with these carbon-based fillers. In their study, Spoerk et al. [28] developed through FDM PP composites reinforced with short CF and studied the effect of the fillers in terms of the improvement of mechanical and thermal properties. The addition of CF was shown to lead to an increase in elastic modulus, flexural strength, and thermal conductivity; however, the increase in these properties turned out to be anisotropic and print direction dependent. Savandaiah et al. studied FDM of PP reinforced with both long and short CF [29]; they observed that mechanical properties, in particular flexural and impact properties, were anisotropic and dependent on printing orientations. Stanciu et al., finally, studied FDM of PP composites reinforced with multi-wall carbon nanotubes (MWCNTs) [30]. They demonstrated the feasibility of both filament extrusion and FDM of these composites; the mechanical properties, however, were more influenced by the printing orientation rather than by the quantity of MWCNTs.

The aim of the present work is the development of two PP composites reinforced with carbon fibers and carbon nanotubes respectively. Starting from commercial pellets of PP, a masterbatch of PP/CNTs, and pristine CF, the first aim has been to assess the outcome of both filament extrusion and FDM of both the composites and the neat matrix. The work was addressed to characterize the developed materials in terms of their thermo-physical, compositional morphological and mechanical properties, with the goal to assess the effect of the carbon-based fillers on the investigated properties.

2. Materials and methods

2.1 Available materials

Polypropylene (PP) (tradename: Hostacom CR 1171 G1A) was provided in pellets by LyondellBasell (Rotterdam, Netherlands). The datasheet provided by the producer reports that this material is a mineral filled polypropylene copolymer designed for injection molding, with Melt Flow Rate of 13 g/10min (230 °C/2.16 kg) and density of 0.99 g/cm³. PP/CNTs pellets were obtained as described in

another work [31]: a masterbatch of PP reinforced with 15% of MWCNTs with average diameter of 9.5 nm, average length of 1.5 mm and purity >90%, was diluted with the matrix to obtain PP filled with 2% of CNTs. Carbon fibers (CF) (tradename: Tenax®-A HT M100 60mu) were purchased from Toho Tenax (Chiyoda, Tokyo, Japan); the fibers feature a diameter of 7.0 μm and density of 1.79 g/cm³. To improve the adhesion between PP and CF, polypropylene grafted with maleic anhydride (PP-g-MA) in form of pellets was used as compatibilizer; this was purchased from Sigma-Aldrich (St. Louis, Missouri, USA). PP-g-MA is the most used compatibilizer for PP-based composites and it is needed to ensure a better interfacial bond between the filler and the matrix, as the performances of the composite strongly depend on the interface between the two phases, and carbon fibers normally have poor interaction at the interface with polymers [32].

2.2. Development of materials

2.2.1. Compound of PP/CF

PP/CF composites were processed using a Process 11 Parallel Twin-Screw Extruder by Thermo Fisher Scientific (Waltham, Massachusetts, USA) having the following characteristics: screw diameter = 11 mm, L/D ratio = 40. This twin-screw extruder has eight thermocouples and it employs two gravimetric feeders: a principal feeder for the pellets (PP and PP-g-MA, which were manually mixed) is positioned at the beginning of the cylinder, while a second feeder for the filler is positioned after the melting of the polymer. The percentage of carbon fibers was equal to 15% wt., while the compatibilizer was added in a percentage equal to 2% wt.. The process parameters were set as follows: screw rotation speed = 300 rpm, temperature of heating elements = 190 °C (apart from the heating element at the inlet of the pellets, set to 150 °C).

2.2.2. Filament extrusion

To produce a filament with a nominal diameter of 1.75 mm, Next 1.0 Advanced filament making machine by 3Devo B.V. (Utrecht, Nederlands) was employed. This instrument consists in a single-screw extruder featuring four heating zones; the main parameters of the instrument are the temperatures of each heating zone, the screw speed, and the fan speed. The extruded filament is cooled using a system made of two fans, adjusted with a home-made flow deviator to provide a

homogeneous cooling to the filament. An inhomogeneous cooling would result in a filament with oval section, due to a higher shrinkage along the cooling direction which is caused by the high degree of crystallinity of PP. The filament is then pulled down using a two counter-rotating wheels system, whose speed can be adjusted either manually or automatically to maintain the desired diameter. The parameters employed for the extrusion of the filaments, which were the result of a long trial-and-error approach, are shown in Table 1. FDM printer normally requires a filament featuring a standard diameter of 1.75 mm. It is worth noting that deviating from this value would risk obstruction or intermittent extrusion of materials for higher or lower values of diameter respectively.

2.2.3. Fused Deposition Modeling

Roboze One 3D printer by Roboze (Bari, Italy) was employed to print the specimens. This is a standard open chamber Fused Deposition Modeling machine, having a build space of 28 cm x 34 cm. The machine was equipped with a 0.6 mm diameter steel nozzle; this was employed as the producer discouraged the use of the standard brass nozzle with diameter of 0.4 mm for printing composites, due to possible damages to the extruder head caused by the hard fillers.

A polypropylene adhesive plate with rough surface was applied to the printing bed using double-sided tape to ensure good adhesion between the printed part and the build platform, as PP presents very low adhesion with the standard materials used in FDM 3D-printers (glass, blue tape), as mentioned before in the Introduction paragraph.

Each material was printed with a flat arrangement (i.e., the surface with higher area parallel to the printing bed) and with a linear cross pattern ± 45 °, consisting of a succession of layers with the filament deposited at 45 ° alternating with layers with the filament deposited at -45°. The infill density was set at 100% for each layer; moreover, two perimeter contours were printed for each layer. The parameters used in the FDM process are shown in Table 2.

The software Simplify3D was used to implement all the process parameters and create the *gcode* file, which was then used in the FDM 3D-printer.

2.3. Characterization methods

Differential Scanning Calorimetry (DSC) analyses were performed using the Perkin Elmer Pyris 1 DSC instrument. Every sample underwent a heating ramp from 50 °C to 220 °C which was performed to eliminate the thermal history of the sample, then a cooling stage from 220 °C to 50 °C and a second heating stage from 50 to 220 °C were performed. All the heating and cooling ramps were carried out in nitrogen atmosphere (30 ml/min) with a heating/cooling rate of 10 °C/min.

Thermogravimetric analyses (TGA) were conducted with the Mettler Toledo TGA/SDTA851 instrument, interfaced with METTLER Star software. Each material was placed in an alumina crucible with a capacity of 150 µl and was analyzed carrying out the test both in inert atmosphere (argon flow; 50 ml/min) and oxidizing atmosphere (air flow; 50 mL/min). The analyses were performed from 25 °C to 900 °C with a heating rate of 10 °C/min.

Spectroscopic analysis was performed using a Perkin-Elmer Fourier-transform infrared spectroscopy (FT-IR) Frontier spectroscope. The transmission spectrum relating to the various samples was examined using infrared radiation from 4000 cm^{-1} to 400 cm^{-1}, with a resolution of 1 cm^{-1}.

The X-ray diffraction (XRD) was conducted using the Malvern Panalytical X'PERT PRO PW3040 / 60 diffractometer with Cu Kα radiation at 40 kV and 40 mA. The employed analysis program involved the scanning of the samples varying the 2θ diffraction angle from 5 ° to 50 ° with a step size of 0.013 °.

Leica DMI 5000 M optical microscope, using magnifications from 50x to 1000x, was used to estimate the length and arrangement of the carbon fibers, to assess a morphological-structural analysis of the sections of each filament used for FDM printing, and to analyze the microstructure of the sections of the samples obtained by FDM printing.

Fracture surfaces of FDM printed specimens were observed with ThermoFisher Phenom ProX scanning electron microscope (SEM). The samples were previously coated with platinum, in order to allow the observation with the microscope.

The mechanical characterization was carried out by performing tensile tests using an MTS Criterion Model 43 dynamometer, referring to the ISO 527-2:2012 standard, which is recommended in the case of polymeric materials reinforced with short fibers or other fillers. The tested specimens, previously

made by FDM printing, are those of type 1BA, reported in Figure 1, according to the aforementioned standard [33].

The electrical characterization was carried out using a Siglent SDM3065X digital multimeter. The electrical resistance was measured with the two-point method; this instrument can reveal values of resistance not higher than 120 MΩ.

3. Results and discussion

3.1. Distribution of CF

The distribution of the length of the pristine carbon fibers was evaluated using optical microscopy; the fibers were spread over a glass slide and their length was measured using the software connected to the optical microscope. Figure 2a shows some of the fibers examined using this approach. A sampling of 200 fibers were examined to evaluate the length distribution, whose results are shown in Figure 2b; it is possible to see that the average length of the carbon fibers is about 90 μm, which is slightly higher than what reported by the producer.

3.2. Thermal properties: DSC, TGA

The results of DSC analyses are shown in Figure 3. The curves in the graph are related to the cooling ramp and to the second heating stage; the first heating cycle was performed to eliminate the thermal history of the sample and is not considered. From the analysis of the curves, it is clearly possible to see the presence of two endothermic peaks during the heating cycle and two exothermic peaks during the cooling cycle, which are related to phenomena of melting and crystallization respectively.

On the base of the information reported in the literature [34][35][36], it can be supposed that the matrix is made of a blend between PP and HDPE. This hypothesis is consistent with the temperatures at which melting and crystallization phenomena take place, which are typical of these polymers, as well as the shape and disposition of the peaks. In particular, it is possible to suppose that the first and second endothermic peaks are due to the fusion of HDPE and PP crystalline phase respectively; similarly, according to this reasoning, it is possible to assume that the first and second exothermic peaks are due to crystallization processes, relative to PP and HDPE respectively.

Table 3 shows the values of melting and crystallization peak temperatures (T_m, T_c) and enthalpies of melting ΔH_m for every developed material. The table also shows the values of enthalpy of melting referred to a gram of polymer, named ΔH_{pol}. These values are representative of the crystallization of the polymeric fraction of the materials and were calculated by dividing the values of enthalpy of melting by the weight fraction of polymer, obtained using thermogravimetric analyses in inert atmosphere (see next Paragraph); for this reason, the following discussion regarding the values of enthalpies refers to the values of ΔH_{pol}.

As the composition of the blend is not known in terms of the weight fractions of the polymers, it is not possible to calculate the degree of crystallinity. Nevertheless, a qualitative comparison in terms of crystalline part between the materials can be done by looking at their values of enthalpy of melting.

The addition of carbon fibers caused a significant decrease in the value of enthalpy of melting, which can be attributed to a lower degree of crystallinity. This result could be caused by the high reinforcement content, which includes not only the carbon fibers but also the mineral fillers, which might have had a negative effect on crystallization due to interactions at the interface between the matrix and the fillers, as reported by the study of Karsli et al. [37].

The addition of the fibers anticipated the crystallization of HDPE crystals of 3 °C; this is coherent to what is exposed in the study of Zhang et al., who investigated the crystallization of iPP/HDPE blends reinforced with CF [38]. In this study, it is supposed that the fibers are selectively located in HDPE, acting as nucleating agents, and anticipating the crystallization of HDPE. The crystallization of PP occurred at the same temperature compared to the matrix, which may be explained by the fact that the CF acted as nucleating agents only for HDPE phases. Nevertheless, although the crystallization was anticipated, the enthalpy of melting related to the HDPE crystalline phase was lowered, similarly to what happened with the PP phase. This result could be explained by the fact that the interactions at the interface between the matrix and the fillers played a major role on the influence of the degree of crystallinity.

The addition of CNTs brought to a slight increase in the value of enthalpy of melting, which can be related to a rise of the crystalline content. This can be explained by the fact that the presence of CNTs promotes the nucleation process, increasing the amount of crystalline phase, as explained by

Kwiatkowska et al. [39]. The presence of CNTs increased by 3 °C the crystallization temperature of PP phase. It is then possible to suppose that CNTs can act as nucleating agents for the PP crystalline phase; this behavior is also reported in literature in the study of Zhou et al. [40]. Conversely, the crystallization temperature of the HDPE phase was not influenced by the addition of CNTs. This result was also shown in the work by Jeevananda et al. [41], so it is possible to suppose that the nucleating effect of CNTs is limited only to the PP crystalline phase.

Thermogravimetric analyses were performed with the main goals to evaluate the quantity of filler inside the composite, and to assess the influence of the CF and CNTs on the thermal stability of the material, both in oxidizing and inert atmosphere.

Figures 4(a, b) report the results of the TG and DTG analyses carried out in Argon atmosphere. All the materials showed a similar behavior, as the mass loss occurred in a unique step. The PP/CNTs composite exhibited improved thermal stability, since the values of $T_{2\%}$ and of T_{peak} are higher than those of the matrix, as shown in Table 4. It is reported in literature that CNTs can act as thermal stabilizers, and this can be due to different mechanisms, such as barrier effect, thermal conductivity of carbon nanotubes, physical or chemical adsorption, radical scavenging action, or polymer–nanotube interaction [42]. The difference between the residues of PP/CNTs and PP should give the amount of CNTs present in the composite and amounted to 2,7% wt. This value is slightly different to what was calculated in the previous work [24], where the employed pellets were processed; however, if the residue is considered at around 600 °C, where all the degradation curves showed a plateau, the difference between the two materials is around 2% wt., which corresponds to what was previously calculated.

Conversely, the addition of CF brought to an anticipation of the onset of degradation. This was also verified in the work by Savas et al. [43], who attributed this behavior to the increase in the thermal conductivity of sample. This might also be due to a non-perfect insulation of the chamber, as the curve is not perfectly flat after the first degradation step. The difference in the residue between the two runs is equal to 13.3%, which gives the content of carbon fibers. This value is lower than the quantity added during the compound; this difference could be attributed either to some losses during

the compound process, or to the degradation of part of the fibers due to non-perfectly hermetic seal. The last hypothesis could be confirmed by the fact that the weight is equal to 27% at 500 °C.

Figures 5(a, b) show the results of TG (5a) and DTG (5b) analyses for all the developed materials in oxidizing atmosphere; the onset temperature, peak temperature and quantity of residue are shown in Table 5. It is possible to see that, for every material, the samples showed a significant decrease of the weight starting from shortly after 300 °C; this step can be related to the degradation of the matrix. A second degradation step took place between 480 °C and 650 °C and can be attributed to the degradation of the pigment, which might be identified as carbon black, or also to the degradation of the carbon nanotubes, for the case of PP/CNTs composite. Finally, it is possible to identify a third step of degradation for PP/CF composite, occurring between 600 °C and 800 °C and with a maximum of weight loss rate at 700 °C, which is due to the degradation of the carbon fibers [44]. The degradation of all the materials leaded to the formation of a significant percentage of residue, which can be attributed to the presence of a mineral phase, coherently to what was reported in the datasheet. The PP/CNTs composite showed a lower thermal stability than the neat PP. This can be explained by the presence of impurities and structural defects on the surface of the nanotubes which, in an oxidizing atmosphere, can induce an early and more pronounced degradation of the polymer [42]. Conversely, the PP/CF composite showed a slightly improved thermal stability, in contrast to the analysis in inert atmosphere, as the $T_{2\%}$ was increased by 14 °C.

3.3. Compositional analysis: XRD, EDS, FTIR

The results of X-Ray diffraction analyses are shown in Figure 6. From the processing of the output data, it was possible to identify talc ($Mg_3Si_4O_{10}(OH)_2$) as the mineral phase found after the thermogravimetric analyses, in relation to the peaks at 9.5 ° (002), 19.1 ° (004), 28.7 ° (006), 38.6 ° (008), and 48.7 ° (0010).

Regarding the crystalline phases of the polymer matrix, following the DSC analysis, it was assumed that the matrix was made up of a PP/HDPE blend. From the literature search, the characteristic diffraction peaks of the α crystals of polypropylene are found at 14.28 ° (110), 17.14 ° (040), 18.92 ° (130) and 21.4 ° (111), while the peaks relative to polyethylene (HDPE) correspond to 21.6 ° (110) and 23.9 ° (200) [35], [36], [45], [46]. The presence of the characteristic peaks of both polymers is

evident, except for the peak at 21.4 ° (111) of polypropylene and 21.6 ° (110) of polyethylene, in correspondence with which there is, instead, a single peak at 21.6 °. This difference, as reported in the literature, is typical of polypropylene/polyethylene blends [36].

Furthermore, the absence of appreciable amorphous halos overall is found, confirming the high degree of crystallinity calculated following the DSC analysis; both the composites' spectra featured a halo in the area between 15 ° and 25 ° C, attributable to the presence of the carbonaceous fillers, whose XRD showed they are amorphous.

The presence of talc as mineral phase was also confirmed by EDS analyses, which were coupled to the observation of the material morphology using scanning electron microscopy. The morphology of the material, specifically of the PP/CNTs composite, which is show in in Figure 7a, revealed the presence of many lamellae-shaped structures, which featured the presence of silicon, magnesium, and oxygen, as shown in Figure 7b, confirming the hypothesis obtained from the results of the XRD analyses.

The developed materials were analyzed using IR spectroscopy; this analysis was carried out to qualitatively verify the actual composition of the materials under study, in order to provide further confirmation of what was hypothesized following the performed thermal analyses.

Figure 8 shows the spectrum related to the matrix; the composites spectra are not reported as they had negligible differences with the matrix. The identified peaks were compared with the spectra present in the literature, which showed the presence of the characteristic peaks of PP, HDPE, and talc, as reported in Table 6 [47]–[49]. The peak at 1742 cm^{-1} is related to C=O stretching [50], as reported in literature; this might be attributed to an unknown additive. The results thus confirmed what was hypothesized following the DSC and XRD analyzes, concerning the nature of both the matrix and the mineral filler.

3.4. Optimization of FDM process

The adhesion between the first layer and the printing bed is crucial for a successful outcome of the process; for this reason, this aspect was intensively investigated using a trial-and-error approach. It is often suggested to print some layers, which are often called "raft", before the desired object, in order

to increase the adhesion between the first layer of the part and the substrate; nevertheless, difficulties were found in removing the part from the raft without damaging the surface of the first layer. For this reason, the parameter which was mainly investigated and was found to have a key role was the distance between the extruder head and the printing bed. Low offset values caused welding between the part and the plate, which resulted in a difficult removal of the part and also damaging the plate; on the other hand, high offset values resulted in poor adhesion between the part and the bed, which leaded to warping of the object due to the shrinkage of the printed layers. An optimum distance of 250 µm was found to grant the best results in terms of the surface quality of the first layer and reproducibility of the process. Other important parameters were the temperature of the printing bed and the printing speed of the first layer. Lower values of bed temperature led to warping of the part, as the difference of temperature between the extruded material and the printing bed must be kept as low as possible in order to reduce the shrinkage related to the cooling of the material; on the other hand, the double-sided tape could not bear temperature higher than a certain value, which was 50 °C. Finally, the printing speed of the first layer was lowered compared to the speed of the following layers in order to increase the adhesion and to ensure the accuracy of the first layer.

3.5. Morphological analysis of filaments and FDM-printed samples

Optical microscope was used to visualize the cross-sections of the obtained filaments, which are shown in Figure 9a-d. From the images, it is possible to see that the filament showed low roughness; furthermore, there are not significant internal porosities. Figure 9d shows a higher magnification of the PP/CF filament. It is possible to see that the carbon fibers, which sometimes were broken during polishing, feature circular section, which indicates that they are aligned to the direction of extrusion of the filament. It was also possible to calculate the average diameter of the fibers, which was around 7 µm, as reported by the producer.

Figures 10a-d show the micrographs acquired by optical microscopy of the cross sections with respect to the axis of the specimens printed using FDM technology, related to PP/CNTs (a-b) and PP/CF (c-d) composites. It is possible to notice, especially from Figure 10b, a certain irregularity in the matrix, which can be attributable to the presence of talc. Regarding the same image, it can be supposed that the white zones could be attributed to the presence of carbon nanotubes agglomerates.

The cross section of the PP/CF specimen at low magnitudes (Figure 10c) shows very clearly the layer structure of the sample; it is also possible to see some porosities, which are located between the perimeter contour (printed at 0 °) and the inner part of the specimen, printed at ± 45 °. From Figure 10d, finally, it is possible to see that the cross sections of the fibers are not circular anymore, but they show to a greater or lesser extent an oval cross section, due to the printing pattern set at ± 45 °.

The morphology of the FDM samples of both PP/CNTs and PP/CF was also investigated using Scanning Electron Microscopy on the fracture surfaces of specimens submitted to tensile tests. The fracture surface of PP/CNTs composite is shown in Figures 11a, 11b. From Figure 11a, it is possible to see both the "frayed" morphology of the surface; a lamellar particle, which can be identified as talc, can be easily seen. Figure 11b, which was taken using a lower magnification, reports the layer structure of the sample; the staking of the layers is evident, as well as the contrast between the perimeter and the inside of the part. The fracture surface of the PP/CF composite, instead, is reported in Figures 11c, 11d, 11e. Figure 11c shows the morphology of the sample in the internal zone, i.e. that printed following the ± 45 ° architecture. It's possible to see that the fibers are not perpendicular to the surface, denoting that they were probably aligned along the extrusion direction. The interface between fibers and matrix can be better investigated by looking at Figure 11d, which shows the morphology of the perimeter contour, whose direction is characteristic of a filament deposited along the 0 ° direction. The fibers are aligned to the specimen, and most of them are well adhered to the matrix, to demonstrate that the compatibilizer had some good effects on the adhesion between filler and matrix; it is also possible to see some holes, related to the pull-out of the fibers. Finally, Figure 11e shows a lower magnification of the sample; it is possible to see the layers stratification, and both the fillers – fibers and talc lamellae – are clearly visible.

3.6. Mechanical properties

Figure 12 shows the results of the tensile tests; each material is represented by a curve which is representative of the average tensile test values. The mean values of elastic modulus, tensile strength and elongation at break are shown in Table 7.

The addition of the fillers led to different results. The addition of carbon nanotubes caused a slight increase of the average value of the elastic modulus, which was raised by 25% compared to the

matrix; the tensile strength, however, remained almost the same of the matrix. Finally, the PP/CNTs composite showed a much more brittle behavior, as the elongation at break was decreased by 71% compared to the matrix. These minor improvements of mechanical properties might be due to the small amount of carbon nanotubes, but more likely due to the quality of dispersion of the nanotubes; it can be supposed that both during the extrusion of filament and during FDM process the CNTs underwent agglomeration phenomena, which did not bring to relevant improvements.

PP/CF composite exhibited a more significant improvement of mechanical properties. This material showed value of elastic modulus of 2.84 GPa, almost four times higher than the elastic modulus of the pure matrix. The tensile strength was also increased, as it reached the value of 17.5 MPa, resulting in an increase of 29% compared to PP. The increase in mechanical properties demonstrates the effective transfer of stresses at the fiber-matrix interface, which was also confirmed by the fairly good adhesion between fibers and polymer revealed by SEM analyses.

3.7. Electrical properties

For every material, the multimeter measured values of resistance higher that 120 MΩ, meaning that every composite showed an insulating behavior. This could be a proof of the agglomeration of carbon nanotubes, as the percolation threshold, referred to well-dispersed CNTs, is much lower, as reported in literature [51].

4. Conclusions and future developments

The present work was focused on the study of the processability by FDM technology of polypropylene and its related composites, reinforced with carbon nanotubes and carbon fibers. Starting from commercial pellets of PP, a masterbatch of PP reinforced with CNTs, and raw carbon fibers, filaments tailored for Fused Deposition Modeling process were successfully processed. A viable FDM process was studied and satisfactorily developed for all the processed materials.

The characterization was aimed first at deeply investigating the nature of the matrix, and then at assessing the effects of the fillers on the thermo-physical and mechanical properties. By means of DSC, TGA, XRD, FTIR analyses, it was possible to identify the matrix as a blend between polypropylene and high-density polyethylene reinforced with talc. The addition of carbon nanotubes

increased the degree of crystallinity and anticipated the crystallization of the PP phase, while CF brought to a decrease in degree of crystallinity and anticipation of the crystallization of the PE phase. CNTs brought to a higher thermal stability in inert atmosphere but lower in oxidizing atmosphere, while the addition of CF brought to the opposite results.

The addition of fillers led to an improvement in mechanical properties. This was only moderate with the addition of CNTs: PP/CNTs showed an increase of 25% of elastic modulus, while the tensile strength was not increased with the addition of CNTs, probably due to agglomeration of the nanotubes. The increase in mechanical performances was more significant with the addition of carbon fibers, as the PP/CF composite featured an elastic modulus of 2.84 GPa, four times higher than the matrix, and an increase of tensile strength equal to 29%.

CRediT authorship contribution statement

Francesco Casamento: Conceptualization, Validation, Investigation, Data Curation, Writing - Original Draft **Elisa Padovano**: Conceptualization, Writing - Review & Editing, Supervision **Stefano Pappalardo**: Validation, Investigation **Alberto Frache**: Writing - Review & Editing, Supervision **Claudio Badini**: Writing - Review & Editing, Supervision, Project administration

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Figure captions

Figure 1. Type 1BA test specimens, according to BS EN ISO 527-2:2012 standard

Figure 2. (a) Carbon fibers acquired under the optical microscope, (b) CF length distribution

Figure 3. DSC curves for PP, PP/CF, PP/CNTs composites.

Figure 4. (a) TG and (b) DTG curves in inert atmosphere of PP, PP/CF, PP/CNTs.

Figure 5. (a) TG and (b) DTG curves in oxidizing atmosphere of PP, PP/CF, PP/CNTs.

Figure 6. XRD spectra for PP, PP/CF, PP/CNTs.

Figure 7. (a) SEM micrograph of the lamellar particle inside the PP/CNTs composite and (b) relative EDS spectrum

Figure 8. IR spectrum of PP

Figure 9. Cross-section images obtained using optical microscopy of filaments of (a) PP, (b) PP/CNTs, and (c-d) PP/CF.

Figure 10. Cross-section images obtained using optical microscopy of (a, b) PP/CNTs, (c, d) PP/CF specimens processed by FDM

Figure 11. Fracture surface of (a, b) PP/CNTs, (c) PP/CF in the zone printed at ± 45 °, (d) PP/CF along the perimeter contour, and (e) PP/CF at lower magnitude

Figure 12. Tensile test results for PP, PP/CF, PP/CNTs

Tables

Table 1. Parameters of the extrusion of PP, PP+CNTs, PP+CF composites

Barrel zones temperature (° C)				Screw speed (rpm)	Puller speed (mm/min)	Fan speed (%)
T_1	T_2	T_3	T_4	4.8	1585	37
190	195	200	205			

Table 2. Parameters of FDM 3D printing process of PP, PP+CNTs, PP+CF composites

Extruder temperature	Plate temperature	Printing speed	Printing speed (1^{st} layer)	Layer height	Distance between extruder and plate
245 °C	50 °C	40 mm/min	20 mm/min	0.2 mm	250 µm

Table 3. Values of melting temperatures, melting enthalpies, melting enthalpies per gram of polymer, crystallization temperatures for PP, PP/CNTs, PP/CF obtained by DSC analyses

Material	T_m (°C)		ΔH_m (J/g)		ΔH_{pol} (ΔH_m/polymer fraction, J/g)		T_c (°C)	
PP	$T_{m,1}$ = 127	$T_{m,2}$ = 165	$\Delta H_{m,1}$ = 9.6	$\Delta H_{m,2}$ = 78.7	$\Delta H_{pol,1}$ = 11.3	$\Delta H_{pol,2}$ = 92.5	$T_{c,1}$ = 125	$T_{c,2}$ = 116
PP/CF	$T_{m,1}$ = 127	$T_{m,2}$ = 165	$\Delta H_{m,1}$ = 4.8	$\Delta H_{m,2}$ = 38.2	$\Delta H_{pol,1}$ = 6.4	$\Delta H_{pol,2}$ = 50.9	$T_{c,1}$ = 128	$T_{c,2}$ = 116
PP/CNTs	$T_{m,1}$ = 128	$T_{m,2}$ = 166	$\Delta H_{m,1}$ = 10.0	$\Delta H_{m,2}$ = 86.0	$\Delta H_{pol,1}$ = 11.8	$\Delta H_{pol,2}$ = 101	$T_{c,1}$ = 124	$T_{c,2}$ = 119

Table 4. T_{onset}, T_{peak} and residue of PP, PP/CF, PP/CNTs in argon atmosphere.

Material	$T_{2\%}$, argon (°C)	T_{peak}, argon (°C)	Residue, argon (%)
PP	397	461	12.5
PP/CF	389	465	24.9
PP/CNTs	431	469	15.2

Table 5. T_{onset}, T_{peak} and residue of PP, PP/CF, PP/CNTs in air atmosphere.

Material	**$T_{2\%}$, air (°C)**	**T_{peak}, air (°C)**	**Residue, air (%)**
PP	308	411	11.8
PP/CF	322	410	11.6
PP/CNTs	301	405	12.0

Table 6. List of peaks with corresponding wavelengths, induced vibrations, and material correspondences

Wavelength [cm^{-1}]	**Induced vibration**	**Material correspondance**
667	Si-O-Si bend	Talc
719	CH_2 rock	HDPE
730	CH_2 rock	HDPE
973	CH_3 rock, C-C stretch	PP
999	CH_3 rock, CH bend, CH_2 wag	PP
1012	Si-O-Si stretch	Talc
1167	CH bend, CH_3 rock, C-C stretch	PP
1376	CH_3 bend	PP
1463	CH_2 bend	HDPE
1742	C=O stretch	Unknown
2849	CH stretch	HDPE
2916	CH stretch	PP, HDPE
2950	CH stretch	PP

Table 7. Average values of Elastic modulus, Tensile strength and Elongation at break obtained by tensile tests for PP, PP/CF, PP/CNTs materials.

Material	**Elastic Modulus (GPa)**	**Tensile Strength (Mpa)**	**Elongation at break (%)**
PP	0.72 ± 0.07	13.6 ± 0.3	36.5 ± 2.90
PP/CF	2.84 ± 0.24	17.5 ± 1.1	4.78 ± 0.85
PP/CNTs	0.90 ± 0.23	13.4 ± 0.4	9.20 ± 1.75