# **Fused Deposition Modelling of High Temperature Polymers: Exploring CNT PEEK Composites**

S.Berretta1, R.Davies1, YT.Shyng1, Y. Wang1, O.Ghita1

1 College of Engineering, Mathematics and Physical Sciences, University of Exeter, North Park Road, EX4 4QF, Exeter, United Kingdom

*Corresponding author*

Silvia Berretta, [s.berretta@exeter.ac.uk](mailto:s.berretta@exeter.ac.uk)

College of Engineering, Mathematics and Physical Sciences, University of Exeter, North Park Road, EX4 4QF, Exeter, United Kingdom

# **Abstract**

The Fused Deposition Modelling (FDM™) process owes its popularity to its hardware versatility, low cost and wide range of materials (and colours) available. In this study, PEEK was produced with 1% and 5% Carbon NanoTubes (CNTs) loading and processed in a modified FDM system able to operate high temperature polymers. The tensile strength, layer bonding and the microstructure of the plain and CNT loaded PEEK samples were investigated throughout the three steps of manufacturing: compounded composite feedstock filaments, single FDM deposited layers and fabricated testing specimens. Interestingly, every step of processing seems to fabricate structures of lower performance. As part of the methods employed for characterisation of the FDM structures, short shear beam tests were used as a new method to assess layer-to-layer bonding.

# **Keywords**

FDM; PEEK; 3D printing; CNT; filament; extrusion

# **Introduction**

Fused Deposition Modelling (FDM™) is an additive manufacturing process (AM) based on filament extrusion. A polymer filament is heated within a print head (hot end or nozzle) and deposited over a flat surface (build plate) layer upon layer. The hot end is controlled by a number of servo-motors that regulate where the molten filament is deposited. When all the layers are completed, the part is carefully detached from the base plate and it is ready for use. Usually operating as an open system, exposed to environment temperature and air, this technique has been mainly developed and utilised for low melting polymers such PLA, ABS and TPU where high melting temperatures are not needed. Exhaustive reviews on low melting temperature materials for FDM can be found elsewhere [[1](#_ENREF_1), [2](#_ENREF_2)].

The ease of maintenance and upkeep (due to no laser or electron beam), the stability of storage of raw materials, the relatively low cost of the system compared with other manufacturing systems, the availability of open source software for control and operation of the system and the flexibility for relocating and moving the system in offshore facilities, desert regions or spatial systems [2] makes the technology attractive to several industrial sectors.

Several parameters have to be identified during FDM manufacture. The nozzle temperature is the temperature of the hot-end that causes melting of the feedstock filament. Plate or bed temperature is the temperature of the support plate where the molten filament is deposited; this temperature should not be too low in order to induce uncontrolled crystallisation responsible for part distortion and warpage and not too high to hinder the natural cooling of the deposited filament. Nozzle speed is the velocity at which the print end travels over the build plate while depositing the filament. Layer thickness is the height at which the print end deposits sequential layers of materials. Raster angle is the strategy at which the filament is deposited for the creation of a part, e.g. along the X axis (0° raster angle) or along the Y axis (90°raster angle) and raster to raster air gap is the distance between two next lines of the fill pattern (hatch lines).

While low melting polymers and their composite are continuously optimised in FDM, researchers have also started to look at the potential to employ engineering polymers exhibiting high mechanical properties, high thermal and chemical resistance, such as polyethylenimine (PEI), poly ether ketone ketone (PEKK), polystyrene (PS) and poly ether ether ketone (PEEK).

Kishore et al. [[3](#_ENREF_3)] analysed the thermal behaviour and viscosity performance of short carbon fibres (CF) loaded PEKK supplied by Arkema and polyphenylene sulphide (PPS) (40 and 50% CF loads) supplied by Techmer Engineered Solutions. Interestingly, when the rheological properties of the composites were tested in the same shear frequency range as one provided by the print end of a low melting FDM system used for processing 40% CF loaded ABS, all the four materials showed lower viscosity than the ABS composite, thus indicating promising processability in the system.

Valentan et al. [[4](#_ENREF_4)] built two FDM systems able to process two grades of medical PEEK - PEEK OPTIMA®. The ultimate tensile strength (UTS) of the fabricated samples were approximately 50% lower than that of injection moulded counterparts.

Liu et al. [[5](#_ENREF_5)] focused on the deposition of PEEK 450G supplied by Victrex by means of a slot die based mechanism within the FDM. Layers of 50 µm and 1 mm were successfully deposited over a 600 mm² in short times with improved surface roughness.

Vaezi et al. [[6](#_ENREF_6)] developed a FDM system for fabricating PEEK OPTIMA® samples with increasing porosity. A maximum UTS of 75 MPa and flexural strength of 132.4 MPa were found for the sample with 14% porosity.

Wu et al. [[7](#_ENREF_7)] analysed the effect of layer thickness and raster angle on the tensile, compressive and three point bending performance of FDM parts made with ABS and PEEK obtained from the Jilin University Special Plastic Engineering. Specimens built with layer thickness of 300 µm and alternating raster angle (0°-90°) had the highest mechanical values (50-60 MPa range) for tensile, compression and 3 point bending strengths. Parts underperformed mechanically when compared to the corresponding injection moulded specimens, thus indicating the high turnaround and freedom of design of the FDM process comes with a price on performance, which could or not be at all limiting according to the specific application.

Rahman et al. [[8](#_ENREF_8)] provided an extensive characterisation of a CF loaded PEEK grade produced by Arevo Labs [[9](#_ENREF_9)], an FDM and material manufacturer. The horizontal raster was found to lead to the highest mechanical results with UTS up to 73 MPa, a 10-20% improvement when compared to previous studies, followed by the alternating raster angle and the only-vertical raster angle. This is not surprising as the latter angle is likely to negatively affect the existing layering structure.

Cicala et al. [[10](#_ENREF_10)] analysed PC filament produced by Stratasys for the FDM Fortus® 400 mc and Luvocom® PEEK filament provided by Lehmann&Voss&Co [[11](#_ENREF_11)] in a new high temperature FDM system: Roboze one 400+ [[12](#_ENREF_12)]. The authors found a UTS value of approximately 70 MPa for FDM PEEK tensile bars extruded at 420 °C, the highest nozzle temperature so far found in the literature. The authors refer to the material as PEEK throughout the study and compare the value with other neat PEEK FDM specimens. Unfortunately, the PEEK samples used in this study appeared to be black in colour, thus indicating the presence of carbon loading of unknown formulation which invalids comparison with neat PEEK.

Majority of these studies propose new material options for the high temperature FDM technology relying on a trial-and-error approach and presenting mechanical performance of fabricated parts with little detail on the methodologies used to define the thermal processing parameters, key aspects affecting FDM parts. This is the first study investigating mechanical testing of single FDM deposited layers to help define nozzle temperature and applies the short shear beam strength test, known for investigating inter-laminar shear strength of parallel fibres in composites, for defining layer-to-layer bonding.

Also, this study firstly presents the processing and characterisation of PEEK filament containing carbon nanotubes (CNT) with 1% and 5% wt loading in an FDM desktop modified system through all the steps of the process: (1) filament feedstock production (2) analysis of the extruded single filaments and (3) mechanical characterisation of FDM components.

# **Manufacturing of samples**

## **Materials**

Two PEEK grades have been used in this study. PEEK 450G, supplied by Victrex, is an unreinforced grade for injection moulding and extrusion. Plasticyl PEEK 101 is a PEEK composite with 10% loading by weight of multi walled CNTs, supplied by Nanocyl [[14](#_ENREF_14)]. PEEK101 has been used as masterbatch material to form new PEEK composites with formulations at lower CNT content. The masterbatch was used for safe handling of the CNTs.

## **Compounding of composite filaments (Feedstock filaments)**

PEEK 450G and CNT Plasticyl PEEK 101 were manually mixed prior to loading into the feed hopper of a CT twin-screw extruder (Chareon Tut Co ltd). The processing temperatures and their corresponding locations are reported in Table 1.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Die Temp (°) | Barrel 6 Temp (°) | Barrel 5 Temp (°) | Barrel 4 Temp (°) | Barrel 3 Temp (°) | Barrel 2 Temp (°) | Barrel 1 Temp (°) | Screw Speed (RPM) | Melt Temp (°) |
| 360 | 360 | 360 | 360 | 360 | 325 | 53 | 90 | 344 |

Table 1. Processing temperatures within twin-screw extruder

Die, barrel and melt temperatures are set in the extruder and measured within the instrument.

Filaments of PEEK 450, 1% CNT PEEK 450 and 5% CNT PEEK 450 were produced. All the filaments had a diameter of 2.7 ± 0.3 mm and were dried in an air-conditioned oven for 5 hrs at 150°C prior to mechanical test and use in the FDM system.

## **FDM system**

A MendleMax v2.0 (Figure 1) from Maker’s Tool Works was chosen as the base FDM framework to modify for the processing of high temperature polymers. A V6 all metal hot-end supplied by E3D-online was selected with a number of interchangeable brass extrusion tips of varying diameter.

Figure 1. MendleMax V2.0 framework (left) V6 Hot-end mounted on the Mendlemax v2.0 [[16](#_ENREF_16)] (right)

This design features an aluminium heater block and heat sink, with stainless steel centre tubing and no PEEK or PTFE internal liner, which restricts high temperature processing. The processing temperature range of the material extrusion systems is limited by the use of thermistors to measure the temperature of the extrusion head. Commonly used is the ATC Semitec Ltd product 100k Ohm NTC Thermistor. This thermistor has an operating temperature range of -50°C to 300°C [[17](#_ENREF_17)]. When attempting to process materials with higher melting temperatures like PEEK, the thermistor needs to be replaced with a thermocouple capable of operating at a higher temperature. A Type K welded tip thermocouple (with additional circuit extension board), able of operating between -50°C to 1100°C, above the melting point (660°C) of the aluminium heater block, was used in the E3D Online v6 extrusion head.

Modifications were also made to the printer’s firmware to enable use of the replacement thermocouple. The system was checked for thermal accuracy with an independent handheld digital thermometer with K-type thermocouple positioned in close proximity to the nozzle outlet. An additional heated build base was designed in aluminium and held at 300 °C, thus compensating for the open air building environment, and found to be sufficient for molten PEEK to adhere to. The build plate is usually kept at a lower temperature in standard low melting temperature standard MendleMax systems.

The software automatically determined the filament feed rate based on the input deposition rate. The deposition rate was 4.8 mm3 x s-1 and the deposition speed was 30 mm x s-1. Raster angle was zero with zero raster-to-raster air gap. These manufacturing conditions were used for the manufacture of all samples examined in this study.

### **FDM deposited single layers**

A thin-wall geometry of a single tool-path 10 mm high was selected. Single wall samples were sectioned into approximately 0.2 x 0.8 x 90 mm specimens by “peeling” individual layers. These single wall samples were fabricated to quantitatively assess the processability of the materials in the FDM process before attempting to manufacture full tensile dumbbells.

The FDM single layers were fabricated at 350, 365, 380 and 390°C. The aim of the fabrication and testing of the samples was to define the nozzle and plate temperatures leading to the highest UTS. Those setting were then used for FDM of PEEK, 1% and 5 % CNT. Figure 2 shows the FDM assembly for the single deposited layers.

Figure 2. FDM single filament: (A) assembly, isometric view; (B) Assembly, top view; (C) Pull out of the single filament

## **Tensile bars**

Tensile bars of PEEK, 1% CNT PEEK and 5% CNT PEEK were built according the geometry indicated in ISO 527-2-1BA. The CAD model was sliced using 0.2mm layers and 10 perimeters at a nozzle temperature of 365°C. This generated a tool path file of concentric profiles allowing the gauge length of the test specimen to be built using aligned, unidirectional extrusions.

## **Short Beam Shear Stress (SBSS) samples**

SBSS samples manufactured along the X axis of the building plate were fabricated with PEEK, 1% CNT PEEK and 5% CNT PEEK, according to the ASTM D3244 and ASTM 2344-00. Layer thickness and deposition strategy was equal to the one used for the manufacture of the tensile specimens.

# **Characterisation techniques**

## **Scanning Electron Microscopy (SEM)**

The filament surface and the fracture surface of the test specimens were investigated by SEM (Hitachi S-3200N). The secondary electron images were taken under 25 kV acceleration voltages.

## **Transmission Electron Microscopy (TEM)**

Compounded 5% CNT PEEK 450 were embedded in epoxy resin. TEM samples with thickness of approximately 100 nm were sectioned in a microtone (Ultracut, Reichert-Jung). The TEM specimens were placed on copper grids for analysis. The bright field images were captured using a JEM 2100 (JEOL) at 100 kV acceleration voltage.

## **Tensile testing**

The testing of feedstock composite filaments, single FDM deposited layers and tensile bars were carried out on a Lloyd Instruments EZ20 at room temperature.

The composite filaments (feedstock) of neat PEEK, 1% CNT PEEK and 5% CNT PEEK were tested at a speed of 2 mm x s-1 using a 20 kN load cell. Average sample length was 100 mm, with a 50 mm gauge length and approximately 25 mm clamp area at each end. A minimum of ten specimens were tested for each grade. The filament cross section, necessary for UTS calculation, was calculated as an average value obtained from 6 measurement of feedstock diameters. This precaution was performed in order to compensate for some of the diameter variation encountered in the feedstock filaments.

The deposited FDM layers of neat PEEK, 1% CNT PEEK and 5% CNT PEEK were tested at a speed of 5 mm x min-1 to an extension of 10 mm using a 500 N load cell according to the ASTM D 3379-75. Between 10 and 15 samples were tested for each temperature (350, 365 and 380°C).

The ISO 527 dumbbells (all manufactured at 365°C) were tested at a speed of 5 mm x min-1 to an extension of 10 mm using a 20 kN load cell. Approximately 10 samples were tested for each grade.

## **Short Beam Shear Stress (SBSS) test**

SBSS tests are similar to a 3 point bending test and used to obtain inter-laminar shear strength of composites (Figure 3). In this case the test was used to test the layer bonding of FDM printed components, a critical parameter in all AM processes.

The flexural stresses are minimised by using a specimen that is very short compared to its thickness. The induced shear stress is maximised by configuring the test mechanism to a ratio of 4:1 support span length (S) to specimen thickness (t). The specimens tested were of dimensions 2 x 6.4 x 25 mm.

Figure 3. Short beam shear test (left) and a standard test setup (right)

The SBSS value was calculated as shown in Equation 1.

Equation 1

9 samples for each grade were tested using the Lloyds Instruments EZ20 3 Point Bend jig at a speed of 1.25 mm x min-1.

## **Micro Computer Tomography (CT)**

Micro-CT (CT160Xi, X-Tek Systems) was used for FDM part inspection, and especially porosity measurements. Small cross-section samples were cut from untested tensile dumbbells, and scans were conducted at 65 kV and 50 μA x-ray beam output. The typical location of a CT sample is displayed in Figure 4.

Figure 4. Location the micro CT sample from untested tensile bar. Black lines (hatch lines): FDM deposition strategy; red line: micro CT samples

A small sample can be brought closer to detector and achieve best resolution (3 μm). To ensure accuracy of scan and subsequent porosity analysis, a slow scan with ring artefact correction was used. Scan results were reconstructed automatically by application software, and porosity analysis was carried out based on pixel grayscale variation. To measure porosity, a 3D volume was defined within the sample and extracted. Doing so ensures false features such as surface irregularities are avoided. The porosity was measured by highlighting the region of interest (ROI) on the basis of a contrast threshold defined by the user on the grayscale based micro CT views. The porosity of the same ROI was measured in two ways: (1) subtracting the density obtained by highlighting the solid region from 100% (Figure 5); (2) density obtained by highlighting the voids (Figure 6).

Figure 5. Porosity measurement assessed by highlighting the solid (dense) region

Figure 6. Porosity measurements assessed by considering the voids

Both values are reported in section 4.3. The reason for this methodology was to compensate for any visual operator error created by examination of multiple grayscale images.

## **Differential Scanning Calorimetry (DSC)**

PEEK and 5% CNT PEEK filaments were heated from room temperature to 400°C under nitrogen atmosphere and cooled back to room temperature with heating and cooling rate of 10°C x min-1.

# **Results**

## **FDM processing temperature and single layers**

One of the most decisive parameters in the FDM process is the nozzle temperature of the system as it is in direct contact with polymer and will determine the degree of the melting of the extruded polymer.

Both PEEK and CNTs have well established high onset degradation temperatures, both above 500°C [[18](#_ENREF_18), [19](#_ENREF_19)]. Hence, their thermal degradation behaviour was not included in this study.

Before processing in the FDM system, the thermal behaviour of all feedstock filaments – PEEK 450, 1% CNT PEEK 450 and 5% CNT PEEK 450 -has been investigated in DSC. Details on melting and crystallisation temperatures can be found in a previous study [[20](#_ENREF_20)]. DSC thermoscans of the filaments have been reported in Figure 7.

Figure 7. DSC thermoscan of feedstock filaments of PEEK 450 and 5%CNT PEEK 450 [[20](#_ENREF_20)]

5% CNT PEEK shows a shift of the melting and crystallisation peaks towards higher temperatures compared to plain PEEK (Figure 7). This is expected after addition of CNT in the polymeric matrix [[21](#_ENREF_21)].

Four nozzle temperatures were tested for FDM of PEEK: 350, 365, 380 and 390°C. All are past the materials’ melting regions to ensure melt of the polymer in the FDM nozzle. While PEEK could be easily extruded in the temperature range 350-380°C, the 390°C temperature was found to lead to the formation of darker degraded polymer at the outlet of the nozzle. This finding is not in contradiction with the onset temperature degradation available in the literature: if PEEK is exposed at temperatures higher than 260°C [[18](#_ENREF_18)] it will be expected to show effects of degradation. The temperature range of 350-380°C was then used for the fabrication of FDM deposited layers.

Images of the FDM single layers for neat and 1% CNT PEEK are shown in Figure 8.

Figure 8. FDM assemblies for single layers. A,B: neat PEEK at increasing magnification; C,D:1% CNT PEEK at increasing magnification

## **SEM results**

Figure 9 shows FDM single layers of neat PEEK.

Figure 9. FDM single layers of PEEK manufactured at 350°C (A), 365°C (B) and 380°C (C)

The surface of the PEEK FDM single layers presented various morphologies: very smooth, dense structure (A) and significant cavities (B, C). Although the temperatures are indicated, such structures were found in the samples regardless of the manufacturing temperature utilised. These results indicate that the FDM of PEEK could lead to highly dense and smooth surfaces and structures such as in Figure 9A but the lack of a building chamber in the system might affect repeatability and consistency in the fabrication of deposited filaments, which is a major challenge in many AM processes.

5% CNT PEEK FDM single layers are shown in Figure 10.

Figure 10. FDM single layer of 5% CNT PEEK manufactured at 350°C (A), 365°C (B) and 380°C (C).

Morphology variation appears also in 5% CNT PEEK single layers: a dense and smooth structure (Figure 10B, C) and a porous surface (Figure 10A). Again these structures occurred regardless the extrusion temperature used for their fabrication.

Pores are present in all PEEK formulations, with and without CNTs. Similar remarks were found by other researchers [[4](#_ENREF_4), [10](#_ENREF_10)]. Their origin is still unclear. Filaments were dried prior to FDM, but it is possible that the moisture in the environment as well as any additional moisture trapped in the filaments, not released through drying, evaporates once the molten filament is deposited, causing the cavities.

The two ends fracture surfaces of 5% CNT PEEK single layers are shown in Figure 11.

Figure 11. Single layers 5% CNT PEEK: fracture surface manufactured at 365°C (SEM)

CNTs appears to protrude evenly from the PEEK matrix, indicating good dispersion of the CNTs throughout the FDM printed structure.

The fracture surface of FDM tensile specimens are shown in Figure 12 and Figure 13.

Figure 12. Fracture surface of PEEK manufactured at 365°C (SEM)

Figure 13.1% CNT PEEK showing layering structure and presence of small cavities manufactured at 365°C

In both material formulations, the layering structure, typical of AM processing, of the fabricated samples is clearly visible with indications of material bulge from the extrusion tip to the outside of the part.

The part also showed evident pores that are always positioned close to the surface of an individual layer. This seems the result of the porous surface seen in Figures 9A and D.

## **Micro CT**

Feedstock filaments of PEEK and 5% CNT PEEK were analysed used micro CT (Figure 14).

Figure 14.Micro CT of feedstock filaments: PEEK feedstock filament front view (A) and cross section (B); 5% CNT PEEK filament front view (C) and cross section (D)

Both PEEK and 5% CNT PEEK filaments did not display any obvious voids along their length (Figure 14A, C) while exhibiting an acceptable level of circularity in the cross section views (Figure 14B, D).

Micro CT cross-sections of FDM parts in PEEK and 5% CNT PEEK are shown in Figure 15.

Figure 15. Micro CT views of FDM printed specimens: (A,B) PEEK; (C,D) 5% CNT PEEK

The PEEK sample (Figure 15A, B) shows a number of voids especially towards the centre of the parts. Although this result is not ideal, it is not surprising, especially considering that the centre of the part where the extrusion lines are unidirectional and constituted of 10 concentric profile lines (Figure 4). This indicates that the deposition strategy (raster angle and raster to raster air gap) should be optimised in order to guarantee the same density level found on the sides of the part, which can be addressed with further process optimisation. The smaller voids appear to follow the horizontal layer pattern and could be a result of moisture being trapped during fabrication. With a melting temperature of 343°C [[22](#_ENREF_22)], any moisture is likely to rapidly turn into steam during FDM and cause the small voids seen in Figure 15.

The 5% CNT PEEK specimen (Figure 15C, D) displays lower porosity than the PEEK sample. These results seem to indicate that CNTs can lead to denser parts using the same processing conditions, especially raster angle. The large void running through the centre of the construction can be explained again by considering the deposition strategy lacking of alternating hatch lines (figure 4). This result can be compensated for in the construction software and overall highlights the requirements for process improvements at the early stages of material preparation.

Porosity measurements of PEEK and 5% CNT PEEK FDM samples are presented in Table 2.

|  |  |  |
| --- | --- | --- |
| **Material** | **Porosity (%) [100%- Dense ROI]** | **Porosity (%) [Voids ROI]** |
| PEEK sample 1 | 2.68 | 2.82 |
| PEEK sample 2 | 2.15 | 2.05 |
| 5% CNT PEEK sample 1 | 1.58 | 5.88 |
| 5% CNT PEEK sample 2 | 2.56 | 4.67 |

Table 2. Porosity values of PEEK and 5% CNT PEEK

PEEK exhibits a porosity content of 2.4 ± 0.4 %, while 5% CNT PEEK has a porosity of 3.7 ± 2.0 %.

5% CNT PEEK samples seem to lack homogeneity, having regions where the porosity is much higher than others across the same specimen and compared to neat PEEK samples. If these results are considered in parallel with Figure 15, it appears clear that the higher porosity of the 5% CNT sample is more due to the deposition strategy rather than the material itself, a defect that could be significantly improved with further process optimisation.

The large deviation in porosity measurements found for 5% CNT PEEK samples is due to the lack of a clear contrast during micro CT data processing which then allows for more variation when assessing the thresholds for solid and voids ROIs. As samples were measured by the same person and analysed with the same conditions as neat PEEK, this greater complexity in analysing data seemed to be caused by the structure of the composite material itself.

Hence, the porosity values obtained through micro CT should always be considered in parallel with visual support data.

## **Tensile testing**

The tensile results for the feedstock filaments of PEEK and PEEK with the two CNT loadings are shown in Figure 16.

Figure 16. UTS of feedstock filaments of PEEK and CNT at increasing content

The tensile behaviour of PEEK seems in agreement with the values provide by the main material supplier Victrex (98 MPa)[[22](#_ENREF_22)]. This is a positive result because it indicates that the CNT filament produced by using a PEEK CNT loaded masterbatch did not have a detrimental effect when mixed with PEEK 450. Additionally, CNTs seems to slightly increase the UTS of the feedstock filament only for the 5% loading.

FDM single layers of PEEK were extruded at increasing temperatures, from 350°C to 390°C and tested. The results are shown in Figure 17.

Figure 17. UTS of FDM single layers of PEEK

The temperature range 350-380°C results in a UTS between 70 and 90 MPa, while a significant decrease is seen for the samples fabricated at 390°C. This is not surprising because this temperature was found to hinder the polymer extrusion through the hot end. It was, therefore, discarded for the extrusion of CNT PEEK.

The UTS of CNT/PEEK FDM single layers are shown by comparison with PEEK samples in Figure 18.

Figure 18. UTS of FDM single layers

No significant difference can be found between PEEK and PEEK with CNTs and between the three extrusions temperatures 350, 365 and 380°C. As there are no clear trends between the three material grades, the middle temperature 365°C was then chosen for the fabrication of all mechanical test specimens to satisfy a broader range materials – including plain and composite formulations.

The UTS of FDM tensile dumbbells are displayed in Figure 19.

Figure 19. UTS of FDM printed tensile bars of PEEK, 1% CNT PEEK and 5% CNT PEEK

1% CNT PEEK appears to have slightly higher UTS, followed by PEEK and 5% CNT PEEK. The addition of CNTs seems to improve the UTS of FDM PEEK based parts only at 1% loading. The poor performance of 5% CNT PEEK is not surprising if analysed while considering the porosity results (Table 2) wherein an increase of the CNT loading (5%) seems to create regions within the samples with an elevated degree of porosity. It is possible that CNTs agglomerated in the reheated and re-melted filament in the nozzle of the FDM apparatus just before depositing. It is difficult to directly ascertain agglomeration within the nozzle because of the lack of accessibility. Agglomeration could be caused by two main factors: nozzle temperature and nozzle design.

Nozzle temperature affects the level of viscosity that the PEEK composite reaches. It is well known for many polymers that the addition of CNTs causes a significant increase of the viscosity of the polymeric composites [[23-25](#_ENREF_23)]. It is also well established that the higher the PEEK processing temperature in traditional manufacturing processes such as compression and injection moulding, the lower its viscosity [[26](#_ENREF_26)]. It is, therefore, possible that a higher nozzle temperature for the PEEK composite with 5% CNTs is required for lowering the material viscosity and assuring consequential homogeneity in the deposited material. The need to increase FDM processing temperature for polymer composites was noted in previous studies [[20](#_ENREF_20)]. However, higher nozzle temperature did not produce any positive effect on the tensile results of plain PEEK and 1% CNT PEEK (Figure 18).

Nozzle design could lead to agglomeration for several reasons: if the orifice is too small, polymers at high content of CNTs might not be able to free flow as their plain or lower loaded counterparts; if the internal walls of the nozzle are manufactured with high surface roughness, this might not be notable for low viscosity polymer but could favour wall gripping for viscous materials; lastly, if the internal inclination of the nozzle funnel is not optimised for promoting free flowing this could lead to overbridging and heterogeneous polymer outlet in viscous polymeric composites.

It can also be noted there is a decreasing trend amongst the UTS of raw filament, single deposited layer and FDM part. Every step of processing seems to impact negatively on the final performance of the part. Such result is found to be in agreement with the work of Wu et al. [[7](#_ENREF_7)] on neat PEEK and ABS materials.

Lastly, all materials show a considerable standard deviation. Although this is a well-known challenge in AM processes, it must be highlighted that most air-exposed FDM systems run on components and materials whose critical temperatures (glass transition temperature, melting temperatures) are close to room environment and less challenging than PEEK, which has a melting point above 340°C. Sources of variations in an open air system are numerous: thermal gradient between hot end and surrounding environment, thermal gradient between molten polymers, components and base plate, humidity and water absorption in the filaments and during deposition.

## **Short beam shear stress tests (SBSS)**

The results of the SBSS test for neat and composite CNT PEEK materials are presented in Table 3.

|  |  |
| --- | --- |
| **Polymer** | **SBSS (MPa)** |
| PEEK | 33 ± 10 |
| 1% CNT PEEK | 33 ± 10 |
| 5% CNT PEEK | 21 ± 5 |

Table 3. SBSS values

Shear strength of PEEK and 1% CNT PEEK are not different, whereas 5% CNT PEEK presents a significant decrease. This result can be due to the fact that that the surface characteristics (surface tension, wettability and adhesion when molten) are different for 5% than 1%. 5% is quite a high concentration, whose processability has been found challenging in other works [[27](#_ENREF_27)]. A further study could investigate if a higher deposition temperature in the FDM system can enable the same level of interface bonding within the layering structure of neat PEEK and 1% CNT PEEK.

## **TEM results**

The TEM images of the 5% CNT PEEK feedstock filament are shown in Figure 20.

Figure 20. TEM images of 5% CNT PEEK feedstock filament at low (A) and increasing magnification (B and C)

Cross sections of the 5% CNT PEEK feedstock filament analysed by TEM showed the presence of CNTs relatively well dispersed, thus indicating the potentiality of a promising composite structure. However, such results were not equally matched in tensile test data where the 5% CNT samples showed the lowest UTS value. This finding can indicate that FDM process and parameters are highly sensitive to the good composite polymers conditions and a qualitative examination like TEM might not be rigorous enough to assess a priori the performance of a FDM PEEK CNT sample. It must be noted that TEM imaging was carried out on the feedstock filament and not on the FDM printed part. The pictured composite structure undergoes re-melting in the nozzle of the FDM apparatus before being deposited for the manufacture of a component. This re-melting might lead to potential agglomeration of the CNTs in the nozzle, due to re-melting itself, temperatures or nozzle geometry. Exploring different nozzle designs could help to understand if the lower value of UTS found in the FDM parts is due to re-melting itself regardless of the nozzle geometry or if a specific nozzle design facilitates homogenous melting of FDM filaments preventing agglomerations.

# **Conclusions**

The processability of PEEK CNT polymers in FDM was studied. CNT dispersion within the matrix, FDM conditions and quality of the fabricated filament play an important role in the fabrication of FDM components. The presence of CNTs did not seem to influence the mechanical performance of the PEEK fabricated parts. As filaments are too brittle to be used in a peel-out test, bespoke FDM structures referred to as single layers were firstly designed and tested for understanding micro-mechanical performance and microstructure. Also, the short shear beam test was successfully used for the first time in this type of specimens to investigate layer-to-layer bonding of FDM components. Future works will investigate two main areas: (1) the fabrication and testing of FDM printed components manufactured along the Z axis, ideally in an enclosed FDM system where temperature and humidity are actively controlled; (2) thermal conduction and electromagnetics characterisation of the specimens.

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