In-house Processing of 3-D printable Polyetheretherketone (PEEK) filaments and the effect of Fused Deposition Modelling parameters on 3D Printed PEEK structures

Bharath Tej Challa
Sudeep Kumar Gummadi
Karim Elhattab
Jordan Ahlstrom
Prabaha Sikder (p.sikder@csuohio.edu)
Cleveland State University https://orcid.org/0000-0001-9302-2310

Research Article

Keywords: Fused Deposition Modelling, 3D Printing, Poly-ether-ether-ketone (PEEK), filaments, mechanical properties

Posted Date: March 9th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1404978/v1

Abstract

3D printing, specifically Fused Deposition Modelling (FDM) of Poly-ether-ether-ketone (PEEK), is one of the most powerful and efficient *state-of-the-art* manufacturing techniques. However, FDM of PEEK is challenging. Indeed, it is critical to consider specific 3D printing parameters and filament feedstock quality to achieve optimum mechanical properties in the 3D printed PEEK parts. In this paper, we investigate the effect of specific 3D printing parameters such as nozzle and chamber temperature, print speed, and layer height on the mechanical properties of 3D printed PEEK. Moreover, we explore the effect of filament quality on the structures' mechanical properties. In that regard, we developed PEEK filaments using a customized extruder setup in-house and used those laboratory-developed filaments (LD) to 3D print PEEK structures suitable for mechanical testing (tensile, compression, and flexural testing), and compared them to the mechanical properties of 3D printed parts that were developed using commercially available (CA) filaments. Results indicate that an optimum combination of a nozzle and chamber temperature, print speed, and layer height is appropriate to achieve 3D printed parts with optimum mechanical properties. Notably, results confirmed no significant differences between the specimen groups developed using LD and CA filaments, highlighting that the LD filaments were of comparable quality to the CA ones. The highest mean strengths recorded for the parts printed with the LD filaments were: 106.45 MPa (compressive), 85.43 MPa (tensile), and 102.63 MPa (flexural). This paper confirms that high-quality PEEK-based filaments can be developed in-house to yield 3D printed PEEK parts with optimum mechanical properties.

1.0 Introduction

Poly-ether-ether-ketone (PEEK, $(\text{-}C_6H_4\text{-}OC_6H_4\text{-}O\text{-}C_6H_4\text{-}CO\text{-})_n$) is a semicrystalline, thermoplastic polymer belonging to the poly-aryl-ether-ketone (PAEK) family[1]. As opposed to some well-known polymer counterparts like Polylactic acid (PLA), Polycaprolactone (PCL), and Acrylonitrile Butadiene Styrene (ABS), PEEK exhibits outstandingly high mechanical properties and melting temperature. It has Young's modulus of around 4 GPa, tensile strength around 145 MPa, and a melting point at 343^{O}C[1]. PEEK is also highly resistant to thermal and chemical degradation. These high-quality properties make PEEK one of the most suitable advanced polymers used in a wide variety of high-performance applications in aerospace, automotive, military, oil and gas, and chemical industries [2]. In addition, PEEK is a preferred biomaterial to make craniofacial, maxillofacial, orthopedic, and spinal implants because of its biocompatibility, radiolucency, chemical stability inside the body, and a close match to the mechanical properties of bone [3],[4, 5].

Traditionally, PEEK products are processed by conventional methods such as injection molding, compression molding, or machining extruded PEEK rods. However, these methods require multiple processing steps, lack the capability to make complex-designed products, and involve high chances of dimensional inaccuracies and contamination from machining tools in the final part. Hence, when Additive Manufacturing (AM), better known as 3-dimensional or 3D printing came into the industry and started developing components by a top-down or bottom-up layer-by-layer approach, it eliminated the shortcomings of conventional manufacturing techniques and allowed developers to make PEEK parts of any complex design with utmost precision easily [6].

At first, 3D printing of PEEK was only limited to the Selective Laser Sintering (SLS) technique because SLS is the only 3D printing technique that involves high processing temperature ranges, ones which can accommodate PEEK printing [7]. However, the SLS apparatus is highly sophisticated, involves multiple complicated and expensive components, and requires skilled operators. Also, the starting material needs to be in the form of powder, and SLS processing of PEEK is complicated by its varying particle morphology and size distribution, and the un-sintered powder goes waste [7], [8]. These shortcomings restricted the expansive and broad-ranging development of 3D-printed PEEK products to some extent.

On the other hand, Fused Deposition Modelling (FDM) is the most well-known and widely used 3D printing technique with many advantages, including low cost, minimal waste, and simplicity in which it can be installed on benchtops and it is easy to operate compared to other AM techniques [9]. Also, it is convenient to develop polymer composites compatible with FDM printers [10] [11] [12]. However, FDM of PEEK is complex and requires careful processing, especially when the aim is to print products that exhibit mechanical properties close to those developed in conventional manufacturing techniques such as injection molding. FDM of PEEK requires high thermal processing parameters such as nozzle, bedplate, and chamber temperatures. It is also well known that FDM-developed (FDM-d) PEEK parts are prone to warping, involve high thermal stress, and are prone to poor interlayer adhesion [13]. Since 2014, various research groups have explored FDM of PEEK using customized 3D printers and feedstock filaments. Valentan et al.[14] and Wu et al.[15] were some of the firsts to establish a particular FDM 3D printer that could achieve the required nozzle and chamber temperatures to process PEEK material. Subsequently, other research groups explored the effect of various FDM-specific parameters on the material and mechanical properties of 3D printed PEEK products. In a critical study, Wu et al.[16] investigated the influence of layer thickness and raster angle on the mechanical properties of FDM-d PEEK and further compared the properties with PEEK parts made by injection molding. The study concluded that optimal mechanical properties of PEEK could be observed in samples with 0.3 mm layer thickness and a raster angle of $0^0/90^0$, but the properties of 3D printed PEEK parts were significantly lower than those developed by injection molding. Vaezi and Yang [17] performed a detailed exploration of various thermal parameters on the quality of PEEK parts. The authors observed that nozzle temperatures within the range of 400–430^0C was suitable for 3D printing PEEK. Further, they also indicated that a chamber temperature of 80^0C and a heated build plate at 130^0C are critical to assure a suitable PEEK/substrate and PEEK interlayer bonding, avoid warpage, minimize delamination, and reduce polymer degradation. Yang et al.[18] analyzed the effect of various thermal conditions on PEEK parts and observed that a high chamber temperature (150^0C and 200^0C) and annealing can significantly enhance the crystallinity of PEEK and hence improve the mechanical properties of the printed parts.

In the last few years, many researchers have conducted in-depth studies to analyze the effect of various kinds of FDM processing parameters on PEEK properties [19],[20]. Yet, it should also be noted that apart from FDM processing parameters, the quality of the feedstock filaments also play a significant role in the mechanical properties of the filament. Deviations in the diameter of the feedstock filament can cause material deficit or surplus in layers [14] and air gaps between adjacent filaments in the printed parts [17], leading to mechanical property degradation. Through a series of experiments, Zhao et al.[21] confirmed that the diameter deviation of the feedstock filament was a critical factor in influencing the quality of the printed parts. Lesser variations lead to fewer voids in the printed parts, thus enhancing mechanical property. Many research groups that focused on the FDM of PEEK developed their in-house 3-D printable PEEK filaments, but very few considered the effect of feedstock filament quality. Indeed, it is challenging to form constant diameter PEEK filaments primarily because of the high extrusion temperatures and viscosity of PEEK. In the recent 2–3 years, there has been a surge in the research and development of FDM-d PEEK, because of the availability of various cost-effective, high-temperature 3D printers. Moreover, companies like Invibio, Apium, and 3DXTECH have become well-known 3D printable PEEK filament manufacturers. However, it does not give innovators the chance to develop 3D printable filaments of customized compositions, for instance, PEEK-based composites [22].

In this study, we developed an extrusion setup and used it to form constant-diameter PEEK filaments. Subsequently, the filaments were used in a high-temperature FDM printer to print various PEEK specimens for mechanical testing. We aimed to compare the quality of the laboratory-developed (LD) filaments to one of the most well-known commercially available (CA) filaments. Therefore, we performed a thorough comparative analysis between the tensile, compressive, and flexural strengths of the 3D printed specimens developed from LD and CA filaments. Further, we explored the effects of crucial 3D printing parameters like nozzle and chamber temperature, print speed, and layer height on the mechanical properties of specimens developed from both CA and LD filaments. We expect this study to provide the necessary guidance to researchers and developers about choosing LD or CA filaments and combining them with an optimized set of printing parameters to achieve high-quality FDM-d PEEK parts.

2.0 Experimental

2.1 Raw Materials for 3D Printing

For the LD 3D printable filaments, PEEK 450G Type Unfilled Natural Pellets (Filastruder, Snellville, GA, USA) was used. The filament extruder and filament winder parts were procured from Filastruder and assembled in-house. A 15V, 150W power supply (LRS-150F-15, Mean Well, New Taipei City, Taiwan) was used for increasing the extruder temperature up to 450^0C and a 1" thick Ceramic Fiber Insulation Kao wool insulation blanket (Lynn Manufacturing Inc, Lynn, MA, USA) was wrapped around the extruder barrel to maintain the high extrusion temperature. The CA filament used in this study was Thermax™ PEEK Natural (3DXTECH, Grand Rapids, MI, USA) filament with a diameter of 1.75 mm.

2.2 In-house feedstock filament extrusion

3D printable LD PEEK filament was made by a customized device assembly comprising of **1)** a single-screw extruder, **2)** a sensor controlling the speed of filament winding, and **3)** a filament winding setup as shown in Fig. 1. All the parts were procured from Filastruder. Figure 1 also shows the entire extrusion and filament spooling setup. The PEEK pellets were first dried at 120^0C for 5h in a convection oven and fed to a single-screw extruder with the help of a custom-designed hopper. The single screw extruder (with a Ø1.6 mm nozzle) was kept at a raised angular position with respect to the sensor and the winder setup. The extruder screw (length = 150 mm) speed was set at 10 rpm, and the temperature was maintained at 355^0C throughout. We didn't use any additional quenching step apart from ambient atmosphere cooling as it affected the uniformity in the filament dimension. Once a filament was extruded out, it was guided through a sensor that detects the filament's position and adjusts the speed of the winder. The filament was then guided through a loop of polytetrafluoroethylene (PTFE) tube that provides tension (and stretch) to resist tangles. Once the filament left the PTFE tube, a filament guide evenly spread the filament across the spool to avoid bundling up at only one region. Depending on the positioning of the filament on the spool, the filament winding setup automatically adjusted the speed of spool rotation to induce a favorable tension to the ongoing extruded filaments. After an entire spool of PEEK filament was formed, it was stored at 120^0C until further usage.

2.3 Filament Characterization

To analyze the extent of pores present in the filaments, both LD and CA filaments were cryo-fractured at three random locations along the filament spool length and analyzed using Scanning electron microscopy (SEM).

2.4 FDM-3D Printing Parameters

Both CA and LD PEEK filaments were dried at 120^0C for 5h before using them for 3D printing. We used a FUNMAT HT Enhanced (Intamsys Technology Ltd., Shanghai, China) for 3D printing various PEEK specimens. We varied four different FDM parameters one at a time, keeping the others fixed, as shown in **Table I**. For all the samples, the raster direction was an oblique direction of 45°, and the infill rate was 100%. The protocol of post-heat treatment (annealing) procedure for one set of samples was:160°C for 30 min, followed by 200°C for 2 h, and gradual cooling to room temperature.

Table I The variable and fixed 3D printing parameters followed in this study

Variable Parameter	*Nozzle Temp (^{O}C)*	*Bed Plate Temp (^{O}C)*	*Chamber Temp (^{O}C)*	*Layer Height (mm)*	*Print Speed (mm/sec)*
Nozzle Temp	**380**	130	90	0.2	50
	400				
	410				
Chamber Temp	400	130	**25**	0.2	50
			90		
Layer Height	400	130	90	**0.3**	50
				0.2	
				0.1	
Print Speed	400	130	90	0.2	**30**
					40
					50

2.5 Mechanical Properties

Tensile, compression, and flexural tests were performed on various 3D printed PEEK parts at room temperature. The Instron 3369 Universal Testing Machine (UTM) with a 50kN load cell and specific testing fixtures was used for the different mechanical tests. Compression testing was performed following ASTM D695 with a constant displacement of 1.27 mm/min [23]. The dimensions of the cylindrical specimens are shown in Fig. 2a. Tensile testing was performed following ISO 527-2 [24]. The CAD diagrams and 3D models (STL format) of the dog bone-shaped specimen dimensions are shown in Fig. 2b. A fixed-gauge length 2630 series clip-on extensometer was clipped directly onto the specimen at the beginning of each tensile test. In addition, 5 mm/min strain deformation was used to measure the specimens' tensile strength. A 1kN load cell was used for the flexural tests, and ISO 178 was followed. The rectangular specimen dimensions are shown in Fig. 2c. Flexural strength was calculated using the following equation. $\sigma = \frac{3\mathrm{PL}}{2\mathrm{b}t^2}$

where:

σ = Flexural Stress (MPa)

P = Load (N)

L = Support span (50 mm)

b = width of specimen (mm)

t = thickness of beam (mm)

2.6 Statistical Analysis

All the tests were performed with a sample size n = 4. One-way analysis of variance with Tukey test was conducted to determine the statistical difference between different specimen groups and $\rho < 0.05$ were considered significant.

3.0 Results

3.1 Compressive Strengths

The photograph of a cylinder-shaped compression testing specimen is shown in Fig. 3a. The part exhibits a gradient of dark brown and light beige-colored regions all over the surface. While certain print layers and regions show prominent dark brown color, some regions show beige color. Figure 4**(a-d)** shows the compressive strengths of the specimens developed with LD and CA filaments as a function of various 3D printing parameters such as nozzle temperature, chamber temperature, printing speed, and layer height. Some critical observations can be made from the graphs – **First**, in all the cases of varied printing parameters, the specimens developed with CA filaments exhibited moderately better compressive strengths than those produced with LD filaments. **Second**, higher nozzle temperature helps to enhance the compressive strengths of the 3D printed parts significantly. The highest average compressive strength can be observed in the specimens printed at 410^0C nozzle temperature using CA filaments (105.34 MPa); nonetheless, the parts printed at the same nozzle temperature using LD filaments exhibited an average compressive strength of 104.56 MPa. **Third**, chamber temperature plays a significant role in improving the compressive strength of the specimens. In the case of the CA filaments, we noticed significantly higher compressive strengths of the samples printed at 90^0C (105.34 MPa) compared to those printed at 25^0C (90.28 MPa). The observations were the same for the parts printed with LD filaments; an increase of 18.5% was observed in the compressive strengths of the parts printed at 90^0C (104.56 MPa) over those printed at 25^0C (88.23 MPa). **Fourth**, increasing print speed steadily augments the compressive strengths of the parts printed with both LD and CA filaments. However, there were no significant differences in the compressive strengths of the parts printed at 50 mm/sec compared to those printed at 40 mm/sec. **Finally**, lowering the layer height thickness increases the compressive strengths of the specimens. Notably, a significant difference in the strengths can be noted between the samples printed with layer heights of 0.3 mm (90.23 MPa for LD filaments and 91.54 MPa for CA filaments) and 0.1 mm (106.45 MPa for LD filaments and 108.69 MPa for CA filaments).

3.2 Tensile Strengths

The photograph of a 3D printed PEEK tensile specimen is shown in Fig. 3b. Similar to the compression specimens, a dark brown and beige gradient can be observed all over the printed part. However, as opposed to the compression specimen, the color gradient was more prominent on the top surface of the printed part and not along with the layers, i.e., the part thickness. The deep brown color was evident along with the thickness of the tensile bar. Figure 5**(a-d)** shows the tensile strengths of the specimens printed with LD and CA filaments as a function of various 3D printing parameters. The graphs indicate some essential observations. **First**, like the compressive strengths, specimens printed with CA filaments exhibited better tensile strengths than the ones printed with LD filaments. In the majority of the cases, the differences were not significant, except for the two conditions. At 25^0C, the specimens printed with LD filaments exhibited considerably lower tensile strength values (69.84 MPa) than those printed with CA filaments (78.25 MPa). Similarly, with 0.3 mm layer height, the tensile strengths of the parts printed with LD filaments were significantly lower (16.2%) than those printed with CA filaments. **Second**, higher nozzle temperature helps in a significant increase in the tensile strength of the specimens. Notably, the samples printed at 410^0C and LD filament exhibited a mean tensile strength of 86.57 MPa. In addition, the rise in chamber temperature (90^0C) significantly increases the tensile strength of the samples; in the case of LD filaments, the rise was 21.7%, and in the case of CA filaments, the rise was 11.7%. **Third**, lowering the print speed helped decrease the tensile strength, whereas reducing the layer height thickness increased the tensile strength. Interestingly, as opposed to the significant differences in tensile strengths between the parts printed with LD and CA filaments and 0.3 mm layer height, the parts printed with 0.1 mm layer and LD filaments exhibited comparable tensile strengths (85.43 MPa) to the ones printed with CA filaments.

3.3 Flexural Strengths

A 3D printed PEEK specimen for flexural testing is shown in Fig. 3c. Similar to the tensile test specimens, a dark brown and beige gradient can be seen on the specimen's top surface. Also, the dark brown color was predominant along with the thickness of the specimen. Figure 6**(a-d)** shows the flexural strength of the specimens printed with LD and CA filaments as a function of Some important observations that can be made from the graphs are mentioned in the following. **First**, at every condition, the flexural strengths of the specimens printed with CA filaments were moderately better than those printed with LD filaments. No significant differences were observed between the groups of specimens printed at LD and CA filaments. **Second**, the change in nozzle temperature have a prominent effect on the flexural strength of the specimens printed with CA filaments (21.4%); a marked increase can be observed between the samples printed at 410^0C and 380^0C. Similarly, an increase in the nozzle temperature resulted in a notable enhancement (22.3%) in the flexural strengths of the specimens developed from LD filaments, just like the tensile and compressive strength trends. Similarly, the increase in chamber temperature significantly enhanced the flexural strength of the specimen irrespective of the filaments used. **Third**, flexural strengths of the specimens increase with a rise in printing speed, with the highest values observed at 50 mm/sec. The parts printed at the latter speed and LD filaments exhibit a mean flexural strength of 99.25 MPa, almost similar to those printed with CA filaments (101.46 MPa). Fourth, decreasing print layer height thickness enhances the flexural strength of the specimens. In the case of CA filaments, an enhancement of 13.1% can be observed over the decrease in the layer height. Also, in case of LD filaments, a notable difference of 14.6% can be observed between the specimens printed with 0.1 and 0.3-mm layer height. The highest flexural strength was observed in the specimens with 0.1mm layer height with a mean value of 102.63 MPa, almost similar to those printed using CA filaments.

4.0 Discussion

In this study, we explored PEEK filaments developed in the laboratory and determined their suitability for 3D printing design-specific structures with favorable mechanical properties. Even though in some cases, the PEEK parts developed with the LD filaments exhibited reduced mechanical properties than the ones developed with CA filaments, overall, the results confirm that favorable quality filaments can be developed in-house, and those can be used in a FDM 3D printer to yield mechanically robust 3D printed parts. One of the primary reasons for the degradation of mechanical properties in the parts printed with LD filaments is the presence of pores or defects in the filament that can be seen in Fig. 7. The cross-section of a LD filament shows the presence of such defects. Furthermore, the slight inconsistency in the filament diameter also degrades the mechanical properties of the printed parts. For instance, when the filament diameter is thicker than 1.75 mm at a fixed extruder flow, excess material flow results in buildups in the print layers, as seen in the compression specimen (yellow arrows in Fig. 8). That being said, a controlled amount of excess material flow can also promote a robust filament-to-filament bonding in the lateral direction. Yet, an extra flow results in dimensional inaccuracy surface finish and even affects interlayer adhesion. On the other hand, when the feedstock filament was thinner than 1.75 mm, at a fixed extruder flow, it created voids in the print layers due to a shortage in the material flow (red arrows in Fig. 8). These voids are critical in affecting the load distribution between the layers when the specimens are subjected to stress and degrades the mechanical properties.

Indeed, it is critical to employ an optimum set of FDM processing parameters to achieve the parts with the best mechanical properties. It is evident that printing parameters such as nozzle temperature, chamber temperature, layer height, and printing speed significantly affect the mechanical properties of the printed structure [20, 25]. Temperatures of the nozzle, build plate, and chamber mainly affects the crystalline/amorphous ratio of the 3D printed PEEK structures [18, 26]. PEEK, similar to many other polymers, is semicrystalline, meaning that PEEK in the solid-state consists of crystalline and amorphous structures, each of which has different characteristics [27]. On the one hand, a completely crystalline structure is characterized by its high molecular order, close polymer chain packing, and strong intermolecular forces. Therefore, the crystalline region in PEEK contributes to having a more dense and rigid polymer. On the other hand, the amorphous region is characterized by its random and intertwined structure. Thus, the density and mechanical properties of PEEK depend primarily on the crystalline/amorphous ratio [28, 29]. In the present study, all the test specimen parts exhibit a mixture of amorphous and crystalline PEEK, which is indicated by the mix of dark brown and beige-colored regions (Fig. 3). The dark brown indicates the amorphous regions, and the beige region exhibit the crystalline regions. The amorphous and crystalline combination in a single printed part is not appropriate for obtaining excellent mechanical properties. A good way to address this is to anneal the parts post-printing. To analyze the effect of post-heat-treatment, we annealed one set of tensile specimens printed using: Nozzle Temp.: 410^0C, Chamber Temp:90^0C, Print Speed: 50 mm/sec, and layer height: 0.1 mm. We observed an enhancement of 7% in the mechanical properties and achieved a tensile strength of 114.34 MPa in the annealed parts. This is because annealing crystallizes the amorphous regions and forms a completely crystallized part corroborated by the uniformly beige colored PEEK specimen shown in Fig. 9a. Further, with the help of our DSC results, we observed a 3.21% rise in crystallinity in the annealed parts as compared to the non-annealed ones. (Fig. 9b). However, we did not anneal the other sets as we wanted to analyze the effect of the printing conditions on the mechanical properties of the specimens.

Along the same lines, the mechanical tests, including compression, tensile, and bending, showed increased mechanical properties by increasing the nozzle temperature, which can also be explained by the higher crystallinity of 3D printed PEEK samples produced by higher printing temperature. Furthermore, higher nozzle temperatures decrease the melt viscosity of the polymer/PEEK extrudate, resulting in easy flow of the material through the nozzle, resulting in better filament deposition and filament-to-filament bonding. Also, a more viscous extrudate helps diffuse well with the underlying polymer layer and promotes a strong filament-to-filament bonding in the lateral and vertical direction [30–32]. Similar results have been shown in a study conducted by Yang et al. focusing on the thermal processing effect on the crystallinity of 3D printed PEEK structure [18]. In that study, 3D printed PEEK tensile bars were printed with nozzle temperatures ranging from 360 ^{0}C to 480 ^{0}C, and the results showed an increase in PEEK crystallinity from 16–21%. Also, the results showed that tensile strength and elastic modulus were increased when the nozzle temperature increased from 360 ^{0}C to 420 ^{0}C, accompanied by an increase in crystallinity. However, the tensile properties decreased from nozzle temperature of 440 ^{0}C to 480 ^{0}C due to material degradation [18]. The degradation of PEEK during the 3D printing process above the nozzle temperature of 430 ^{0}C was also captured by Vaezi et al. [17]. A study by Wang et al. [33] investigated the effect of different AM parameters (e.g., nozzle diameter, nozzle temperature, and printing speed) on the mechanical performance of FDM PEEK. Nozzle temperatures of 420 ^{0}C, 430 ^{0}C, and 440 ^{0}C were investigated in the latter study, all of which were more than the highest temperature used in the present study. The authors observed that when optimum printing parameters were combined with the nozzle temperature of 430^{0}C, it produced a structure with higher compression and bending properties compared to the nozzle temperature of 420 ^{0}C [33]. In another study, Ding et al. [30] studied the effect of nozzle temperature on the mechanical properties of 3D printed PEEK samples. The nozzle temperature range used in that study was 360 ^{0}C to 420 ^{0}C with a gradient of 10 ^{0}C, similar to the temperature profile explored in the present study. The results showed that the relative density of the printed PEEK samples increased with the increase in nozzle temperature and achieved the highest relative density (92.5%) at the highest nozzle temperature (420 ^{0}C). Increasing the nozzle temperature improves the fluidity of the polymer melt through the nozzle and eliminates the air particles, which increase the density of the 3D printed structure and improve the adhesion between the printed layers. In the same study, the results showed that increasing nozzle temperature from 360 ^{0}C to 420 ^{0}C significantly increased tensile and flexural strengths [30].

Also, in the present study, mechanical properties were enhanced by increasing the chamber temperature. The chamber temperature affects the cooling speed of the printed layers. Thus, it affects the crystallinity of the printed structure. For instance, a 3D printed PEEK structure at a chamber temperature of 25 ^{0}C will be cooled faster than a structure printed at 90^{0}C, thus increasing the chamber temperature improves the crystallinity of the 3D printed structure. Hu et al. proposed several design structures to improve the mechanical properties of 3D printed PEEK using finite element analysis [34]. The study showed that PEEK structures printed at a chamber temperature of 60 ^{0}C were more crystalline and had better mechanical performance than those printed at 25 ^{0}C [34, 35]. Moreover, the strength of interlayer bonding improves when the temperature field is more uniform [34], which can be achieved by increasing the chamber's temperature and printing bed. A study by Wu et al. [13] also investigated the effect of chamber temperature on the 3D printed PEEK structure quality. In that study, the warp deformation of PEEK structures has been monitored versus chamber temperature of 90 ^{0}C, 100 ^{0}C, 110 ^{0}C, 120 ^{0}C, and 130 ^{0}C. The results showed that increasing the chamber temperature improved the quality of 3D printed structures in which increasing the temperature from 90 ^{0}C to 130 ^{0}C reduced the warp deformation from 1.93 mm to 0.65 mm [13]. In the present study, 90^{0}C chamber temperature helped in elevating the mechanical properties compared to the 25^{0}C; however, it should be noted that 90^{0}C was not sufficient to yield completely crystalline parts (Fig. 3) with optimum mechanical properties.

The layer height is another important factor that has an inversely proportional relationship with the quality and mechanical performance of the 3D printed structures. Smaller layer height provides a better surface finish of the 3D printed structure [20, 36]. Additionally, smaller layer height produces denser structures that significantly increase the mechanical properties of the printed structures [36]. Liaw et al. studied the effect of different 3D printing parameters on the interlayer bonding strength of the 3D printed PEEK structures [37]. In that study, the 3D printed PEEK structures were printed in the vertical direction then the strength of the interlayer was evaluated by conducting a three-point flexure test where the bending load was applied perpendicular to the printing direction. It was noticed that among all the 3D printing parameters investigated in that study, the layer height was the only parameter that affected the flexure modulus significantly. The results showed that reducing the layer height increased flexure stress at break and flexure modulus. We also observed a similar trend in the present study, where decreasing the layer height increased the compressive, tensile and flexural strengths of the 3D printed PEEK parts. Thinner layers eliminate microvoids between printed layers by reducing the layer height, which results in a closely stacked layer and better bonding [37].

Interestingly, printing speed is a complicated factor that can either improve or hamper the mechanical performance of the printed structure when combined with other specific printing parameters. For instance, higher printing speed with a thick layer height and low nozzle temperature reduces the quality and mechanical properties of the printer structure. However, when a higher printing speed is combined with thinner layer height and high nozzle temperature, it improves the quality and mechanical properties of the printed structure, as this parameter combination decreases the interlayer defects and increases interlayer bonding [19]. Geng et al. studied the effect of the FDM extrusion and printing speeds on the accuracy of the extruded PEEK filament [38]. In that study, defects in 3D printed PEEK straight lines were investigated at different extrusion and printing speeds. There were evident defects in the printed line at an extrusion speed of 1 mm/min and printing speed of 6.9 mm/min compared to the printed line at an extrusion speed of 80 mm/min and a printing speed of 335.5 mm/min, which has no apparent defects [38]. This is because the melt flow should have a sufficient pressure drop through the liquefier to move out of the nozzle and be deposited on the printing bed. In the case of slow extrusion speed, therefore, slow printing speed, there will be an insufficient pressure drop in the liquefier zone, creating cavities in the filament [38]. Our observations are similar to the previous studies. Higher printing speeds yields better mechanical properties as it helps in reducing the extent of defects in the print layers, ensures a favorable interlayer adhesion and avoids extrudate build-ups. Indeed, the print speed should be optimized as too high speeds might not give sufficient time to deposit the extrudate and even affect the dimensional accuracy resulting in voids.

Thus, in this study, the most favorable printing conditions identified are Nozzle Temp: 410^0C, Chamber Temp: 90^0C, Print Speed: 50 mm/sec, and layer height: 0.1 mm. We used this printing combination and LD filaments to print a femoral head, as shown in Fig. 10. Indeed, we noticed layers with varying amorphous and crystalline regions but the overall resolution and quality was outstanding, indicating that LD filaments and a combination of optimum 3D printing parameters can yield excellent orthopedic medical devices.

5.0 Conclusion

In this study, we were successful in making quality PEEK filaments in-house. We did not notice any considerable differences in the mechanical properties of the parts printed with LD and CA filaments in almost all the printing conditions. Yet, the slight decrease in the mechanical properties of the parts printed with LD filaments can be attributed to the defects in the filament and variability in the filament diameter. Notably, an increase in nozzle and chamber temperatures significantly enhances the mechanical properties of the specimens. However, the present study's highest thermal conditions, i.e., 410^0C nozzle temperature and 90^0C chamber temperature, were not sufficient to yield completely crystalline PEEK parts. Instead, all the parts contained mix of amorphous and crystalline regions. Also, a high printing speed and lower layer height were promising in considerably improving the mechanical properties of 3D printed PEEK.

Declarations

6.1 Funding

This work was supported by Dr. Sikder’s STARTUP grant at Cleveland State University.

6.2 Competing Interests

All the authors have no financial interests.

6.3 Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Bharath Tej Challa and Sudeep Kumar Gummadi.. The first draft of the manuscript was written by Prabaha Sikder and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

References

1. Rigby RB Polyetheretherketone, Engineering thermoplastics, CRC Press2020, pp. 299–314
2. Park SJ, Lee JE, Park J, Lee N-K, Son Y, Park S-H (2021) High-temperature 3D printing of polyetheretherketone products: Perspective on industrial manufacturing applications of super engineering plastics. Mater Design 211:110163
3. Panayotov IV, Orti V, Cuisinier F, Yachouh J (2016) Polyetheretherketone (PEEK) for medical applications. J Mater Science: Mater Med 27(7):1–11
4. Kurtz SM, Devine JN (2007) PEEK biomaterials in trauma, orthopedic, and spinal implants. Biomaterials 28(32):4845–4869
5. Elhattab K, Sikder P, Walker JM, Bottino MC, Bhaduri SB (2020) Fabrication and evaluation of 3-D printed PEEK scaffolds containing Macropores by design. Mater Lett 263:127227
6. Berman B (2012) 3-D printing: The new industrial revolution. Bus Horiz 55(2):155–162
7. Schmidt M, Pohle D, Rechtenwald T (2007) Selective laser sintering of PEEK. CIRP Ann 56(1):205–208
8. Bourell DL, Watt TJ, Leigh DK, Fulcher B (2014) Performance limitations in polymer laser sintering. Physics Procedia 56:147–156
9. Elhattab K, Hefzy MS, Hanf Z, Crosby B, Enders A, Smiczek T, Haghshenas M, Jahadakbar A, Elahinia M (2021) Biomech Additively Manufactured Metallic Scaffolds—A Rev Mater 14(22):6833
10. Han X, Yang D, Yang C, Spintzyk S, Scheideler L, Li P, Li D, Geis-Gerstorfer J, Rupp F (2019) Carbon fiber reinforced PEEK composites based on 3D-printing technology for orthopedic and dental applications. J Clin Med 8(2):240
11. Oladapo BI, Ismail SO, Bowoto OK, Omigbodun FT, Olawumi MA, Muhammad MA (2020) Lattice design and 3D-printing of PEEK with Ca10 (OH)(PO4) 3 and in-vitro bio-composite for bone implant. Int J Biol Macromol 165:50–62
12. Elhattab K, Bhaduri SB, Lawrence JG, Sikder P (2021) Fused Filament Fabrication (Three-Dimensional Printing) of Amorphous Magnesium Phosphate/Polylactic Acid Macroporous Biocomposite Scaffolds. ACS Appl Bio Mater 4(4):3276–3286
13. Wu WZ, Geng P, Zhao J, Zhang Y, Rosen DW, Zhang HB (2014) Manufacture and thermal deformation analysis of semicrystalline polymer polyether ether ketone by 3D printing. Mater Res Innovations 18(sup5):S5–12
14. Valentan B, Kadivnik Ž, Brajlih T, Anderson A, Drstvenšek I (2013) Processing poly (ether etherketone) an a 3D printer for thermoplastic modelling. Materiali in tehnologije 47(6):715–721

15. Wu WZ, Geng P, Zhao J, Zhang Y, Rosen DW, Zhang HB (2014) Manufacture and thermal deformation analysis of semicrystalline polymer polyether ether ketone by 3D printing, Materials Research Innovations 18(sup5) S5-12-S5-16
16. Wu W, Geng P, Li G, Zhao D, Zhang H, Zhao J (2015) Influence of layer thickness and raster angle on the mechanical properties of 3D-printed PEEK and a comparative mechanical study between PEEK and ABS. Materials 8(9):5834–5846
17. Vaezi M, Yang S (2015) Extrusion-based additive manufacturing of PEEK for biomedical applications. Virtual and Physical Prototyping 10(3):123–135
18. Yang C, Tian X, Li D, Cao Y, Zhao F, Shi C (2017) Influence of thermal processing conditions in 3D printing on the crystallinity and mechanical properties of PEEK material. J Mater Process Technol 248:1–7
19. Wang P, Zou B, Xiao H, Ding S, Huang C (2019) Effects of printing parameters of fused deposition modeling on mechanical properties, surface quality, and microstructure of PEEK. J Mater Process Technol 271:62–74
20. Wang Y, Müller W-D, Rumjahn A, Schwitalla A (2020) Parameters influencing the outcome of additive manufacturing of tiny medical devices based on PEEK. Materials 13(2):466
21. Zhao F, Li D, Jin Z (2018) Preliminary investigation of poly-ether-ether-ketone based on fused deposition modeling for medical applications. Materials 11(2):288
22. Sikder P, Ferreira JA, Fakhrabadi EA, Kantorski KZ, Liberatore MW, Bottino MC, Bhaduri SB (2020) Bioactive amorphous magnesium phosphate-polyetheretherketone composite filaments for 3D printing. Dent Mater 36(7):865–883
23. Standard A (2008) D695: Standard test method for compressive properties of rigid plastics. ASTM International, West Conchohocken
24. Iso UE (2012) Plastics-Determination of tensile properties-Part 2: Test conditions for moulding and extrusion plastics. Switzerland, International Organization for Standardization
25. Deng X, Zeng Z, Peng B, Yan S, Ke W (2018) Mechanical properties optimization of poly-ether-ether-ketone via fused deposition modeling. Materials 11(2):216
26. Mrówka M, Machoczek T, Jureczko P, Joszko K, Gzik M, Wolański W, Wilk K (2021) Mechanical, Chemical, and Processing Properties of Specimens Manufactured from Poly-Ether-Ether-Ketone (PEEK) Using 3D Printing. Materials 14(11):2717
27. Mark JE (2007) Physical properties of polymers handbook. Springer
28. Jaekel DJ, MacDonald DW, Kurtz SM (2011) Characterization of PEEK biomaterials using the small punch test. J Mech Behav Biomed Mater 4(7):1275–1282
29. Rae PJ, Brown EN, Orler EB (2007) The mechanical properties of poly (ether-ether-ketone)(PEEK) with emphasis on the large compressive strain response. Polymer 48(2):598–615
30. Ding S, Zou B, Wang P, Ding H (2019) Effects of nozzle temperature and building orientation on mechanical properties and microstructure of PEEK and PEI printed by 3D-FDM. Polym Test

78:105948

31. Zalaznik M, Kalin M, Novak S (2016) Influence of the processing temperature on the tribological and mechanical properties of poly-ether-ether-ketone (PEEK) polymer. Tribol Int 94:92–97
32. Zanjanijam AR, Major I, Lyons JG, Lafont U, Devine DM (2020) Fused filament fabrication of peek: A review of process-structure-property relationships. Polymers 12(8):1665
33. Wang Y, Müller W-D, Rumjahn A, Schmidt F, Schwitalla AD (2021) Mechanical properties of fused filament fabricated PEEK for biomedical applications depending on additive manufacturing parameters. J Mech Behav Biomed Mater 115:104250
34. Hu B, Duan X, Xing Z, Xu Z, Du C, Zhou H, Chen R, Shan B (2019) Improved design of fused deposition modeling equipment for 3D printing of high-performance PEEK parts. Mech Mater 137:103139
35. Kurtz SM (2019) An overview of PEEK biomaterials, PEEK biomaterials handbook 3–9
36. Fischer D, Eßbach C, Schönherr R, Dietrich D, Nickel D (2022) Improving inner structure and properties of additive manufactured amorphous plastic parts: the effects of extrusion nozzle diameter and layer height,Additive Manufacturing102596
37. Liaw C-Y, Tolbert JW, Chow LW, Guvendiren M (2021) Interlayer bonding strength of 3D printed PEEK specimens. Soft Matter 17(18):4775–4789
38. Geng P, Zhao J, Wu W, Ye W, Wang Y, Wang S, Zhang S (2019) Effects of extrusion speed and printing speed on the 3D printing stability of extruded PEEK filament. J Manuf Process 37:266–273

Figures

Figure 1

Photograph of the entire laboratory extruder setup that was used to develop the PEEK filaments. The major components that assemble to make the setup are the high temperature extruder, sensor that detects the filament position and an automatic guided spooling system. A photograph of a spool of laboratory-developed (LD) PEEK filaments is also shown.

Figure 2

CAD diagrams and corresponding 3D models (as obtained from the slicing software) of the **(a)** compression, **(b)** tensile and **(c)** flexural test specimens.

Figure 3

Photographs of 3D printed PEEK specimens developed by LD filaments for **(a)** compression, **(b)** tensile and **(c)** bending tests. All the parts show a mix of amorphous (dark brown color regions) and crystalline regions (beige color regions). The FDM parameters that were used to print these parts are as follows: Nozzle Temp: 410^0C, Chamber Temp: 90^0C, Print Speed: 50 mm/sec, and layer height: 0.2 mm

Figure 4

Comparison of compressive strengths of specimens developed by commercially available (CA) and laboratory developed (LD) filaments as a function of (a) printing speed (b) layer height, and (c) nozzle temperature. * means that value is statistically significant with the values at 380^0C, 25^0C and 0.3 mm.

Figure 5

Comparison of tensile strengths of specimens developed by commercially available (CA) and laboratory developed (LD) filaments as a function of (a) printing speed (b) layer height, and (c) nozzle temperature. ***** means that value is statistically significant with the values at 380^0C, 25^0C, 30 mm/sec, and 0.3 mm. # means statistically significant between LA and CA filaments within the same 3D printing condition.

Figure 6

Comparison of flexural strengths of specimens developed by commercially available (CA) and laboratory developed (LD) filaments as a function of (a) printing speed (b) layer height, and (c) nozzle temperature. * means that value is statistically significant with the values at 380^0C, 25^0C, 30 mm/sec, and 0.3 mm.

Figure 7

(a) SEM image showing the cross-section of a LD PEEK filament. A high magnification scan of the red dotted region in (a) is shown in (b). One can notice the pores and defects present in the PEEK filament which causes a detrimental effect on the printed structure.

Figure 8

Photograph of the topmost layer of a 3D printed compression PEEK specimen showing the effect of inconsistencies in filament diameter. Yellow arrows indicate the portions where excess material was deposited due to a thicker filament diameter and red arrows indicate the portions that received lesser material due to thinner filament diameter.

Figure 9

Effect of annealing on 3D printed PEEK. (a) Photographs of non-annealed and annealed compression test specimen. While the non-annealed part show a mix of amorphous (dark brown color regions) and crystalline regions (beige color regions), the annealed part is totally crystalline (completely beige color). (b) Differential Scanning Calorimetry (DSC) plots of annealed and non-annealed 3D printed PEEK parts. The 3D printing parameters that were used to print this parts are as follows: Nozzle Temp: 410^0C, Chamber Temp: 90^0C, Print Speed: 50 mm/sec, and layer height: 0.2 mm

Figure 10

Photograph of a femoral head as developed by the optimized set of printing parameters (Nozzle temp: 410^0C, Chamber temp.: 90^0C, Printing speed: 50 mm/sec, Layer height: 0.1 mm) and LD filaments.