3D printed Polyether ether ketone (PEEK), Polyamide (PA) and its evaluation of mechanical properties and its uses in healthcare applications.

Sandeep Shetty, Nandish B T, Vivek Amin, *Jayaprakash K, Shahira, Stanly Selva Kumar G S, Faizan Khan, Pooja Harish

Department of Orthodontics, Yenepoya (Deemed to be University), Mangalore, Karnataka, India.

*Corresponding author: Dr. Jayaprakash K, jayanperla@gmail.com

Abstract. Additive manufacturing (AM) is evolving continuously which enables 3D printing a given idea into a functional prototype, the complex structures can be 3D printed with versatility of changing the density depending on the in-fills programmed during printing thus it can be light in weight with less material wastage which cannot be achieved by other methods. Polyether ether ketone (PEEK) is widely used in implantable devices such as spinal, dental and orthopedic implants due to its superior biocompatibility and nearly matching properties with bone. Polyamide (PA) is another biomaterial widely used as sutures, catheters, and dentures due to its biocompatibility. In the present study, the specimen of PEEK and polyamide were 3D printed and the mechanical properties evaluated and compared for healthcare applications.

Methodology: In this work, a comparison of mechanical strength such as compressive strength (CS), tensile strength (TS), flexure strength (FS), and impact strength (IS) of 3D printed PEEK samples by fused deposition modelling (FDM) and PA specimens by selective laser sintering (SLS), respectively. Samples for mechanical strength were prepared according to ASTM and ISO specifications. Result: The strength of the Polyether ether ketone was higher than that of Polyamide. Conclusions: The results of this experiment provide a comprehensive understanding of the mechanical strength of PEEK and PA, that can be used as a valuable guide for their healthcare applications.

Keywords: 3D printing, SLP method, mechanical strength, healthcare

1. Introduction
Additive manufacturing (AM), is a fastest evolving technology that has been evolving continuously and have grown exponentially since a decade. The basic principle of this technology is to fabricate objects from Stereolithography (STL) format from 3D design data, extruding the molten polymer from the printer layer by layer, also enabling the printing of lightweight and complex structures [1]. 3D printing is used to accurately fabricate complex structures in a wide range of materials such as polymers, metals, rubbers, or ceramics. It reduces the wastage of materials compared to the CAD-CAM technique [2,3,4]. 3D printing creates objects based on digital models created by computer aided design software which then fed into to printer for the manufacturing [3,4]. Polyamide 12 (PA12) has a broad temperature range and is able to lessen the crystallization of printed parts during the printing processes hence it is widely used polymer for powder bed fusion (PBF) processes because [3]. Polyamide (PA) is a biomaterial widely used as suture materials and catheters
due to its biocompatibility. It has a tunable mechanical properties and desirable chemical stability making it an ideal material of choice for sutures. PA can be drawn easily into fibres, and molded parts, and is also used in orthopedic applications [5]. One of the recent advances in medical and dental biomaterials is PEEK polymer known for its superior biocompatibility, high strength, light in weight and superior tissue acceptability, these are some of the properties that drawn an attention towards its use in orthopedic, spinal and dental implants [6]. One of the major advantages of this biomaterial is the radiolucent feature of the PEEK, which aid in the diagnosis which otherwise by using metal implant causes artifact in the imaging. This study aimed to compare and evaluate the mechanical properties between Polyamide and PEEK for various healthcare applications.

2. Materials and methods:

The specimens for the mechanical test were designed digitally by using Autodesk Fusion 360. The specimens for mechanical tests of PEEK have been prepared at the Prototyping Lab with a 3D-Printer - INTAMSYS - FUNMAT HT by using unreinforced PEEK (450G - Victrex Plc., Lancashire, UK) (Fig. 1). PA specimens were prepared with a 3D-Printer -Sinterit Lisa Pro and PA12 smooth v2 (Fig. 1). The details of printer parameters used during were given in table 1. The compressive, tensile, and flexure tests were performed using an electromechanical universal testing machine (UTM) model-Zwick/Roell Z020 with a 20kN load cell. The setup of a specimen and test fixture for mechanical tests was shown in Fig. 2-A, B, C. The impact strength was tested using Zwick/Roell HIT 50P impactor with a pendulum weight = 5.5J (Fig 2-D). Specimens were tested in triplicate for the mechanical test. The geometrical details of digitally 3D designed test specimens for mechanical tests such as compression, tension, flexure, and impact test (Unit: mm) were shown in Fig. 3. Graphical representations of Stress-strain behavior of two tested materials for various mechanical properties are shown in Fig. 4.

Samples for compressive strength were prepared according to EN ISO 604. The cylindrical specimens a diameter-height ratio (x/L) greater or equal to 0.4. Consequently, a cylindrical specimen with a diameter of x=10mm and a height L=25mm was prepared. The tests were performed with UTM at a crosshead speed of 5 mm/min, until failure of the specimen [7].

For tensile strength evaluation, specimen was prepared according to ASTM D368 and designed with a dimension L = 135 and, Width = 10 and thickness = 4mm. The samples were loaded up to material failure at a displacement rate of 50mm/min. until failure of the specimen [8]. Flexural strength by 3-point bending test was performed according to ASTM D7264 at a loading rate of 2mm/min until failure of the specimen. The load applied at the time of fracture was noted. The flexural strength of the specimen was calculated using a standard equation, S= 3FL/2bd2 Where, F= Fracture load, L= Distance between two supports, set at 25mm, b= Width of the specimen, and d= Thickness of the specimen [9,10,11].

To determine the impact strength of the PEEK and PA by the amount of energy absorbed during the fracture, an un-notched impact test was performed according to ASTM D4182. A rectangular specimen of dimension 64 mm length, 13mm depth, and 3 mm thickness was made according to ASTM D4182 using the 3D printing technique. The specimens were clamped into the pendulum impact test fixture with a thin edge facing the striking edge of the pendulum. The pendulum was released and allowed to strike through the specimen. The impact strength was calculated by dividing the impact energy in J by the thickness of the specimen (m) [12].

Results

The results of this study are shown in table 2 and fig. 5. Analysis of the results was conducted using SPSS software (V-22). Tests were performed at a confidence level of 95% and with a significant P-value of (P ≤0.05). These statistical tests included inferential statistical analysis of variation (ANOVA). A one-way ANOVA (Post-hoc, Tukey test) showed statistically significant differences (P < .001) in mechanical properties evaluated between PEEK and PA. The PEEK showed higher mechanical properties such as tensile, compressive, flexural, and impact strength than PA.
Discussion

The ability to process powders by laser sintering (e.g., ease of deposition and spreading over the powder bed) and the quality of laser-sintered parts (e.g., surface roughness, density/porosity) depend on the powder morphology, size, and size distribution. Particles that are too large negatively influence surface finish and part density and powder particles with too small a diameter exhibit poor bulk flow at high temperatures, presumably due to the higher interparticle friction found in extremely fine powders. The optimum particle size in processing ability is generally around 45–90 lm for laser sintering of macro-sized parts. Spherical with regular morphology is the ideal powder for laser sintering. Powders tend to arrange themselves more efficiently with spherical morphology that increases the density of parts. In contrast, powders with irregular morphology cannot achieve this form of efficient arrangement resulting in low-density parts.

Moreover, spherical morphology will help powder flow and ensures that a flat and thin powder layer is deposited during the sintering process. The PA12 powder used in this study was PA12 smooth v2. The mechanical parameters, resistance to heat and flexibility, are ideal for functional prototypes. PA 12 by Laser printing does not require supportive structures and hence it enables printing the most complicated designs [13].

In this study, the PEEK demonstrated superior mechanical properties such as higher tensile, compressive, flexural, and impact strength and lower plastic deformation in the elastic region than PA. On the other hand, the PA polymer’s flexibility and highly flexible nature, as shown in the stress-strain curve (fig. 4), could potentially improve the retention of the partial denture, which are the most desirable properties required for partial denture in dentistry.

Polyamide has a tunable mechanical properties and desirable chemical stability making it an ideal material of choice for sutures. PA can be drawn easily into fibres, and molded parts, and is also used in orthopedic applications [14]. PEEK materials are currently used in dentistry for temporary clinical abutments, temporary bruxism devices, long-term implant fixtures into bone, implant-supported prosthetic substructures, crowns and bridges, removable dentures [15]. PEEK is widely used in medical implants due to its approximate properties with bone, excellent biocompatibility, mechanical properties similar to those of human cortical bones and radiolucency which prevent imaging artifacts [16,17].

The following conclusions may be made within the limitations imposed by the methods of the current study:

- PEEK showed higher mechanical properties than PA.
- PEEK materials are currently used in dentistry for temporary clinical abutments, temporary bruxism devices, long term implant fixtures into bone, implant-supported prosthetic substructures, crowns, and bridges, removable dentures, and also used as medical implants due to its approximate property with bone.
- Polyamide can be drawn easily into fibres, and molded parts, and is also used in orthopedic applications. Due to its biocompatible nature, has a tunable mechanical properties and desirable chemical stability making it an ideal material of choice for sutures, etc.
- Even though two materials tested in this study show different mechanical properties, each material has advantages and diverse healthcare applications.

Conflict of Interests

There is no conflict of interest regarding the publication of this paper.
FIGURES, TABLES, AND LEGENDS

Fig. 1 3D Printer used for PEEK (A) and PA (C), printed specimens PEEK (B), and PA (D)

Fig. 2 Experimental set-up for compression (A), tensile (B), flexural (C) and impact (D) test
Fig. 3 Geometrical details of tested specimens for tensile (A), impact (B), compression(C), and flexural test (Unit: mm)

Fig. 4 Machine diagram shows the Stress-Strain behavior of PEEK and PA specimen during compression (A), tensile (B), flexural(C) and impact test (D)
Fig. 5 Mechanical properties of PEEK and Nylon

Table 1: Printing parameters details for PEEK and PA

| Printing parameters for PEEK | Printing parameter for PA |
|-----------------------------|---------------------------|
| Printing temperature: 380-410°C | Build volume: 150×200 ×260[mm] |
| Build plate temperature: 130-160°C | Laser system: IR laser diode 5[W] |
| Printing speed: 15-40mm/min | Wavelength =808[nm] |
| Color: Natural | Min wall thickness: from 0.4[mm] |
| Raft top layer thickness: 0.3mm | Min detail size: from 0.1mm |
| Raft top layer width: 0.4mm | Heating system: heated-piston, cylinder, feed bed, print bed. |
| Raft middle layer thickness: 0.15mm | Max temp in chamber 200[°C]/392°F |
| Raft base layer thickness: 0.36mm | |
| Raft base layer width: 0.8mm | |
| Raft top printing/scan speed: 25mm/s | |
| Raft middle printing speed: 18.75mm/s | |
| Raft base printing speed: 18.75mm/s | |
| Ambient temperature: 24°C | |
| Nozzle temperature: 400°C | |
| Nozzle diameter: 1.75mm | |
| Bed temperature: 145°C | |

Table 2: Mechanical properties of PEEK and Nylon with mean values and standard deviation (SD)

| Test materials | Compressive strength (MPa) Mean(SD) | Tensile strength (MPa) | Flexural strength (MPa) | Impact strength J/m |
|----------------|--------------------------------------|------------------------|-------------------------|---------------------|
| PEEK           | 95.8(SD=3.3)                          | 77.5(SD=5.6)           | 85.5(SD=8.4)            | 301(SD=22.2)        |
| Nylon          | 34.5(SD=4.6)                          | 23.5(SD=4.56)          | 23(SD=4.09)             | 132.6(SD=6.2)       |
REFERENCES:

1. Martynkova GS, Sliva A, Krotosova G, Barbaszova KC, Studentova S, et al. Polymers 2021, 13, 810. https://doi.org/10.3390/polym13050810.

2. Bhat VS, Nandish BT, K Jayaprakash., Science of Dental Materials with Clinical Applications, 3rd ed., CBS Publishers and Distributors, P:230 (2019).

3. Cai C, Tey WS, Chen J, Jhu W, Liu X et al. Comparative study on 3D printing of polyamide 12 by selective laser sintering and multi-jet fusion Journal of Materials Processing Tech. 2021; 288 :116882.

4. Ngo, T.D., Kashani, A., Imbalzano, G., Nguyen, K.T., Hui, D., 2018. Additive manufacturing (3D printing): A review of materials, methods, applications, and challenges. Compos. Part B-Eng. 143, 172–196.

5. Shakiba M, Ghomi ER, Khosravi F, Jouybar S, Bigham A et al. Nylon—A material introduction and overview for biomedical applications. Polym Adv Technol. 2021;32:1–16.

6. McNamara A, Turner RM. Potential of polyetheretherketone (PEEK) and carbon-fibre-reinforced PEEK in medical applications. J Mater Sci Lett; 1987;6:188-90.

7. Percoco G, Lavecchia F, Galantucci LM. Compressive properties of FDM rapid prototypes treated with a low-cost chemical finishing. Res. J. Appl. Sci. Eng. Technol 2012(19):3838-42.

8. Liu Z, Lei Q, Xing S. Mechanical characteristics of wood, ceramic, metal and carbon fiber-based PLA composites fabricated by FDM. J Mater Res and Technol. 2019:8(5):3741-51.

9. Caminero MA, Rodríguez GP, Muñoz V. Effect of stacking sequence on Charpy impact and flexural damage behavior of composite laminates. Composite Structures. 2016;136:345-57.

10. D7264/D7264M.ASTM standard test method for flexural properties of polymer matrix composite materials. Annual book of ASTM standards 2007;7:1–1.

11. Jayaprakash K, Nandish BT, Rijesh M, Nayak J, Bhat SM et al. Fabrication of Hair and Copper Fiber Reinforced Polymethyl Methacrylate (PMMA) Composites and Evaluation of Their Mechanical Properties, Thermal Conductivity and Color Stability for Dental Applications, Trends Biomater Artif Organs., 30, 8-12 (2016).

12. Lay M, Thajudin NLN, Hamid ZAA, Rusli A, Abdullah MK, et al. Comparison of physical and mechanical properties of PLA, ABS, and nylon 6 fabricated using fused deposition modeling and injection molding. Composites Part B: 2019;176:107341.

13. Bai J, Goodridge RD, Hague RJM, Song M. Improving the Mechanical Properties of Laser-Sintered Polyamide 12 through Incorporation of Carbon Nanotubes. Polym. Eng. Sci. 2013. DOI 10.1002/pen.23459.
14. Ghomi ER, Khosravi F, Jouybar S, Bigham A, Mina Zare et al. Nylon—A material introduction and overview for biomedical applications. Review. Polym Adv Technol. 2021;1–16. DOI: 10.1002/pat.5372.

15. Siewert B, Plaza-Castro M, Sereno N, Jarman-Smith M. PEEK Biomaterials Handbook P: 333-42. https://doi.org/10.1016/B978-0-12-812524-3.00020-X.

16. Hořík Z, Pokorný D, Fulín P, Slouf M, Jahoda D, Sosna A. Polyetheretherketone (PEEK). Part I: Prospects for use in orthopaedics and traumatology. Acta Chir Orthop Traumatol Cech 2010;77 (6):463-9.

17. Guo Y, Chen S, Wang J, Lu B. Medical applications of polyether ether ketone. Transl Surg 2018;3:12-6.

Acknowledgment:

This work was supported by the BIRAC (Project number- BIRAC/KIIT0555/BIG-14/19) and Yenepoya Research Centre (Yenepoya University). The authors would like to thank Mr. Asim Syed Sheeraz, Incubator Manager, Yenepoya Technology Incubator, and Dheeraj Poojary, Design Engineer, Yenepoya Technology Incubator, for assisting in preparing specimens for the mechanical test.