CHARACTERIZATION OF ELASTIC AND RESISTANCE BEHAVIOURS OF 3D PRINTED CONTINUOUS CARBON FIBRE REINFORCED THERMOPLASTICS

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Abstract
The aim of this research is to evaluate the mechanical properties of 3D printed continuous carbon fibre polyamide composites using a novel composite Fused Filament Fabrication (FFF) printing process. The FFF process is one of the most popular 3D printing processes due to its simplicity, low cost of the printers and the possibility of combining different materials. The printer used in this study is Mark Two® from Mark Forged®. The ply and interlaminar behaviours are characterized to determine elastic and strength properties. The longitudinal and transverse tensile strength, and the in-plane and interlaminar shear resistances have been determined for polyamide resin unidirectionaly reinforced with carbon-fibres. The values are in general lower than those of an equivalent material made by hot compression moulding. These effects are likely to be associated with observed microstructure defects produced during the printing process, such as a high void content, highly non-uniform fibre distribution (resulting in matrix-dominated and fibre high-density regions), and weak bonding between filaments. Despite these constraints, the current FFF 3D printing process of thermoplastic composites has great potential due to a flexible laminate and component design including possibly fibre hybridization, and filament orientation in non-conventional directions or steered to high curvatures.

1. Introduction

The 3D printing technology of continuous fibre reinforced thermoplastics has a great potential because it allows obtaining complex geometry parts reinforced with fibres in non-conventional orientations. This novel process is still under development, being the main challenge to leap from prototyping to industrial applications. In this respect, great efforts are being conducted on improving the mechanical properties of the material, printing greater volume pieces and increasing the productivity of the printers [1]. Fused Filament Fabrication (FFF) is one of the most popular 3D printing processes due to its simplicity, low cost of the printers and the possibility of combining different materials. In this layer by layer fabrication process, a thermoplastic or a fibre reinforced thermoplastic filament is extruded through a heated printer head to shape and fill each layer [2, 8]. The printer used in this study is Mark Two® from Mark Forged®, which is able to print continuous carbon, glass or aramid fibre reinforced polyamides [3].

Due to particularities associated with the process, mainly the lack of a significant pressure on the deposited filaments, several defects result on the printed parts, such as bad adhesion between layers, voids and non-homogeneous distribution of fibres. Dependence of mechanical properties of these defects on printed specimens is, at this moment, not well understood. Overall, the existing knowledge on the mechanical behaviour of the printed continuous fibres composites is limited, as judged by the reduced number of publications in the literature [4-9]. To impulse the use of this new technology in the design of complex composite parts, further knowledge of the mechanical behaviour of the material is compulsory.

In this study, the ply and interlaminar behaviours of a 3D printed continuous carbon fibre reinforced polyamide laminate are characterized to determine elastic and strength properties. Different orthotropic directions and load cases are addressed, i.e. longitudinal and transverse tension, in-plane shear and interlaminar shear resistance. The obtained properties are compared to an equivalent material made by hot compression moulding [10, 11] to assess the performance of this novel FFF process. In addition, the microstructure is observed through different microscopy techniques, which allows identifying both the defects associated with the printing process and the most relevant fracture mechanisms.

2. Material and test methods

2.1. Materials and printing process

The materials that can be printed in the Mark Two® printer are limited and the matrix-fibre relation of the filaments is predetermined. The only non-reinforced material that can be used is PA6 plain polyamide. In the case of reinforced materials, the reinforcements can be discontinuous or continuous: as a discontinuous reinforcement composite a PA6 polyamide with a chopped carbon blend, called Onyx is available; and finally, continuous carbon, glass or aramid fibre reinforced polyamide composites can also be used. During the printing process, top and bottom layers and vertical external layers of unreinforced polyamide or Onyx are included in the samples by default, which are termed roof, floor and vertical walls by the software, respectively. In this study, continuous carbon fibre reinforced polyamide composite and the unreinforced polyamide covering material have been used to print the specimens.

The extrusion parameters of the printing process of different materials on the Mark Two® are fixed, and the ones shown in Table 1 correspond to the continuous carbon fibre composite. Regarding the filling parameters, different filling patterns can be chosen; in this case, a straight filling pattern with parallel filament extrusion, called 'isotropic' by Mark Forged®, has been used with a 100% fill density. The aim of this study is to characterise continuous carbon fibre reinforced composites, therefore the amount of un-reinforced polyamide material is reduced to minimum, only one wall contour and one roof and floor layer has been printed in the specimens.

Table 1. Extrusion and filling parameters of the printing process.

Extrusion parameter	Value
Layer thickness (mm)	0.125
Nozzle diameter (mm)	0.9
Extrusion temperature (°C)	252
Printing speed (mm/s)	15

Filling parameters	Value
Filling type	Isotropic
Fill density	100%
Number of wall contours	1
Number of roof and floor layers	1

2.2. Analyses of the quality of materials and process

The quality of both, supplied carbon composite filament and printed samples, have been examined to detect the presence of process-induced defects. Both microstructures have been examined by optical microscopy. In the filament, the quantity, size and distribution of the fibres have been observed, as well as the presence of voids. In the specimen, the sizes of the extruded filament and layers, the fibre distribution and the presence of pores have been investigated. The analysed printed sample is a longitudinal tension specimen with a $[0]_8$ carbon composite lay-up. The samples have been prepared in two steps. First, samples have been sanded using 600, 1200 and 4000 grit SiC paper consecutively, and after that, the samples have been polished using 6 µm and 3 µm monocrystalline diamond suspensions on polishing cloth. The optical microscope used is a Leika DM IRM.

In addition, the content of fibre and voids in both, supplied composite filament and printed sample, have been measured. The subtraction of the fibre has been done according to ASTM D3171 by matrix digestion in sulphuric acid/hydrogen peroxide. In the study of the quality of printed parts, square samples of 25.5 mm in side and 2 mm in thickness have been printed. The samples were composed of 16 layers, two polyamide external layers (roof and floor layers) and 14 carbon composite internal layers. The filling pattern was 'isotropic' with 100% fill density and the lay-up configuration of the composite was $[0/90]_7$.

2.3. Measurement of mechanical properties

The ply and interface behaviours of the composite has been characterized to determine the elastic moduli, Poisson's ratio and strength values. For this purpose, different fibre orientations and load cases have been addressed, i.e. longitudinal tension, transverse tension, in-plane shear and interlaminar shear resistance. The three types of tests have been done according to ASTM standards: ASTM D 3039 for tensile properties, ASTM D 3518 for in-plane shear properties using tensile tests of ±45º laminated specimens and ASTM D 2344 for interlaminar strength by short beam test method.

Five specimens have been produced for each test. The dimensions (width × length × thickness) in millimetres of the specimens were 15 × 250 × 2.25 for longitudinal tension, 24 × 175 × 2.5 for transverse tension and 22 × 190 × 2.5 for in-plane shear. The lay-up of the carbon composite is $[0]_{16}$ for the longitudinal tension samples, $[90]_{18}$ for the transverse tension samples and $[+45,-45]_9$ for the in-plane shear samples, and as mentioned before, all the specimens have one floor and one roof of external polyamide layer. All these specimens have been cut from a printed plate by water jet machining in order to avoid edge effect of the polyamide and composite fill contour in the mechanical properties. In longitudinal and transverse specimens glass fibre composite tabs have been used according to the standard. The tensile tests have been performed in a Zwick/Roell universal testing machine equipped with a 50 kN load cell, and the longitudinal and transverse strains have been measured with a GOM-ARAMIS digital image correlation system. The testing speeds were 1 mm/min for longitudinal and transverse tension tests and 5 mm/min for in-plane shear tests. The fractured surfaces have been observed in a scanning electron microscope (FEI Nova NanoSEM 450).

In the case of the short beam tests, the dimensions of the specimens were 12 × 40 × 6 mm^3. The lay-up of the carbon composite was $[0]_{46}$ with two external polyamide layers (floor and roof). The 5 specimens have been cut from a printed plate by machining in order to avoid edge effect (IsoMet 1000 precision saw). The tests have been performed in a Zwick/Roell universal testing machine equipped with a 5 kN load cell at a 1 mm/min load rate. The delamination has been observed in a macroscope (model Leica Z16 APO) after sanding and polishing the tested specimens.

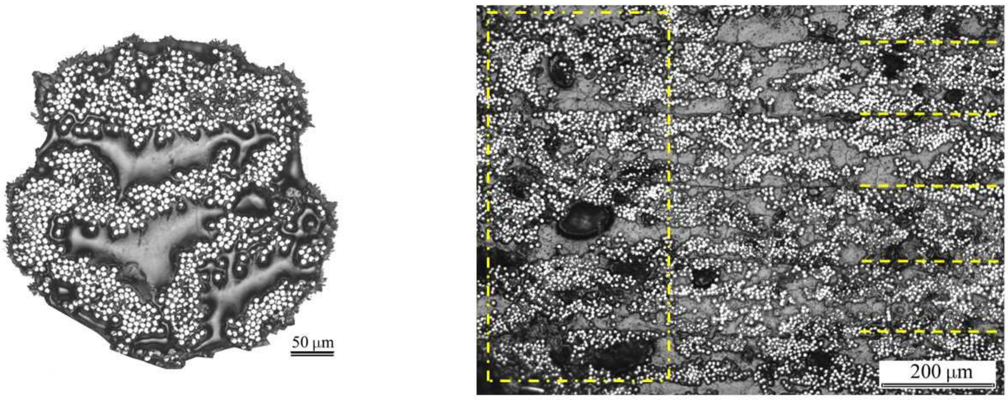
Polyamide is a hygroscopic polymer, hence its mechanical properties depend on the quantity of absorbed moisture. To ensure the same testing conditions in the different configurations, all the specimens have been conditioned in a climatic chamber at 23ºC and 50% relative humidity for at least 4 days before testing.

3. Results and discussion

3.1. Process and material quality

Microstructure of carbon pre-extruded filament has been examined using an optical microscope. Microscope images of the cross section show non-uniform distribution of the fibres, in fact matrix-dominated and fibre high-density regions have been observed (Figure 1a). The fibres appear to be well impregnated in the resin and the amount and size of pores, which appear mainly in densely packed fibre regions, is very low. Cross sections for four carbon filaments have been analysed by the microscope. The mean area and diameter of the filament cross section are 0.104 mm^2 and 363 µm, respectively. Carbon filament contains around 1000 fibres and each fibre has a 33 μm^2 mean area and 6.5 µm mean diameter. The ratios of fibres to filament areas represents the fibre volume fraction of the filament, which is estimated to be around 32% from the pictures.

Microstructure of a printed longitudinal tensile specimen has been also examined by the optical microscope. The cross section of the specimen is shown in Figure 1b. Interlayer limits are visible, which indicates that the diffusion of the matrix is incomplete during the deposition process. Similarly to the filament, the fibre distribution is non-uniform and large matrix-dominated zones exist. However, the printed specimen presented large voids, mainly at the interfaces between extruded filaments (black zones in marked box in Figure 1b). This fact indicates printing process is unable to adequately compact the extruded filament onto the printed part.



(a) (b)

Figure 1. Cross section of the pre-extruded carbon fibre composite filament (a) and cross section of a unidirectional laminate printed specimen (b).

As explained above, fibres and voids concentration for pre-extruded carbon filament and for printed sample have been measured by matrix digestion method. First, densities of both samples have been determined and then fibre and voids volume fractions have been calculated. Measured density of the filament was 1.348 $kg/dm^3$and corresponding fibre volume fraction was 34.6% (in accordance with micrographic analysis estimation), and the volume fraction of voids was below 1%. For the printed sample, the measured density was 1.154 kg/dm^3, the corresponding fibre volume fraction was 24.1%, and it shows a high voids volume fraction : 11.9%. The decrease of the fibre content from the filament to the sample is significant. Similar values have been obtained by van der Klift *et al.* [4], Justo *et al.* [6] and Goh *et al.* [7] by matrix burn-off technique. The overlapping of the extruded filament is shown by Goh *et al.* [7]. This reduction can be associated to the presence of the unreinforced nylon in the external layers of the printed parts, and also to the large quantity of voids produced during the printing process.

In summary, fibre volume fraction obtained by FFF process is low and the voids quantity is high in comparison with traditional composite manufacturing processes (more than 40% fibre volume fraction and less than 3% in voids volume fraction).

3.2. Mechanical properties

The ply and interface behaviours of the composite has been characterized to determine elastic and strength properties. At ply level, three tests have been performed: longitudinal tension, transverse tension and in-plane shear. Fibre volume fraction of the ply-level test specimens was estimated to be 27%. On the other hand, fibre volume fraction of short-beam test specimens was around 30%; higher than the tensile specimens due to a greater number of carbon composite layers.

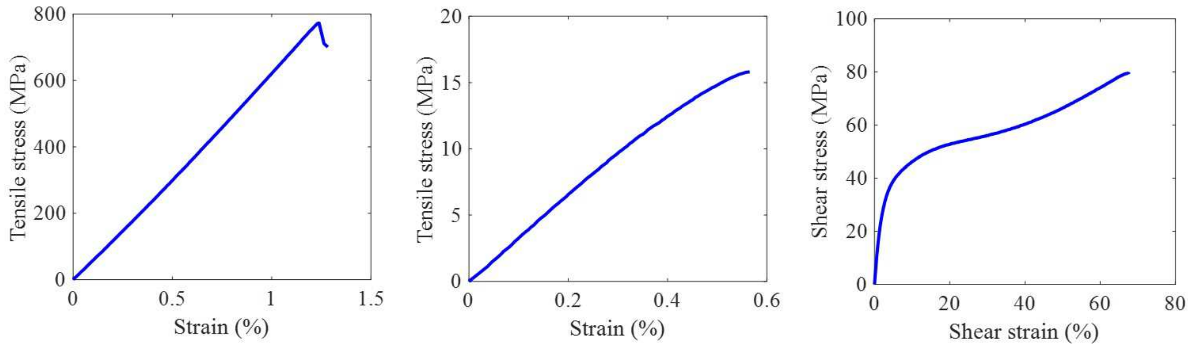
In order to evaluate the performance of printing process and the quality of printed material, obtained mechanical properties have been compared to the ones of an equivalent material made by means of hot compression moulding [10, 11]; Ma *et al.* [10] compared tensile properties of carbon fibre/epoxy and carbon fibre/polyamide 6 unidirectional composites. Yi *eta al.* [11] analysed the effect of different fibre coatings on the interlaminar shear strength of PA6 composites. The measured mechanical properties and reference data are shown in Table 2. The value shown in brackets correspond to the fibre volume fraction from the reference data. Stress-strain curves obtained for one repetition of each test are shown in Figure 2.

Table 2. Mechanical properties of the printed carbon fibre composite.

Test	Property	Average ± stand. dev.		Reference data [10, 11]	
Longitudinal tension	Tensile modulus (GPa)	60.9	± 1.1	65.4	(27.0%)
	Poisson's ratio	0.41	± 0.0	-	
	Tensile strength (MPa)	779.8	± 6.2	900.0	(27.0%)
	Ultimate tensile strain (%)	1.24	± 0.0	-	
Transversal tension	Tensile modulus (GPa)	3.13	± 0.1	7.4	(42.3%)
	Tensile strength (MPa)	15.8	± 1.8	33.0	(42.3%)
	Ultimate tensile strain (%)	0.58	± 0.1	-	
In-plane shear	Shear modulus (GPa)	1.58	± 0.1	-	
	Shear strength at 5% (MPa)	39.3	± 3.0	-	
	Shear strength at 27% (MPa)	56.7	± 3.8	-	
Short beam test	Interlaminar strength (MPa)	34.1	± 0.1	38.8-46.7	(20.7%)

For the longitudinal tensile tests, brittle fracture has been observed at 1.24% strain. The average values of tensile modulus and of tensile strength are slightly higher than the one reported by Mark Forged® (54 GPa and 700 MPa respectively). Similar stiffness and higher strength have been obtained by Blok *et al.* [8] but with thinner specimens. As seen in Figure 2a, the stress-strain behaviour is approximately linear-elastic, in spite of a slight stiffening effect which is characteristic continuously fibre reinforced composites and is likely to be caused mainly by the change of morphology of the fibres under increasing load, as discussed in [12]. With regard to the fracture behaviour, fibre breakage mechanisms, fibre pull-out and fibre bundles have been observed (Figure 3a). Fracture SEM images indicate a good interfacial bonding between matrix and fibres. Mechanical properties in longitudinal direction are similar to values reported for samples made by hot pressing with the same fibre volume fraction [10].

For transeversal tensile test, very low plastic strain has been observed and the fracture can be considered to be brittle (Figure 2b). Mechanical properties obtained are lower than the reference data obtained by hot pressing process for higher fibre volume fraction [10]. The fracture is produced in a plane perpendicular to the load and parallel to the fibres. Fracture SEM images show localized matrix plastification zones, voids and fibre bundles debonding zones (Figure 3b). In the case of the transversal tensile strength, the cause of the early fracture may be the high stress concentrations that are produced in the matrix near fabrication defects like voids and high-density fibre zones.

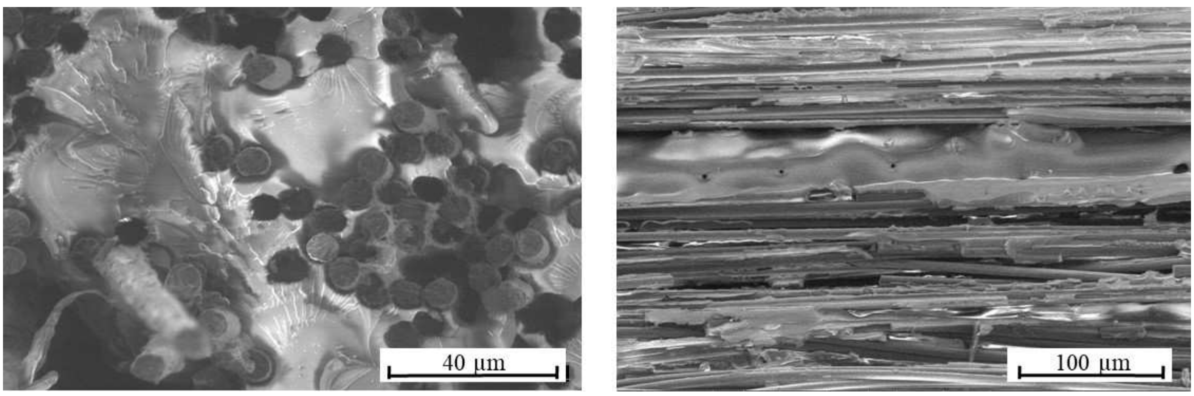


(a) (b) (c)

Figure 2. Stress-strain curves of (a) longitudinal tensile test, (b) transveresal tensile test and (c) in-plane shear test.

Stress-strain curve of one sample for the in-plane shear test is shown in Figure 2c. A very high strain has been observed, in contrast to the behaviours of the longitudinal and transversal configurations. In the final part of the test, a stiffening effect behaviour can be distinguished. This may be due to the alignment of the fibres to the load direction. Shear strength value has been considered just before the alignment phenomenon, at inflexion point, which corresponds to a 27% shear strain level (Table 2).

During the short beam test, small delamination has been produced between the load and support points in the zone of maximum shear stress. Similar behaviour and interlaminar shear strength values have been reported by Caminero *et al.* [9]. In comparison with reference data obtained by hot pressing and less fibre volume fraction, interlaminar strength of the printed specimens is 27% lower (Table 2), indicating plies bonding is a weak zone in the parts produced by FFF 3D printing process.



(a) (b)

Figure 3. Fracture images of (a) longitudinal tensile test fracture surface and (b) transversal tensile test fracture surface.

4. Conclusions

The quality of a novel composite FFF printing process and the mechanical properties of the printed continuous carbon fibre composite have been studied. The results show that the microstructure of the material is heterogeneous, with a fibre volume fraction of around 27%, high quantity of voids (around 12% in volume fraction), and a non-uniform matrix and fibre distribution. These results can be associated to actual process limitations, mainly an insufficient thermo-mechanical consolidation in the filaments bounding. The mechanical properties obtained in the fibre direction are high (60.9 GPa tensile modulus and 779.8 MPa tensile strength) and similar to those obtained by hot pressing process. However, mechanical properties in other directions are strongly influenced by defects produced by the process (voids, non-uniform distribution of fibres and bad adhesion between filaments), and are lower than expected.

Despite of these constraints, the current FFF 3D printing process of thermoplastic composites have great potential. On the one hand, the process offers considerable freedom in the design of a component and in the printing configuration of each layer. This means that if a good component and process design is performed, the negative influence of the material defects can be minimised. On the other hand, in this process, continuous fibre filaments can be steered to high curvatures and oriented in non-conventional directions; this is not possible with traditional processes and therefore it could be one of the major advantages of this 3D printing process. Another possibility is hybridization between different reinforcements. To improve and impulse the use of this new technology in the design of complex composite parts, further exploration of the design and manufacturing spaces is necessary.

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