Solid Freeform Fabrication 2021: Proceedings of the 32nd Annual International
Solid Freeform Fabrication Symposium – An Additive Manufacturing Conference
Reviewed Paper

Mechanical Properties of High-Performance Plastic Polyether-ether-ketone (PEEK) Printed by Fused Deposition Modeling

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Abstract

Polyether-ether-ketone (PEEK) is a high-performance thermoplastic material with high heat resistance, high chemical resistance, high water resistance, and high wear resistance. Due to its distinguished strength and durability, PEEK is extensively used for aerospace, automotive, and medical applications. 3D printing PEEK filaments offer a new approach to make PEEK parts, fulfilling specific requirements of geometrical complexity. But the mechanical properties of 3D printed PEEK materials are not further explored. This study investigated the mechanical properties of PEEK materials fabricated using the fused deposition modeling (FDM) 3D printing process. Tensile test, hardness test, and impact test were conducted to the PEEK samples, in compliance with ASTM standards. The testing results were summarized and discussed, compared to the conventionally manufactured PEEK materials. This study also provides insights on employing FDM 3D printing process for making PEEK parts, based on its special mechanical properties and failure mode.

Introduction

Polyetheretherketone (PEEK) is a semi-crystalline thermoplastic material, firstly developed by British scientists in 1978 [1]. PEEK has high heat resistance, high chemical resistance, high water resistance, and high wear resistance, making it widely used as a high-performance material. For conventionally manufactured PEEK parts, injection molding is the most commonly used process which supplies PEEK pellets into barrel and then mold to obtain a molded product [2]. However, the high tooling cost, long lead time, and design restrictions make injection molding a less accessible technology for producing PEEK parts. In recent years, more and more attention has been focused on the use of additive manufacturing or 3D printing methods to accommodate plastic materials. Selective laser sintering (SLS) and fused deposition modeling (FDM) are two popular additive manufacturing methods [3]. Since the cost of SLS is relatively high, and the PEEK powders are difficult to recycle after printing, the FDM 3D printing process is economically preferred than SLS. Some preliminary progress has been reported. Li et al. [4] studied different FDM printing temperature, printing direction, and layer thickness and their effects on the crystallinity and bending strength of PEEK parts. It is extremely possible to improve the mechanical properties of PEEK parts by changing 3D printing parameters. In addition, Yang et al. [5] studied how heat treatment conditions affect the crystallinity and mechanical properties of 3D printed PEEK parts. The results confirmed the key role of the temperature during the crystallization and its influences on the mechanical properties of PEEK parts.

Some studies on 3D printed PEEK parts for application are also published. The high chemical resistance, radio transparency, biocompatibility and lower shear modulus than metals make PEEK material and its variant materials a good option for medical implants as a substitute for metal [6]. For example, as dental implants such as dentures, PEEK/hydroxyapatite composite materials are used as orthopedic implants and for spinal surgery [7, 8, 9]. PEEK material can also be sterilized repeatedly, which is strongly suitable for medical equipment [10,11]. In addition, its high strength-to-weight ratio, high Young's modulus, and high tensile strength make it a promising substitute for aluminum and steel parts in the aerospace and automotive fields [12,13]. 3D printing process provides a high degree of freedom for low-volume production and geometrical complexity for special designs of PEEK parts. This has greatly increased the research interests in 3D printing PEEK materials in various aspects.

Therefore, this paper aims to provide a comprehensive study in the mechanical properties of FDM 3D printed PEEK materials. The purpose is to give end users to general idea of how 3D printed PEEK material performs under the external loads. Through the tensile test, hardness test, and impact test, the strength and toughness of the material can be understood. Guidance is given for the characteristics of PEEK parts printed using FDM. At the same time, the test results are compared and discussed with conventionally manufactured PEEK materials.

Experimental

CreatBot F430 3D printer was used for printing PEEK test specimens in this study. The printer has two nozzles, one of which can be heated up to 420°C to print high-temperature thermoplastics such as PEEK, PEKK, and Ultem, as shown in Figure 1. In this study, PEEK filament with a diameter of 1.75 mm was selected. PEEK is a semicrystalline thermoplastic material with a melting temperature of 343°C and a glass transition temperature of 143°C [14]. Because PEEK is characterized for its rapid solidification from molten phase to solid. It is necessary to tune the chamber temperature during 3D printing to ensure good bonding between layers. The 3D printer exerts printing specimens for a 100% fill rate to the infill region (45° raster angle scan) after double contouring scans. The direction of the infill scan is re-oriented 90° every layer to ensure good bonding. The major 3D printing parameters are listed in Table 1. The printed parts were then annealed to improve the crystallinity. The annealing temperature is shown in Figure 2.

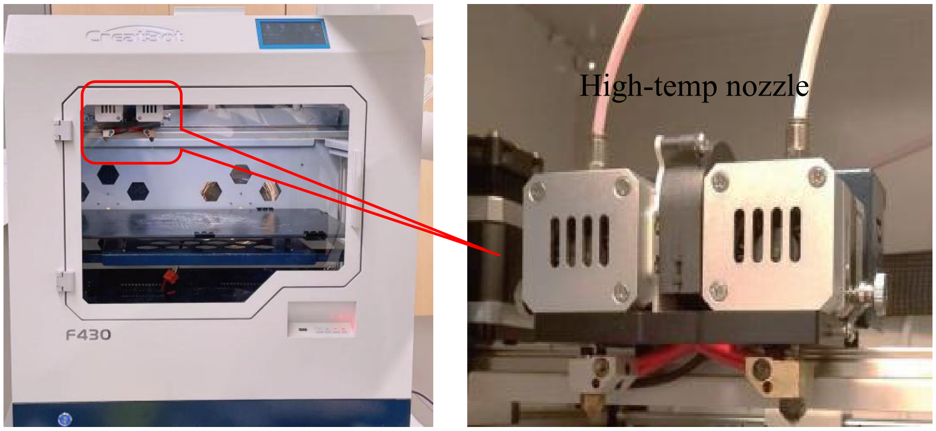

Figure. 1 High-temperature 3D printer and nozzles

Table 1. 3D printing process parameters

Layer thickness (mm)	0.15
Fill density (%)	100
Nozzle temperature (°C)	420
Bed temperature (°C)	100
Chamber temperature (°C)	65
Scan speed (mm/s)	15

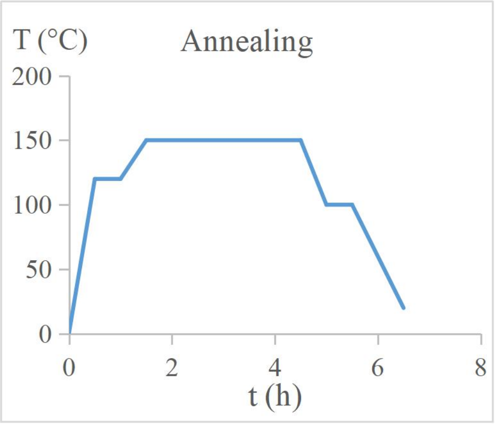

Figure. 2 Annealing temperature

The tensile test specimens have type I standard dimensions (gage length 2.25 inch, thickness 0.25 inch) in accordance with ASTM D638. The test sample was vertically fixed by two clamps, and the load was continuously applied at a known strain rate until it breaks. The machine used for tensile strength testing was MTS Criterion 43. The stress-strain curve can be plotted for acquiring yield strength, Young's modulus, and tensile strength. The impact test specimens have dimensions in compliance with ASTM D256 standard for Izod pendulum impact testing. The energy required to break the specimen was estimated by the test. A hammer rated with energy of 5.5J was selected. The hammer rised to 150°, then released to swing downwards. There are two ways to generate a notch on the impact testing specimen. The notch can be directly formed during 3D printing or cut by an ancillary notching device. Two types of notches were generated to see whether the printed notches and cut notches affect the experimental results. The hammer hits the notched specimen and the energy absorbed by the specimen is measured to calculate the impact strength. In this experiment, the Instron CEAST 9050 pendulum impact tester was used to measure the Izod impact strength. According to the ASTM D2240 standard, Mitutoyo Hardmatic durometer was used to perform Shore D hardness testing on specimens. The size of the hardness test specimen was dimensioned 1 × 1 × 0.5 inch. The hardness measurement was conducted on both top surface and side surface of the testing specimen.

Results and Discussion

Deformation and interlayer crack

Warping is a common problem of the 3D printed PEEK parts. The thermal strain generated by temperature gradient results in detachment of PEEK part from the build plate, as shown in Figure 3(a). An over-warped PEEK specimen may interfere the motion of the printing head, causing printing failure (Figure 3(b)), or part thickness inconsistency. In addition, the 3D printed PEEK specimens (pre-annealing) exhibit weak layer-to-layer bonding strength. Interlayer cracks are usually developed when removing specimen from the build plate, as shown in Figure 3(c). Especially, the bottom layer is easily unbonded when separating raft structure from PEEK part. The delamination is deteriorated after annealing (Figure 3(d)).

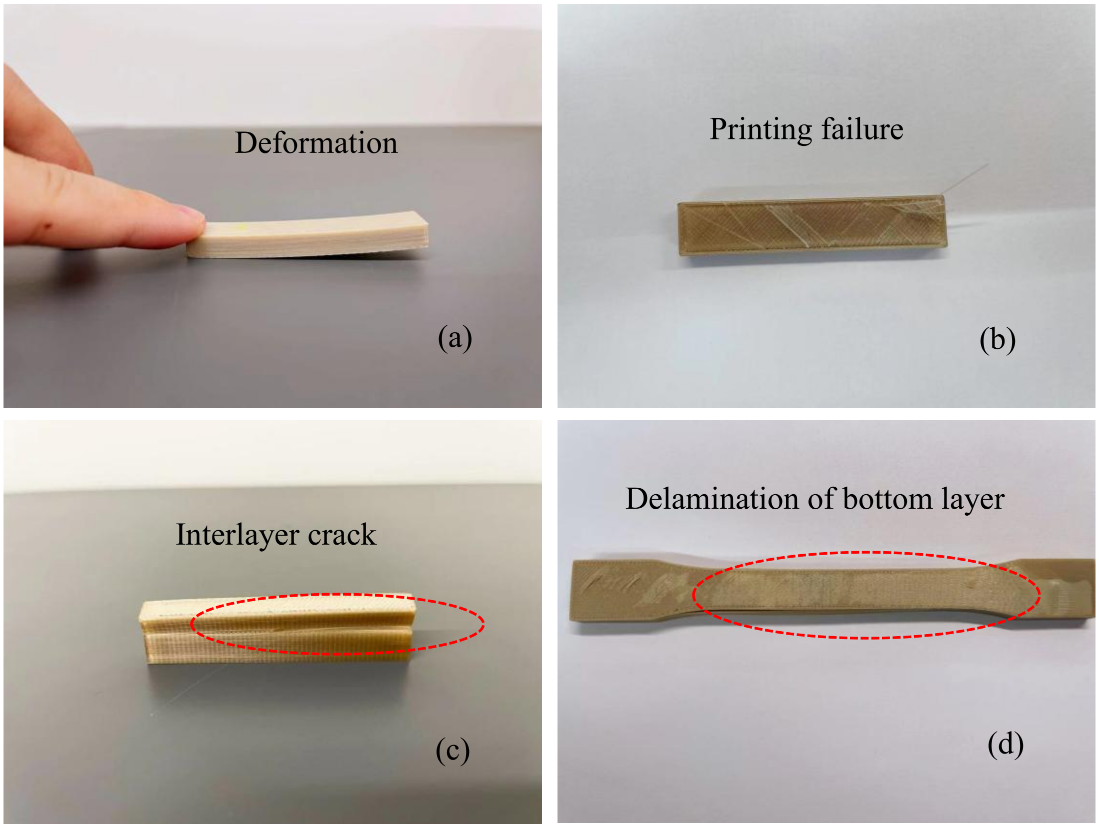

Figure. 3 Common problems of the 3D printed PEEK parts (a) Deformation (b) Printing failure (c) Interlayer crack (d) Delamination after annealing

Tensile Strength

The stress-strain curves of the 3D printed PEEK specimens are shown in Figure 4. A total of 4 samples were tested, and the results of tensile property are summarized in Table 2. The reference values of conventionally processed PEEK parts are also included for comparison. Stable tensile property values were observed on the stress-strain curves, in terms of Young's modulus, Tensile strength at yield, and Tensile strength at break (UTS). The standard deviations confirm the consistency of tensile strength. The Young's modulus of 3D printed PEEK parts is approximately 3.26 GPa, which is similar to 3.6 GPa of conventionally processed PEEK materials. However, the yield strength of 3D printed PEEK parts is only 22.5 MPa, which is significantly different from the 110 MPa of conventional processing. This result may be related to the weak bonding between layers (Figure 5). There are still many tiny pores on the surface of 3D printed PEEK parts, which affect the yield strength of the parts.

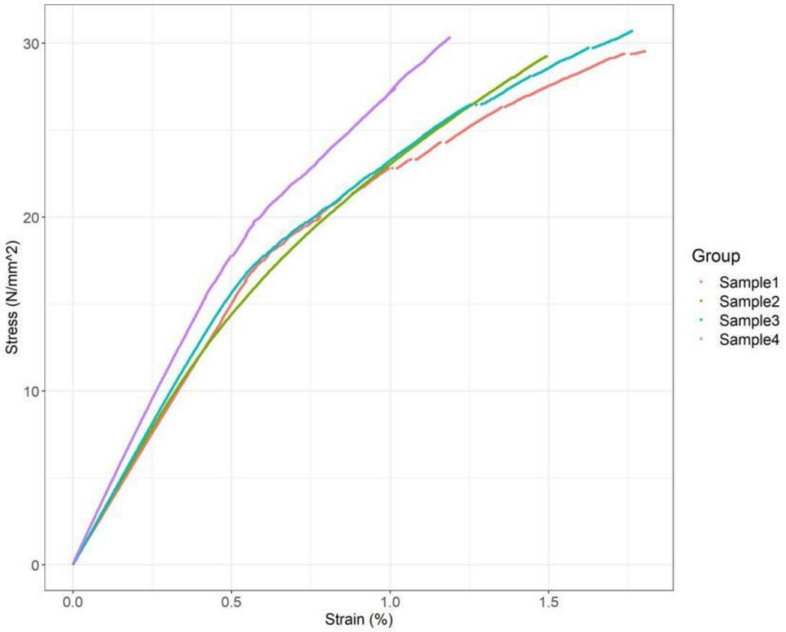

Figure. 4 Stress-strain curve of the 3D printed PEEK (4 samples)

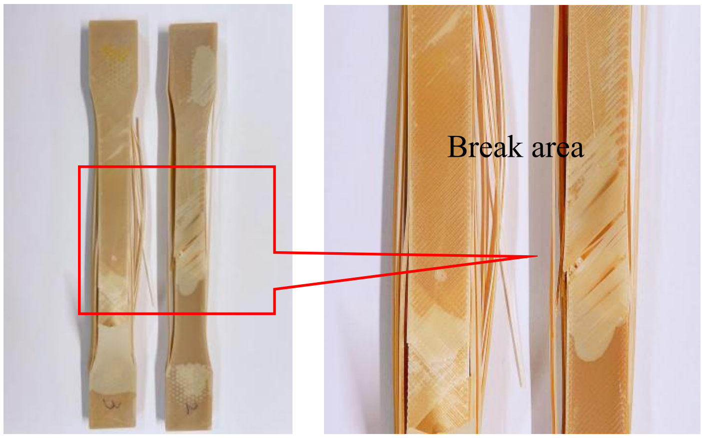

Figure. 5 Specimens after tensile test

Table 2. Tensile test results

Sample	Young's Modulus (GPa)	Tensile strength at yield (MPa)	Tensile strength at break (UTS) (MPa)
1	2.99	22.04	29.54
2	3.07	21.72	29.25
3	3.21	21.52	30.71
4	3.78	24.59	30.33
Mean	3.26	22.47	29.96
Std	0.36	1.43	0.68
Conventional PEEK value*	3.60	110	

* Data source: www.cctprecision.com/materials/peek-all/

Hardness.

The average hardness values (Shore D) of the 3D printed PEEK specimens (Figure 6) on both top surface and side surface are shown in Figure 7. Compared to conventionally processed PEEK materials, the hardness of the top is D 77.58 in average, and the average hardness of the sides is D79.11. This indicates that the hardness of the top and the side is not significantly different, and the overall hardness of the specimen is uniform, which is slightly lower than the hardness D85 of the conventionally processed PEEK material.

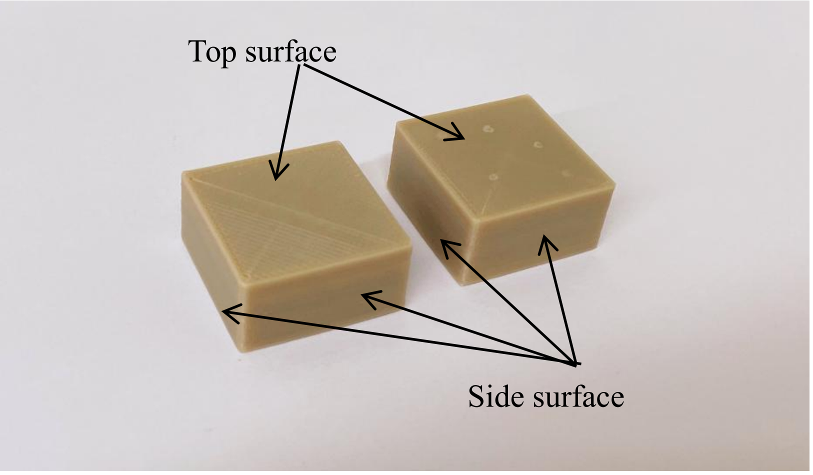

Figure. 6 Top surface and side surface

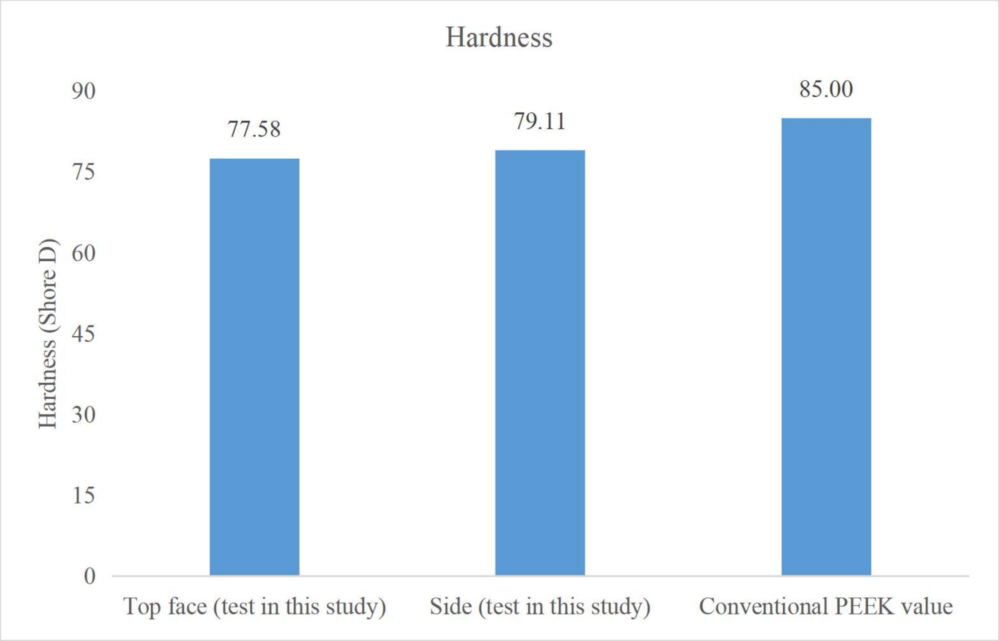

Figure. 7 Hardness of the 3D printed PEEK specimens

Impact strength

The impact strength of the 3D printed PEEK specimen is shown in Figure 8. A total of eight specimens were tested, specimens #1-3 were 3D printed with notches, and specimens #4-8 were cut for notches. The impact strength of the printed notched PEEK specimen is 38±4 kJ/m², which is much higher than the impact strength of the cut notch specimen (18±4 kJ/m²) and the conventional processed PEEK material (8 kJ/m²).

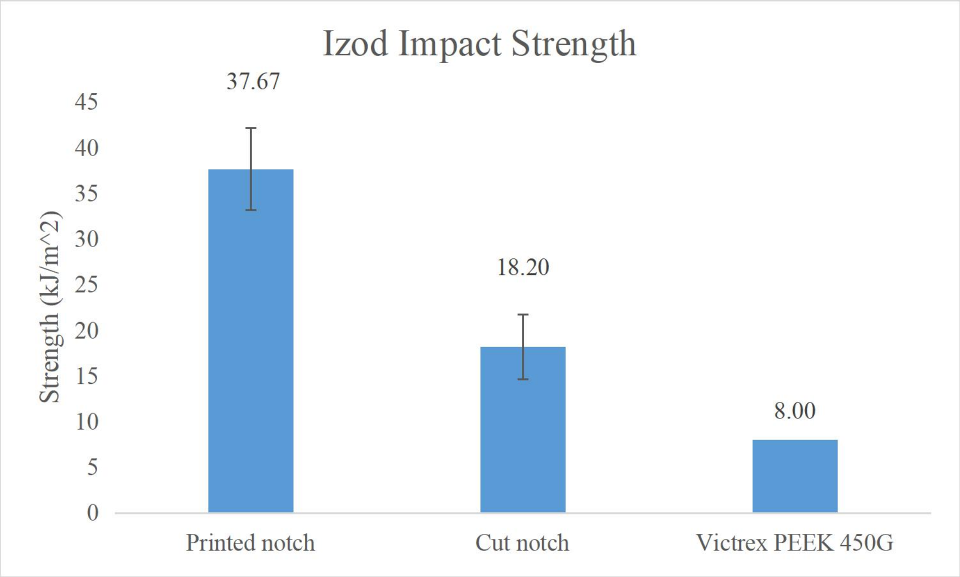

Figure. 8 Impact Strength of the 3D printed PEEK specimens

The comparison of the impact testing specimen fractures is shown in Figure 9. After the specimen with printed notch was hit by a hammer, the specimen did not completely break. The impact load did not cause catastrophic cracks from the notch (Figure 9(a)). The outer edge (contouring of 3D printing) of the specimen is separated. but the impact load caused interlayer debonding slightly on the rear face of the specimen (Figure 9(b)). Both outer edge detaching and interlayer debonding contributed to the impact energy absorption. As for the specimen with the cut notch, the impact load starts from the notch and causes cracks (Figure 9(c)). At the same time, it caused severe interlayer debonding of the rear face. This is due to the notch types are different. The printed notch is not easy to develop a crack. So even though the notch sizes are the same, the printed notch is not characterized as an artificial crack or defect, like the cut notch.

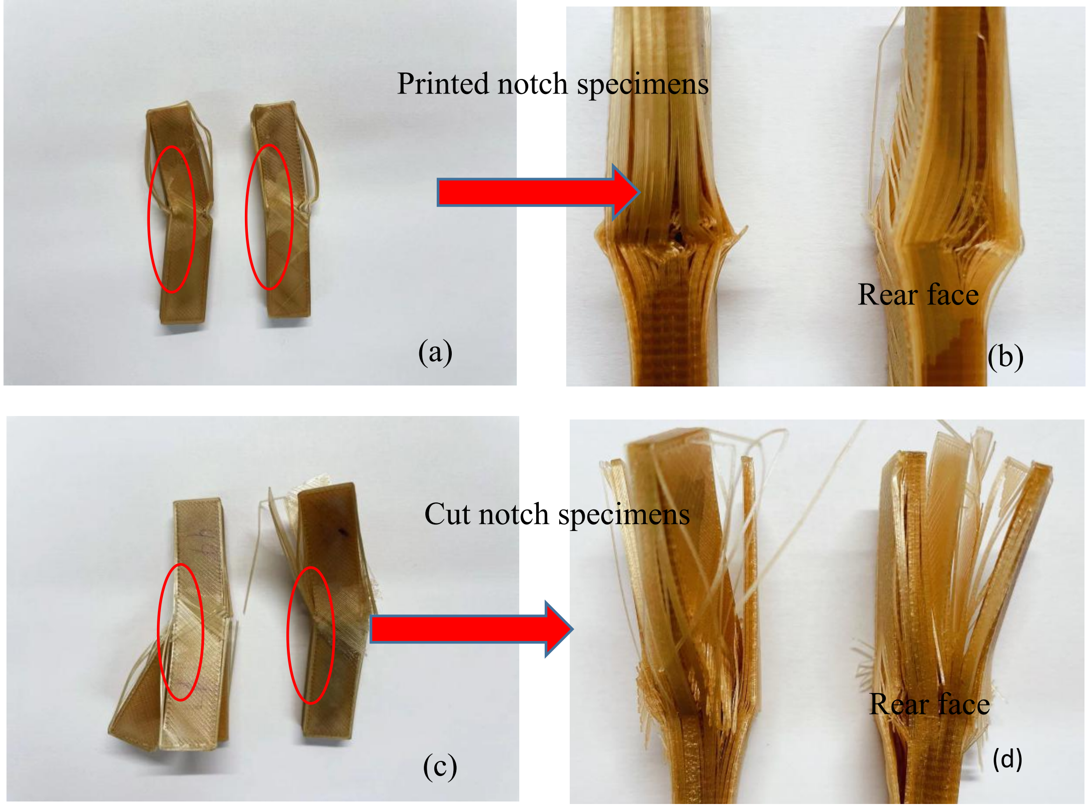

Figure. 9 Comparison of two types of notched specimens after impact load

A general guideline for 3D printing PEEK

According to the mechanical testing results of this study, the 3D printed PEEK parts exhibits weak interlayer bonding. The material is easily deformed (warping) due to the difference in temperature gradient during the printing process. Cracks usually occur under the influence of weak interlayer bonding. The PEEK filament is heated to molten phase and then extruded from the nozzle. The extruded material falls onto the designated position of the build platform and solidifies quickly. The material temperature finally drops to the same temperature of the chamber. Because the chamber temperature is somewhat lower than the build plate. The temperature gradient is generated after the part is printed for a period of time. The temperature in the middle of the part is lower than the temperature of the top and bottom surfaces. The PEEK material is susceptible to the temperature gradient in the 3D printing process, resulting in apparent thermal deformations and then cracks. Most of the cracks occurred near half of the design thickness of the specimen in this study. Therefore, when determining 3D printing orientations of PEEK parts, it is recommended to align the part direction of large dimension with the horizontal build plate to reduce the overall height in z direction for avoiding the occurrence of cracks. To mitigate the temperature gradient issue, it is also recommended to remove PEEK parts when the printing chamber has completely cooled down after the part has been printed. In addition, a PEEK part with a size of high aspect ratio also easily causes cracks in the 3D printing process. For example, when printing Izod impact test specimens, the specimen printed vertically on the build platform (Figure 10, aspect ratio 10:1) has a higher probability of cracking than the specimen printed horizontally on the build platform (aspect ratio 5:1). It is important to notice such type of designs restrictions in the 3D printing PEEK application.

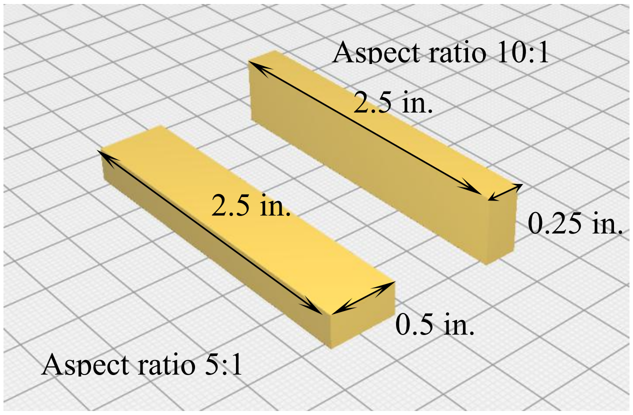

Figure 10 schematic of 3D printing PEEK part of varied aspect ratio

3D printed PEEK parts have higher impact strength than conventionally processed PEEK parts. The Izod impact test results show that the parts with printed notch have higher impact strength than the parts with a cut notch. This is mainly due to the continuity of the outer edges (contouring of 3D printed notch). Since the existing software cannot remove the contouring and then print the impact test specimens, it is impossible to further confirm the specific influence of the continuous outer edge on the impact strength. The impact test without outer edge specimens will be perfected in future research. Also, the post-cutting to 3D printed PEEK materials causes a reduced impact strength. When design a PEEK part for 3D printing, all design features are better to be included for printing, instead of secondary cutting. The results also show that the main problem of impact specimen failure is weak interlayer bonding. The impact load on the specimen is higher than the bonding force between the layers so that no obvious cracks occur at the notch and it failed due to interlayer cracking. High impact strength suggests a better shock resistance which is suitable for medical implants or aerospace applications. On the other hand, the failure of the specimen under tensile load is also related to weak interlayer bonding. The sample did not completely break to form a section. The tensile failure is mainly attributed to the interlayer cracks at the failure location. Therefore, 3D printed PEEK parts have low tensile strength and should not be loaded with high tensile stress.

Annealing is necessary to improve crystallinity and mechanical properties, such as hardness. But the weak interlayer bonding cannot be addressed by the annealing process. PEEK is a semi-crystalline polymer, which is affected by many factors, including repeating unit shape, molecular weight, and temperature control. Ordered polymer long chains pile together to form crystals, while the chains in other regions are disordered (amorphous). The effect of temperature on the crystallinity of 3D printed PEEK material is significant. Rapid cooling results in a limited time for polymer chains to arrange into crystalline domains and thus low crystallinity. In the 3D printing process, the material extruded from the nozzle is cooled fast. So, an annealing process is necessary to improve the PEEK part crystallinity. However, in the annealing process, the increased crystallinity does not improve much to solve the weak interlayer bonding issues. Therefore, it is recommended to increase the 3D printing temperature and chamber temperature to ensure a good bonding in between layers. A new annealing recipe also deserves further study to improve the mechanical properties of 3D printing PEEK parts.

Conclusion

This research focuses on the tensile, hardness, and impact testing of 3D printed PEEK materials. At the same time, it is compared with conventional processing PEEK materials. The weak interlayer bond affects the tensile strength of the specimen. This indicates that more tests are needed to improve the level of interlayer bonding by changing the chamber temperature and annealing recipe. In addition, 3D printed notches are different from cut cuts. The extruded outer edge fine lines significantly increase the impact strength of the specimen. The general guideline of 3D printing PEEK material provides some recommendations when designing and printing. This is helpful for the future research and application of 3D printing PEEK materials.

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