Short Communication

Rapid injection moulding process of polyether ether ketone based on stereolithography

Xuewen Zong[1,2,3] · Jiayang Ruan[1,2] · Huilong Liu[3] · Wensen Sun[3] · Yaxiong Liu[3]

Abstract
In this study, photosensitive resin mould was made by stereolithography technology to inject individualized polyether ether ketone (PEEK) parts. In simulation experiment, the temperature field of the PEEK injection mould was analysed by finite element analysis; it was preliminarily determined that the resin mould will not be deformed during the injection process. The optimum parameters of PEEK injection process were obtained by orthogonal experiment: injection temperature 373 °C, injection pressure 11 MPa and injection speed 70%. Mechanical tests were carried out on PEEK samples injected by this process. The results showed that the average tensile strength was 96.4 ± 2.28 MPa, the average bending strength was 147.654 ± 9.36 MPa, and the impact strength was higher than 10 kJ/m^2. The experimental results show that it is feasible to produce photosensitive resin mould to inject individualized PEEK parts by stereolithography. Photosensitive resin mould has lower cost, shorter production cycle and no waste of PEEK material during injection process. The injection method in this study greatly reduced the production cost of individualized PEEK parts and can obtain PEEK parts with good mechanical properties in a relatively fast time.

Keywords Polyether ether ketone · Additive manufacturing · Personalized parts · Engineering plastics

1 Introduction

Polyether ether ketone (PEEK) is an inert polymer material with excellent properties. It has good high-temperature resistance, fatigue resistance, high strength and corrosion resistance. It has been widely used in aerospace, automobile and other fields [1–9]. The advantage of additive manufacturing (AM) technology is that it can quickly manufacture parts with complex structures and individual structures and has high material utilization [10]. The traditional PEEK processing methods mainly include injection moulding, machining and the like. Injection moulding needs to be matched with the corresponding mould design and manufacturing. The traditional mould costs are high, the production cycle is long, and the PEEK material is wasted during the machining process.

The flexural properties and interlaminar shear strength of PEEK moulded parts made by fused deposition modelling (FDM) forming technology are poor [11–13]. The edges of PEEK parts manufactured by FDM are easy to warp and deform, and the mechanical properties of PEEK parts are difficult to meet the requirements of using parts [14–18]. Traditional injection moulding is suitable for high-volume, standardized PEEK parts manufacturing. Individualized PEEK parts are injection-moulded with metal moulds, which have the disadvantages of high processing cost, serious material waste, low efficiency and cumbersome processes. Generally, the photocuring forming speed is fast, the photosensitive resin material used has thermosetting property, and the manufacturing precision can reach 0.1 mm or more [19].

✉ Xuewen Zong, zongw007@xust.edu.cn | [1]College of Mechanical Engineering, Xi'an University of Science and Technology, Xi'an 710000, China. [2]Institute of Adding Manufacturing Technology, Xi'an University of Science and Technology, Xi'an 710000, China. [3]State Key Laboratory for Mechanical Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an 710054, China.

SN Applied Sciences (2019) 1:1388 | https://doi.org/10.1007/s42452-019-1385-4

Received: 30 June 2019 / Accepted: 28 September 2019 / Published online: 12 October 2019

The process for quickly printing a mould using a stereolithography technique to inject individualized PEEK parts through a thermosetting photosensitive resin mould was proposed in this study. The finite element simulation experiment was done to evaluate the temperature change of resin mould during the injection process. The PEEK samples were injected, and nine groups of experiments were done; the orthogonal experimental results were analysed by variance analysis, and the optimum injection process parameters were obtained. Under these process parameters, the mechanical properties of PEEK parts are the best. Mechanical experiments were carried out on the samples with the best injection process parameters. The experimental results show that the strength of PEEK parts produced by this process meets all the mechanical properties' requirements. The experimental results prove that the injection process of PEEK parts by photosensitive resin mould is feasible, and the PEEK parts with good mechanical properties and complex shape can be obtained quickly by this process.

2 Experiment

2.1 Materials and methods

Differential scanning calorimetry (DSC) experimental equipment was DSC200F3 differential scanning calorimeter; the mould was made by Shaanxi Hengtong Intelligent Machine Co., Ltd., in SPR6000 photosensitive resin.

In the simulation experiment, finite element simulation was used to simulate the PEEK injection process, and ANSYS was used to simulate the temperature change process of the mould in the PEEK injection process. The resin used for 3D printing is a new material developed exclusively by Shaanxi Hengtong Intelligent Machinery Co., Ltd. According to the literature, SPR6000 is a light-cured printing material developed on the basis of ABS performance, and many properties are similar to ABS performance. In the case that the heat conduction parameters of SPR6000 cannot be obtained completely, some parameters are supplemented by the parameters of ABS materials.

The injection equipment and method of PEEK sample used in orthogonal experiment are as follows. The test equipment is BABYPLAST 610VP injection moulding machine. The heating temperature range of the injection moulding machine is from 0 °C to 400 °C, and the injection pressure range is from 0 bar to 150 bar. The PEEK granule used in the test is PEEK330G. The manufacturer is Zhongyan High Performance Engineering Plastics Co., Ltd. The average molecular weight of PEEK330G is 1.0×10^5. The injection temperature of PEEK is generally 360 °C to 380 °C. The injection process of individual PEEK parts is based on the experience of traditional injection PEEK. According to the parameters' range of the injection machine used, appropriate injection parameters are designed to test the injection performance of the mould.

Following is the orthogonal experimental injection mould design process. The properties of PEEK samples are evaluated by tensile strength. The mould structure of PEEK test sample was designed according to the required dimensions of tensile strength sample in GB/T 1040-2006 standard. The tensile strength standard is a symmetrical model with a simple structure. Using the maximum contour parting surface design, the upper and lower moulds have the same structure, which facilitates assembly interchangeability, saves resin usage and facilitates injection moulding installation operations. The thickness of a single mould cavity is 2 mm. After mould closing, it can be injection moulded to obtain PEEK tensile strength standard parts with a thickness of 4 mm. Other design dimensions of the standard parts are shown in Fig. 1. Mould closing mode is designed with dense bolt connection mode, which has higher closing strength, higher precision of injection parts and no problem of PEEK spillover along parting surface. The design mould model is completed by 3-matic software.

The PEEK mechanical properties of test samples are all made by injection moulding with resin mould. The injection parameters are obtained by orthogonal experimental variance analysis. The experimental equipment used in tensile mechanics experiment is CMT4304, a multifunctional static experimental machine of the State Key Laboratory of Mechanical Manufacturing System Engineering. According to GB/T 1040-2006 plastic tensile test standard, PEEK injection mould was designed and manufactured by light curing technology. According to the standard of GB/T 9341-2008 for measuring the bending properties of plastics, the bending strength experiment designed the sample size of 80 mm × 10 mm × 4 mm, and the experimental instrument was a multifunctional static testing machine. The impact strength experiment chooses experimental instruments: XJJ50 impact test prototype, no notch simply supported beam impact test machine. PEEK impact strength sample size standard is 80 mm × 10 mm × 4 mm,

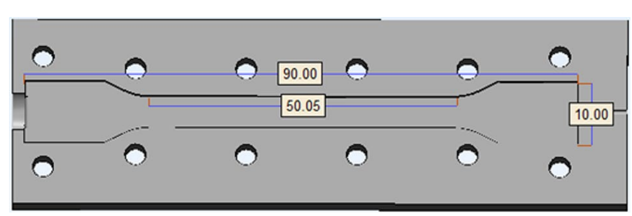

Fig. 1 Tensile strength standard parts mould and relevant dimensions

pendulum impact energy is 7.5 J, and sample cross-sectional area is 40 mm^2.

A finite element model of PEEK injection moulding is established. In this study, PEEK injection moulding process is studied, which is mainly the close contact between PEEK melt colloid and moulds. Heat conduction is the main heat transfer mode, and Fourier's law is followed:

$$q = -\lambda \frac{dT}{dx}$$

where λ is the heat conductivity, $\frac{dT}{dx}$ is the temperature gradient, and q is the heat flux.

The heat transfer process can be divided into two types: steady-state process and unsteady-state process, according to whether the temperature change of the object is time dependent or not. The heat transfer process simulated by the finite element model is unsteady heat transfer process, and the temperature of the polymer die increases first and then decreases with the cooling of PEEK.

2.2 Experiment

The solidification process of PEEK undergoes a phase change from melt state to solid state, and the composition of SPR6000 material is confidential. In order to simulate the heat transfer in PEEK injection process, the following simplified model is established on the basis of reasonable assumptions: the mould will not soften, change or change the shape and position at high temperature, and the density is uniform and isotropic. PEEK melt colloid fills the die cavity completely and contacts closely. The density is uniform and isotropic. The influence of different crystallization rates of PEEK on the density was neglected, and the average density in the forming temperature range was calculated. The latent heat of phase transformation is taken into account when the material is transformed from melt state to solid state. The latent heat is treated by equivalent hot melting method, assuming that the latent heat is uniformly released. The thermal conductivity and specific heat capacity of SPR6000 refer to ABS.

The finite element simulation model is established. The structure of individual PEEK parts and injection moulds is complex, and it is difficult to generate high-quality finite element meshes. In order to obtain high-quality meshes and improve the accuracy of finite element simulation, the finite element model is 2-D: the square with 60 mm edge represents the resin mould, and the circle with 12 mm diameter represents the PEEK part in the centre. The mould temperature was set to 25 °C at normal temperature; the molten PEEK colloid temperature was set to 380 °C; the finite element unit was selected as Plane 55. A quarter of the model was used for the analysis. The photosensitive resin used in the PEEK 450G and 3D printing in the experiment was an injection-moulded pellet with standard parameters. The thermal conductivity, specific heat capacity and density were found according to the literature [20]. The material parameters of the finite element model are shown in Table 1.

Table 1 Material parameters of heat transfer model

Thermal properties	Unit system	PEEK	SPR6000 (class ABS)
Thermal conductivity	W/(m °C)	0.29	0.18(ABS)
density	Kg/m^3	1300	1200
Specific heat capacity	J/(kg °C)	2200	1300(ABS)

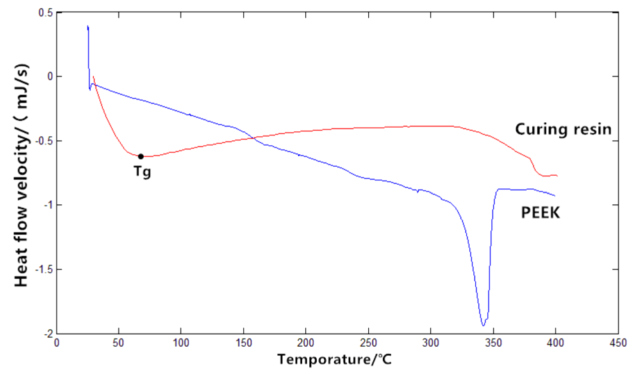

Fig. 2 DSC heat absorption diagram of PEEK and photosensitive resin mould

Firstly, the time integration was closed and the steady-state analysis was carried out to obtain the initial temperature field of the transient analysis, and then the transient analysis was carried out. We opened time integral, set the time of transient analysis to 1800, set the time step of load step to 30, minimum 2, maximum 200; automatic time step opening removed the temperature load applied in steady-state analysis.

3 Results and discussion

3.1 DSC experimental results and analysis

Amorphous polymers have three mechanical states, namely glassy, highly elastic and viscous. According to the DSC curve of the experimental results of the photosensitive resin mould and the PEEK sample, the glass transition temperature (T_g) of the photosensitive resin is 71 °C as shown in Fig. 2, and the endothermic decomposition is started at about 400 °C, and the PEEK melting temperature is 343 °C. According to the injection temperature of PEEK, it can be inferred that as the PEEK melt colloid falls from the high temperature of 380 °C, the resin mould will be softened to some extent, and even a certain degree of pyrolysis and deterioration will occur [21]. Since the volume of the resin mould is much larger than the volume of the PEEK part, it is not certain that the PEEK injection moulding will cause the resin core to directly soften and collapse, which requires experimental verification.

During the injection process, most of the heat of PEEK melt is transferred to the mould, and the other part is discharged into the air through the exhaust holes. During the injection process, the heat in the mould is limited. When the melt fills the mould, the heat does not increase. The exhaust hole is located at the last position of the melt, which ensures the exhaust of gas and the forming of parts. The diameter of the exhaust hole is generally 0.7 mm.

3.2 Analysis of simulation results

The heat transfer finite element simulation results of PEEK for resin injection moulding are shown in Fig. 3a–h. Set t as loading time and take simulation screenshots of different loading times.

The density and size of contours in temperature field cloud picture are divided according to glass transition temperature (71 °C) and PEEK melting temperature (343 °C) of resin mould. Temperature field cloud picture: PEEK did not solidify at 380 °C–343 °C and PEEK solidified at 343 °C–190 °C. When the temperature is between 190 °C and 71 °C, the mould is higher than the glass transition temperature, and the mould of this part may be deformed. When the temperature is between 71 °C and 25 °C, the mould does not reach the glass transition temperature.

Figure 3b shows that the temperature at the edge of the contact between the PEEK melt and the mould has exceeded 71 °C, at which time the surface layer of the mould has softened and the softening thickness is increased; Fig. 3c shows that the outer layer of PEEK decreases below the melting point (343 °C), and PEEK begins to solidify and its thickness increases continuously. Figure 3d shows that the temperature of the mould is mostly below the glass transition temperature (71 °C). Figure 3e shows that at the loading time $t = 33$ s, the PEEK temperature drops below 343 °C and the PEEK sample is completely solidified.

As the resin on the inner surface of the mould begins to soften, the outer surface of the PEEK solidifies a solidified shell, making it possible to mould the PEEK parts with a resin mould. Since PEEK has less injection volume and less total heat loss, the softening speed of the mould is lower than the solidification speed of PEEK. Most of the temperature of the mould is below 71 °C, which can maintain the shape characteristics of the mould. The softening resin and PEEK parts inside the mould are in extrusion state, which is conducive to the formation of PEEK parts. Therefore, it is theoretically feasible to inject PEEK parts with resin mould.

3.3 Orthogonal experiment and result analysis

According to the experience of traditional PEEK injection moulding, injection temperature, injection pressure and injection speed have the greatest influence on the mechanical properties of PEEK products. Therefore, the orthogonal experiment chooses three factors as variables: injection temperature (°C), injection pressure (MPa) and injection speed (%). Each variable is designed at three levels, as shown in Table 2 [22].

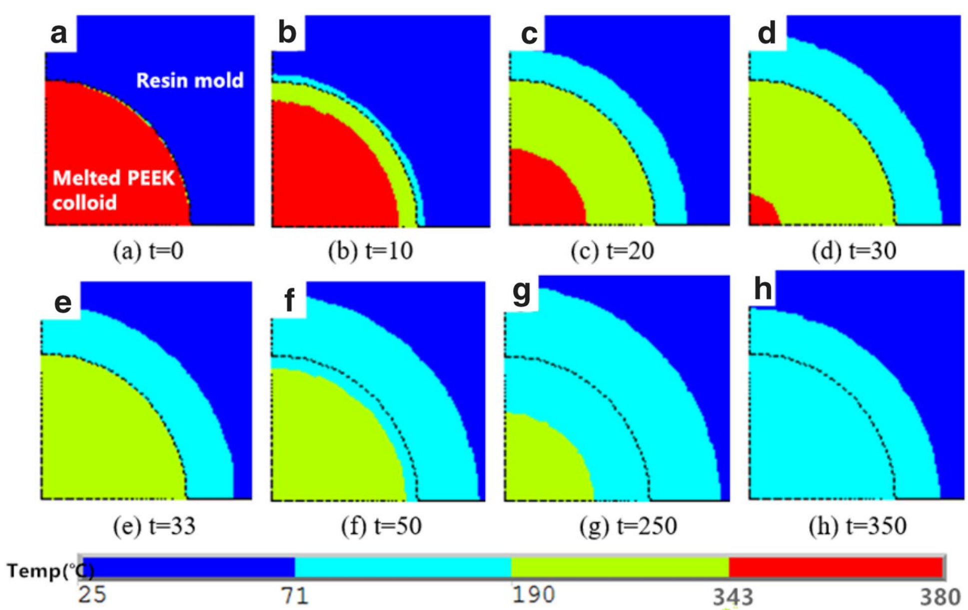

Fig. 3 Temperature field nephogram of die with different loading times

Table 2 Selection table of orthogonal test parameters

	Injection temperature/°C	Injection pressure/MPa	Injection speed/%
1	360	9	50
2	373	11	70
3	385	12.5	90

According to the orthogonal test parameter table, the optimum injection parameters of polymer core injection PEEK were explored. Nine groups of injection PEEK experimental parameters, each group of parameters need to be injection moulded 5 PEEK standard samples. Tensile standard samples were obtained by 3D printing resin mould and PEEK injection experiment. LCD1100 is chosen as resin. BABYPLAST 610VP Injection Moulding Machine is shown in Fig. 4a. The mould before injection is shown in Fig. 4b. The mould after injection is shown in Fig. 4c. PEEK samples were obtained by injection moulding of resin mould, as shown in Fig. 4d.

The mechanical tensile test equipment is a multifunctional static test machine of the State Key Laboratory of Mechanical Manufacturing System Engineering. Tensile strength data of PEEK samples manufactured by nine groups of injection parameters were obtained by stretching. Mean values of five tensile strength data were taken as evaluation criteria for the same injection parameters, and orthogonal test results are given in Table 3.

Tensile strength results of nine groups of orthogonal experiments were analysed by variance analysis. The variance analysis results are shown in Table 3. The results of orthogonal experiment show that injection temperature and injection pressure have the greatest influence on the strength of injection parts, while injection speed has little effect. The PEEK sample obtained by core injection has the best tensile strength when the injection temperature was 373 °C, the injection pressure was 11 MPa, and the injection speed was 70%.

Table 3 Orthogonal test results and analysis

	A Injection temperature/°C	B Injection pressure/MPa	C Injection speed/ %	Mean tensile strength/MPa
1	360	9	0.5	78.86 ± 2.53
2	360	11	0.7	72.8 ± 1.87
3	360	12.5	0.9	69.45 ± 3.87
4	373	9	0.7	80.1 ± 1.66
5	373	11	0.9	86.72 ± 0.98
6	373	12.5	0.5	74.2 ± 4.53
7	385	9	0.9	71.08 ± 2.93
8	385	11	0.7	71.38 ± 2.02
9	385	12.5	0.5	68.2 ± 3.8
I	221.11	230.04	221.26	
II	241.02	230.9	224.28	
III	210.66	211.85	227.25	
K1	73.70	76.68	73.75	
K2	80.34	76.97	74.76	
K3	70.22	70.62	75.75	
R	10.12	6.35	2	

3.4 Mechanical Experiments and Result Analysis

The optimum injection parameters obtained by orthogonal experiments were used to inject PEEK mechanical experimental samples. The experimental data of tensile strength of PEEK samples are shown in Fig. 5a. The experimental results show that the average tensile strength is 96.4 ± 2.28 MPa, the elongation at break of the specimens

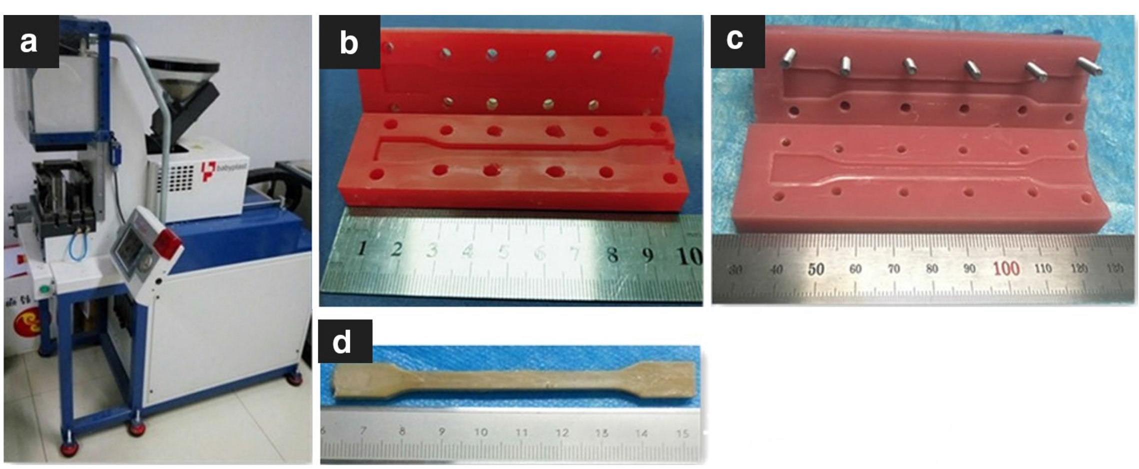

Fig. 4 **a** Injection machine, **b** resin mould before injection, **c** resin mould after injection, **d** orthogonal test PEEK sample

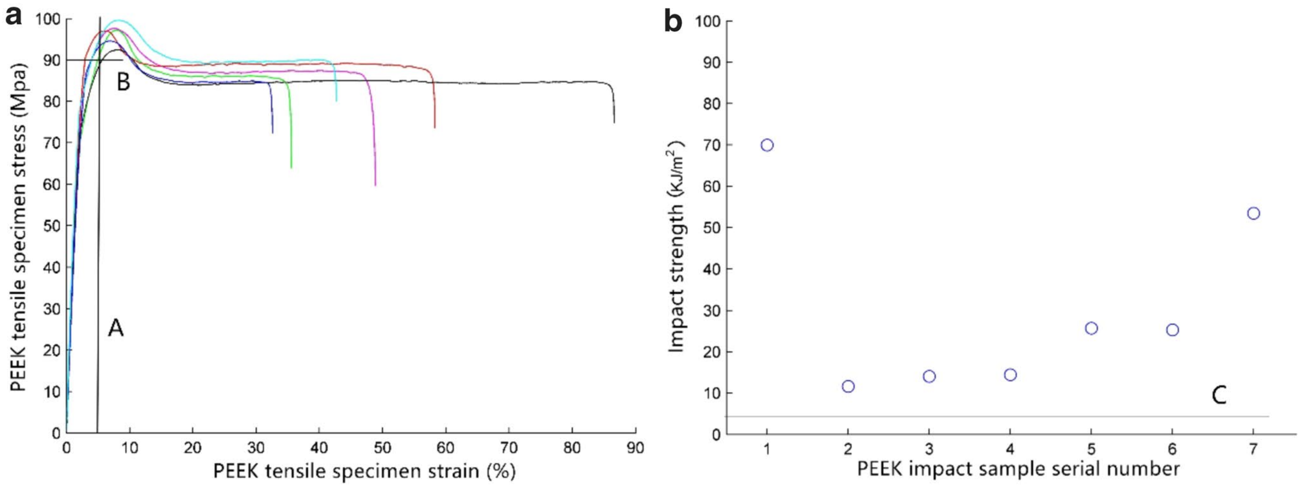

Fig. 5 Experimental results: **a** stress–strain curve diagram of tensile samples. **b** shock test distribution spot diagram (A is the lowest standard line of elongation at break, B is the lowest standard line of tensile strength, and C is the lowest standard line of impact strength)

is above 30%, and the average is 50.7 ± 18.1%. Obviously, the minimum tensile strength is 90 MPa with reference to ISO 527, the minimum elongation at break is 5% with reference to ISO 527, type 1B, the PEEK specimen meets the tensile standard of PEEK polymer: the elongation at break is not less than 5%, and the tensile strength is the lowest of 90 MPa.

The experimental results show that the bending strength and flexural modulus of the sample are 147.654 ± 9.36 MPa and 3.344 ± 0.255 GPa. The minimum bending strength is 110 MPa with reference to ISO 178, and the minimum flexural modulus is 3 GPa. The bending strength standard of PEEK polymer is as follows: the lowest bending strength is 110 MPa, and the bending modulus is not lower than 3GPa. PEEK impact strength sample size standard is 80 mm × 10 mm × 4 mm, pendulum impact energy is 7.5 J, and sample cross-sectional area was 40 mm^2. The experimental results are shown in Fig. 5b, and the impact strength was higher than 10 kJ/m^2. The minimum notched impact strength is 4/KJ/m^2 with reference to ISO180. The impact strength standard for PEEK polymers is as follows: notched impact strength is not less than 4 kJ/m^2. All the experimental results are higher than the minimum standard, which shows that the mechanical properties of the sample are up to the standard, and the PEEK sample is successfully injected by resin mould.

4 Conclusion

In this study, the simulation software ANSYS was used to analyse the temperature change of the PEEK injection mould. It was concluded that the resin mould can withstand the PEEK injection temperature of 380 °C. The optimum parameters of injection moulding were obtained by orthogonal experiments. The mechanical properties of PEEK samples were tested by mechanical experiments. The results showed that the mechanical properties of PEEK samples conformed to the standard of PEEK parts. This study presents and proves that resin mould with low glass transition temperature can be used for injection moulding of PEEK parts with high melting point, and samples with good mechanical properties have been obtained. The PEEK parts with complex shape and strength can be obtained quickly by the injection process in this study.

Acknowledgements This research was supported by Natural Science Foundation of China (No. 51875452,51675416) and the National Key Research and Development Program of China (2018YFB1106904).

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interest

References

1. Zhou H, Goel VK, Bhaduri SB (2014) A fast route to modify biopolymer surface: a study on polyetheretherketone (PEEK). Mater Lett 125:96–98
2. Wang L, Weng L, Song S, Sun Q (2010) Mechanical properties and microstructure of polyetheretherketone–hydroxyapatite nanocomposite materials. Mater Lett 64(20):2201–2204
3. Oliveira TP, Silva SN, Sousa JA (2018) Flexural fatigue behavior of plasma-sprayed hydroxyapatite-coated polyether-ether-ketone (PEEK) injection moldings derived from dynamic mechanical analysis. Int J Fatigue 108:1–8
4. Ma R, Weng L, Bao X, Ni Z, Song S, Cai W (2012) Characterization of in situ synthesized hydroxyapatite/polyetheretherketone composite materials. Mater Lett 71:117–119

5. Puhan D, Wong JS (2019) Properties of Polyetheretherketone (PEEK) transferred materials in a PEEK-steel contact. Tribol Int 135:189–199
6. Järvinen S, Suojanen J, Kormi E, Wilkman T, Kiukkonen A, Leikola J, Stoor P (2019) The use of patient specific polyetheretherketone implants for reconstruction of maxillofacial deformities. J Cranio-Maxillofac Surg 47(7):1072–1076
7. Panin SV, Anh ND, Kornienko LA, Alexenko VO, Buslovich DG, Ovechkin BB (2018) Wear-resistant polyetheretherketone composites: with carbon nano-and microfibers. Mater Today Proc 5(12):25976–25982
8. Schwitalla AD, Zimmermann T, Spintig T, Kallage I, Müller WD (2017) Fatigue limits of different PEEK materials for dental implants. J Mech Behav Biomed Mater 69:163–168
9. Ma J, Xue Y, Liang X, Liao C, Tan Z, Tang B (2019) Bi-directional regulatable mechanical properties of 3D braided polyetheretherketone (PEEK). Mater Sci Eng C 109811
10. Liu K, Zhang X, Zhou K, Shi L, Chen Z, Li W, Chen P (2019) Scaffolds Prepared with Bovine Hydroxyapatite Composites by 3D Printing. J Wuhan Univ Technol-Mater Sci Ed 34(1):230–235
11. Wu W, Jiang J, Jiang H, Liu W, Li G, Wang B, Zhao J (2018) Improving bending and dynamic mechanics performance of 3D printing through ultrasonic strengthening. Mater Lett 220:317–320
12. Zuo Z, Gong J, Huang Y, Zhan Y, Gong M, Zhang L (2019) Experimental research on transition from scale 3D printing to full-size printing in construction. Constr Build Mater 208:350–360
13. Yang W, Jian R (2019) Research on intelligent manufacturing of 3D printing/copying of polymer. Adv Ind Eng Polym Res
14. Dawoud M, Taha I, Ebeid SJ (2016) Mechanical behaviour of ABS: an experimental study using FDM and injection moulding techniques. J Manuf Proces 21:39–45
15. Sood AK, Ohdar RK, Mahapatra SS (2010) Parametric appraisal of mechanical property of fused deposition modelling processed parts. Mater Des 31(1):287–295
16. Rodríguez JF, Thomas JP, Renaud JE (2003) Mechanical behavior of acrylonitrile butadiene styrene fused deposition materials modeling. Rap Prototyp J 9(4):219–230
17. Pham DT, Gault RS (1998) A comparison of rapid prototyping technologies. Int J Mach Tools Manuf 38(10–11):1257–1287
18. Vega V, Clements J, Lam T, Abad A, Fritz B, Ula N, Es-Said OS (2011) The effect of layer orientation on the mechanical properties and microstructure of a polymer. J Mater Eng Perform 20(6):978–988
19. He F, Wang Y, Huang Y, Wan Y (2006) Preparation and mechanical properties of 3-D braided glass fiber reinforced light-cured resin composites. Mater Lett 60(28):3339–3341
20. Fu G, Liu H, Zhang B, Han Gu (2006) Characteristics and application of PEEK (Doctoral dissertation)
21. Mirkhalaf SM, Pires FA, Simoes R (2017) Modelling of the post yield response of amorphous polymers under different stress states. Int J Plast 88:159–187
22. Zhao C, Zhang Y (2008) Polyetheretherketone