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Influence of thermal processing conditions in 3D printing on the crystallinity and mechanical properties of PEEK material

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A B S T R A C T

Poly-ether-ether-ketone (PEEK) is a high-performance, temperature-resistant semicrystalline polymer which is frequently used as a replacement for metals in a wide variety of high-performance end-use application. Thermal processing conditions during manufacturing process for PEEK can implement a significant impact on its crystallinity and mechanical properties directly and indirectly. In this paper, we have used a temperature-control 3D printing system to prepare all the PEEK samples for calculating crystallinity and performing tension tests, in order to investigate the relationship between various thermal processing conditions (the ambient temperature, the nozzle temperature and heat treatment methods) in FDM process and crystallinity and mechanical properties (tensile strength, elastic modulus and breaking elongation) of pure PEEK material. All experiment results show temperature-control 3D printing method has tremendous potential to design, control and realize different degrees of crystallinity and mechanical properties for different PEEK parts, even in different regions of the same PEEK part.

Keywords: PEEK; 3D printing; Thermal processing; Crystallinity; Mechanical properties; Fused deposition modeling

1. Introduction

Poly-ether-ether-ketone (PEEK) is a high-performance, temperature-resistant semicrystalline polymer which is considered as one of the most excellent thermoplastic. Zalaznik et al. (2016) thought PEEK would be frequently used as a replacement for metals in a wide variety of high-performance end-use application, such as cars, aircraft, industrial pumps, etc. Accordingly, as Vaezi and Shoufeng (2015) expressed, manufacturing methods of PEEK materials with complex structure also has been widely investigated for use in different industries. Among these manufacturing methods, Valentan et al. (2013) reported that fused deposition modeling (FDM), as one of the most commonly used and low-cost 3D printing technologies for thermoplastic materials, has been an alternative method to process PEEK parts. In FDM process, the PEEK filament can be continuously fed into a nozzle and heated to a semiliquid state, and then extruded onto the previous layer along the cross section contour and the filling trajectory. At the same time, the extruded material rapidly solidifies and adheres with the surrounding material to accumulate the required complex PEEK parts. Magalhães et al. (2013); and Weng et al. (2016) considered that PEEK parts can be manufactured rapidly and directly from CAD model without expensive moulds, geometry limitation and specific tooling, and with high material utilization by this 3D printing process.

However, it is quite challenging to fabricate ideal-performance PEEK parts through FDM process due to its very high melting temperature, great melting expansion and especially its semicrystalline property (Garcia-Gonzalez et al. (2015);, Wu et al. (2014)). Valentan et al. (2013) developed a special 3D printer for high-performance thermoplastic modelling which could achieve the required melting and environment temperatures to process PEEK material. Wu et al. (2014) and Wu et al. (2015) investigated the mechanical strengths and the thermal deformation performance of PEEK material with different printing process parameters in FDM. Vaezi and Shoufeng (2015) found that heat management during print process and heat distribution in the environment surrounding the part were identified as important parameters to decide a good PEEK/substrate and PEEK interlayer bonding, and to affect the level of crystallinity in the 3D printed PEEK structure. Additionally, Jin et al. (2014) also demonstrated that PEEK, as a semi-crystalline polymer, exhibits varying degrees of crystalline perfection which can be influenced by thermal processing conditions, such as rate of cooling or thermal gradient, which exists during crystallization from the melt. PEEK’s mechanical properties can be influenced by the level of crystallinity of the material: increasing crystallinity can increase the range of working temperatures, elastic modulus and yield strength, while conferring lower toughness and different tribological behaviours (Conrad et al. (2013)). Obviously, the thermal processing conditions of FDM technology to process PEEK can implement a significant impact on the crystallinity and mechanical properties of PEEK materials.

Therefore, the main aim of this research was to investigate the influence of various thermal processing conditions in FDM, such as the ambient temperature, the nozzle temperature and heat treatment methods, on the crystallinity and mechanical properties of pure PEEK material. In order to do this, we used a temperature-control 3D printer, which was designed and developed by ourselves, to prepare all the PEEK samples. Tension tests were carried out to evaluate the mechanical properties (tensile strength, elastic modulus and breaking elongation) of these samples, while the crystallinity of PEEK was calculated by the Differential Scanning Calorimetry (DSC) method. All experiment results show it has tremendous potential to control the crystallinity and mechanical properties of PEEK materials by adjusting processing temperatures of 3D printing methods.

2. Experimental

2.1. Equipment and material

As shown in Fig.1, in this paper, a temperature-control 3D printing system for high-performance polymer was independently developed and set up, which consists of an extrusion head, temperature-control system, building platform, X-Y-Z motion mechanism etc.. The ambient temperature of this 3D printer can be controlled within a stable temperature from 25℃ to 200℃, and the nozzle temperature of its extrusion head can be kept in a appropriate temperature for printing PEEK (from 360℃ to 500℃). Moreover, it is available for this machine to perform some heat post-treatment methods for printed PEEK. The PEEK filaments, as the material for 3D printing in this paper, were reprocessed from the PEEK pellets (450G, VICTREX Corp. in UK).

As a reference to objectively assess the results in this paper, some properties of molded PEEK and some 3D printing process parameters for PEEK specimens except the thermal processing conditions are listed in Table 1.

Table 1

Some properties of molded PEEK material and some 3D printing process parameters for PEEK specimens except the thermal processing conditions.

	Description	**Value**
Properties	Glass-transition temperature T_g	143 ℃
	Melting temperature T_m	343 ℃
	Typical crystallinity of molded PEEK	35 %
	Tensile strength of molded PEEK	100 MPa
	Elastic modulus of molded PEEK	4 GPa
	Breaking elongation of molded PEEK	45 %
Process parameters	Nozzle diameter	0.4 mm
	Bead width	0.4 mm
	Layer thickness	0.2 mm
	Printing speed	40 mm/s
	Raster angle	Consistent with the longest edge

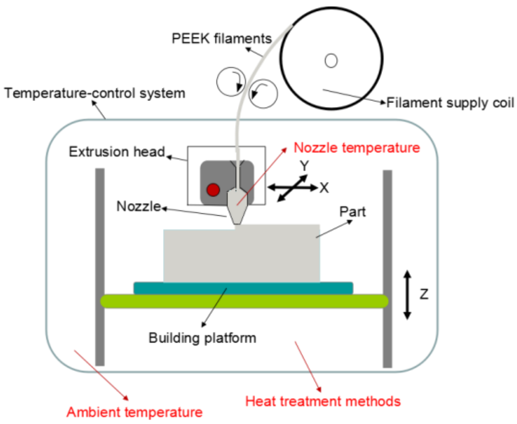


Fig.1. A temperature-control 3D printing system for high-performance polymer, which can control the temperature of nozzle and ambient, and perform some heat treatment methods for PEEK.

2.2. Thermal processing conditions

Different ambient temperatures, nozzle temperatures and heat treatment methods were considered as the thermal processing conditions in FDM process for PEEK in this paper. Table 2 shows that different groups of tension specimens were prepared in different thermal processing conditions by 3D printing to study the relationship between these different thermal processing conditions and PEEK's crystallinity as well as mechanical properties. Fig.2 presents the specific descriptions of temperature variation in different heat treatment methods detailedly.

Table 2

Different groups of tension specimens with different thermal processing conditions.

Specimens	**Ambient temperature (℃)**	**Nozzle temperature (℃)**	**Heat treatment methods**
1-5	25 50 100 150 200	420	Air cooling
6-12	25	360 380 400 420 440 460 480	Air cooling
13-17	100	420	Air cooling, Furnace cooling, Quenching, Annealing, Tempering

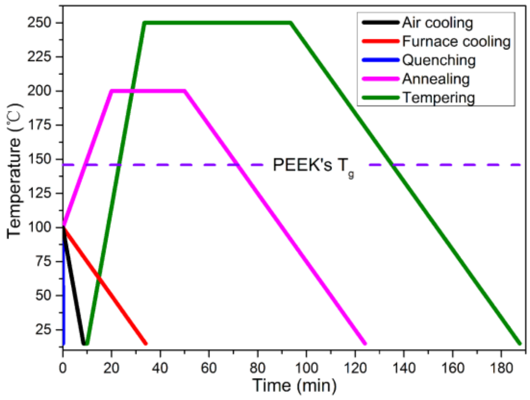


Fig.2. Specific descriptions of temperature variation in different heat treatment methods.

2.3. Tensile test

The samples were dog bone shape tensile testing specimens (90 mm × 5 mm × 4 mm) according to ISO 527 (Plastics -- Determination of tensile properties) standard. Tensile testing was carried out by using an electro-hydraulic servo mechanical testing machine (CMT4304, MTS Corp., USA). Testing speed for all samples was 2 mm/min and the gauge length was 25 mm. 5 samples were tested for each batch and the testing was performed at ambient temperature (20 ℃). Fracture surfaces of the tested specimens were observed with a Hitachi S-3000N SEM at an acceleration voltage of 15 kV after the surfaces were sputter-coated with conductors.

2.4. Differential scanning calorimetry (DSC)

Thermal analysis measurements were carried out using a Mettler-Toledo DSC machine under a 60 ml/min nitrogen flow. All samples were heated and from cooled between 20 ℃andto 400 ℃at 10 ℃/min. The measurements were all cut from the core of the dog bone specimens, in order to avoid producing any additional variation in data due to differences in skin and core crystalline structure. It is well known that the skin of a sample experiences a more rapid cooling rate which reduces the degree of crystallinity, compared to the slower cooling core, which often demonstrates a higher degree of crystallinity McLauchlin et al. (2014). The ratio of the enthalpy of melting during the first heating cycle, and the enthalpy of fusion of an 100% crystalline PEEK sample (130 J/g) (Blundell and Osborn (1983)), was used to determine crystallinity.

3. Results and discussions

3.1. Ambient temperature

Fig.3 shows the result that the ambient temperature during 3D printing PEEK performs a crucial and great factor to affect the crystallization behavior, while the nozzle temperature was 420 ℃ and the air-cooling method was used for all these samples. As shown in Fig.3a, as the ambient temperature increases from 25 ℃ to 200 ℃, the crystallinity grows from 16.937 % to 31.16 % accordingly. The crystallization processes are also different in accordance with the comparison between the ambient temperatures and PEEK's glass-transition temperature (143 ℃): if the ambient temperatures are below 143 ℃ (i.e., 25 ℃, 50 ℃, 100 ℃) , the molten material which is extruded from the nozzle would experience a nonisothermal crystallization process, and the higher ambient temperatures would provide more energy and time to improve the crystallinity of PEEK; Relatively, these ambient temperatures (150 ℃, 200 ℃) would cause an isothermal crystallization process, in which the amorphous polymer chains have sufficient energy to transform and crystallize in the degree of around 31 %, but still less than the typical crystallinity (35 %).

Mechanical properties results (tensile strength, elastic modulus and breaking elongation) are found to own a close relationship with the ambient temperature directly and indirectly. The tensile strength in Fig.3b keeps going up to the maximum (84 MPa) along with the ambient temperature and the crystallinity as well, less than the typical value of molded PEEK (100 MPa) because of the more structure defects in 3D printed part (Turner and Gold (2015)). Moreover, the elastic modulus curve in Fig.3b also shows the similar tendency with the crystallinity curve in Fig.3a and it can reach, even exceed the typical level of molded PEEK (4 GPa). The breaking elongation behaves quite disparate in different degrees of crystallinity. As shown in Fig.3a, the breaking elongation of low-crystallization samples can be greater than 130 %, presenting an excellent plasticity, and when the crystallinity increases to surpass 20 %, the elongation would dropped to 20 % dramatically.

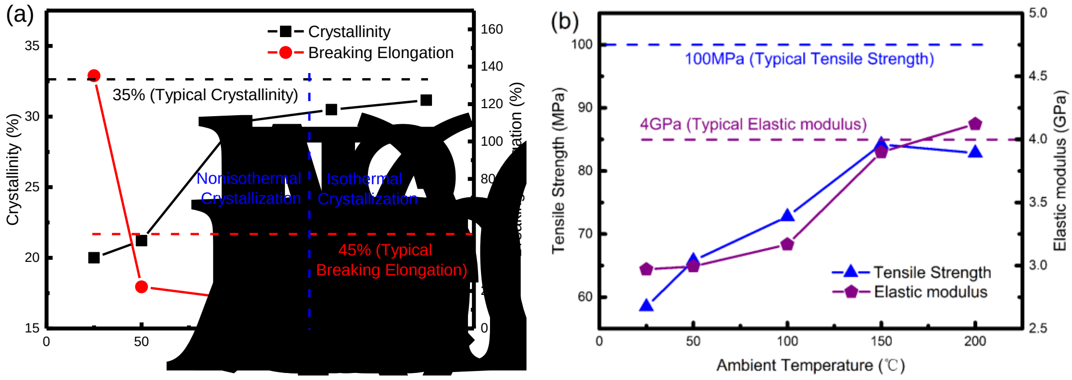


Fig.3. Crystallinity and mechanical properties results of different PEEK samples with different ambient temperatures (25℃, 50℃, 100℃, 150℃, 200℃): results of crystallinity and breaking elongation (a), and results of tensile strength and elastic modulus (b).

According to the theory of polymer physics (Mark (2007)), mechanical properties of polymers have a close relationship with the state of aggregation of macromolecular chains: the macromolecular chains in crystalline region align in better order and own stronger intermolecular forces, causing greater strength and rigidity; the macromolecular chains in amorphous region prefer to intertwine loosely, and are easy to be scattered and stretched, showing a good extensibility. Therefore, Aa model in Fig.4a was proposed to explain the experimental results that higher crystallinity of PEEK material means higher percentage of crystalline region in the 3D printed PEEK part, which could improve the tensile strength and the elastic modulus of these samples, while the amorphous region could greatly increase the breaking elongation along the printing orientation. Moreover, different from the one of molded PEEK parts, the macromolecular chains in 3D printed PEEK appear an orientational arrangement (>90%, tested by wide angle X-ray diffraction method) because of the melt-extrusion process and the unidirectional printing method in FDM technology, result in a greater breaking elongation (135%) or elastic modulus (4.1 GPa) in the printing orientation of 3D printed PEEK than the typical values of molded PEEK. Therefore, the ambient temperatures can be used as a primary factor to adjust the degree of crystallinity of PEEK material to acquire various rigidity-plasticity parts in Fig.4b for different applications.

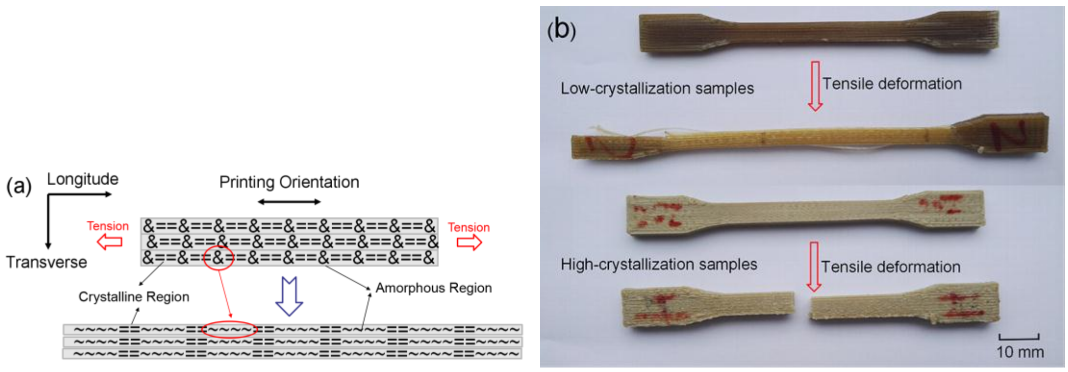


Fig.4. A model about crystalline region and amorphous region in 3D printed PEEK part (a), and various rigidity-plasticity PEEK parts with different degrees of crystallinity (b).

3.2. Nozzle temperature

As shown in Fig.5a, nozzle temperature is found to be a complicated factor to PEEK's crystallinity when the ambient temperature was kept at 25 ℃ and the air-cooling method was used to process all these samples, because this temperature can both influence the crystal melting process and the crystallization process. The crystallinity first reduces from 18.829 % to 15.96 % when the nozzle temperature increases from 360 ℃ to 380 ℃, which can be explained as an incomplete melting result of crystalline region in the nozzle with a lower and non-uniformity temperature inside. Then the crystallinity turns into a moderate growth until a relatively stable value (21 %), as the nozzle temperature goes up to 480 ℃. It is obvious that the nozzle close to the printed part can be considered as a local thermal source in FDM process, which can influence the crystallization process of the molten and extruded PEEK material. Higher nozzle temperature can supply more energy and time for PEEK to crystallize. Furthermore, if the nozzle temperature is close to the decomposition temperature of PEEK (500 ℃), polymer chains are more likely to be broken into short ones and then crystallization process is easier to proceed.

Tensile strength and elastic modulus grow up rapidly when the nozzle temperature increases from 360 ℃ to 420 ℃ in Fig.5b, but then they begin to decline at a slower pace which is probably caused by the deterioration phenomenon of polymer materials because of the excessive melting temperature. The breaking elongation curve in Fig.5a appears a rapid decline first and a followed slow raise. These mechanical results are explained as the comprehensive result of the crystallinity, the interface between printing lines and the deterioration phenomenon of polymer materials. Accessibly, as shown in Fig.5c, the fluidity of melted PEEK with higher nozzle temperature could be improved and have a better adhesion to previous depositional material, that is, the interface between printing lines have been strengthened. In the contrary, the printing lines of the samples in Fig.5d with low nozzle temperatures would be separated from each other easily. So, as for the low-crystallization PEEK samples printed in a low ambient temperature, the nozzle temperature perform a more important role in the internal pore structure than crystallinity, which could both exercise an important influence on the mechanical properties of these samples with different nozzle temperatures.

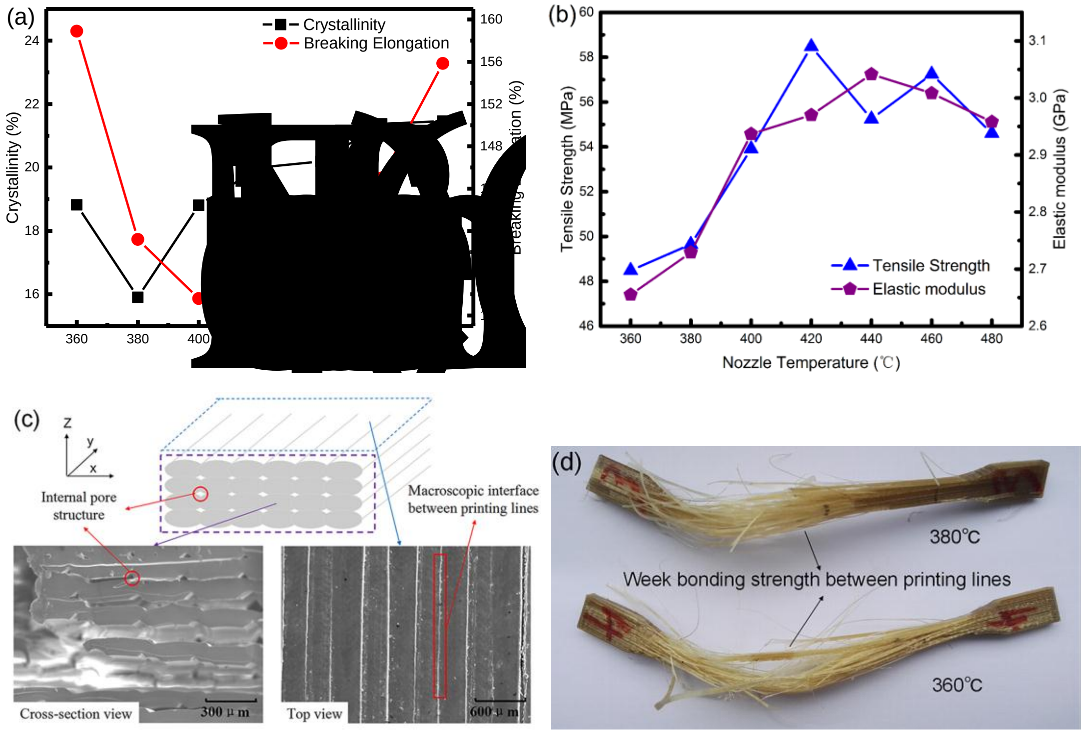


Fig.5. Crystallinity and mechanical properties results of different PEEK samples with different nozzle temperatures (360℃, 380℃, 400℃, 420℃, 440℃, 460℃, 480℃): results of crystallinity and breaking elongation (a), results of tensile strength and elastic modulus (b), the internal pore structure (c), and the weak interface between printing lines with lower nozzle temperatures (d).

3.3. Heat treatment methods

As shown in Fig.6a, different heat treatment methods for 3D printed PEEK samples could result in a quite striking difference of crystallinity and crystallization process, while the ambient temperature was kept at 100 ℃ and the nozzle temperature was 420 ℃. Furnace cooling and annealing method could be the more efficient approaches to get a higher degree of crystallinity (36.2 % and 37.558 %) rather than tempering method (33.84 %). This result indicates that the cooling down stage before the heating up stage in the tempering method might influence the crystal size and structure to decrease the final crystallinity. Air cooling and quenching methods would lead to lower degrees of crystallinity (29.630 % and 27.718 %), because there were not enough energy and time for molten PEEK to crystallize in these two methods.

The tensile strength and elastic modulus curves in Fig.6b shows the similar rules with the crystallinity, but the samples with furnace cooling method, which has a quite high degree of crystallinity. The slow cooling down stage in furnace cooling method would lead to an adequate shrinkage distortion to cause internal defects and residual stress, which can decrease the mechanical performance of PEEK parts. Obviously, annealing and tempering methods can not only increase the degree of crystallinity, but also relieve the residual stress, which can both improve the tensile strength and elastic modulus. Therefore, in addition to crystallinity, the different residual stress, internal defect and structural distortion caused by different heat treatment methods can also have a certain level of influence on the mechanical properties, especially for the results of the breaking elongation in Fig.6a.

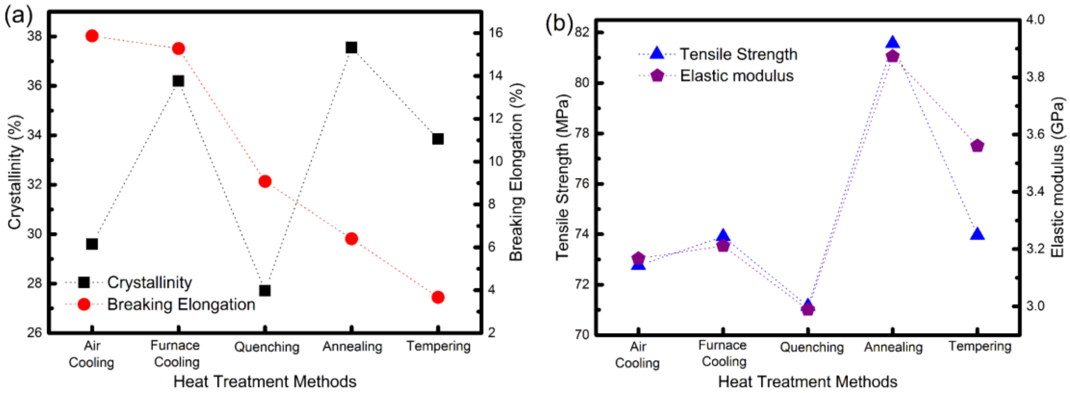


Fig.6. Crystallinity and mechanical properties results of different PEEK samples with different heat treatment methods: results of crystallinity and breaking elongation (a), and results of tensile strength and elastic modulus (b).

3.4 Controllable crystallinity and mechanical performance of PEEK material by 3D printing method

As a semi-crystalline polymer, the degree of PEEK’s crystallinity would greatly influence its various properties. However, it is not easy to process PEEK parts with appropriate degree of crystallinity by traditional manufacturing methods. The experimental results show that FDM technology could be a feasible access to realize the satisfactory crystallinity of PEEK material. What is more, due to the line-by-line and layer-by-layer prototyping characteristic of 3D printing technology, different degrees of crystallinity can be implemented in different regions in one PEEK part to show the compound mechanical/functional properties. As shown in Fig.7a, the ambient temperature near the nozzle could be controlled at a required degree by the thermostat to change the rate between crystalline region and amorphous region in the polymer chain of PEEK, result in the high-crystallization regions and the low-crystallization regions in one PEEK part. Nozzle temperature could be used to make some slight adjustment of PEEK’s crystallinity, especially for the low-crystallization regions.

The results of tensile test show that the mechanical performance of these PEEK samples is a comprehensive result of multiple factors, including the printing parameters, the degree of crystallinity, the multi-scale interfaces between printing lines, the residual internal stress and the deterioration phenomenon of polymer materials. The 3D printed parts are probable to be mechanical anisotropy depend strongly on the angle of the printing trajectory: because of the continuous extrusion process in 3D printing, the polymer chains prefer to be arranged along the orientation of these printing lines (i.e., the longitude direction). Moreover, the degree of crystallinity decided by the thermal processing conditions would be an important factor to decide the longitude mechanical performance: the parts with the higher crystallinity manifest the higher tensile strength, the greater elastic modulus and the worse plasticity in this direction. In addition, the interfaces shown in Fig.7b, including the microcosmic interface between polymer chains in different printed lines and the macroscopic interface about the internal pore structures, are crucial to the transverse mechanical performance, which also could be a nonnegligible factor for the longitude mechanical performance. FDM-based 3D printing is a thermal process and inevitably cause the residual internal stress and the deterioration phenomenon of polymer materials, which could have a complicated influence on the mechanical performance of 3D printed PEEK.

However, it is relatively simple to change and control the processing conditions in FDM-based 3D printing method. So, thermal processing conditions (the ambient temperature, the nozzle temperature and heat treatment methods), and other 3D printing process parameters can be used to achieve controllable crystallinity and mechanical performance of PEEK material.

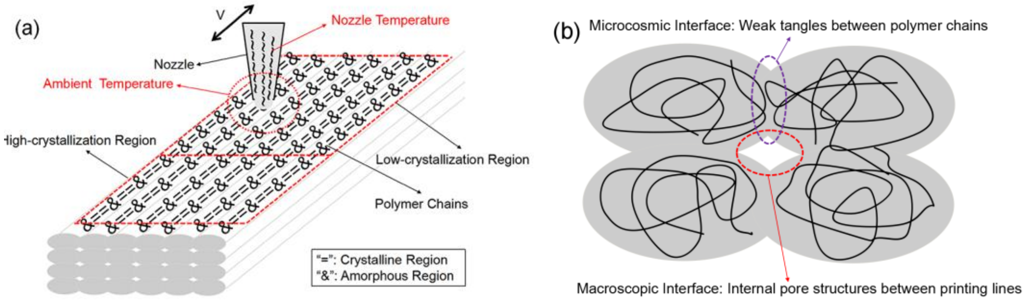
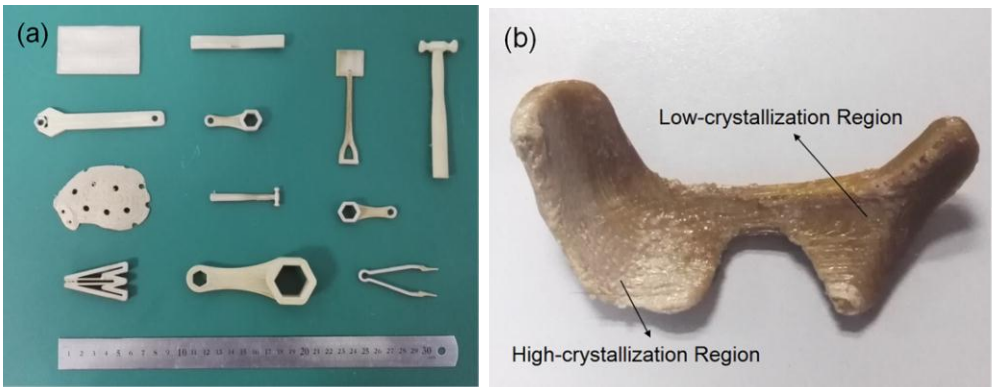


Fig.7. Different degrees of crystallinity can be implemented in different regions in one PEEK part by 3D printing method (a), and the interfaces, including the microcosmic interface between polymer chains in different printed lines and the macroscopic interface about the internal pore structures, are crucial to the transverse mechanical performance (b).

3.5 Demonstrations of the controllable process

Fig.8a shows some demonstrations for different applications with different degrees of crystallinity under the different thermal processing conditions in 3D printing. Fig.8b shows an implantable bone which has different crystallinity regions: the low-crystallization region can be applied to connect the cartilage, and the high-crystallization region can used to attach the surrounding bones. The implementation of the heat treatment methods should be necessary and important, because these methods are the pretty valid way to obtain a very high degree of crystallinity of PEEK materials. As shown in Fig.8c, a piece of PEEK cranium implant was heat-treated to improve its mechanical performance greatly.



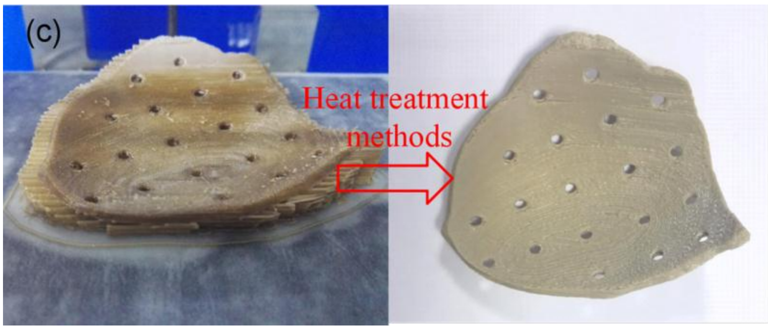


Fig.8. Some demonstrations of the controllable process: some parts with different degrees of crystallinity under different thermal processing conditions in 3D printing (a), an implantable bone which has different crystallinity regions (b), and a piece of PEEK cranium implant (c).

5. Conclusions

In this paper, we have used a temperature-control 3D printing system to prepare all the PEEK samples for calculating crystallinity and performing tension tests, in order to investigate the relationship between various thermal processing conditions in FDM process and crystallinity and mechanical properties of pure PEEK material. The results show that the crystallinity grows from 16.937 % to 31.16 % accordingly, as the ambient temperature increases from 25 ℃ to 200 ℃, and mechanical properties results are found to own a close relationship with the ambient temperature directly and indirectly. Nozzle temperature is found to be a complicated factor to PEEK’s crystallinity and mechanical properties, because this temperature can both influence the crystal melting process, the crystallization process, the interface between printing lines, and the deterioration phenomenon of polymer materials. Different heat treatment methods for 3D printed PEEK samples could result in a quite striking difference of crystallinity and crystallization process: furnace cooling and annealing method could be the better and more efficient approaches to get a higher degree of crystallinity (36.2 % and 37.558 %) and better mechanical performance rather than tempering method or quenching method. Some PEEK parts of this process had been manufactured to demonstrate the controllable crystallinity and mechanical performance of PEEK material by 3D printing method. All experiment results show temperature-control 3D printing method has tremendous potential to design, control and realize different degrees of crystallinity and different mechanical properties for different PEEK parts, even in different regions of the same PEEK part.

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