Performance of biocompatible PEEK processed by fused deposition additive manufacturing

M.F. Arifa, S. Kumara,⁎, K.M. Varadarajanb,c, W.J. Cantwelld

aDepartment of Mechanical and Materials Engineering, Khalifa University of Science and Technology, Masdar Institute, Masdar City, P.O. Box 54224, Abu Dhabi, United Arab Emirates
bDepartment of Orthopaedic Surgery, Harris Orthopaedics Laboratory, Massachusetts General Hospital, 55 Fruit St, Boston, USA
cDepartment of Orthopaedic Surgery, Harvard Medical School, A-111, 25 Shattuck Street, Boston, USA
dDepartment of Aerospace Engineering, Khalifa University of Science and Technology, P.O. Box 127798, Abu Dhabi, United Arab Emirates

HIGHLIGHTS

• Horizontally 3D printed PEEK with raster angles of 0° and 90° exhibits tensile flexural and fracture properties comparable to those of molded PEEK
• Specimens built vertically are prone to delamination, exhibiting poorer mechanical performance due to high thermal gradient in the build-direction
• Stick-slip fracture and lower Poisson’s ratio are observed for specimens built vertically, due to the presence of interfacial voids.
• Minimizing thermal gradients across beads is the key to producing parts with excellent macroscopic properties

GRAPHICAL ABSTRACT

ABSTRACT

In this study, the tensile, flexural and fracture behavior of PEEK processed by fused filament fabrication (FFF) is reported. Three different configurations, viz., specimens built horizontally with a raster angle of 0° (H-0°) and 90° (H-90°), and vertically with a raster angle of 90° (V-90°) are examined. The best performing specimen in terms of its tensile, flexural and fracture toughness properties is H-0°, followed by H-90° and V-90°. The H-0° and H-90° specimens exhibit 85% and 75% of tensile and flexural strengths of molded bulk PEEK, respectively. However, the fracture toughness of the H-0° and H-90° specimens are 78% and 70% of molded bulk PEEK, respectively. The fracture surface and microtomography analyses indicate that the degree of interfacial bonding between beads during layer-by-layer buildup, is affected by the thermal gradient across the beads. The PEEK specimen configurations examined here have different thermal gradient in the build directions and such variations manifest themselves in their macroscopic mechanical behavior. The findings of this study provide guidelines for FFF of PEEK to enable its realization in applications such as orthopedic implants.

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* Corresponding author.
E-mail address: s.kumar@eng.oxon.org (S. Kumar).

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1. Introduction

Compared to established technologies, additive manufacturing (AM) offers the possibility of cost-effective automation of the fabrication process, it enables a digital inventory, and provides greater flexibility to locally design the material architecture in three-dimensions [1–4]. Fused filament fabrication (FFF), also known as fused deposition modeling (FDM) is the most commonly used AM technique for thermoplastic polymers. In the FFF process, a thermoplastic filament is fed into a heated nozzle, melted or liquefied, and subsequently extruded and deposited onto a build plate. A gantry moves the nozzle in the horizontal \(x\) – \(y\) plane as the molten material is deposited. The build plate then moves vertically (in the \(z\) axis) after completing the deposition in the \(x\) – \(y\) plane. The deposited layers solidify and bond/weld with adjacent layers, forming the desired 3D geometry. FFF has been used in the AM of numerous thermoplastics. The most widely used polymer for FFF is acrylonitrile butadiene styrene (ABS) [5,6] and poly lactic acid (PLA) [7]. Moreover, high impact polystyrene [8], Nylon [8], Ultem® [9], polycarbonate [8], poly(vinyl alcohol), polypropylene [10] and the mixtures of any two thermoplastics [11] or reinforced thermoplastic composites [12,13] are suitable for FFF. Nanocomposite feedstocks, such as graphene [14,15] or CNT [16] reinforced filaments, are currently attracting interest, due to their superior thermal, electrical and mechanical properties.

Processing parameters, material type and geometrical features were found to influence the final properties of the products made by FFF. For optimal properties of components or devices manufactured by FFF, temperature control is critical. The distribution and variation of temperature and residual stresses in structures or parts produced by FFF must be optimally controlled so as to ensure sufficient internal stress relaxation and a good bonding quality between the adjacent polymer beads. For example, warping and interlayer delamination are frequently observed due to the residual stresses accumulated during the layer-by-layer build up. These stresses originate from the thermal gradient generated during the solidification process that influence the layer’s volume contraction, warping and bonding/diffusion quality between beads [17,18]. This has shown to pose important challenges particularly for processing of semicrystalline polymers as a high degree of crystallinity and high shrinkage coefficient can negatively affect the dimensional stability of the part [19]. By using a heated build plate and by controlling the temperature of the 3D printer chamber, thermal gradients and their effects, such as warping can be minimized [20,21].

In recent years, there has been a growing interest in the fabrication of high-performance polymers such as polyphenylene sulfone, polyether ether ketone (PEEK), polyether ketone ketone (PEKK), etc. via AM due to their outstanding mechanical properties and chemical stability. PEEK is an expensive thermoplastic having excellent mechanical and chemical resistance properties even at temperatures up to 240 °C. PEEK also exhibits excellent hydrolisis resistance and provides fire, smoke, and toxicity performance. PEEK is one of the few polymers considered for metal replacement in high temperature applications. PEEK has been used in automotive, aerospace, oil & gas and space applications. This study focuses on FFF of PEEK for bioimplants in order to effectively utilize its properties such as biocompatibility, excellent fatigue and wear resistance for such applications [22]. PEEK is typically fabricated by an injection molding or extrusion process. AM of high performance PEEK in particular, holds tremendous promise for biomedical applications, such as for design of novel knee replacement implants that more closely mimic native physiology. Effort has been made to additively manufacture PEEK via the selective laser sintering (SLS) method [23]. Oxford Performance Materials, Inc. has developed OsteoFab® technology for 3D printing of facial and cranial implants for bone replacement using PEKK powders via SLS process [24]. SLS uses a high power laser to selectively sinter powders, which causes them to coalesce together due to interfacial and free surface diffusion. SLS can be used to fabricate very complex geometries because it uses the same powder to support the overhang portions, unlike FFF which requires supporting parts. However, the inherent cost of SLS is high, owing to relatively expensive capital costs and high power laser source.

Recently, FFF has been promoted as a cost-effective alternative to SLS for the fabrication of high-performance polymers, such as PEEK. Valentan et al. [25] developed FFF systems to fabricate two grades of PEEK-Optima®. The strength of the FFF samples in their study was approximately half of the tensile strength of molded PEEK (∼100 MPa). Vaezi and Yang [26] developed the FFF system to fabricate PEEK-Optima® samples. A nozzle temperature of 400–430 °C, an ambient temperature of 80 °C and a build plate temperature up to 130 °C were identified as optimal parameters. The FFF process with 100% infill density results in a sample porosity of 14% and a tensile strength of 75 MPa. Wu et al. [27] showed that the warping deformation of FFF-PEEK samples reduces with increasing chamber and nozzle temperature. Wu et al. [28] evaluated the influence of layer thickness (200, 300 and 400 μm) and raster angle (0°, 90°, 30°/–60° and 45°/–45°) on the mechanical properties of FFF–PEEK samples. A maximum tensile strength of 56.6 MPa was achieved for samples with a 300 μm layer thickness and a 0°/90° raster angle. Cicala et al. evaluated the tensile properties of PEEK-PEEK samples with raster angle of 0°/90°, 30°/–60° and 45°/–45° and found an average tensile strength of 69.04 MPa and a tensile modulus of 3.35 GPa for all tested samples [29]. Yang et al. [30] studied the effect of ambient temperature, nozzle temperature and post heat-treatments on crystallinity and tensile properties of FFF–PEEK with a 0° raster angle. In general, a higher ambient temperature, higher nozzle temperature and a higher post treatment temperature and time resulted in higher crystallinity, strength and stiffness. The maximum tensile strength and modulus were found to be 84 MPa and 4 GPa, respectively.

The aforementioned studies mostly focused on the development of new FFF machines to accommodate the high processing temperature of PEEK, and to evaluate the effect of process parameters on the final properties of the samples. However, for the latter, the analysis of the mechanical performance of the fabricated parts is presented with little detail, especially on how the spatial thermal gradients during the layer by layer build-up of the sample, can influence the properties. In the current study, the tensile and flexural properties of samples built horizontally (\(x\) – \(y\) plane) with raster or bead angles of 0° and 90°, and vertically with a bead angle of 90° with respect to loading direction are evaluated. These three configurations are associated with different thermal histories during FFF-PEEK part build up. Digital image correlation (DIC) analysis is used to measure the axial and lateral strains in the gauge length zone of dogbone specimens. Moreover, the fracture behavior of FFF-PEEK samples is also investigated. The fracture study is important, since formation of micro-cracks, particularly in the diffusion/bonding zones between beads, could lead to premature failure of fabricated parts during their service life. To date, the fracture behavior and interlayer cohesion studies of FFF fabricated samples are limited to ABS [31,32] and PLA [33,34] through single edge notch bending (SENB) or double cantilever beam (DCB) testing configurations. In this work, the fracture behavior of FFF-PEEK specimens is evaluated for the first time using compact tension tests for the same fabrication configurations as those used in tensile and flexural testing.

2. Experimental methods

The configurations used to fabricate the specimens by FFF are discussed, followed by tensile, flexural and fracture toughness testing, including optical strain mapping with DIC.

2.1. FFF configurations

FFF specimens were fabricated using an Indmatec HPP 155 device (Apium Additive Technologies GmbH). This FFF device is able to fabricate samples with a maximum build volume of 135 × 145 × 148 mm³.
Filaments with 1.75 mm diameter made of Victrex® PEEK 450G were used. The filament exhibited glass transition and melting temperatures of 153 °C and 340 °C, respectively, based on the 2nd heating cycle data from a differential scanning calorimetry (DSC) investigation with a heating rate of 10 °C/min. These transition temperatures closely correspond to those found in the Victrex® PEEK 450G database [35]. The filament was fed into a 0.4 mm diameter nozzle by a feeding pressure mechanism via a driver motor and a counter-rotating set of grooved gears. The Simplify3D software package was used to determine the slicing sequence and define the FFF process. The FFF process parameters used in this study were as follows:

- Nozzle movement speed: 800 mm/min; first layer: 300 mm/min
- Nozzle temperature: 410 °C; first layer: 390 °C
- Bed temperature: 100 °C
- Layer height: 0.1 mm; first layer: 0.18 mm
- Extrusion width: 0.48 mm
- Infill pattern: Rectilinear
- Infill density: 100%

The nozzle movement speed, nozzle temperature and layer height for the first layer were set differently in order to enhance adhesion between the sample and the glass build plate. Adhesion was further enhanced by applying a glue on the plate surface and by the addition of brim. Brim is an outline to create a fabricated large ring that surrounds the part and is attached to it. This holds the edges of the FFF fabricated part and thus helps to improve bed adhesion and prevent warping. After fabrication, the chamber was cooled to room temperature by natural convection and the parts were then removed from the build plate. The brim structure surrounding the specimen was detached by hand.

Three FFF configurations for the tensile, flexural and compact tension specimens used in this work are depicted in Fig. 1.

One specimen for each of the configurations was produced per fabrication cycle, except for V-90°, tensile and flexural specimens. Four and three V-90° tensile and flexural specimens were fabricated respectively in a single fabrication sequence. The molten polymer in the V-90° dogbone and flexural samples is deposited onto a small cross-sectional area, as seen in Fig. 1b and thus the nozzle travel time in the x − y plane is very short prior to moving in the z direction. This can induce a fabrication failure, since the molten polymer is deposited onto a layer that is still in a molten state. To avoid this, we increased the number of specimens so that the fabrication cycle could be done successfully, while ensuring acceptable degree of adhesion between the beads normal to the loading direction (z-direction). A reduced number of specimens resulted in fabrication failure while increasing the number of specimens might increase the thermal gradient between beads in the vertical direction, \( \Delta T / \Delta z \), due to the longer travel time in x − y plane, leading to a weak bonding. The length of the clamping zone of V-90° sample was reduced to reduce the fabrication time, as seen in Fig. 2. H-90° samples

![Fig. 1. AM of PEEK by FFF: FFF configurations of tensile and compact tension specimens. The specimens were fabricated either a) horizontally or b) vertically. The deposition pattern of specimens fabricated horizontally with either c) 0° beads orientation or d) 90° beads orientation, and e) specimens fabricated vertically with 90° beads orientation. Sub-figures p and q in c) and d) illustrate the magnified view of the corresponding regions p and q in a). Similarly, r and s in e) illustrate the magnified zone of corresponding regions r and s in b). Flexural specimen configuration is similar to that of tensile specimen.](image-url)
were fabricated without outside perimeter/outline in order to avoid beads with opposing orientations. In H-0° sample, the polymer melt was initially deposited in the x−y plane following the outline contour of the dogbone sample and was continued until completely printing the entire gauge length zone, leaving the gap only at the central areas of the clamping zone. These clamping zones were then fabricated with beads of 45°/−45° orientation to ensure sufficient strength in the transition zone and thus avoiding sample failure in this zone.

2.2. Tensile testing

Tensile tests were performed according to ISO 527 at a constant crosshead speed of 1 mm/min at ambient temperature (~20 °C) on a Zwick-Roell Z005 universal testing machine (UTM) with a 2.5 kN load cell. The load cell accuracy was ±0.25% for a load > 10 N and ±1% for a load range of 2.5 to 10 N, and crosshead travel resolution was 0.041 μm. DIC technique was used for full-field measurement of strain on the specimens. Random black–white speckle patterns of acrylic paint were sprayed on the specimen using an airbrush prior to testing. Consecutive speckle images were acquired as a function of load using a monochrome 5.0 MP camera for strain evaluation. The average engineering strain in the axial and lateral directions over the gauge length zone was evaluated using Vic-2D software. The tensile properties of the samples were extracted from the stress-strain curve. Each of the specimen configurations was tested at least three times to ensure repeatability. The FFF–PEEK tensile specimens are shown in Fig. 2.

2.3. Flexural testing

Three point flexural tests were performed according to ISO 178 at a constant crosshead speed of 2 mm/min at ambient temperature (~20 °C) on a Zwick-Roell Z005 universal testing machine (UTM) with a 2.5 kN load cell. The H-0° specimens slipped from the supports after the maximum load had been reached but didn’t exhibit final failure. Therefore, testing for H-0° was stopped when the load had reduced by 20% from the maximum. Each of the specimen configurations was tested three times to ensure repeatability.

2.4. Fracture tests

Fracture tests were conducted to evaluate the Mode I fracture toughness of the 3D printed PEEK. The compact tension fracture properties of FFF-PEEK specimens were evaluated following ASTM D5045-14 standard for measuring the plane strain fracture toughness of polymers. Compact tension samples were fabricated in the configuration shown in Fig. 3a, where W = 13−15 mm. After fabricating rectangular blocks, holes for loading pins (Ø 3 mm) were drilled using a benchtop drilling machine. A notch was introduced by a high precision circular saw of 152.4 mm diameter and 0.508 mm thickness. A sharp notch was subsequently generated by a slow tapping motion with a fresh razor blade. These specimens were manufactured without either holes or a notch, to ensure a consistent thermal history. The FFF of the holes and the initial cracks would clearly require a change in the deposition patterns of the filament beads, leading to a change in specimen’s thermal history. Prior to testing, the samples were kept in oven for 12 h at 70 °C to remove moisture. A crosshead speed of 1 mm/min in a Zwick-Roell
2005 UTM was used. Critical stress intensity factor $K_C$ was determined following the method given in ASTM D5045. The adopted scheme assumes a linear elastic fracture behavior of compact tension specimen and therefore restriction on linearity of load-displacement response was imposed. The 5% secant line criterion of the load-displacement curve was employed to ensure validity of the $K_C$ values as described in ASTM D5045 Section 9.1.1. Moreover, the specimen size was appropriately chosen to ensure a plane strain-state at the crack tip. The size criterion stipulates that the value of $2.5\sigma_C/b$ must be less than the specimen thickness, crack and ligament lengths. In the current study, the specimen thickness, crack and ligament lengths. In the current study, the yield strength ($\sigma_y$) of the molded PEEK was used as a reference due to different thermal histories associated with 3D printed tensile and compact tension specimens. Moreover, introducing a sharp crack exactly terminating at the bead-to-bead interface is practically impossible.

3. Results and discussion

3.1. Tensile and flexural properties

The tensile performance of specimens fabricated in three different configurations was evaluated. According to ISO 527-1:2012, tensile strength is the stress at which the first local maximum is observed during a tensile test. Therefore, the tensile strength of the H-0° sample was evaluated at the yield point while those of the H-90° and V-90° specimens were evaluated at the failure point, as seen in Fig. 4. The H-0° specimen exhibited the highest Young’s modulus and tensile strength. The H-90° offered a Young’s modulus and tensile strength values that were 7% and 12% lower than those of H-0°, respectively. The H-90° specimens exhibited properties approaching those of the H-0° specimen, due to the excellent interfacial bonding between beads. The H-90° had a short bead deposition path in the horizontal plane as the nozzle travelled across the width of the specimen, as seen in H-90°.
The gauge length zone of the H-0° specimen with a higher thermal gradient between beads in the x − y plane, and thus weak interfacial bonding, had a brownish color. While the H-90° specimen that had a lower thermal gradient between beads in the x − y plane, and thus better interfacial bonding between beads, had a more pale or whiter color. This color was relatively similar to that of the clamping zone for the H-0° specimen which was purposely fabricated with alternating 45°/−45° bead orientations to have a shorter deposition path, and to avoid failure in the transition or clamping zone during tensile testing. Moreover, the surface finish can be used as an indicator of the degree of diffusion between beads. As seen from Fig. 2, the surface finish of the H-90° specimen was relatively rough. Since the molten polymer was deposited next to a bead that was still in its molten state (due to the short deposition path), the beads flowed more easily, forming an overlap region between beads. In contrast, the H-0° specimen had a relatively smooth surface, since the molten polymer was deposited next to a bead that had started to solidify. However, even though the interfacial bonding in H-90° was better than that in H-0° specimen, the H-0° specimen exhibited superior properties, since the macroscopic performance was primarily due to the strength and strain tolerance of the filament, as discussed earlier.

The interfacial bonding between beads is critical, especially between the layers in the vertical direction, particularly for V-90° specimens where the loading direction is normal to the interface between beads in the z direction (see, Fig. 5c). A lower thermal gradient between beads in the z direction required for promoting interfacial adhesion in vertically-fabricated specimens was restricted by the fact that the preceding layer should be fully or partially solidified so as to lay the succeeding layer properly. Therefore, four tensile specimens of V-90° configurations were fabricated simultaneously to increase the deposition time in the horizontal plane (x − y), and thus reducing the build-rate of H-90° in the vertical (z) direction and avoiding the fabrication failure. Results show that the tensile strength and modulus of V-90° samples were significantly lower compared to those of H-0° and H-90° samples, as seen in Fig. 4 and Table 1. These results indicate incomplete sintering between layers in the vertical direction due to unavoidable large thermal gradient in the vertical fabrication direction (z). This can be seen from the SEM image of V-90° sample where brittle-like fracture surface is observed, as seen in Fig. 6c. It can also be seen clearly from the SEM images of the H-0° and H-90° specimens where the weak interface can be observed between the beads in vertical fabrication direction (Fig. 6a and b). It should be noted that, the time to build a single layer in the horizontal plane (x − y) of H-0° and H-90° samples was 1.52 min, which was approximately five times higher than that of the V-90° samples (0.28 min), due to larger x − y deposition area compared to that of V-90° samples. Therefore, the H-0° and H-90° samples had lower build-rate (0.07 mm/min) in vertical direction than that of V-90° samples (0.36 mm/min), as seen in Table 2, and thus larger thermal gradient in z direction. Therefore, we expect poorer interfacial bonding in the vertical direction for H-0° and H-90° samples. However, the effect of thermal gradient in the z direction has less influence on the mechanical properties of the H-0° and H-90° samples since the weak interfaces between beads in the z direction do not experience normal traction under tensile loading. A heating zone at the top of the printer’s chamber has been installed to maintain the top surface temperature of the sample and to regulate the chamber temperature, with temperature control being a proprietary technology of the manufacturer. Though it ensures that the top surface of the sample remains heated, it cannot fully eliminate the low interfacial bonding in the z direction as the minimum thermal gradient between beads is restricted by the fact that the preceding

### Table 2

| Build-rate (V) in x, y and z directions, and the deposition time (t<sub>dep</sub>) in a single horizontal plane during the FFF-PEEK process. |
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layer should be fully or partially solidified so as to lay the succeeding layer.

To further confirm the interfacial defects and morphology in the z direction, micro-computed tomography (μCT) images of the H-0°, H-90° and V-90° tensile samples under no-load have been acquired via Phoenix Nanotom® m system. μCT analysis is important to complement the SEM observations since it provides details of 3D microstructure and enables visualization of cross-sectional 2D image from the 3D volume, though it has lower resolution than that of the SEM images. As seen in Fig. 7a and b, the interfacial defects between the beads in the vertical direction in H-0° and H-90° samples cannot be seen as the void dimensions were mostly below the μCT voxel size or resolution (3 μm). However, the presence of interfacial defects between beads in the vertical fabrication direction was confirmed earlier from the SEM images of tensile fracture surface, as seen in Fig. 6a and b, and also from the SEM images of fractured surface of compact tension H-0° and H-90° samples (see, Fig. 11a and b). In fact, some interfacial defects were found in the μCT H-0° and H-90° samples. However, the number of defects observed was small and the defects were randomly scattered in a few zones of the sample volume. It is interesting to note that our H-0° and H-90° samples possess qualitatively a very low void fraction, although FFF process tends to produce large gaps or voids between deposited beads. A low void fraction was achieved in this study by choosing a 100% infill density, a small layer height (0.1 mm) and high nozzle temperature (410 °C) that allowed an optimum viscous flow of the molten polymer. Moreover, the vertical build-rate for the H-0° and H-90° samples was lower (0.07 mm/min) due to the large fabrication area in the x−y plane and thus the preceding layer had sufficient time to solidify. Therefore,
the succeeding horizontal layer was deposited onto a surface that had already solidified, inducing a stable deposition of the polymer melt and thus preventing a void formation at the interface. Concomitantly, this led to weak interfacial bonding due to high thermal gradient between beads along the vertical direction. Different interfacial defects and morphologies were observed for V-90° tensile samples under no-load, and those results were further confirmed from the V-90° compact tension samples. Voids at the interfaces between beads were observed in both tensile and compact tension V-90° samples, as seen in Fig. 7c and d. As discussed earlier, the deposition of molten polymer in V-90° configuration occurred on the surface of the preceding horizontal layer that was not fully solidified in order to promote an acceptable degree of interfacial adhesion between the beads in the vertical fabrication direction, without inducing a fabrication failure. Consequently, good adhesion between beads was achieved over a certain area of the interface, but voids were created primarily due to undulations of the molten layer being laid on a partially solidified preceding layer, and shrinkage of the polymer. Inserts in Fig. 7c and d show the 3D reconstructed image of V-90° tensile and compact tension samples, respectively, which describe more clearly the voids formed at the interface between the beads in the vertical fabrication direction. It should be noted that, these voids cannot be seen clearly from the SEM images of tensile and compact tension samples in Figs. 6c and 11c. These images were taken on the interfacially debonded surfaces between beads in the vertical fabrication direction. Voids were mostly developed between the undulating beads normal to surface view and thus they cannot be seen clearly. Some voids were also observed in H-0° samples particularly at the cross-junction between beads, as seen in insert of Fig. 7a. It shows an average bead dimension of 0.5 × 0.1 mm², which corresponds to a layer height of 0.1 mm and extrusion width of 0.48 mm.

Samples loaded below the yield point (for H-0°) and below failure point (for H-90° and V-90°) showed uniform axial strain along the gauge length zone, as can be seen in Fig. 4b, with the maximum standard deviation in longitudinal strains of 0.15%, 0.12% and 0.019%, respectively. This indicates that the samples were macroscopically uniform, even though the samples were built layer-by-layer. The sample loaded beyond the yield point for H-0° didn’t exhibit a uniform axial strain along the gauge length, with the maximum strain occurring in the middle portion due to its excessive straining. The Poisson’s ratio of the H-0° and H-90° samples were approximately the same (see the mean values and their corresponding standard error, in Table 1). Much lower Poisson’s ratio was observed in V-90° sample and this could be attributed to two factors, namely, the bead orientation and the proliferation of voids during loading. The tensile loading in V-90° specimen is normal to numerous weak bead-to-bead interfaces. This results in significant void growth during loading and thus exhibits lower Poisson’s ratio.

The flexural properties of the FFF-PEEK were also evaluated. It was found that the flexural properties followed the same trend as those of tensile properties, as the H-0° specimen had the highest flexural strength and modulus, followed by the H-90° and V-90°, as seen in Table 1 and Fig. 8. This is due to nearly the same build-rate and deposition time in x – y plane for tensile and flexural samples, as seen in Table 2. The flexural properties reported here confirms the observation of the effect of printing configurations on tensile properties discussed earlier. Both tensile and flexural strength of H-0°, H-90° and V-90° specimens were 15%, 25% and 90% lower than those of molded PEEK 450G, respectively (Table 1). However, the tensile and flexural moduli didn’t exhibit similar levels of reduction compared to the PEEK 450G. The tensile and (flexural) moduli of the H-0°, H-90° and V-90° specimens were 5% (19%), 11% (19%) and 24% (33%) lower than those of molded PEEK 450G, respectively. This is due to the fact that the interface zones of the layered structure of the FFF-PEEK samples provide strain-tolerance to the system (due to their lower compliance) under bending load and thus lower the flexural modulus of the samples. The Young’s modulus and tensile strength of the H-0° and H-90° specimens were similar to those reported elsewhere [30] or indeed higher [25,26,28,29] than the previously reported FFF-PEEK samples. The flexural modulus and strength of the H-0° and H-90° specimens were higher than the
In-plane crack rate in bonding between beads, as discussed earlier. Interestingly, the build-rate in bonding between beads compared to those of tensile and flexural samples. Regardless of these limitations, it can be seen that the trend of $K_{IC}$ was almost the same as those observed for the tensile and flexural tests. Results indicate that the bead orientation with respect to the loading direction contributes the most to the mechanical performance, followed by the interfacial adhesion between beads. Interfacial adhesion is affected by the thermal gradient dictated by the in-plane and out-of-plane build-rates (see Table 2).

The crack tip in H-90° and V-90° compact tension specimens exhibited a higher probability of advancement through the bead-bead interface where the interfacial zone between beads acted as the weakest link, unlike the H-0° specimen wherein the crack tip advanced normal to the bead orientation (see, Fig. 10). The crack tip in H-0° specimen required more energy to break the beads transversely, resulting in higher fracture toughness. This effect can also be seen on the fracture surface, where the crack path in H-0° specimen sometimes deflected into the weakest link, leading to out-of-plane crack propagation, while the crack propagation in H-90° and V-90° specimens consistently delaminated along the bead-bead interface, as shown in Figs. 10 and 11. The difference in performance between H-90° and V-90° specimens was related to the different degree of interfacial bonding between beads associated with the different thermal gradients, as discussed in the previous section. After the maximum load had reached, a softening response was observed as seen in Fig. 9b due to the deflection of crack into neighboring weak bead-bead interface. The SEM images of the fracture surfaces of compact tension samples shown in Fig. 11a, b and c helped to draw a similar conclusion to those of tensile samples as weak interfacial bonding can be found between beads in the vertical fabrication direction. The stick-slip crack growth (after the maximum load) was observed in V-90° sample under constant applied extension rate loading conditions due to the presence of voids at the interface between beads. These voids act as a crack arrester. Stick-slip fracture in this case was characterized by oscillatory crack tip velocities and crack growth jumps resulting in periodic load fluctuations (see, Fig. 9c) [41]. The strain contour at maximum load of the three sample configurations was evaluated. It showed that the strain was a maximum at the crack front, as seen in Fig. 12. The highest value of maximum strain was found in H-0°, followed by H-90° and V-90° specimens. The H-0° specimen had the highest strain tolerance as the crack tip advanced normal
to the bead orientation, and thus the highest fracture toughness of the sample. While comparing the current results with those from tests on bulk, molded PEEK using compact tension geometry at room temperature, we noticed that the fracture toughnesses of H-0° and H-90° samples, respectively were 78% and 70% of the molded PEEK fracture toughness (see, Table 3). The low fracture toughness in the V-90° configuration reduced the full potential of PEEK to be applied in high load-bearing applications but the value was still within the range of brittle polymers such as acrylic, epoxy and polystyrene [42].

4. Summary

The tensile and flexural properties of PEEK fabricated by FFF have been studied. The fracture behavior of FFF-PEEK has been reported for the first time. Three specimen configurations; H-0°, H-90° and V-90° have been tested to failure in conjunction with optical strain mapping. The configuration that exhibited a superior performance, in terms of tensile strength and modulus, flexural strength and modulus, and fracture toughness, was H-0°, followed by H-90° and V-90°. The H-0° and H-90° showed 85% and 75% attainable tensile and flexural strengths of the bulk molded PEEK respectively. The fracture toughnesses of the H-0° and H-90° specimens were 78% and 70% of the molded PEEK fracture toughness, respectively. However, the V-90° sample exhibited low tensile, flexural and fracture toughness properties compared to those of H-0°, H-90° and bulk PEEK. The performance of these three configurations represents different thermal gradients between beads during layer by layer buildup in FFF.

It was found that different fabrication path can promote a different degree of interfacial adhesion between beads which in turn can have a significant influence on the tensile and fracture toughness properties. This information is directly relevant to the fabrication of biomedical implants with sufficient mechanical strength for long-term in-vivo applications. Short polymer deposition path in x – y plane promoted the best bead-to-bead interfacial adhesion since the diffusion is faster when the beads were in molten condition. However, it had drawback in the final surface roughness due to the formation of bead-to-bead overlap zone. Therefore, short deposition path could be considered for the inner part of the sample while the long deposition path could be employed for the outer surface to obtain better surface quality. The short deposition path need not necessarily be implemented with a 90° bead orientation as alternate bead orientations such as 45°–90° and 60°/60° also exhibit almost the same thermal gradient in the horizontal layer as that of the 90° bead orientation.

Diffusion lines (interfaces at which the bonding is weak) were found at the interface between the beads in the vertical fabrication direction in all specimen configurations due to high thermal gradient across beads. This had a dramatic effect when the load was applied normal to this weakest zone, as exemplified by the tensile, flexural and fracture toughness properties of V-90° samples. Results suggest that minimizing thermal gradients across beads during FFF of thermoplastics with a high melting temperature is the key to producing parts with excellent macroscopic material properties and dimensional stability. Thermal gradient effects remain an important issue in FFF, leading to limitations in mechanical performance relative to conventionally molded samples. Ways such as precise control of the chamber temperature, post heat-treatment of the FFF fabricated samples [30] and microwave heating of FFF samples fabricated with coated-CNT filament [43], would help to minimize these limitations. The Poisson’s ratio calculation can be used as a comparative indicator of the specimen’s quality. For example the V-90° specimen had much lower Poisson’s ratio compared to the H-0° and H-90° specimens which was mostly due to the opening of the voids during loading. The current study serves as an important first step in the development of comprehensive guideline for the FFF of high temperature and high performance thermoplastics (e.g. PEEK) to enable high-end engineering applications such as for biomedical implants.

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