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Preparation of short CF/GF reinforced PEEK composite filaments and their comprehensive properties evaluation for FDM-3D printing

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ABSTRACT

Fused deposition modeling (FDM) has been successfully applied to fabricating short fiber reinforced polymer composites parts. However, due to the intrinsically limited mechanical properties of matrix polymers, there is critical need to develop fiber reinforced high-performance thermoplastic composites for FDM-3D printing to expand engineering applications. In this work, the potential of FDM-3D printing short carbon fiber (CF) and glass fiber (GF) reinforced high-performance PEEK composites has been investigated. Composite filaments with fiber contents of 5 wt%, 10 wt% and 15 wt% were prepared using extrusion process and characterized by micro-morphology observation; and thermal properties testing demonstrated its better thermal stability than pure PEEK. The performance evaluation of printed CF/GF-PEEK parts was focused, including mechanical properties, microstructure, surface quality and porosity. The results indicate that the addition of CF/GF to PEEK can significantly enhance the tensile and flexural strength at the cost of ductility. Lower fiber content of 5 wt% is conducive to increasing mechanical properties, improving surface quality and reducing porosity of printed CF/GF-PEEK. GF/PEEK has better interfacial bonding than CF/PEEK due to the different surface treatments on fibers. Furthermore, microstructure observation suggests that fibers aligned along the printing orientation can strengthen the properties, while pores lead to performance degradation of 3D printed CF/GF-PEEK.

1. Introduction

3D printing technology has been widely applied to replace those parts [1–4,40,42], that are difficult to be fabricated by traditional processing methods, in aerospace, biomedical, automotive, architecture and education fields since its rapid development in the 1990s [3]. It has the advantage of low-cost, freedom of design and directly rapid manufacturing for structures with complicated geometries. Over the recent 30 years, 3D printing has advanced in various technological forms [3]. Fused deposition modeling (FDM) becomes one of the main streams of 3D printing which uses thermoplastic filament as feedstock and achieves stacking layer by layer by depositing material extruded from a heated nozzle in accordance with the filling path generated by the slicing software [[5–7]]. Despite of its simplicity and convenience, so far FDM process creates parts with pretty weak mechanical properties which curb the applications of this technology attributing to the inferior characteristics of thermoplastics used, such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polycarbonate (PC) and polyamide (PA) [[8]]. Scholars have conducted complete investigations on optimizing the main printing parameters of FDM process parameters [[9]], including nozzle temperature, layer thickness, printing speed, platform temperature, raster angle, feed rate, building orientation, but such efforts cannot significantly increase the mechanical performance of FDM printed parts [[8]].

On the other hand, composite material modification by adding short or continuous fibers into thermoplastic matrix has attracted much attention and improves mechanical properties [[10–14]] significantly. Since using short fibers rather than continuous fibers is more economical and feasible in terms of preparation technique of filament, there have been some studies focusing on short fibers reinforced polymer composites for FDM process. Caminero et al. [[15]] have proved the feasibility and potential of FDM process to fabricate PLA-graphene

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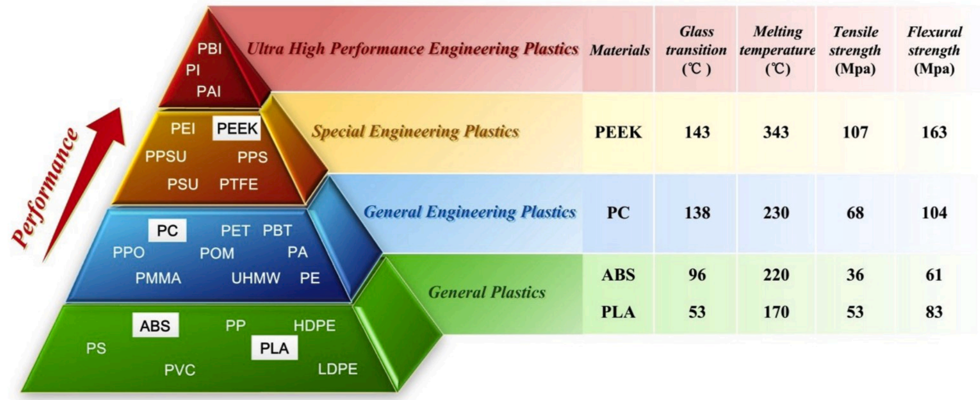

Fig. 1. Thermophysical properties of PEEK and other general plastics [[20],[21]].

Table 1
Characteristic of CF and GF.

Property	Density (ρ)	Tensile strength (σ)	Tensile modulus(E)
CF	1.72 g/cm^3	3.9 GPa	220 GPa
GF	2.61 g/cm^3	2.1 GPa	70 GPa

composites by analyzing the mechanical performance, dimensional accuracy and surface roughness of 3D printed PLA-based and graphene nanoplatelets (GNPs) reinforced composites. Gray et al. [[16]] proposed to prepare composite filaments by adding thermotropic liquid crystalline polymers (TLCP) to polypropylene (PP) for FDM-3D printing. The tensile modulus of TCLP/PP (40/60 wt%) was 150% higher than those of pure PP via FDM process. Zhong et al. [[17]] found that short glass fibers can significantly enhance the tensile strength and surface rigidity of printed ABS parts at the cost of flexibility and ductility. Further research indicated that reducing fiber content or adding appropriate plasticizer could improve the toughness of composites. Moreover, nano carbon fibers also have a dramatically effect on the increase of tensile strength and modulus of FDM printed ABS [[18]]. Previous studies have demonstrated convincingly that the content, length and distribution of fibers have great influence on the mechanical properties of short fiber reinforced polymer composites in compression molding (CM). For FDM-3D printing, Tekinalp et al. [[5]] conducted the tensile testing of CF/ABS composites with fiber contents ranging from 10 wt% to 40 wt%. Fracture morphology of printed samples showed that with increasing fiber content, internal porosity of FDM printed beads enlarged. Even so, the better tensile strength and Young's modulus of CF/ABS are also obtained at higher fiber content. Fiber orientation in FDM printed samples is highly consistent with the printing direction. Additionally, Ning et al. [[6]] reported that the tensile strength of FDM printed CF/ABS composites improved with the increase of fiber length. Besides, other short fiber reinforced thermoplastic composites have been developed for FDM to expand the range of printable materials including GF/PP [[19]], CF/PLA [4], KBF/PLA [1]. Although the mechanical properties of these fiber reinforced composites printed by FDM are stronger than those unfilled fibers, they are still inadequate to satisfy the requirements of industrial applications.

Polymeric materials with excellent mechanical, thermal, and physicochemical properties can be defined as *special engineering plastics* or *ultra-high performance engineering plastics*. Their superior performances make them well-qualified in various fields. Polyetheretherketone (PEEK), a semi-crystalline special engineering plastic, that owns much higher mechanical properties than those general plastics used for FDM process [[20],[21]], such as ABS, PLA and PC, as shown in Fig. 1. In this study, the hybrid chopped carbon fiber (CF) and glass fiber (GF) reinforced PEEK filaments were successfully fabricated by extrusion process, respectively. Comprehensive evaluations were carried out to explore the effect of fiber types (CF, GF), fiber contents on micromorphology, thermophysical properties and rheological behavior of fabricated filaments, mechanical (tensile, flexural, impact) properties, surface quality, and microstructure observation of printed composites parts. Recently, some investigations were concentrated on printing PEEK, as well as improving mechanical properties of printed PEEK parts (including tensile strength, flexural strength, and impact strength) with FDM equipment and process parameters [[22]]. However, the properties of PEEK parts manufactured by FDM are still inferior to those of traditional compression-molded PEEK owing to its process characteristics. Although adding fibers into the matrix, i.e. developing reinforcement plastic matrix composites, has been proposed to improve the mechanical properties of FDM-3D printed parts, only a few studies have been reported on FDM-3D printing carbon fiber reinforced PEEK filaments [[23–26]], due to high melting point and high viscosity of PEEK composites which make it challenging to produce filaments for FDM-3D printing. Compared with short carbon fiber, glass fiber has different aspect ratio, surface structure and mechanical characteristics. However, it has not been reported that GF/PEEK can be used as a potential feedstock for 3D printing.

In summary, the purpose of this study is to explore the potential in engineering application of FDM-3D printing short fiber reinforced PEEK composites. This work is aimed to provide a rapid prototyping approach for complicated shape, high-strength, and lightweight applications to meet diverse manufacturing requirements effectively.

2. Experimental work

2.1. Preparation procedure of filaments

In this work, polyetheretherketone (PEEK 450G, from Jinlin Zhongyan High Performance Plastic Co., Ltd, China), an emerging high-performance thermoplastic for FDM-3D printing, is selected as matrix material. The density of PEEK is 1.3 g/cm^3 and the melting temperature (T_m) of PEEK is 343 °C. The tensile strength, flexural strength and Charpy unnotched impact strength of PEEK are 107 MPa, 163 MPa and 136 kJ/m^2, respectively. Two types of chopped fibers, carbon fiber (CF, Zoltek Co., Ltd, USA) and glass fiber (GF, Jushi Group Co., Ltd, China), were added into PEEK respectively as reinforcement to fabricate composites filaments. The characteristic of CF and GF are listed in Table 1.

Prior to blending, the carbon fiber and glass fiber were treated by anodic oxidation and silane coupling agent, respectively. Silane coupling agent and anodic oxidation methods are commonly used to improve fiber-matrix interfacial bonding [[27–29]]. The stable bonds of -Si-O-Si- are formed among GF and silane coupling agent. In addition, active functional groups are formed on the surface of GF, which are beneficial to the curing reaction of PEEK [[27]]. The surface roughness

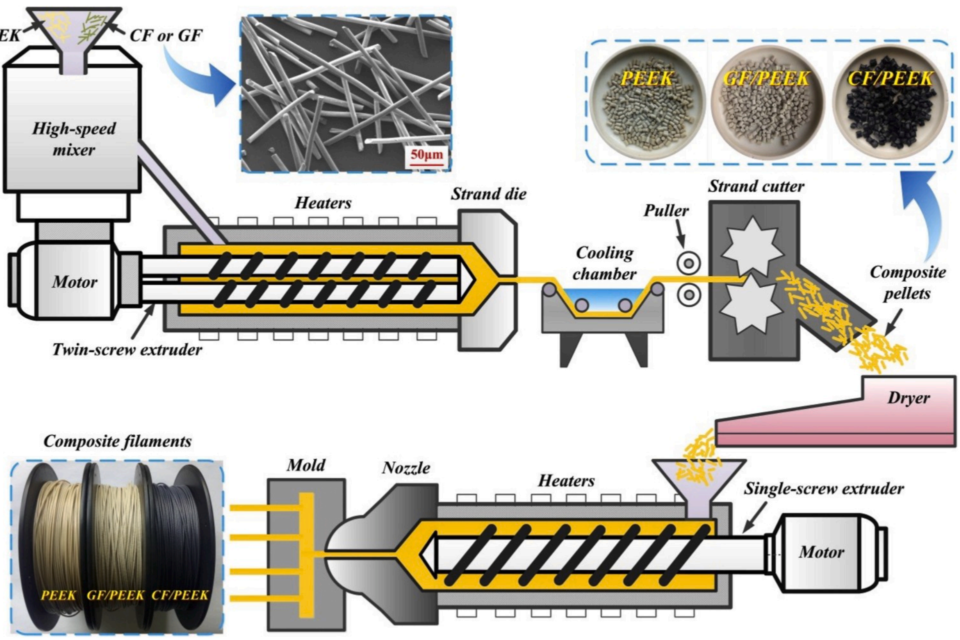

Fig. 2. Preparation process of composite filaments.

Table 2
Fiber volume fraction and theoretical density of varied composite filaments.

Samples	Fiber volume fraction (%)	Theoretical density (g/cm^3)
5 wt%CF/PEEK	3.83	1.316
10 wt%CF/PEEK	7.75	1.333
15 wt%CF/PEEK	11.77	1.349
5 wt%GF/PEEK	2.55	1.333
10 wt%GF/PEEK	5.24	1.369
15 wt%GF/PEEK	8.08	1.406

of CF increases effectively through anodic oxidation treatment which also improves the amount of oxygen functional groups on the surface of CF. However, the active functional groups on CF after anodic oxidation gradually decrease with the increase of time [[28],[29]].

The preparation process of filaments is illustrated as Fig. 2. It is noteworthy that manufacturing PEEK composites filaments with fiber weight fraction more than 20% are unachievable in this series of experiments, because fiber content exceeding this critical value causes excessive melt viscosity in the temperature range of 360–400 °C. This has been proved by the previous works [[23]]. Moreover, higher fiber content also leads to greater brittleness, which makes it difficult to succeed in extrusion. Thus, the fiber contents of composites (wt% Fiber/PEEK) in this work are 5 wt%, 10 wt% and 15 wt%, respectively. Besides, the fiber volume content and theoretical density of composite filaments can be given by Eq. (1) and Eq. (2) successively.

$$Vol\% = \frac{V_{Fiber}}{V} = \frac{w \cdot \rho_{PEEK}}{w \cdot \rho_{PEEK} + (1-w) \cdot \rho_{Fiber}} \tag{1}$$

$$\rho_{composites} = \frac{m}{V} = \frac{\rho_{Fiber} \cdot \rho_{PEEK}}{w \cdot \rho_{PEEK} + (1-w) \cdot \rho_{Fiber}} \tag{2}$$

where $Vol\%$ is defined as fiber volume fraction, w denotes the fiber weight fraction, ρ_{Fiber}, ρ_{PEEK} and $\rho_{composites}$ represents the density of fiber, PEEK and composite filaments, respectively. The composition and density of varied composite filaments are presented in Table 2. It is noteworthy that with the same fiber weight fraction in composites, the volume fraction of CF is larger than that of GF, which is due to the distinction in density between CF (1.72 g/cm^3) and GF (2.61 g/cm^3).

Prior to preparing filaments, all materials were dried at 150 °C for 24 h to remove any moisture. Afterwards, PEEK and fibers were blended sufficiently in the high-temperature twin-screw extruder to fabricate

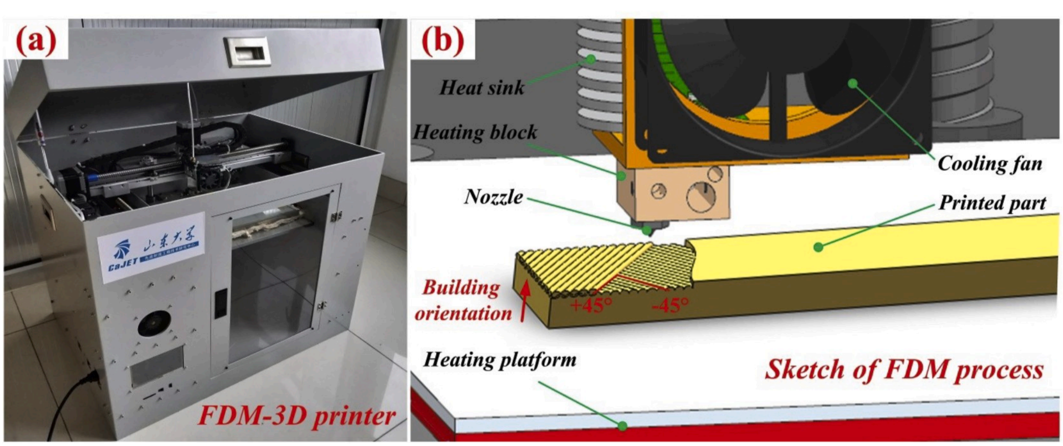

Fig. 3. (a) Home-made heat resistant FDM-3D printer [[31]], (b) Sketch of FDM process.

Table 3
FDM 3D printing parameters for fiber reinforced PEEK composites.

Printing parameters	Value
Nozzle diameter (mm)	0.4
Nozzle temperature (°C)	440
Platform temperature (°C)	260
Layer thickness (mm)	0.2
Printing speed (mm/s)	15
Infill density (%)	100
Wall thickness (mm)	0.8
Infill pattern	Lines
Raster angle (°)	[-45°, +45°]
Overlap interval (mm)	0

composite filaments. During the extrusion processes, heater temperature, filament yield speed, and strand die diameter were set at 400 °C, 1.8 m/min, and 2.5 mm, respectively. Then the filaments were successively cooled down, pulled into strand cutter and chopped to pellets, dried for the second extrusion carried out by a single-screw extruder (Jiangsu Junhua PEEK, China). After twice extruding, composite filament filled with well-distributed fibers was obtained consequently. The filament diameter and cylindricity was strictly controlled to be ∅ 1.75± 0.1 mm using a customized mold and an automatic tension control system. The prepared composite filaments were dried in a drying oven at 80 °C for 24 h in preparation for 3D printing.

2.2. FDM-3D printing specimens

A home-made heat resistant FDM-3D printer was used to fabricate test samples of Fiber/PEEK composites, as illustrated in Fig. 3. Previous studies have been demonstrated the feasibility of this equipment, and some parameters have been optimized for printing PEEK [30–32,41]. The primary 3D printing parameters used for fiber reinforced PEEK composites are listed in Table 3. Moreover, the raster angle [-45°, +45°] means that the infill line directions for different layers were −45° and +45°, alternately, as illustrated in Fig. 3 (b).

Tested samples were printed in accordance with above printing parameters, in order to measure mechanical properties including flexural strength, impact strength and tensile strength. The shape and dimensions of prepared samples are exhibited as Fig. 4. Furthermore, these samples were also used to investigate surface roughness, density, thermal properties and micromorphology etc.

2.3. Testing and analysis

2.3.1. Physical properties testing

Following the standards ISO 527–2: 2012, ISO 178: 2010 and ISO 179–1: 2010, the tensile test, flexural test as well as unnotched impact test of 3D printed fiber reinforced PEEK composite parts (as shown in Fig. 4) were performed at room temperature (25 °C), respectively. The tensile strength and flexural strength were measured using a computer-controlled universal testing machine (WDW-50E, Shidai, China) under 10 kN force transducer capacity with a loading velocity of 2 mm/min. The simply-supported beam impact test was conducted by an impact tester (XJJ-50, Jinjian, China) equipped with a pendulum of 7.5 J. Five tested samples were prepared by FDM for each composition.

In order to evaluate the degree of porosity, Archimedes principle was applied to measure the actual density of raw filaments and parts printed by FDM using a digital balance (DH-120, Shimadzu, China).

2.3.2. Thermal properties analysis

Thermal transitions of fiber reinforced PEEK composite filaments were obtained by differential scanning calorimeter (DSC, TAQ2000, USA), which was used for verifying the effect of fiber content on the thermal properties of the composites as melting temperature (T_m), glass transition temperature (T_g) and crystallinity. About 10 mg of dried filaments underwent a thermal cycle, heating from 30 °C to 400 °C, then cooling down to 150 °C in nitrogen atmosphere. The heating rate and cooling rate are both set to 10 °C/min. Thermal stability of pure PEEK and fiber reinforced PEEK composite filaments were conducted by thermogravimetric analysis (TGA, 5500, USA). Samples were subjected to a heating process from 30 to 1000 °C at a heating rate of 20 °C/min in nitrogen atmosphere. XRD analysis (Ultima IV, scan angle 5–75°, step 0.02°) of filament was made to assess crystal structure.

The melt fluidity of composites is characterized by the melt flow rate (MFR). MFR of PEEK composites with different fiber content in the melting state was measured by melt flow indexer (μPXRZ-400A, Jiangsu Junhua PEEK, China). The test was carried out at temperature of 400 °C with weight of 2.16 kg, measuring the melt weight through the standard die every 30 s. The final results recorded the melt weight for 10 min.

2.3.3. Morphology observation

Microstructures of filaments cross-section and fractured tensile samples surface were surveyed by means of scanning electron microscope (SEM, JSM-7610F Japan), in order to observe internal defects and analyze fracture mechanism. Besides, the fiber morphology was also investigated using SEM. The composite filaments were kept at 600 °C for 3 h until matrix material PEEK was completely decomposed, then fibers can be observed clearly under SEM. Image analysis program (Halcon, MVtec, Germany) combined with manual calculation was used to determine the fiber length distribution.

Following the standard ISO 25178, the surface topography and roughness of PEEK and fiber reinforced PEEK composite parts printed by FDM were investigated via laser scanning microscopy (VK-X200 K, Keyence, Japan). The surface roughness (Sa) was measured at three different positions of the horizontal forming surface for which average values were calculated.

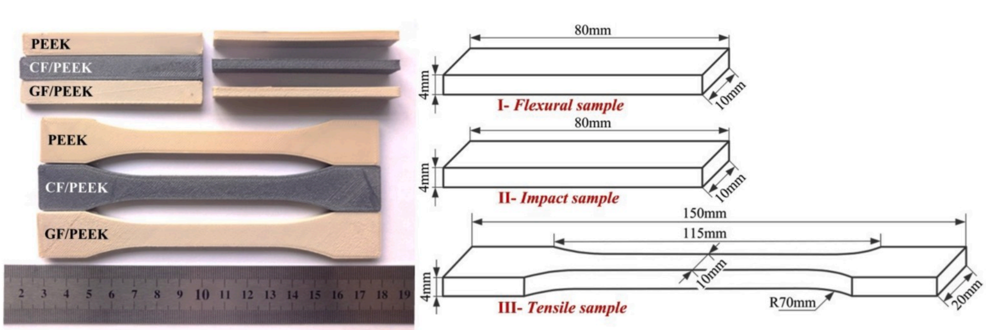

Fig. 4. FDM-3D printed samples, I- Bending sample, II- Impact sample, III- Tensile sample.

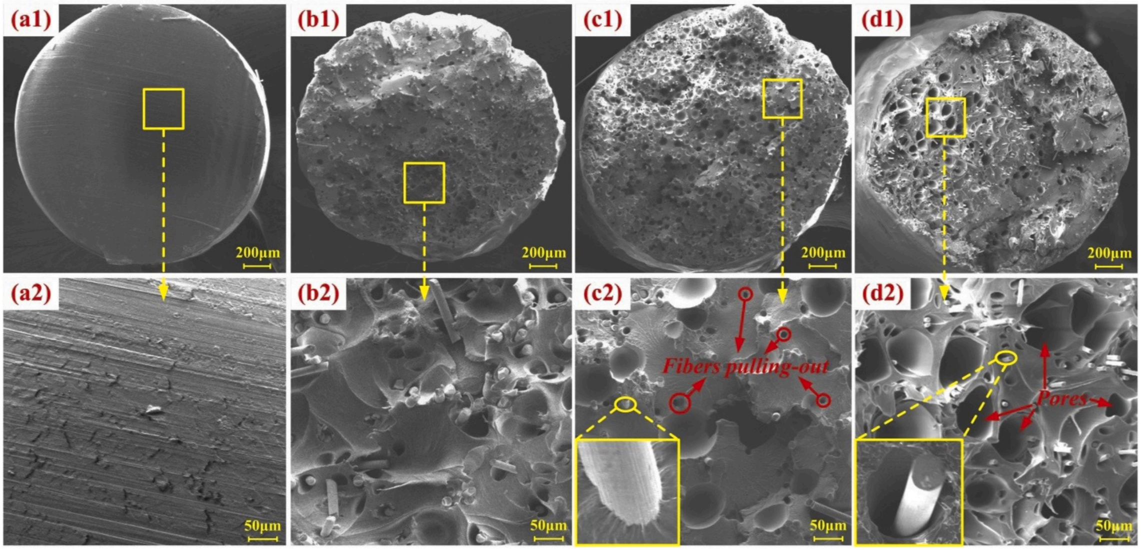

Fig. 5. Scanning electron micrographs of cross-section of PEEK(a1, a2), 5 wt% GF/PEEK(b1, b2), 10 wt% GF/PEEK(c1, c2), 15 wt% GF/PEEK(d1, d2) filaments.

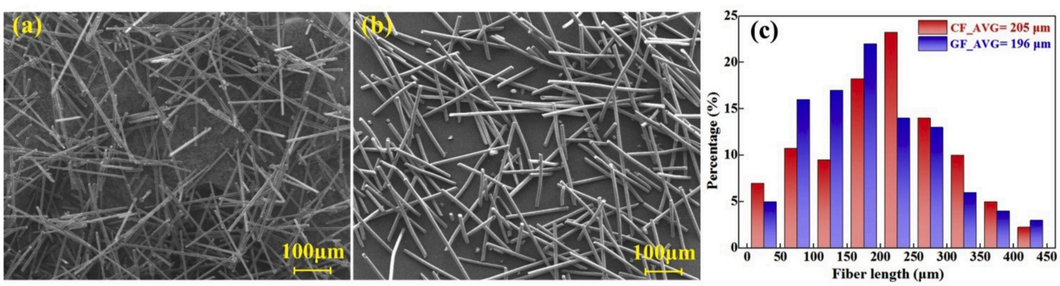

Fig. 6. Fiber morphology observed using SEM and statistics of average fiber length, (a) 15 wt%CF/PEEK, (b) 15 wt%GF/PEEK, (c) CF and GF length distribution.

3. Results and discussion

3.1. *Characterization of 3D-printed short fiber reinforced PEEK composite filaments*

3.1.1. *Micromorphology*

Micrographs of composite filaments cross-section with different GF contents were taken by SEM, as illustrated in Fig. 5. What can be seen from Fig. 5 (a1)-(d1) is that the cross-sectional shape of filament is close to a circle with diameter of 1.75 mm. The uniformly distributed fibers and voids are clearly observed through the whole of filament cross-section. Nevertheless, with the increase of GF weight fraction, rougher filaments surface and higher porosity are viewed. In these voids, some small holes are caused by fibers fracture and extraction, while most of them are air pores formed in the fabrication process of composite filaments. Higher fiber content makes it more difficult to mix the raw particle evenly and the composite filaments doped more air, which is inevitable in this series of experiment. Besides, the inconsistent shrinkage of PEEK resin and fiber during cooling process may results in pores enlargement which can be indicated from magnified micrograph in Fig. 5 (d2). But in most cases, it can be obviously seen that fibers are wrapped by PEEK resin, demonstrating good interfacial adhesion among GF and PEEK matrix (Fig. 5 (c2)).

The properties of fiber, including fiber type, content and length, all have significant impact on the performance of composite filaments as well as FDM-3D printed parts [1,[5],[6],[17]]. Table 2 has shown the weight fraction and corresponding volume fraction of CF and GF in prepared composite filaments. For better characterizing the fiber length, SEM was used to observe the fiber morphology and estimate the fiber length; the number-average was used to illustrate the fiber length distribution, as shown in Fig. 6. What can be seen from Fig. 6 (a) and 6 (b) is that the carbon fiber diameter (∅ 6.5 μm) is less than that of glass fiber (∅ 11.7 μm). From the perspective of fiber length distribution, the fiber length ranges from 5 μm to 450 μm, and the average length of CF and GF are 205 μm and 196 μm, respectively. It is worth noting that the average fiber length is about 50% of nozzle diameter (∅ 400 μm), which implies that the nozzle would basically not be congested by fibers in this work.

3.1.2. *Thermal properties*

DSC curves of fabricated PEEK and fiber reinforced PEEK composites filaments with varied fiber weight fractions are portrayed as Fig. 7 (a) heating scan and Fig. 7 (b) cooling scan, and the main thermal parameters obtained from DSC curves, including the melting temperature (T_m), the crystallization temperature (T_c) and the percentage of crystallization (X_c), are recorded in Table 4. The X_c is determined by the following Eq. (3) [[33],[34]]:

$$X_c = \frac{\Delta H_m}{(1-w)\cdot \Delta H^0_{m,\ PEEK}} \cdot 100\% \tag{3}$$

where ΔH_m is the apparent melting enthalpy of composite material, w represents the weight fraction of fiber and $\Delta H^0_{m,\ PEEK}$ denotes the theoretical melting enthalpy corresponding to a 100% crystalline pure PEEK. The reference value of $\Delta H^0_{m,\ PEEK}$ is 130 J/g taken from literature [[35]].

As can be seen from Fig. 7(a) and (b), compared with pure PEEK, the maximum increment in T_m and T_c of fiber reinforced PEEK composite filaments are 5.39 °C 15 wt% GF/PEEK and 12.5 °C for 10 wt% CF/PEEK respectively, indicating that the addition of CF and GF can strengthen

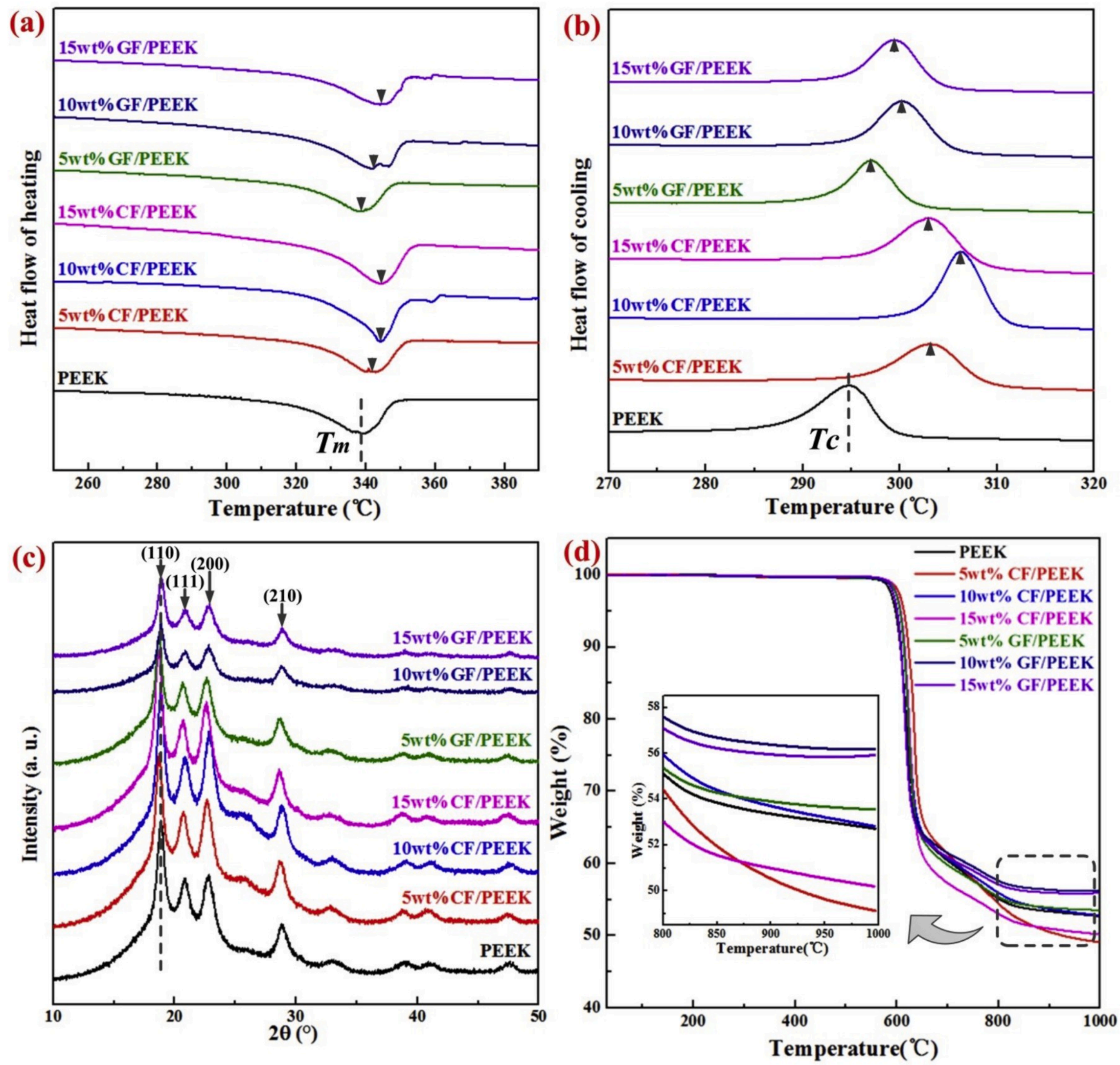

Fig. 7. The DSC curves (a) heating scan and (b) cooling scan, (c) XRD spectra, (d) TGA curves of PEEK, CF/PEEK and GF/PEEK filaments.

Table 4
Thermal properties of PEEK, CF/PEEK and GF/PEEK filaments.

Sample	T_m(°C)	ΔH_m(J/g)	T_c(°C)	ΔH_c(J/g)	X_c(%)	T_d(°C)	Weight loss (%)
PEEK	338.87	38.22	294.76	41.46	29.41	616.29	47.33
5 wt%CF/PEEK	342.72	32.77	303.44	39.50	26.53	627.90	50.96
10 wt%CF/PEEK	343.17	33.25	307.26	45.44	28.42	624.79	47.13
15 wt%CF/PEEK	342.98	35.95	303.42	39.61	32.53	626.36	49.81
5 wt%GF/PEEK	338.91	35.02	297.12	41.25	28.36	623.40	46.44
10 wt%GF/PEEK	341.33	30.07	300.66	37.45	25.70	617.22	43.81
15 wt%GF/PEEK	344.26	28.36	299.94	33.78	25.66	616.50	44.07

the thermal stability of PEEK obviously. Hence, the nozzle temperature of 3D printing fiber reinforced PEEK composites is 20 °C higher than that of printing pure PEEK (420 °C) [[30–32]] to expand the feasibility of printing. And the melting temperature of composite filaments tends to rise with the increase of fiber weight fraction. However, the T_c of CF/PEEK is much higher than that of GF/PEEK as illustrated in Fig. 7(b), which is due to the stronger heterogeneous nucleation ability of CF with more volume content and larger aspect ratio enlarging the crystallization temperature [[36]]. On the other hand, according to the calculation results of X_c in Table 4, the crystallinity of GF/PEEK decreases to 25.66% as the growing fiber weight fraction to 15 wt%, demonstrating that immense interaction among GF and PEEK which limits the movement of polymer molecular chain and leads to inferior crystallinity. This can be explained by more active functional groups existing on GF surface treated by silane coupling agent, resulting in stronger interfacial bonding performance. Since PEEK is classified as a semi-crystalline resin, both crystalline and amorphous regions are contained in PEEK. Hence, lower crystallinity is relevant to the excellent fluidity of polymer segment in the amorphous area, which may be beneficial to enhance the toughness of PEEK [[37]].

Fig. 7 (c) shows the XRD patterns of PEEK, CF/PEEK as well as GF/PEEK filaments, all indicate four reflections at about 18.8°, 20.7°, 22.7°

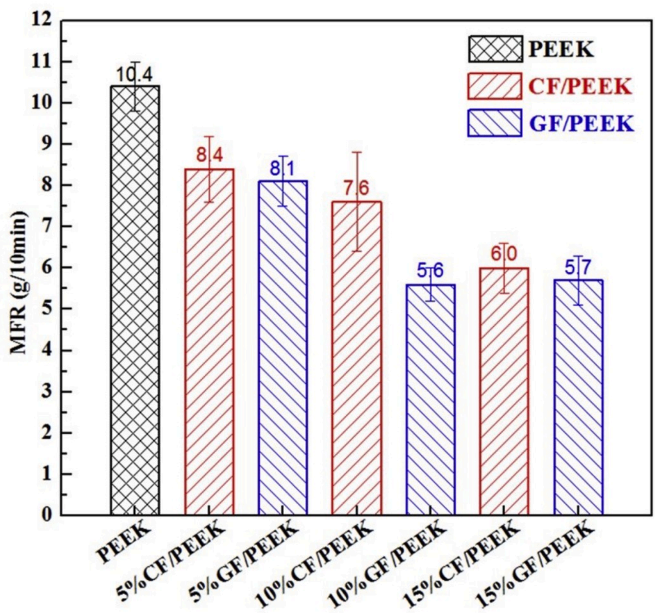

Fig. 8. MFR of fiber reinforced PEEK composite filaments with different fiber types and contents.

and 28.8° associated with (110), (111), (200) and (211) planes respectively, which is related to the orthorhombic structure of PEEK [[38], [39]]. This suggests that the addition of fiber has no distinct change on the crystal structure of PEEK. Moreover, the characteristic peak $2\theta = 18.8^{\circ}$ shows the greatest intensity of all reflections, revealing $2\theta = 18.8^{\circ}$ is the favored orientation for molecular alignment in fiber reinforced PEEK composite filaments. While in comparison of fiber type on characteristic peak $2\theta = 18.8^{\circ}$ intensity, it is found that the intensity of GF/PEEK filaments is weaker than that of CF/PEEK, which also implies lower crystallinity existence in GF/PEEK filaments. Besides, the strongest characteristic peak $2\theta = 18.8^{\circ}$ intensity among all samples is 15 wt % CF/PEEK in Fig. 7 (c) corresponding to the calculated maximum X_c (32.53%) in Table 4.

Further analysis concentrated on TGA is to study the thermal stability of composite filaments, as shown in Fig. 7 (d). Thermal decomposition temperature (T_d) and weight percent loss of filaments with different fiber contents are listed in Table 4. It can be seen that the decomposition temperature of composite filaments exceeds that of pure PEEK, demonstrating that fibers inhibit the dehydrogenation and the destruction of polymer chains at this thermal decomposition stage. Compared with CF/PEEK, GF/PEEK possess minor weight percent loss (43.81%), indicating better thermal stability of GF/PEEK filaments which is ascribed to strong interface performance among PEEK and GF, preventing the movement of polymer chains [[38]].

Fig. 8 describes the MFR of composite filaments with different fiber types and contents. It is evident that the addition of fiber results in decreasing MFR of material, suggesting the increase in viscosity of composite filaments. And with the rising of fiber content, the viscosity of the material develops gradually. As shown in Table 2, although the volume fraction of GF is less than that of CF at the equal weight fraction, the viscosity of GF/PEEK far exceeds that of CF/PEEK under such circumstance, which also can be interpreted by excellent interfacial bonding between reinforced GF and matrix PEEK. Despite the viscosity of composite filaments is approximately 50% higher than that of pure PEEK, based on previous experience on 3D printing PEEK, lower printing speed of 15 mm/s was applied in this experiment to improve the feasibility of 3D printing fiber reinforced PEEK composites.

3.2. Characterization of comprehensive properties of 3D-printed short fiber reinforced PEEK parts

3.2.1. Mechanical properties

Fig. 9 shows the comprehensive mechanical properties of FDM-3D printed short fiber reinforced PEEK composites. Effect of fiber type and fiber weight fraction on tensile strength, flexural strength and impact strength of composite samples are illustrated as Fig. 6(a)–(c). It can be found that the drop of mechanical properties within the added fiber weight fraction increasing from 5% to 15%, which probably caused by increased porosity in the high fiber content composite filaments. However, it is significant that the tensile strength and flexural strength of printed composite parts in this series of experiments are all improved by comparing with printed pure PEEK without fiber reinforcement. The most excellent enhancement of tensile performance is for 5 wt% CF/PEEK which possesses a maximal tensile strength reached to 94 MPa equivalent to 90% of injection molded PEEK (107 MPa). And the greatest flexural strength for 5 wt% GF/PEEK is 165 MPa, which is higher than that of injection molded PEEK (163 MPa), as listed in Table 5. Considering FDM-3D printing is almost an extrusion forming process without pressure, the mechanical properties of short fiber reinforced PEEK in this study are satisfactory and superior to previous 3D printing research results of short fiber reinforced polymer composites [[8],[9]].

It is noteworthy that with the same fiber weight fraction, the performance of printed GF/PEEK is better than that of CF/PEEK under out-of-plane loading, such as bending test and impact test, as shown in Fig. 9 (b) and (c). This can be explained by strong interfacial bonding among GF and PEEK which makes it difficult to separate fiber from PEEK. In addition, the volume content and aspect ratio of CF is larger than that of GF at the same weight fraction. Consequently, when the fabricated part sustains tensile load paralleling to the printing direction, more carbon fibers and wider interaction bonding region on the tensile section can provide bigger bearing capacity.

Moreover, study on elongation at break shows that the addition of fibers results in a reduction of ductility comparing with pure PEEK (Fig. 9 (d)). This is due to the short fibers hinder the ordered arrangement of PEEK polymer chains, which cases the polymer chains to break down easily. The type and content of fibers have no obvious effect on the elongation at break of polymer. All tensile fractures of fiber reinforced PEEK composites are brittle rather than ductile with necking characteristics, as exhibited in Fig. 9 (e).

3.2.2. Microstructure and porosity

In order to further analyze the failure mechanism, the tensile fracture surfaces of printed fiber reinforced PEEK composite samples were observed by SEM, as shown in Fig. 10. It can be seen that with the enlargement of fiber content, the number of fibers on the fracture section increases from Fig. 10 (d2) to Fig. 10 (f2), and the porosity grows from Fig. 10 (a1) to Fig. 10 (c1). These small pores are generated during the preparation of filaments by extrusion as shown in Fig. 10 marked with red dashed circle, while large air pores are gaps among stacked paths and layers in the FDM process as shown in Fig. 10 marked with yellow dashed circle. As shown in the magnified image of Fig. 10 (a2), the CF is wrapped by PEEK polymer which indicates superior bonding interface and mechanical properties at lower fiber content. The larger interlayer gaps existed on the fracture interface of 15 wt% GF/PEEK as shown in Fig. 10 (c1), which is due to the weak molecular diffusion among adjacent filaments caused by huge melting viscosity. All these pores at fusion boundary are the origin of cracks which lead to the failure of printed parts [[30]]. Besides, defect of fiber aggregation was observed in 15 wt% GF/PEEK which may cause fast crack propagation in the tensile process [[36]]. Comparing the fracture surface of CF/PEEK and GF/PEEK, it can be noticed that GF/PEEK has better densification. Furthermore, the fiber orientation in deposited filaments is consistent with the printing direction as shown in Fig. 10 (c1) and Fig. 10 (f1),

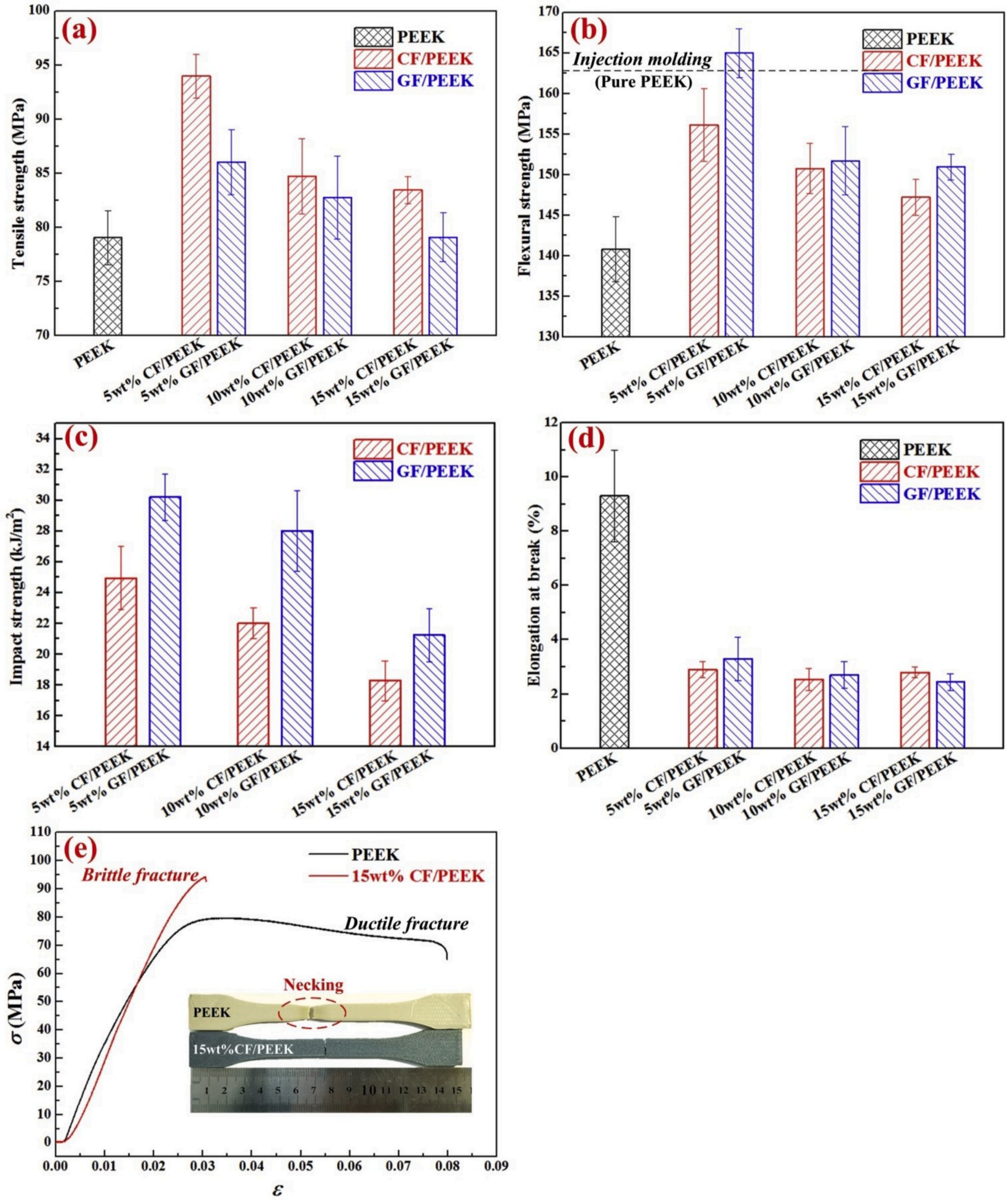

Fig. 9. (a) Tensile strength, (b) Flexural strength, (c) Impact strength, (d) Elongation at break of FDM-3D printed fiber reinforced PEEK composites, (e) Stress-strain curves of PEEK and 15 wt% CF/PEEK for tensile tests.

which is conducive to improving the mechanical properties of composite parts.

Previous studies have reported that porosity is crucial to the mechanical properties of FDM-3D printed fiber reinforced polymer composites [41]. Effect of fiber type and fiber content on the porosity of filaments and printed PEEK composite parts respectively has been conducted by Archimedes principle, and the results are illustrated in Fig. 11. It is remarkable that the density of all composite filaments is greater than 93.5% and thus the void fraction is less than 6.5%. Besides, the porosity of filaments presents a slight growth trend as the rising of CF content and GF content respectively which corresponds to the results of microscopic observation in Fig. 10. Furthermore, fewer air pores can be observed in GF/PEEK fracture surface than that of CF/PEEK at the same fiber weight fraction, due to larger volume fraction of CF than that of GF under this circumstance. According to above analysis on SEM of filaments cross-section (Fig. 5) and fractured surface (Fig. 10), it can be known that pores in composites are mainly formed by inhomogeneous mixing of fibers and PEEK particles during filament fabrication process, and the characteristic of forming porous structure by FDM process itself.

Further study shows that the increase of porosity caused by the filament preparation process is approximately 4–6%, while that of 8–10% is due to FDM process for fiber reinforced PEEK composites. The effect of filament preparation process and FDM process on porosity of composites is 2.5–4.5% and 1.8–3.8% higher than that of pure PEEK, respectively.

3.2.3. Surface quality

3D printed fiber reinforced polymer composite parts should not only possess excellent mechanical properties, but also need to meet the requirements of application for surface quality. Effect of fiber type and

Table 5
Mechanical test results of printed samples with varying fiber contents.

Samples	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (kJ/m^2)	Elongation at break (%)
5 wt% CF/PEEK	94.0 ± 2.0	156.1 ± 4.5	24.9 ± 2.1	2.9 ± 0.3
5 wt% GF/PEEK	86.0 ± 3.0	165.0 ± 3.0	30.2 ± 1.5	3.3 ± 0.8
10 wt% CF/PEEK	84.7 ± 3.5	150.8 ± 3.1	22.0 ± 1.0	2.5 ± 0.4
10 wt% GF/PEEK	82.8 ± 3.9	151.7 ± 4.2	28.0 ± 2.6	2.7 ± 0.5
15 wt% CF/PEEK	83.4 ± 1.3	147.2 ± 2.2	18.3 ± 1.3	2.8 ± 0.2
15 wt% GF/PEEK	79.1 ± 2.3	150.9 ± 1.6	21.2 ± 1.7	2.4 ± 0.3

fiber content on surface quality of FDM-3D printed fiber reinforced PEEK composite parts has been studied, as shown in Fig. 12. The measured surface roughness of printed composites grows when the fiber weight fraction increase from 5% to 15%. Fig. 13 illustrates the surface topography of printed GF/PEEK surveyed via laser scanning microscopy. Distinct deposited paths can be viewed on the surface, however, clear signs of stacking on the fill paths are observed in Fig. 13(b–d) indicating poorer surface quality. Due to enormous viscosity of fiber reinforced PEEK composites, the flow resistance of melting polymer in the nozzle channel increases, hence during the deposition process the nozzle would scratch the surface of deposited filaments resulting in uneven deposition path. Even so, the printing surface quality of PEEK composites by addition 5 wt% fiber is equivalent to that of not containing fiber.

In summary, although the addition of fiber leads to the porosity increase of composites, and the ductility of the material is also reduced, the maximum tensile strength of 5 wt% CF/PEEK in this experiment is 94 MPa which is about 19% higher than that of 3D printing pure PEEK, and the maximum flexural strength of 5 wt% GF/PEEK is 165 MPa which is even higher than that of injection molded PEEK. Such mechanical properties are superior to those short fiber reinforced polymer composites that have been reported in previous studies [[8],[9]]. Besides, the thermal stability of composites is also improved compared with that

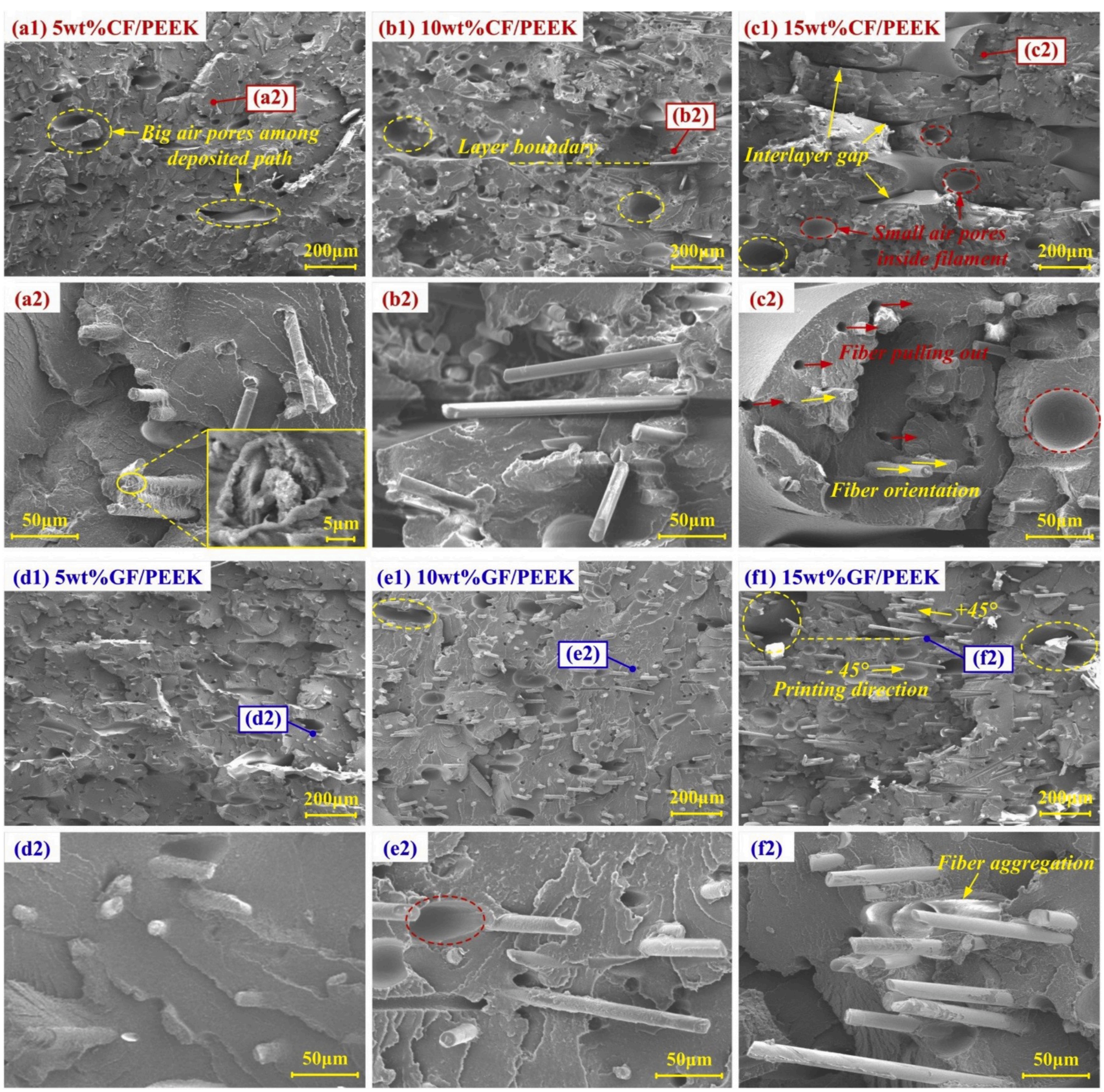

Fig. 10. SEM of tensile fracture surface of 3D printed CF/PEEK and GF/PEEK with varied fiber weight fraction.

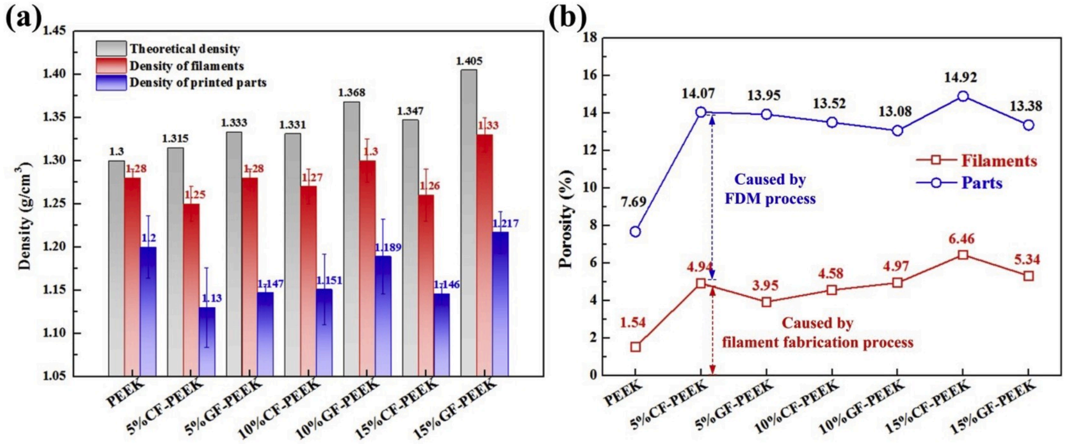

Fig. 11. (a) Theoretical density, filaments and printed parts density, (b) Porosity of filaments and printed parts with varied fiber contents.

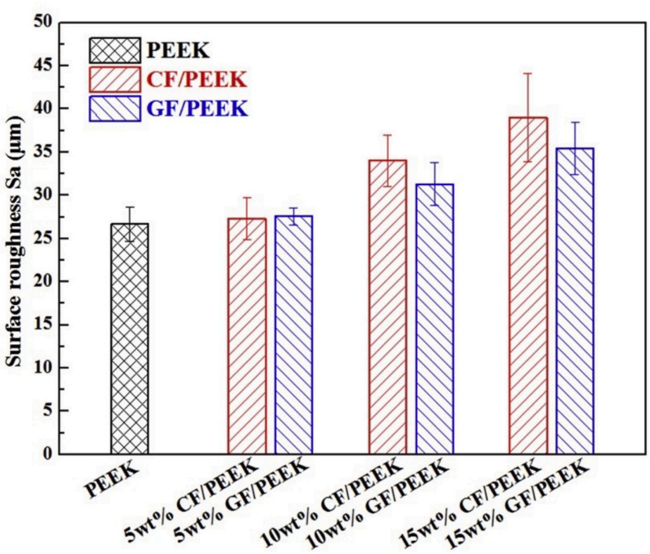

Fig. 12. Surface roughness Sa of printed CF/PEEK and GF/PEEK with varied fiber weight fraction.

without addition of fiber. This research also proved the potential of 3D printing short fiber reinforced PEEK composites with complex shape, as shown in Fig. 14. High temperature resistant PEEK polymer was applied to FDM process, and reinforcement fiber was also introduced into the filaments to achieve high strength, light-weight and complex shaped fiber reinforced PEEK composite parts, enriching the application of PEEK under extreme situations.

4. Conclusions

In this research, fiber reinforced PEEK composites filaments with two types of fibers (carbon fiber, glass fiber) and varied fiber contents from 5 wt% to 15 wt%, were prepared by extrusion process. Experimental investigations on cross-section morphology, thermal properties and crystallinity of composite filaments have been carried out. The mechanical properties (including tensile strength, flexural strength, impact strength and ductility), microstructure, porosity and surface quality (surface morphology, surface roughness) of FDM printed composite samples were studied. The following conclusions can be drawn based on the research results:

(1) With the increase of fiber weight fraction, the melting point, thermal decomposition temperature and crystallization temperature of composites are obviously higher than pure PEEK, indicating greater thermal stability of fiber reinforced PEEK composites. GF/PEEK has better fiber-matrix interfacial bonding than CF/PEEK which is due to more active functional groups on GF after surface treatment. The better interfacial bonding among GF and PEEK limits the movement of PEEK molecular chains, leads to poorer melting fluidity and lower crystallinity than that of CF/PEEK.
(2) In this experiment, the tensile strength, flexural strength, impact strength and ductility all drop with the increase of fiber weight fraction from 5 wt% to 15 wt%. Nevertheless, the tensile strength and flexural strength of printed composite parts are still stronger than that of pure PEEK. The greatest tensile properties and flexural properties are 5 wt% CF/PEEK (94 MPa) and 5 wt% GF/PEEK (165 MPa), with an increase of 19% and 17% than that of printed pure PEEK respectively. The surface roughness of composite with fiber content of 5 wt% reaches the minimum value (27 μm) which is equivalent to that of pure PEEK.
(3) The addition of fibers with the content rising from 5 wt% to 15 wt % leads to an increase in the porosity. Since the volume fraction of CF is larger than that of GF at the same mass fraction, the porosity of CF/PEEK is slightly larger. Studies on microstructure show that the porous structure shaped by FDM process, air pores formed in the fabrication process of filaments, and fibers aggregation are the main causes of composites fracture failure. In addition, the fibers orientation in the deposited path is consistent with the printing direction, indicating the improvement of mechanical properties. Larger flow resistance of melting composites causes the nozzle to scratch the deposited surface, resulting in worse surface quality.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work.

CRediT authorship contribution statement

Peng Wang: Investigation, Writing - original draft. **Bin Zou:** Conceptualization, Methodology, Project administration. **Shouling Ding:** Data curation. **Chuanzhen Huang:** Supervision. **Zhenyu Shi:** Resources. **Yongsheng Ma:** Conceptualization. **Peng Yao:** Resources.

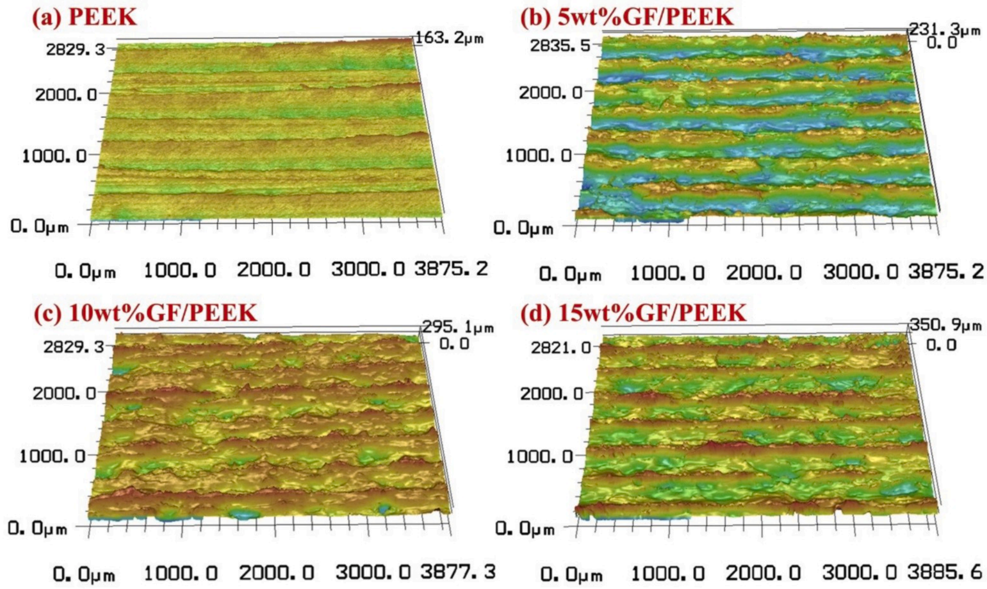

Fig. 13. Surface topography of FDM-3D printed GF/PEEK composites with varied fiber weight fraction, PEEK (a), 5 wt% GF/PEEK (b), 10 wt% GF/PEEK (c), 15 wt GF/PEEK (d).

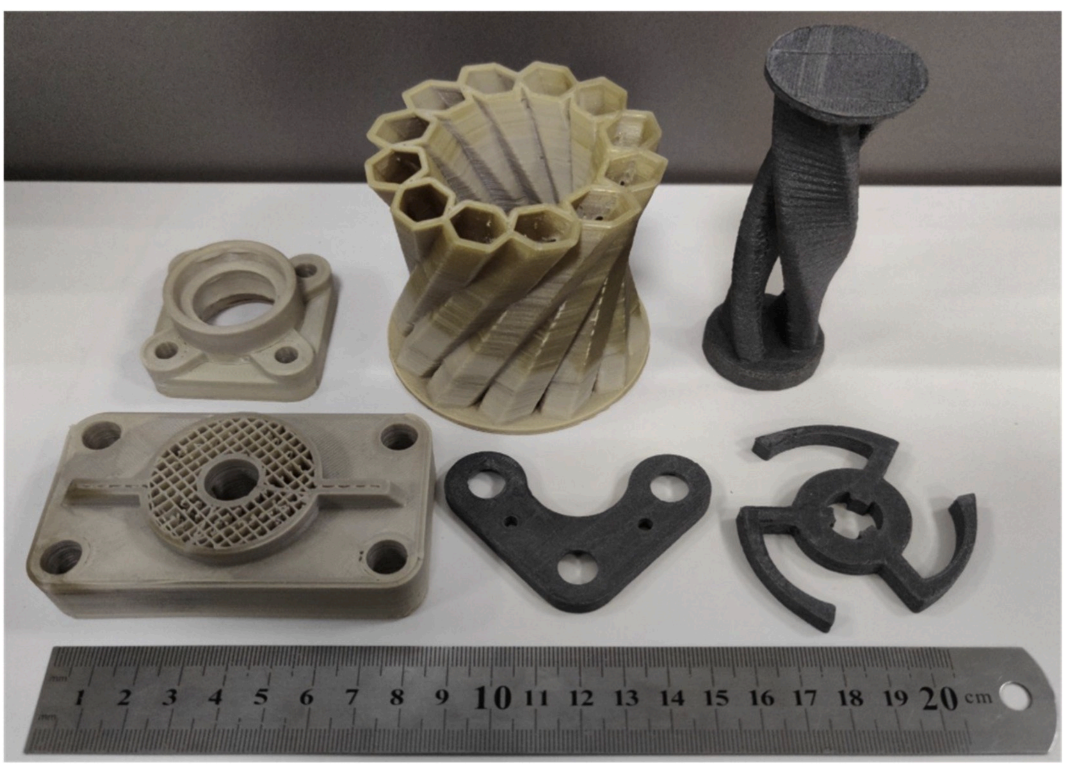

Fig. 14. FDM-3D printed PEEK and fiber reinforced PEEK composite parts with complex shapes.

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