Prog Addit Manuf (2017) 2:117–123
DOI 10.1007/s40964-017-0023-1

FULL RESEARCH ARTICLE

The manufacture of 3D printing of medical grade TPU

Jianhua Xiao[1] · **Yanfeng Gao**[1]

Received: 29 September 2016 / Accepted: 24 April 2017 / Published online: 8 May 2017

Abstract There is a critical need for developing medical grade polymer filament to be used for 3D printing. In this work, a new filament made by medical grade thermoplastic polyurethanes (TPU) was produced by a single-screw extruder, and then tensile dumbbell specimens were printed by a fused deposition modeling (FDM) machine. In the FDM process, the effects of the orientation angle and printing temperature on part quality were studied. For each process, we aimed to achieve good quality parts by evaluating their tensile strength and break elongation. Microstructure analyses were performed on the dumbbell center and fracture surface of the tensile specimens, through the use of USB dignity microscopy. TPU specimens with the best mechanical properties made by FDM have 46.7 MPa tensile strength and 702% break elongation; they were processed under the condition of 215 °C temperature and a 45° orientation angle.

Keywords Medical grade TPU · 3D printing · Tensile test · Dumbbell specimen · FDM

1 Introduction

FDM, using a layer-based approach, is a solid free-forming technology for various applications [1]. Due to its ability to produce complex geometrical parts for personalized customization, it has been widely used for rapid prototyping technology, especially in medicine and health care [2–6], such as the fabrication of customized implants and scaffolds for rehabilitation, human bone techniques, and drug delivery device fabrication.

However, poor mechanical properties of fabricated parts have always been a major issue that restricts their medical applications. Ozan et al. [7] studied the effects of softeners on the PLA filament yarns derived from corn starch. The iconicity softener appeared not to play a significant role. Wu et al. [8] reported that using 1 wt% nano-SiO_2 modified by KH-550 of PLA filament could improve the break elongation to 33.36%. Randa and Selling [9] pointed out that the tensile strength of PLA/Starch composite filaments, with the draw ratio 2:1, can be increased to 92 MPa, and the break elongation can be improved to 136%. Apart from PLA, PCL is usually used to fabricate bone tissue engineering scaffolds because of its biodegradability [10]. Zein et al. [11] found that the compressive strength of PCL could reach 4–77 MPa, and the yield strength can reach 0.4–3.6 MPa, depending on the pore size and porosity. Hutmacher and Cool [12] found that during the FDM process of the PCL scaffold, the compressive strength could vary from 2.4 to 20.2 MPa due to different pore structures. Qing et al. [13] chose composite materials of PCL–HA (mass ratio 7:3) to construct the scaffolds; the maximum pressure value was 472 ± 20N. While the PLA and PCL biodegradable materials showed some defects in their elasticity properties, there is a very critical need for the development of new medical grade polymers to be used for 3D printing machines. But hitherto, only a limited amount of work has been reported on the development of new materials to replace PLA and PCL, which are presently used in most FDM machines for medical applications.

In this paper, we have presented a medical grade polymer TPU to process filament for FDM printing technology.

✉ Jianhua Xiao
xjh3500021002@163.com

[1] School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang, People's Republic of China

Firstly, medical grade TPU is processed into filament that is compatible to the FDM process. Process parameters in fabricating the TPU filament are studied, in order to guarantee the filament's quality for 3D printing. Following this, we investigated the impact, of different FDM process parameters such as tensile strength and break elongation, on quality. The microstructure of tensile specimens revealed different fracture modes related to the process parameters. Lastly, the effects of TPU process parameters on the mechanical properties of 3D printing of a dumbbell specimen were also analyzed.

2 Experimental section

2.1 Materials

Medical grade TPU was purchased from Lubrizol Advanced Materials Inc. The type of Tecoflex LM-95A is an aliphatic polyether-based thermoplastic polyurethane. It is a semi-crystal polymer. The density is 1.10 g/cm^3, and tensile strength is assessed as 49.99 MPa with the ASTM D412 test method.

2.2 Processing

2.2.1 Extrusion TPU filament

TPU is hygroscopic, and will absorb and retain water from the air. Therefore, prior to processing, it should be dried at 45 °C for 4–8 h under vacuum conditions. Depending on the applied processing technique, the maximum moisture level should be 0.10%.

A single-screw extruder (Yiyang plastic machine Co, China, SJ-20), with a screw diameter of 20 mm and *L*/*D* ratio of 24 was used to extrude the TPU filament. The die is *L*/*D* = 30, with diameter 1.3 mm. Figure 1 shows the extrusion equipment.

Fig. 1 TPU filament extrusion equipment

Table 1 shows the setting of the TPU extrusion parameter values. The melt temperature is 176 °C, assessed by DSC detection; it is preferable for the extrusion temperature to be 10–20 °C higher than the melting point. Higher temperatures result in a melt viscosity level lower than that needed to maintain a viable form when exiting the die. Also, temperatures higher than 210 °C may cause polymer degradation as evidenced by bubble formation within the TPU melt.

2.2.2 TPU 3D printing

The 3D printing machine that we used is a MakerPi M14 (Shenzhen Soongon Technology Co., Ltd). The process parameters of this machine have been modified to print TPU material. Table 2 shows the parameter values of 3D printing TPU material. The extruding temperature should exceed the melting temperature of the TPU to guarantee that the TPU filament is molten, and can be smoothly squeezed out from the nozzle. If the extruding temperature is not high enough, the TPU may have high viscosity, leading to difficulty in filament extrusion. In fact, 180 and 190 °C have been used to write the TPU model by 3D printing, but no material flowed out through the nozzle because of the short duration of heating. Therefore, the nominal values of the extruding temperature were set to 200, 215, and 230 °C, higher than the melting temperature.

To evaluate how 3D printing parameters affect printing quality, a dumbbell model shown in Fig. 2 is used. Two samples of a fabricated TPU dumbbell model are shown in Fig. 2c. For the sample on the left side, the orientation angle is 0°, and for the sample on the right side is 45°. The infill percentages for all printing samples are set to 100%. In this research, the quality of the printed part is assessed by tensile strength and break elongation.

2.3 Characterization methods

Tensile strength tests were conducted on a tensile instrument 5567 (Instron, Norwood, USA) with a speed of 500 mm/min at 25 °C. The mean value of five replicated measurements was taken for each sample.

Table 1 TPU extrusion parameters values

Parameters	Values
Zone 1 (°C)	190
Zone 2 (°C)	195
Zone 3 (°C)	200
Die head (°C)	200
Screw speed (rpm)	10

Table 2 Primary parameters of 3D printing machine MakerPi M14

Parameters	Values
Printing temperature (°C)	200, 215, 230
Build plate temperature (°C)	20–25
Printing speed (mm/s)	120
Nozzle diameter (mm)	0.40
Layer thickness (mm)	0.20
Fill percentage (%)	100

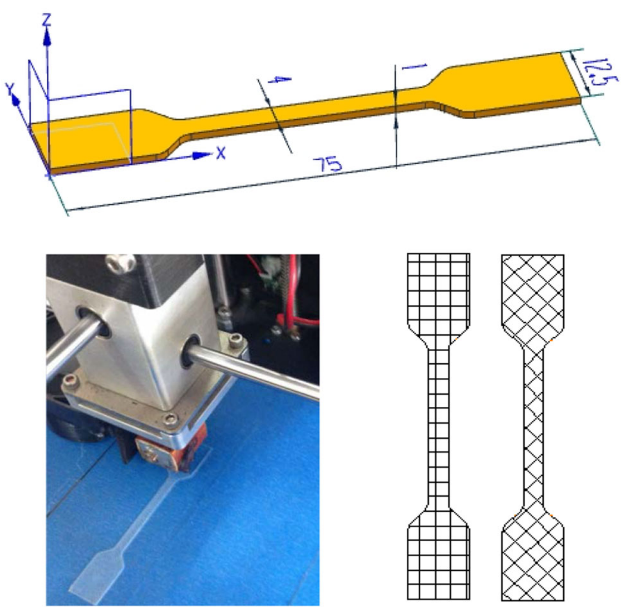

Fig. 2 Dumbbell model design (**a** model, **b** FDM print model, **c** orientation angle 0° and 45°)

Microstructure and fracture cross-sectional images of the dumbbell samples were obtained using a USB digital microscope (OEM CO, China, AM204); this microscope magnifies an object 220 times.

3 Fabrication of TPU filament

The postprocessor for extruding the TPU filament is illustrated in Fig. 3.

The diameter of the TPU filament should be controlled to 1.75 mm to meet the requirement of FDM printing. Figure 3 shows the process of cooling and rolling of TPU filament. When the TPU melt flows out of the extrusion die, it is still in a viscous flow state. At this moment, the material modulus is very small and easy deformation. The enamel tray is placed about 10 cm under the extrusion die. If this distance is too large, the diameter of the TPU filament would become smaller than 1.75 mm under the action of gravity. If the distance is too small, the time of polymer melt leaving extrusion die is too short, so that the material is still sticky and easy to cohere together. When the extruded filament is deposited on the tray, it is semi-cooled by heat conduction to the tray, and heat convection to the surrounding air. After the filament has been on the tray for several seconds, it has been fully cooled and can be rolled.

Fig. 3 Extruded TPU filament through single-screw extrusion

All the TPU filaments produced by a single-screw extruder were packed in a plastic bag for FDM printing, as shown in Fig. 3.

4 TPU 3D printing

Figure 4 shows the FDM prints of TPU dumbbell parts with orientation angles 0° and 45° at printing temperatures of 200, 215, and 230 °C. The first layer thickness is set to 0.30 mm to add adhesion to the platform of the FDM machine, then other layer thicknesses are set to 0.20 mm; every dumbbell specimen is printed to five layers. It is clear that the orientation angle of the first and second layer, and two adjacent layers, is arranged at 90°.

4.1 Tensile test result

Figure 5 shows the tensile strength and break elongation of TPU specimens made by 3D printing, with different printing temperatures and orientation angles. Detailed values are shown in Table 3.

Figure 5 explores the relationship between the tensile test results and printing temperatures. From Fig. 5, it can be seen that the tensile strength at the break of the samples first increased then slowly decreased with increasing printing temperature of TPU, for both orientation angles 0° and 45°. The printing temperature was controlled at 215 °C; the tensile strength of TPU by 3D printing reached the highest values with 46.7 MPa tensile strength and 702% break elongation. TPU is a kind of temperature–sensitivity polymer [11], and if the nozzle temperature is controlled at 230 °C, the temperature may be too high to

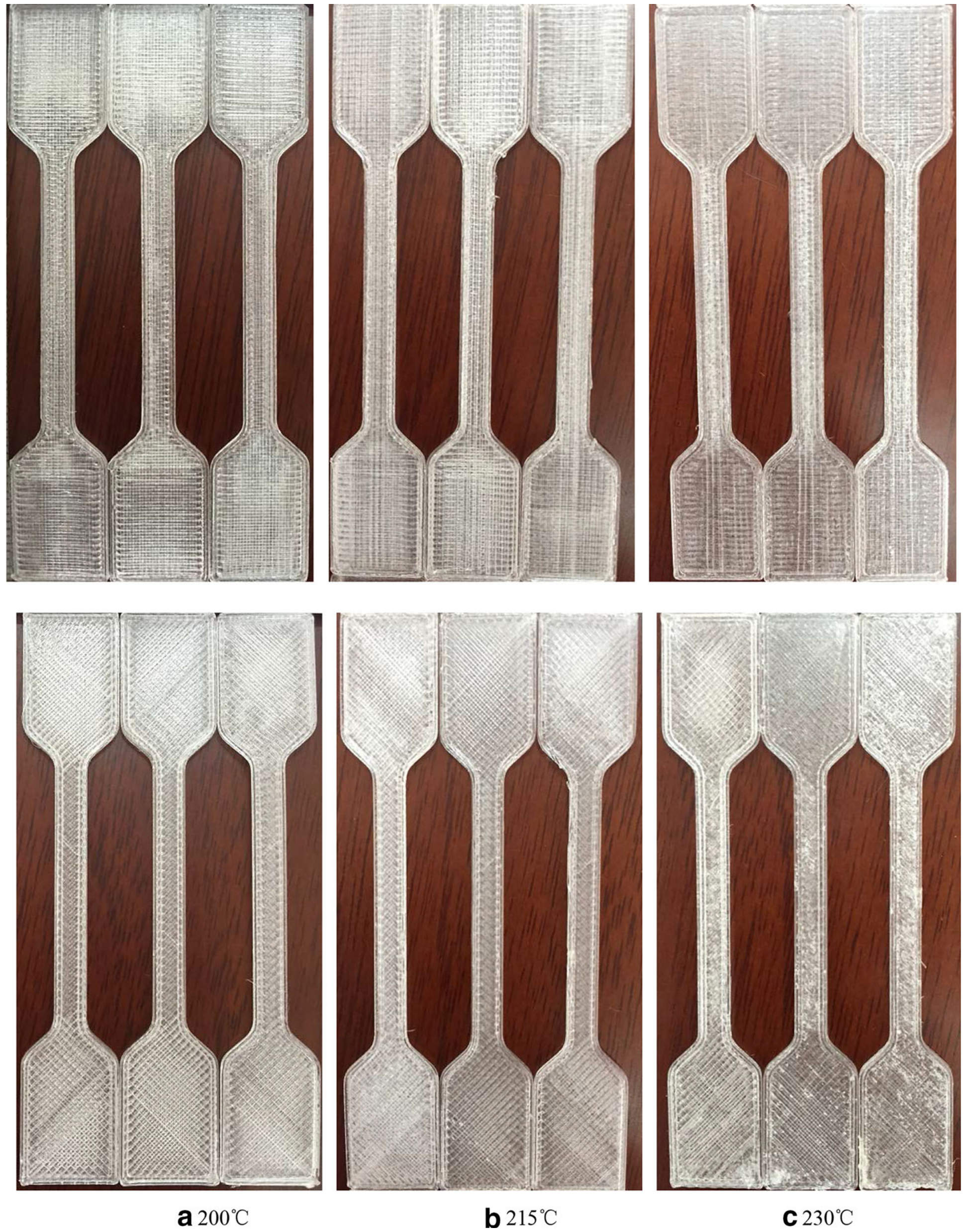

Fig. 4 FDM print of a TPU dumbbell model in different printing temperatures with orientation angles 0° and 45°, respectively

result in few instances of TPU thermal degradation and, therefore, the tensile strength may slightly decrease.

4.2 Orientation angle

The orientation angle has an effect upon tensile strength and break elongation. At all printing temperature settings (including 200, 215, and 230 °C), the tensile strength of TPU samples printed with 45° orientation angle is higher than the strength for the 0° orientation angle. Examining Fig. 6 may give an explanation.

Figure 6 shows the microstructure of the dumbbell center surface of the TPU 3D print with different orientation angles. In Fig. 6, all the specimens were magnified 220 times by using a USB digital microscope. The center surface of the TPU dumbbell specimens has been observed for comparison purposes. Figure 6a–c shows the orientation angle of 0°, while Fig. 6d–f shows the orientation angle of 45°. There are three typical stages in tensile testing: before stretching, stretching, and after stretching.

In Fig. 6a, d, the TPU dumbbell is at the stage of before stretching. The width of the specimen is 4 mm. In Fig. 6b, e, the TPU dumbbell is at the stage of stretching. The specimen is highly stretched, the deformation is nearly 300%, and the width of specimen becomes thin. From the picture, it appears to be about 1/2 of the width before stretching. In Fig. 6c, f, the TPU dumbbells are at the stage of after stretching. All the tensile stresses applied to the

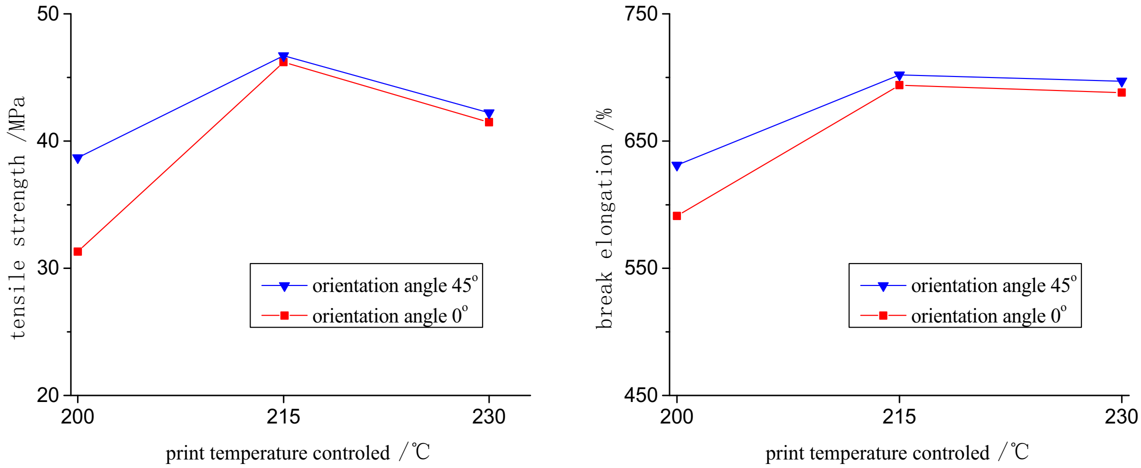

Fig. 5 TPU tensile test by 3D printing in different parameters (**a** tensile strength; **b** break elongation)

Table 3 Tensile test of TPU dumbbell specimens by 3D printing

Printing temper (°C)	Orientation angle (°)	Tensile strength (MPa)	Elongation at break (%)
200	0	31.3	591
215	0	46.2	694
230	0	41.5	688
200	45	38.7	631
215	45	46.7	702
230	45	42.2	697

specimens have disappeared, specimens were in an unstressed state, and specimens have reverted from the highly stretched state to the lowest energy state. Elastic deformation is restored, but a small amount of plastic deformation is difficult to retrieve after the high stress and high tensile deformation. The width of the specimen has become larger. From the picture, it appears to be about 3/4 of the width of before stretching.

All the specimens were printed to five layers. In Fig. 6a, the orientation angle of one layer is set to 0°, the other layer is set to 90°, and five layers are overlapped together.

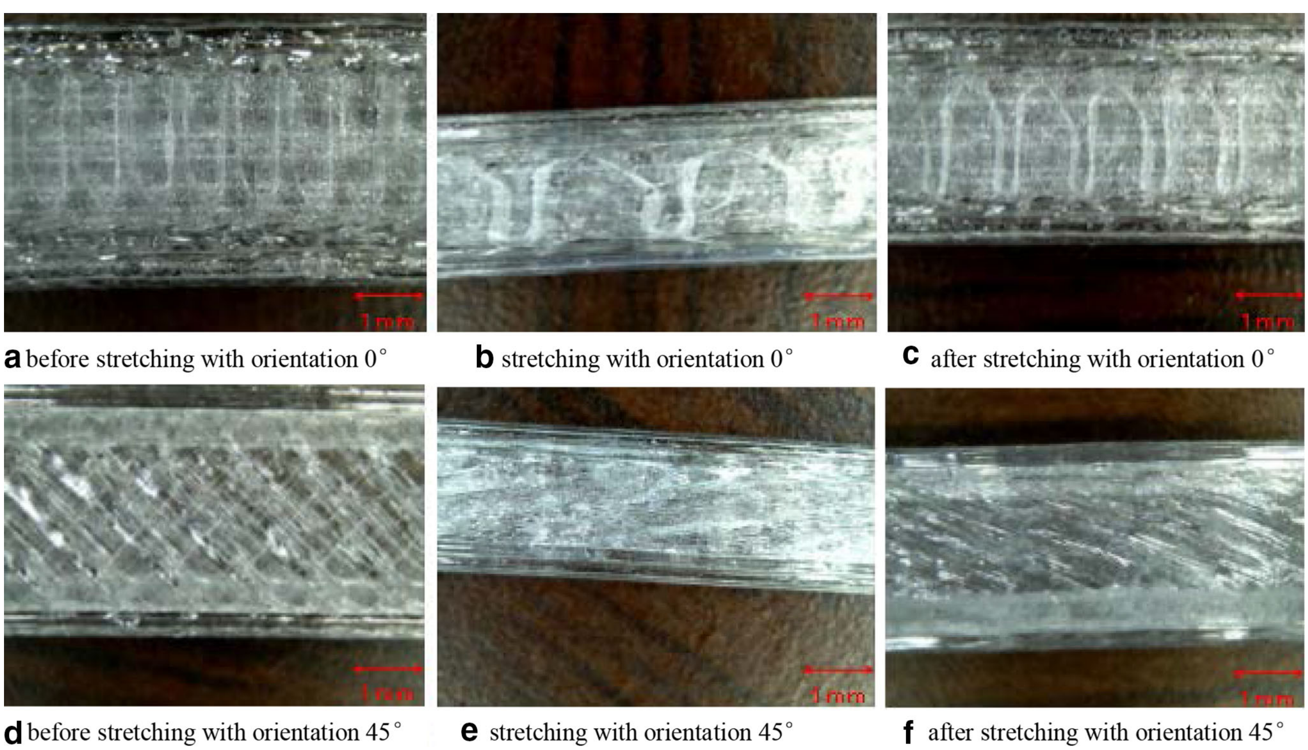

Fig. 6 Microstructure of TPU dumbbell specimen center with different orientation angles

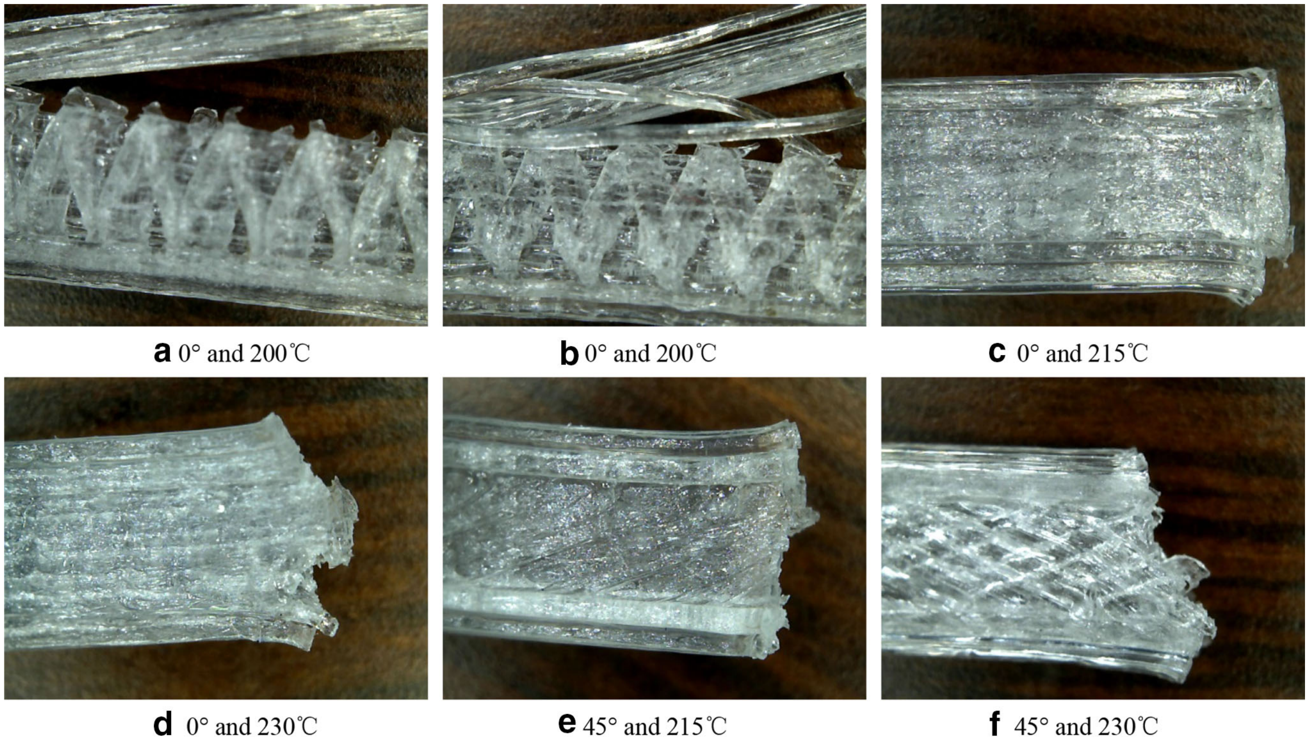

Fig. 7 Microstructure of fracture surfaces in 3D printing TPU with different orientation angles and nozzle temperatures

The intervals between two adjacent filaments are very small, essentially closed together. When the specimen was highly stretched under high stress, the filaments lying parallel to the stretching direction became strongly oriented along the direction of force, and the filaments lying perpendicular to the stretching direction were also strongly oriented along the direction of the force, while the gap between two adjacent filaments with a 90° orientation angle became bigger. When the stress disappeared, the material recovered, and the gaps between two adjacent filaments became smaller. The specimens with 45° orientation angle experience the same situation as the specimens with 0° orientation angle. In Fig. 6d, the orientation angle of one layer is set to +45°, while another layer is set to −45°, and five layers are overlapped together. When the specimen is highly stretched, the orientation angles change to nearly ±0°, and all the filaments are oriented parallel to the stress direction, which may explain why the specimen with a 45° orientation angle has higher tensile strength and break elongation than the specimen with 0° orientation angle.

4.3 Printing temperature

Table 3 shows that printing temperature may have a great impact on tensile performance. The specimen printed at 200 °C with orientation angle 0° has 31.3 MPa tensile strength and 591% break elongation. The specimen printed at 200 °C with orientation angle 45° has 38.7 MPa tensile strength and 631% break elongation. Contrary to other specimens made from the third to the sixth processing parameters, it has lower strength and elongation. The other four specimens printed at 215 and 230 °C have larger values with tensile strength from 41.5 to 46.7 MPa, and elongation from 688 to 702%. Some explanation can be obtained by examining Fig. 7.

Figure 7 displays the microstructure of fracture surfaces in 3D printing TPU with different orientation angles and printing temperatures. All the fractures occurred in the center of the dumbbell specimen. Strong adhesion between five layers avoids the lamination phenomenon in the broken head. Considering the broken head as a whole, the fact of no significant lamination appears to prove that TPU parts have good adhesion between layers.

Figure 7a, b shows the fracture surface of the specimen printing at 200 °C with a 0° orientation angle. The edge of the dumbbell-shaped specimen has 0° orientation angle, which is parallel to the stretching direction. Under a highly stretched condition, the edges of the specimens sustain large deformation, while the interior of the specimen sustains relatively small deformation due to the restriction of 90° orientation angle. The deformation in the edge and in the interior of specimen is not along the stretching direction, and internal stress is generated at the interface of the edge and the interior junction. If this internal stress is greater than the thermal bonding between the edge and the interior junction, cracking and rupturing will occur. After rupturing and cracking between the edge and the center of the specimen, the actual effective area that endures the tensile stress will be decreased, resulting in reductions, at 200 °C and 0°, to break strength and elongation of the dumbbell-shaped specimen.

Figure 7c, f shows some of the typical fracture surfaces of the specimens printed at 215 °C with 0° orientation, 230 °C with 0° orientation, 200 °C with 45° orientation, 215 °C with 45° orientation, and 230 °C with 45° orientation. The fracture surfaces are very similar, some cross-sections are flat, and some are uneven. When the temperature is raised to 215 °C or 230 °C, the thermal bonding between the edges and the interior of the specimen are reinforced. Because the thermal bonding is greater than the internal stress, rupturing and cracking will not occur anymore. Compared to 200 °C, the tensile strength and break elongation at 215 or 230 °C have been greatly improved. If the orientation angle was changed from 0° to 45°, things would become better still. Despite the deformation at the edge and interior of the specimen being unequal, there is smaller restriction and lower internal stress from 45° orientation filament than from 90°, and no rupture occurs at the junction of the edge and interior of the specimen.

5 Conclusion

Medical grade TPU has natural translucent, good biocompatibility and superior strength, so it has a potential application to produce medical devices and surgical tools. In this paper, TPU material was used to produce 1.75 mm filament through a single-screw extruder, then TPU filament was printed at different parameters by FDM machine. The effects of orientation angle and extrude temperature on the tensile properties of 3D printing thermoplastic TPU have been explored; all the experimental results are summarized here:

- With a tensile strength of 46.7 MPa and break elongation of 702% at 500 mm/min stretching rate, medical grade TPU can be one of the strongest FDM thermoplastics. The superior strength and toughness can give the durability to endure demanding in medical tools.
- The orientation angle and printing temperature have effect on tensile strength and break elongation. 45° orientation angles and 215 °C are the optimum printing parameters for the TPU FDM process. It provides small internal stress and good thermal bonding between layers and adjacent filaments.

Acknowledgements This research is supported by China National Natural Science Foundation project (21464010) Grant, and Jiangxi Province Technology Foundation project (20161BBG70046).

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