

Progress on High-Performance PEEK Material for 3D Printing

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Abstract. Amidst the rising demand for lightweight, sturdy, and durable materials across various industries, the research emphasizes the widespread application of polyetheretherketone (PEEK) due to its superior characteristics. This paper inquiry scrutinizes the advanced potential of three-dimensional printing utilizing high-performance PEEK material, with a concentrated examination of the Fused Deposition Modeling (FDM) and Selective Laser Sintering (SLS) methodologies. These technologies have been verified to fabricate complex structures and customized components accurately. The analysis investigates how key printing parameters such as printing temperature, bed temperature, laser power, and scanning speed influence the mechanical properties and microstructure of PEEK components. Nonetheless, the study acknowledges the difficulties encountered with FDM and SLS processes, including high-temperature operations, insufficient adhesion, warping deformation, and inconsistent powder density challenges. Addressing these issues is essential to fully harness the advantages of 3D printing with PEEK material. The paper proposes several avenues for future research aimed at mitigating these challenges, such as optimizing printing parameters to enhance stability and component quality, developing improved thermal management systems and print bed surface treatments to boost adhesion and minimize warping, exploring material research for additional 3D printing substances, and refining models based on empirical data to enhance printing precision and efficiency. This study underscores the considerable potential of 3D printing with high-performance PEEK material to transform manufacturing processes, facilitating the production of high-performance components with complex geometries and customized designs, thereby promoting innovation across various industries.

Keywords: PEEK material, 3D printing, FDM, SLS, Printing parameter.

1. Introduction

In the swiftly evolving technological landscape, various sectors are increasingly requiring more rigorous material specifications. The aerospace sector, for instance, necessitates titanium alloy materials with tensile strengths of 1000MPa or greater, while maintaining densities below 4.5g/cm³ to fulfill objectives of lightweight construction and high strength [1]. Likewise, the electronic information sector, along with the biomedical field, which requires semiconductor materials or biocompatible and biodegradable substances, underscores the significance and complexities inherent in materials science. These metrics clearly illustrate the relentless pursuit of optimal material performance across diverse industries. PEEK, a specialized high-performance engineering plastic, is characterized by remarkable mechanical strength, thermal resistance, wear resistance, fatigue resistance, and self-lubricating capabilities. It boasts a high glass transition temperature ($T_g=143^{\circ}\text{C}$) and a melting point ($T_m=343^{\circ}\text{C}$) [2]. Additionally, it can withstand a high load thermal deformation temperature of up to 316°C and an instantaneous service temperature reaching 300°C [3]. Its tensile strength exceeds 100GPa, with some measurements surpassing 200GPa [4], thereby satisfying the demands of the most rigorous application environments. With a density of 1.29g/cm³ [5], it enables the creation of lightweight components of equivalent volume. PEEK's excellent self-lubricating properties render it particularly suitable for bearing applications. These attributes contribute to PEEK's status as one of the most sought-after high-performance engineering plastics today, with primary applications in the aerospace, automotive, electronics, and medical sectors. For instance, in the context of bone defect repair, scaffolds made from PEEK can facilitate bone tissue regeneration

and enhance the healing process. In spinal fusion procedures, these scaffolds can aid in spinal bone fusion, thereby increasing the likelihood of successful outcomes. Furthermore, in cases of bone reconstruction following tumor resection, scaffolds can restore bone function and assist patients in resuming normal activities [6]. The processing techniques for PEEK are varied, encompassing conventional methods such as injection molding, extrusion molding, mechanical processing, and hot-pressing molding. Hot pressing molding is effective for creating simple symmetrical items; however, it has limitations when it comes to processing intricate and detailed structures, and the high expense of molds renders it impractical for new product development or small-scale production. Extrusion molding allows for continuous production but necessitates significant investment in equipment, has stringent raw material requirements, and is susceptible to issues like melt fracture and production instability, making it ill-suited for complex product shapes. Mechanical processing of PEEK demands meticulous regulation of processing temperatures and parameters to prevent material degradation or subpar results. Furthermore, PEEK's inadequate cutting performance results in elevated cutting forces, increased temperatures, and rapid tool wear during processing, thereby escalating overall processing costs. These considerations collectively influence the selection and applicability of PEEK processing technologies.

Given PEEK's high melting point and low thermal conductivity, traditional injection molding techniques often lead to internal stresses and thermal cracking. In contrast, 3D printing technology can effortlessly produce complex geometries that are challenging to achieve through conventional methods, allowing for the layer-by-layer construction of materials in accordance with precise product designs and intricate architectures, thus ensuring seamless integration from design to final product. Additionally, 3D printing technology enhances the control over temperature and uniformity of crystallinity. For PEEK materials, this approach not only significantly enhances manufacturing flexibility and accuracy but also markedly reduces material waste, shortens production timelines, and decreases costs. Moreover, the implementation of 3D printing technology may offer innovative solutions to improve recycling rates.

Consequently, 3D printing presents novel opportunities for utilizing PEEK materials in advanced manufacturing. The integration of additive manufacturing techniques in the processing of PEEK represents not only a transformation of conventional manufacturing practices but also a crucial factor in enhancing the extensive use of PEEK materials across various high-performance sectors. As technology continues to progress and costs decrease, 3D-printed PEEK materials are anticipated to emerge as essential high-performance solutions across numerous industries in the future.

2. Research on 3D Printing of PEEK

2.1. Research on FDM Printing of PEEK

2.1.1 Process parameters

2.1.1.1 Layer thickness

According to prior researchers' inquiries, layer thickness greatly impacts FDM printing PEEK materials. Wu et al. obtained the average mechanical test results for 3D-printed PEEK samples with varying layer thicknesses by a series of studies. As is shown in Table 1, samples with a 300 μ m layer thickness demonstrated the greatest strength in all experiences, while samples with 400 μ m layer thickness showed a significant downward trend in the mechanical strength [7]. Meanwhile, although layer thickness plays an important role in tensile strength, it has relatively little impact on bending strength and compressive strength. Liu et al. conducted a three-factor interaction analysis and got to know that shorter print times and less material use are caused by thicker layers, with a first decline in storage modulus before an increase [8]. This phenomenon is caused by the fact that the increase in layer thickness will reduce the number of layers which will ulteriorly minimize the print time [9]. Wang et al. showed that layer thickness had a negative effect on mechanical properties, with a minimum point of 0.3mm [10]. Pulipaka et al. carried out a positive association between layer

thickness and surface roughness, surface roughness would increase from 4.600 to 21.569 μm as the layer thickness increased from 0.1 to 0.3 mm [11].

Table 1. Mechanical properties in different layer thicknesses [7]

Factor		Tensile strength (MPa)	Bending strength (MPa)	Compressive strength (MPa)
Layer Thickness (μm)	200	40.1	52.1	53.6
	300	56.6	56.1	60.9
	400	32.4	48.7	54.1

2.1.1.2 Temperature

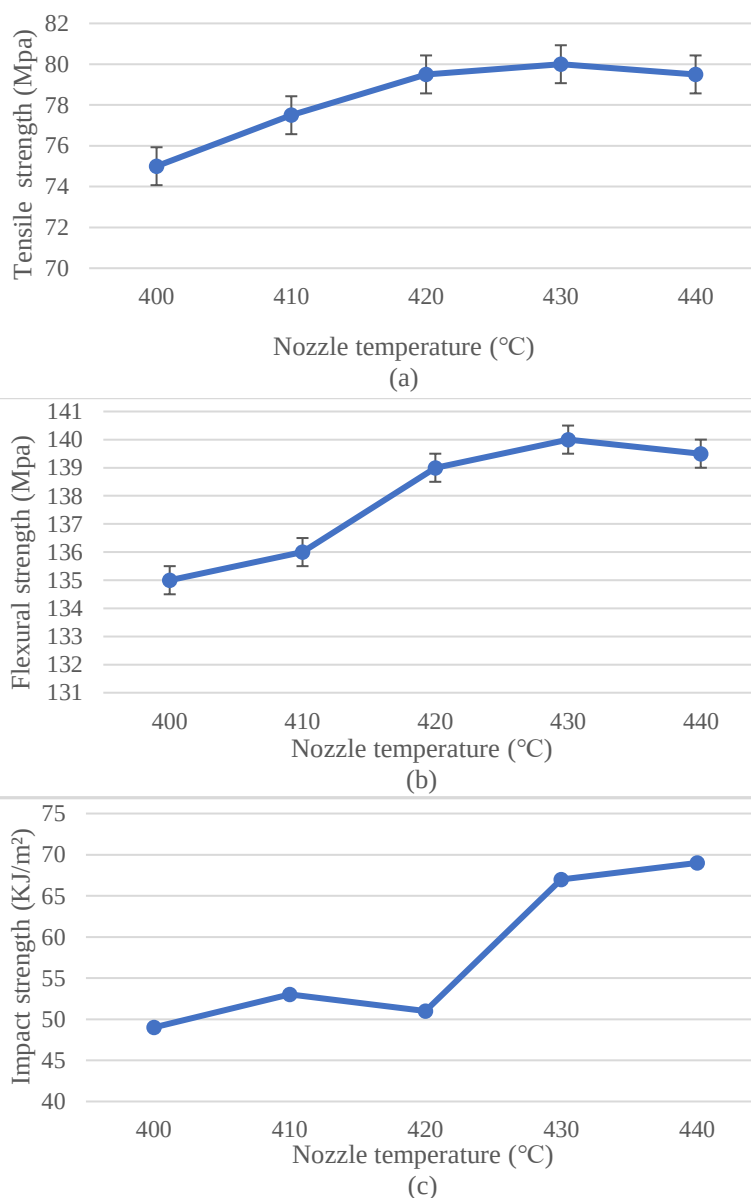


Figure 1. Effect of nozzle temperature on mechanical properties. (a) Tensile strength; (b) Flexural strength (c) Impact strength [10]

Nozzle temperature, Pulipaka et al. came to the conclusion that as the nozzle temperature increased from 390 to 420°C, the hardness would increase from 0.229 to 0.235GPa [11]. This is in line with other previous studies which showed that increasing nozzle temperatures can improve hardness in a manner similar to the crystallinity-dependent effect of elastic modulus [12, 13]. Wang et al. recognized that as nozzle temperature increase, the tensile strength and the flexural strength would increase as well, while the impact strength would keep stable, as is shown in Fig. 1 [10]. Ding et al.

analyzed PEEK's surface morphology, chemical composition, and scanning electron microscopy to find the relationship between nozzle temperature and material properties [14]. As for flexural strength, as is shown in Fig. 2, it is clear that there is a positive correlation between flexural and nozzle temperature before the flexural strength keeps stable after 390°C. Meanwhile, as is shown in Fig. 3(a), the tensile strength of PEEK will first increase before declining as the temperature rises. As is shown in Fig. 3(b), the breaking elongation increased from 6.1% to 16.7% in the study. The effect of nozzle temperature on the sample structure was also noticeable, there was decollation in interlayer at the nozzle temperature of 360°C and fissures were still visible at 370°C, 380°C and 390°C, while they disappeared completely after 390°C. This leads to the conclusion that there is a positive correlation between nozzle temperature and interfacial bonding.

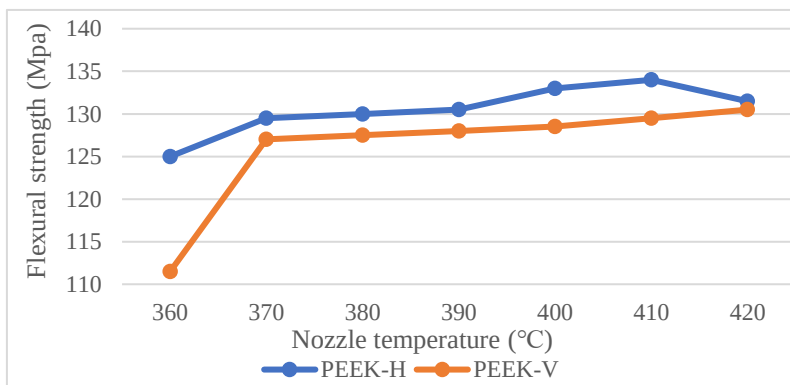


Figure 2. The relationship between bending strength and nozzle temperature [14]

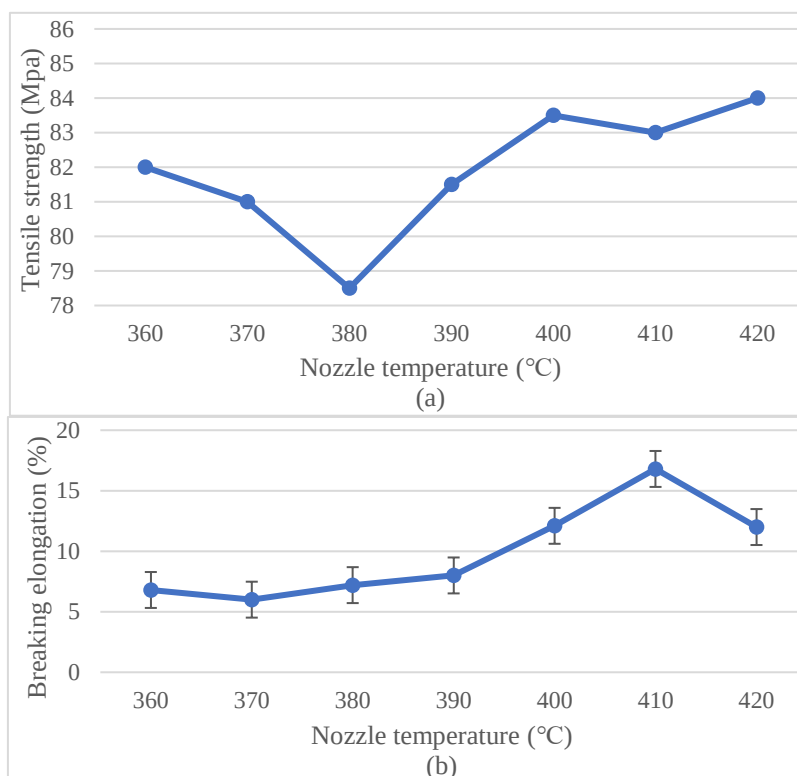


Figure 3. The relationship between tensile strength and nozzle temperature. (a) Tensile strength; (b) Breaking elongation [14]

Platform temperature, Wang et al. drew the conclusion that higher platform temperature would create more energy which would make materials difficult to solidify by observing the tensile fracture surface in scanning electron microscopy [10]. Therefore, sufficient infiltration and diffusion between fibers can enhance the interlayer bonding effect. This phenomenon is similar to the property enhancements achieved through heat treatment processes, which can enhance molecular mobility and

reduce internal defects of PEEK [15]. Meanwhile, as is shown in Fig. 4, there is a positive correlation between the tensile strength and flexural strength of PEEK and the platform temperature.

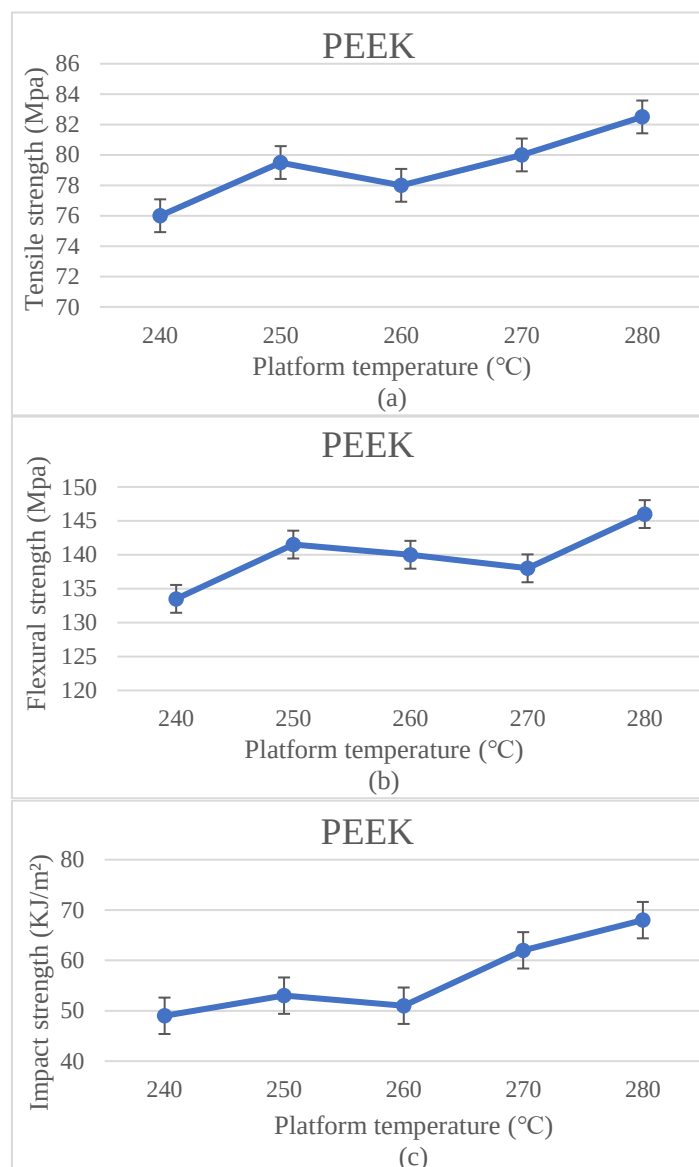


Figure 4. Effects of platform temperature on mechanical properties. (a) Tensile strength; (b) Flexural strength; (c) Impact strength [10]

2.1.1.3 Speed

Printing speed, Ding et al. demonstrated that higher printing speed will cause higher surface roughness [14]. Wang et al. 's result is shown in Fig. 5, which showed that as printing speed rose, the tensile strength and flexural strength of PEEK would respectively lower 10% and 11%. A high printing speed above 30mm/s is not suitable for PEEK as a higher printing speed would lower the extrusion volume of molten material and reduce printing stability. Besides, there is a negative correlation between the mechanical strength of stacked macromolecular chains and printing speed [10]. Higher extrusion speeds, on the other hand, can remove extrusion flaws, increasing the filament density even more. Furthermore, as Fig. 6 illustrates, the melt diameter increases linearly beyond 80mm/min of extrusion speed, making it challenging for the extrusion system to deliver sufficient power.

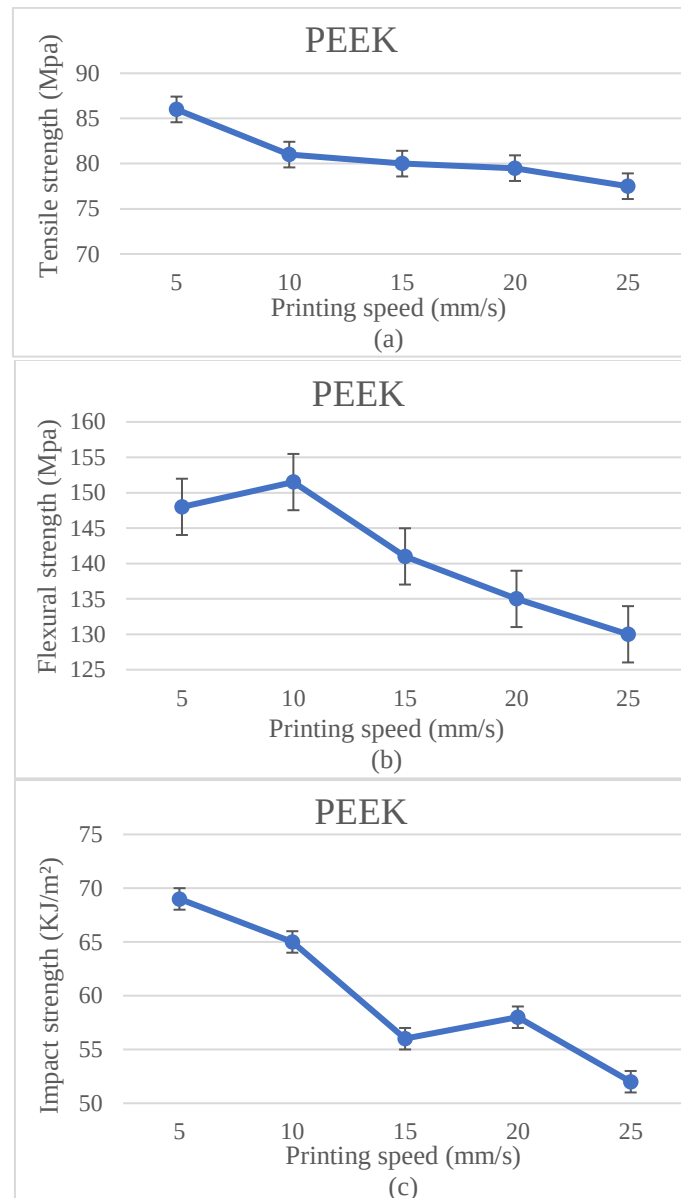


Figure 5. Effects of printing speed on mechanical properties. (a) Tensile strength; (b) Flexural strength; (c) Impact strength [10]

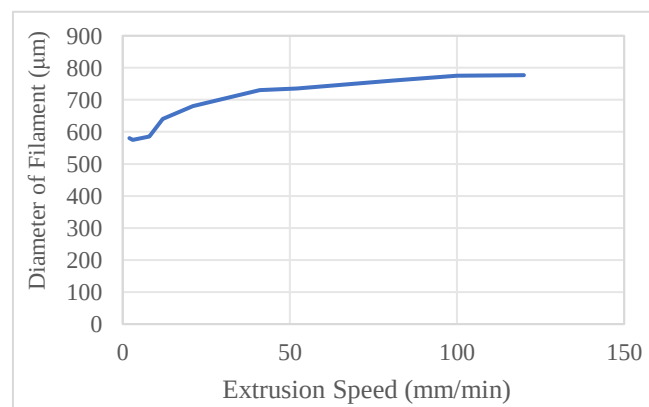


Figure 6. The correlation between filament diameter and extrusion speed [16]

Extrusion speed, Geng et al. obtained that as extrusion speed lowered, there would be surface defects on the filament because of the insufficiency of extrusion pressure. In contrast, higher extrusion speed can eliminate extrusion defects which can further increase the density of the filaments. Besides, as is shown in Fig. 6, the melt diameter grows linearly when the extrusion speed surpasses 80 mm/min,

which makes it difficult for the extrusion system to provide enough power. Therefore, the extrusion speed cannot be increased blindly in the actual FDM process [16].

2.1.2 Path parameters

2.1.2.1 Extrusion Rate

Samples with a conventional extrusion rate (1.0 times) exhibit a tensile strength of 69.35MPa, higher than samples with modified extrusion rates, according to Zhen et al. [17]. Flexural strength rose from 144.16 to 160.08MPa as the extrusion rate increased, while the marginal improvement became minimal when the rate exceeded the standard rate. In comparison to the sample with the standard extrusion rate, the sample with the highest extrusion rate (1.2 times) had a decrease in tensile strength of 16.87% and an increase in flexural strength of 11.04%. As a result, it is believed that the conventional extrusion rate is the superior option.

2.1.2.2 Print Direction

Zhen et al. [17] have found that print direction has little effect on tensile strength but effects significantly on flexural strength. When printing is done vertically instead of horizontally, the flexural strength improves by 27.83%, from 122.53MPa to 156.84MPa.

2.2. Research on SLS Printing of PEEK

SLS is a method of 3D printing in which a laser rapidly melts powder to form a molten pool, which is then moved by the laser to solidify and stack layer by layer to form the final three-dimensional object. Heat loss needs to be controlled during the process to keep the molten pool stable and ensure that the materials are tightly bonded [18].

2.2.2 Laser parameters

2.2.2.1 Laser power

After the printing process was finished, the degree of warpage and dimensional accuracy of the workpieces were examined using range analysis of orthogonal tests to determine the optimal process parameters. Tan et al. found that PEEK powders could not be sintered correctly when less than 10W of laser power was used, and that the formation of “necks” between powder particles became apparent at 12W. The sintering effect improved with increasing laser power, and the samples made with laser power lower than 16W were easily delaminated at the edges. As the laser power increased, the sintering effect improved, and samples made at laser powers lower than 16W were easily delaminated at the edges and poorly bonded between layers. However, too high laser power (e.g. 28W) may lead to material charring and degradation. Therefore, they concluded that a laser power setting between 16W and 21W is preferable [19]. Scott Edwin Snarr investigated the effect of laser powers of 1.81W, 7.62W, and 16.71W on the sintering effect at a scanning speed of 1500mm/s. He qualitatively assessed the sintering effect mainly by sintering color and depth. At 7.62W and 16.71W laser power, the sintering color was dark and close to black, indicating that the material was close to complete melting, in contrast to the light gray color at 1.81W laser power. 16.71W laser power had a deeper melting depth than 7.62W, but too much laser energy may lead to degradation of the material, such as loss of small features and rounded corners [20].

After the printing process was finished, the degree of warpage and dimensional accuracy of the workpieces were examined using range analysis of orthogonal tests to determine the optimal process parameters. Range analysis of the warpage is seen in Table 2, and range analysis of dimensional accuracy is seen in Table 3. comparing the laser power: 8W, 9.8W, 11.6W, and 13.4W. The dimensional accuracy was high with 9.8W, and the degree of warpage was 13.4W. The laser power of 9.8W had a high degree of dimensional accuracy, and that of 13.4W warpage was small [18].

Table 2. Range analysis of warpage [18]

Range	A: Laser Power (W)	B: Scanning Speed (mm/s)	C: Layer Thickness (mm)	D: Scanning Interval (mm)
1	0.34	0.33	0.54	0.41
2	0.37	0.38	0.3	0.41
3	0.43	0.36	0.35	0.35
4	0.26	0.33	0.22	0.24
R	0.18	0.06	0.33	0.17
Optimum assembly	A4B1C4D4			
Order of priority	CADB			

Table 3. Range analysis of dimensional accuracy [18]

Direction	Range	A: Laser Power (W)	B: Scanning Speed (mm/s)	C: Layer Thickness (mm)	D: Scanning Interval (mm)
X direction	1	1.46	1.31	1.3	1.42
	2	1.34	1.43	1.4	1.31
	3	1.34	1.37	1.39	1.38
	4	1.34	1.37	1.4	1.37
	R	0.13	0.13	0.1	0.11
Y direction	Optimum assembly	A2B1C1D2			
	Order of priority	BADC			
	Optimum assembly	A2B1C1D4			
Z direction	Order of priority	BADC			
	Optimum assembly	A2B1C4D1			
Z direction	Order of priority	CBAD			

2.2.1.2 Laser power

There are four scanning speeds available, and the maximum is 800mm/s. See Tables 2 and 3, Zeng et al. concluded that 800mm/s has the best warpage and dimensional accuracy of the workpiece [18]. Besides, Zhang et al. explored this factor, they pointed out that the destructive strength first falls and subsequently increases as the powder spreading speed increases. Fig. 7 shows the SLS-CF/PEEK intensity development with paving speed. The faster the powder spreading speed, the higher the destructive strength. The destructive strength was ranked as follows 230mm/s > 130mm/s > 180mm/s [21].

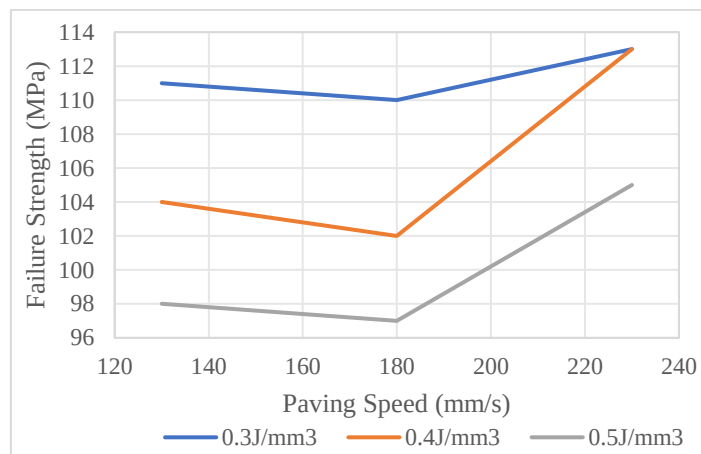


Figure 7. Evolution of SLS-CF/PEEK intensity using paving speed [21]

2.2.1.3 Scanning distance

Wei et al. and some academics reduced the scanning spacing can boost the density and tensile strength of SLS products. This happens as a result of the molten powder's decreased viscosity, which lowers porosity and increases density [22-24]. Zeng et al. compared the scanning intervals: 0.16mm, 0.20mm, 0.24mm, and 0.28mm. See Tables 2 and 3, the scanning interval of 0.28mm workpieces have the best warpage and dimensional accuracy [18].

2.2.1.4 Laser beam diameter

Fang F Z et al. pointed out that the laser beam diameter has a direct impact on the bonding process and polymer degradation of the powder because it is a surface that is strongly related to the heat flux input to the powder surface [25].

2.2.2 Layer thickness

Wei et al. recognized that reducing the layer thickness improves the surface roughness, but the construction time is longer [22]. In terms of strength, Zhang et al. noted that when layer thickness decreases, ultimate tensile strength rises. When the layer thickness is low, along the direction that the powder is spreading, the fibers are more perfectly aligned. This means that along the powder's spreading route, higher strength can be achieved [21]. Zeng et al. used range analysis of orthogonal experiments to investigate the degree of warpage and dimensional accuracy of the workpiece after printing was completed, see Tables 2 and 3, comparing the layer thicknesses: 0.15mm, 0.18mm, 0.21mm, 0.24mm. a layer thickness of 0.24mm was the best [18]. The micro-CT results of Liu and Hou showed that the porosity of the samples increased with the increase of the print height [26].

2.2.3 Laser volumetric energy density (LVED)

Zeng et al. considered the LVED to be derived from the following equation:

$$LVED = \frac{P}{H \times v \times t} \quad (1)$$

Where H is the scanning interval, v is the scanning speed, t is the layer thickness, and P is the laser power [18].

Fig. 8 visualizes the specific effect of LVED on the dimensional accuracy and warpage of sintered parts. The dimensional errors show significant differences and clear trends in the X, Y, and Z dimensions. See Fig. 8(a), as LVED increases, the X and Y axes' dimensional errors have positive values that gradually decrease; on the contrary, the dimensional errors in the Z direction are negative and their absolute values increase with the increase of LVED. Further analyzed, the increase of LVED may also exacerbate the inhomogeneity of the temperature gradient, which in turn induces the warpage deformation of the part. As shown in Fig. 8(b), the warpage of the part exhibits an obvious increasing trend with the gradual increase of LVED [18].

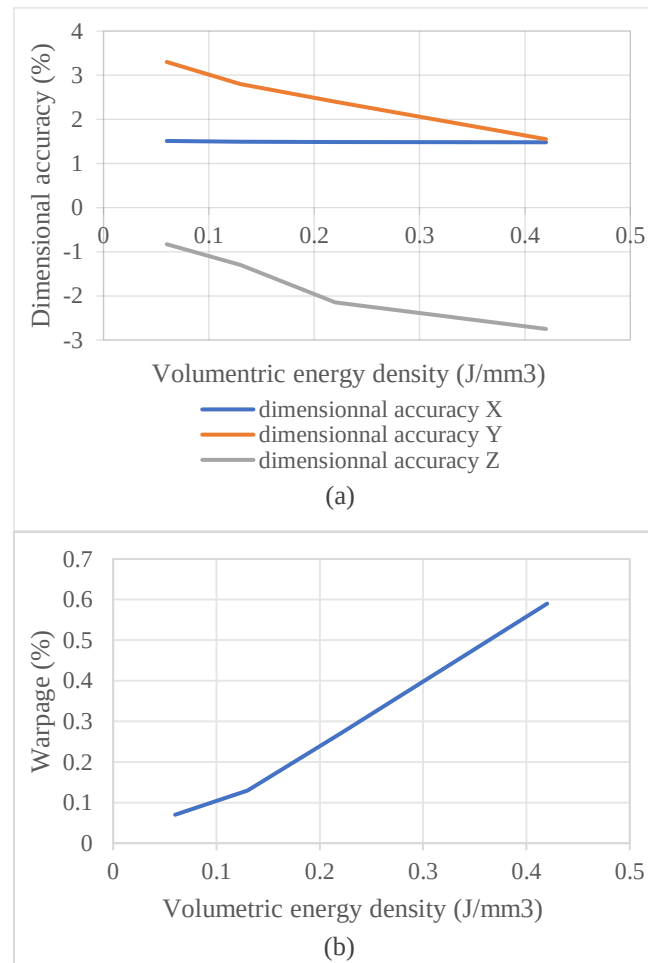


Figure 8. The impact of the fluctuation in laser volumetric energy density. (a) Dimensional accuracy; (b) warpage [18]

Wei et al. concluded that the laser power and scanning speed primarily determine the energy density of the laser filling of the powder surface. Both insufficient and excessive energy density are problematic; if the laser energy density is too low, it will lead to insufficient interlayer adhesion and is prone to delamination, which will result in a weaker part. Conversely, if it is too high, it may cause warping and deformation of the part [22].

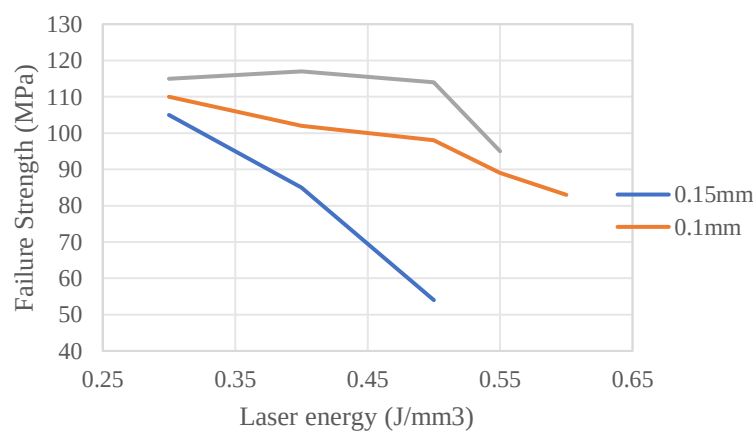


Figure 9. Evolution of SLS-CF/PEEK intensity using laser energy [21]

Zhang and colleagues observed that the greatest value of laser energy density is followed by a drop in the ultimate tensile strength. Fig. 9 shows the intensity evolution of SLS-CF/PEEK utilizing laser energy. Using the 0.08mm group's layer thickness as an example, the ultimate tensile strength improves with increasing laser energy density in cases where the density is 0.4J/mm or less. The

energy was insufficient for CF/sintered PEEK powder during this time. The aggregation of the powder was impacted by the partial melting of the powder surface. The process of CF/PEEK powder bonding during SLS is improved and the powder agglomeration is typically more compressed as the laser energy density increases [21].

2.2.4 Bed temperature

Different bed temperature settings were used by Tan et al. Specifically, the specimens fabricated at a partial bed temperature of 140°C had more pronounced necking and improved sintering compared to those at 110°C. Therefore, they concluded that the most favorable SLS process parameter setting for the fabrication of PEEK stents should be 140°C [19]. Liu and Hou pointed out that the powder bed temperature influences both structural defects and sintered layer distribution, and the presence of over-sintered zones in the sintered samples is usually accompanied by increased porosity, which proves that the temperature variations are an important factor affecting the formation of structural defects. When the area temperature is high, the melt surface tension decreases, which affects the distribution uniformity of the sintered layer. Porosity or unfused flaws in the sintered layer arise when the region temperature is low because the laser energy is insufficient to melt the powder entirely [26].

3. Conclusion

This study offers a comprehensive analysis of the challenges and opportunities associated with high-performance PEEK 3D printing technology. The research methodology includes a thorough investigation of how various printing parameters—such as print temperature, print bed temperature, laser power, and scanning speed—affect the mechanical properties and microstructure of PEEK components. Additionally, the study assesses the difficulties faced during FDM and SLS processes, which encompass issues like elevated temperatures, poor adhesion, warping, inconsistent powder density, and sintering defects.

The focus of this research is to identify the constraints of FDM and SLS technologies while formulating strategies to mitigate these challenges. The findings reveal that optimizing printing parameters, upgrading printing equipment, increasing sample sizes, performing cross-material studies, and refining models can significantly enhance the maturity, efficiency, and reliability of the technology. By adjusting the models based on experimental findings, this research has shown that both the accuracy and efficiency of the printing process can be markedly improved. The results indicate that by tackling the challenges and capitalizing on the strengths of FDM and SLS technologies, it is feasible to produce high-performance components with intricate geometries and tailored designs, fostering innovation across various sectors. However, the current investigation is somewhat limited, primarily focusing on PEEK materials, which may not fully represent the performance characteristics of other high-performance polymers. Future research should strive to include a broader range of materials and explore the interplay between PEEK 3D printing and other manufacturing techniques to enhance the production of complex components.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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