ADDITIVE MANUFACTURING BY SELECTIVE LASER SINTERING: POLY(ETHER ETHER KETONE) PROCESSING DEVELOPMENT

Cristiane A. Pimentel
cristianepimentel@ufrb.edu.br
RODRIGO ALVARENGA REZENDE
rodrigo.rezende@cti.gov.br
Marcelo Oliveira
marcelo.oliveira@cti.gov.br
Jorge Vicente Lopes da Silva
jorge.silva@cenpra.gov.br
Marcus Vinícius Lia Fook
marcusvinicius@dema.ufcg.edu.br

Poly-ether-ether-ketone (PEEK) is a high-performance, low weight, temperature-resistant semicrystalline polymer which is frequently used in medical device instead of metal. This material could be processed by Selective Laser Sintering (SLS), which allows to obtain a desired customized shape, excelent to prepare implants molds. Thermal processing conditions during Additive Manufacturing (AM) is significant influence on crystallinity and morfology conditions. In this research, we have studied the relationship between SLS parameters and the desired PEEK morphology, roughness and crystallinity. All results showed that the temperature-control of the 3D printing method has a potential influence on the morphology layer by layer and it could be a potential to produce cranial implants, especially due to rough surface presented. However if uncontrolled the cooling temperature can reduce crystallinity probably impacting the 3D structure resistance.

Palavras-chave: 3D Printing, Additive Manufacturing, Polymer, Thermal processing, Processing Development

1. Introduction

Poly(ether ether ketone) (PEEK) is a bioinert and a high temperature resistant, semi-crystalline thermoplastic polymer. O'Reilly et al. (2015) emphasized that the properties of radiolucency and elasticity modulus similar as bone allowed to use this material at biomedicine, on the fields of orthopedics, neurosurgery and trauma. Accordingly to Roskies et al. (2016), it is so important the design to apply at biomaterials due to their complex forms, especially prostheses. Shuai et al. (2016) reported the advanced techniques in additive manufacturing to fabricate scaffolds with biomaterials. Selective Laser Sintering (SLS) technique is used to fabricate customized 3D pieces with complex internal geometries with PEEK.

However, one of the fastest growing applications on the market is medical implants, especially those used for cranioplasty. Mohan et al. (2016) and Liang et al. (2016) presented the importance of implant morphology for use in cranial reconstruction. The 3D printing by SLS can help in this quick and adapted implant to each individual.

The SLS process was explained by Kumar (2014), at first step of SLS process, the powder is placed in a container and it is protruded from the container by adjoining piston, a substrate is lowered down to a depth equal to layer thickness, a powder layer is spread on the substrate, and the deposited powder layer is scanned by the laser beam to fuse powders at the selected area, repeating all sequence until the fabrication of product is complete. Shuai et al. (2016) and Wudy et al. (2017) considered the SLS process an excellent choice to produce models quickly and provide planned architecture.

Another challenge of the PEEK processing is to reach the melting temperature, but Schmidt et al. (2007) showed for SLS process the necessary adaptations in systems technology and material modifications and Peyre et al. (2015) explained the importance of the initial temperature process, not to promote thermal shrinkage during crystallization and deformation of the layer to obtain the best morphology.

Additionally, Jin et al. (2014) demonstrated that PEEK 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. Thus, the thermal processing conditions of SLS process could influence on the crystallinity and morphology properties of PEEK 3D structures. Therefore, the aim of this study is to evaluate

the influence of SLS parameters on the PEEK piece formation to be used at cranioplasty posteriorly.

2. Experimental

2.1. Material and SLS equipment

For the experiments, Poly(ether ether ketone) was provided by Victrex Technology Centre, powder grade 702, manufacture date 08/03/2014, Food and Drug Administration Register (FDA) 21 C.F.R. 177.2415.

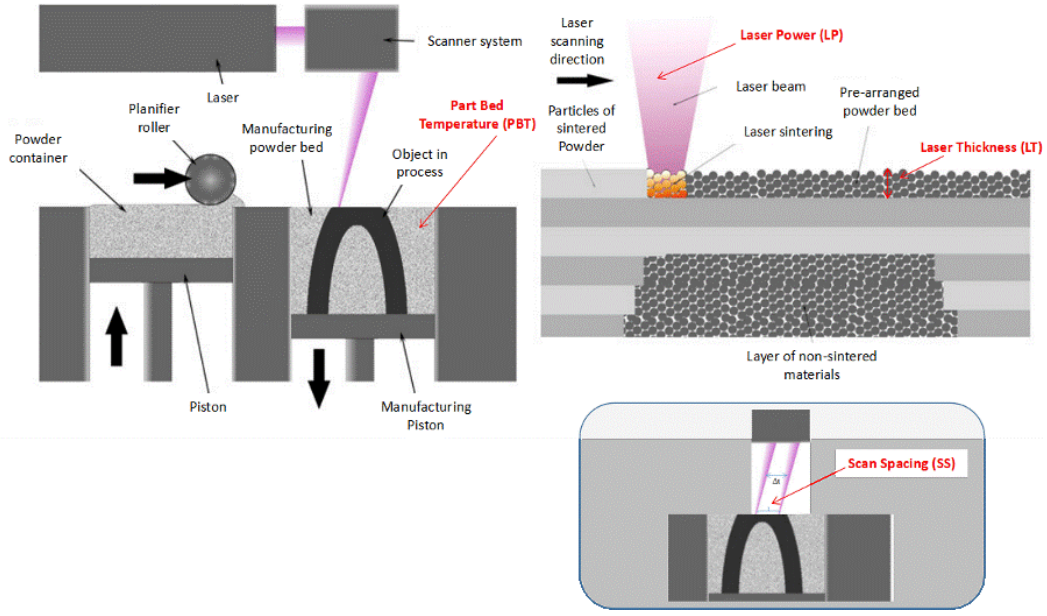
The Selective Laser Sintering Equipment was a Sinter Station 2000 Model, manufactured by DTM Corporation, belonging to the Renato Archer Information Technology Center, and Laser Specifications are detailed in Table 1.

Table 1 - Laser Specifications at SLS Equipment

Parameter	Unit
Spot (beam diameter)	450 um
Power Rating	50 W (max)
Laser Type	CO_2 pulsed (without continuous option)
Wave-length	450 nm (infrared spectrum)

Kwon et al. (2017) explained that the chamber of the SLS machine is pre-heated near the melting temperature of the material. The powdered material is then loaded into the chamber in a workspace, in which a thin layer of the material is spread over. Computer controlled laser scanning selectively fuses the powdered material according to the part design, which is referred to as partial melting. After finishing laser scans at the given layer, the workspace is lowered by a predetermined increment, and another layer of powdered material is spread over the previously sintered layer. This process repeats until all the layers are sintered. The powder volume that has not been sintered works as support for the next layers. Once the printed part and the surrounding materials cool down below the glass transition and the oxidation temperatures, the 3D printed part can be obtained by brushing off the non-sintered powders. In Figure 1 the schematic of SLS Process is presented.

Figure 1 - The schematic of SLS process showing all the parameters related to the device



The SLS equipment process parameters tested during this research are: Part Bed Temperature (PBT) which is related to the temperature at the workspace; Laser Power (LP); Scan Spacing (SS) which is related to the distance between the laser beam scans; and Layer Thickness (LT).

2.2. Samples characterizations

- *Optical Microscopy (OM)*

The analysis were carried out in a Hirox Optical Microscope for reflection and transmission with 2D accessories and 50X-400X variation, coupled to an image analysis station with a magnitude of 60X.

- *Surface Roughness*

An Optical Microscopy (Hirox Optical Microscope) was used to analyze the surface roughness of the PEEK samples at 60X of magnitude. Gwyddion 2.50 software was used to calculate the arithmetic average of the absolute values of the surface height distribution (Ra).

- *Differential Scanning Calorimetry (DSC)*

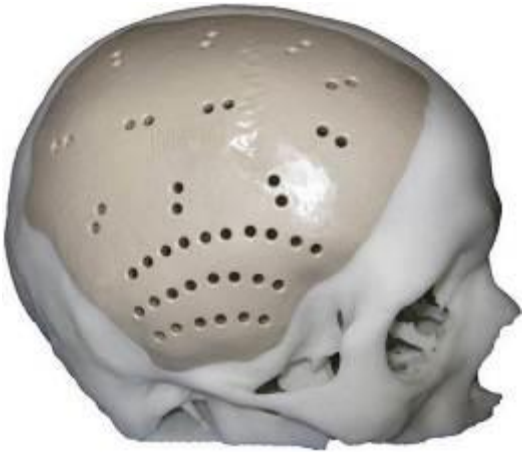
Thermal analysis measurements were carried out using a Universal DSC Q20 TA Instruments under a 50 ml/min nitrogen flow. The heating range was considered from 30 °C to 450 °C at rate of 10 °C/min. The ratio of the enthalpy of melting during the first heating cycle, and the enthalpy of fusion of an 100% crystalline PEEK sample (130 J/g) (Blundell and Osborn, 1983) was used to determine the crystallinity.

3. Results and discussions

3.1. Morphology of PEEK samples in terms of the SLS parameters setting

Since PEEK can be applied as a biomaterial especially for cranioplasty, which means that this biomaterial will be used three-dimensionally, the first step of this study was to obtain a PEEK multilayer structure (three-dimensional). Lethaus et al. (2011) demonstrated the importance of craniofacial reconstruction. Surgeries are still challenging because of the difficulties in defining and repairing the bone defect. The dimensional definition of the implant is the first challenge since each patient has an individual anatomy and each defect has a specific shape, especially with bone defects caused by trauma or tumors. Thus, it is very important to evaluate the morphology of the sample in function of the SLS parameters adjustment. Figure 2 shows an example of a PEEK cranial implant.

Figure 2 - Example of a PEEK cranial implant



Source: Lethaus et al. (2011)

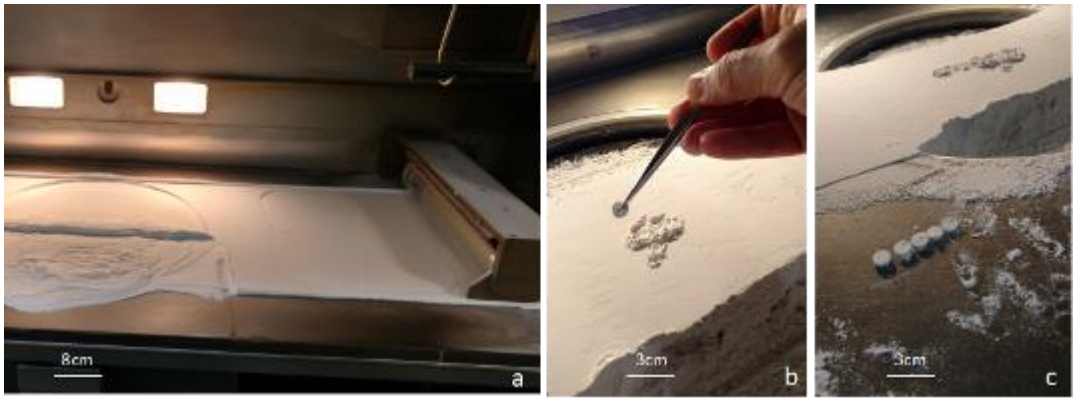
As the material is in powder form, it was initially increased these parameters in order to obtain a temperature close to the melting point of PEEK material (T_m = 343°C). At Table 2 the parameters analysed are presented.

Table 2 - SLS parameters (PBT: part bed temperature; LP: laser power; SS: scan spacing; LT: layer thickness) modified during the experiments

Parameters	Unit	Sample 1 (a)	Sample 2 (b)	Sample 3 (c)	Sample 4 (d)
PBT	°C	140	160	180	200
LP	W	25	5	7	8
SS	mm	0.15	0.30	0.20	0.20
LT	mm	0.10	0.10	0.15	0.15

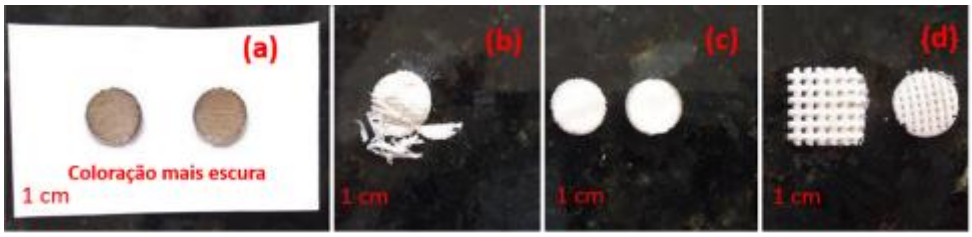
Figure 3 shows the start of the process to obtain the PEEK samples at SLS equipment. At first step, the powdered material was loaded into the chamber as part of the 3D printer workspace (Figure 3a). After the whole sinterization process, withdrawn PEEK samples can be seen (Figures 3b and 3c).

Figure 3 – (a) Overview of the SLS equipment workspace where the PEEK powder was deposited to be irradiated by infrared laser, (b) one small PEEK sample removed from the workspace after being sintered, (c) a collection of sintered PEEK samples at the end of the process



Initially, for the Sample 1 it was adopted a PBT close to the glass transition temperature of PEEK (T_g = 143°C) and an intermediate value for LP reached by the equipment, expecting that the power was enough to melt the material and regarding lower values for SS and LT. Sample 1 got dark after being processed, as shown in Figure 4 (a). Probably occurred the PEEK reasoned to the high Laser Power.

Figure 4 - Samples after SLS processing (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4



The sample color aspect motivated the modifications of Sample 2 that is the increase of the PBT and the reduction of LP, besides the double value of SS. The visual appearance of Sample 2 clearer compared with the color of Sample 1, presenting a beige tone closer to PEEK powder, however it presented a "crumbled" appearance, Figure 4 (b). Probably, the temperature required to melt the material was not reached.

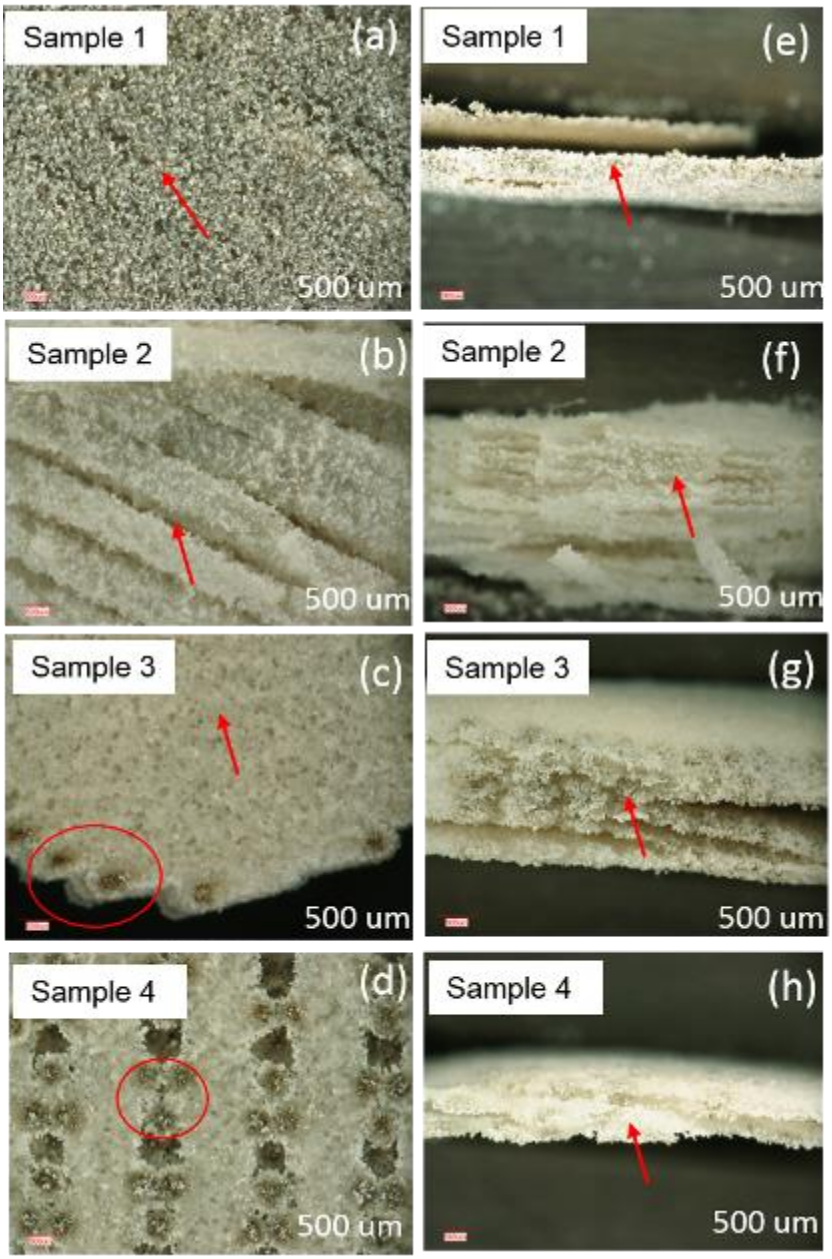
Thus, for the Samples 3 and 4, it was decided to increase the thermal parameter PBT and a smooth variation at the other three parameters. As shown in Figure 4 (c) and 4 (d), respectively. Samples 3 and 4 became higher-stiffnesses when compared to Sample 2. Moreover, Sample 4 presented that the PEEK multilayer was formed, Figure 4 (d).

These visual samples aspects above were compared with OM micrographs of all samples and their surfaces views are presented in Figure 5, surface and cross-section. Figure 5

(a) presented darken spots probably by the material degradation, corroborating the decision to reduce LP at Sample 2.

Still at Figure 5 (b), Sample 2, the "crumbling" appearance is observed. At Sample 3, it was observed a more compact material and the beginning of mesh formation in edges and rough surfaces (Figure 5 (c)). These characteristics were presented at Sample 4 and showed the crosslinking in the mesh formation (Figure 5 (d)).

Figure 5 - Surface OM: (a) Sample 1 (b) Sample 2 (c) Sample 3 (d) Sample 4; Cross-section OM (e) Sample 1 (f) Sample 2 (g) Sample 3 (h) Sample 4

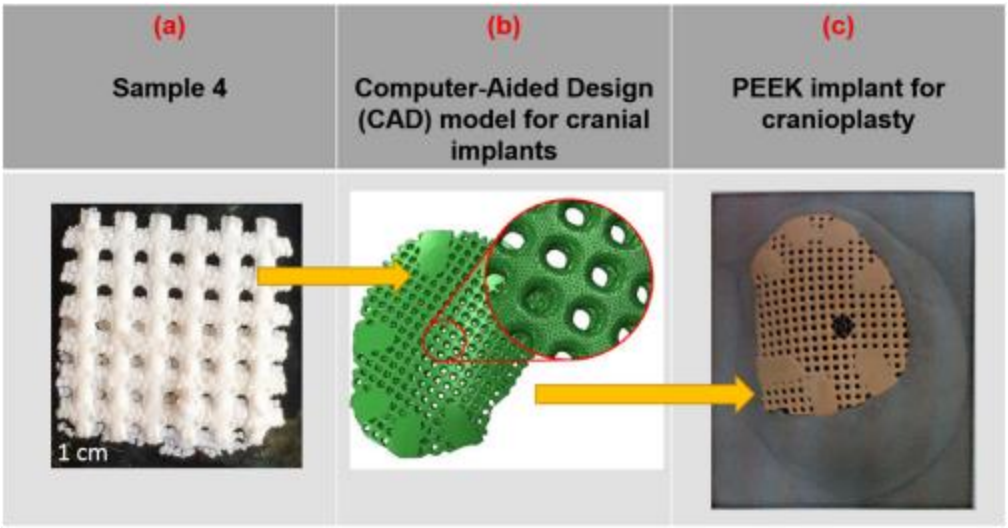


For all samples at cross-section delamination effect was observed. At Sample 1 the layers were more compact, probably because of the higher laser power (Figure 5 (e)). Comparing the cross-sections between samples 2 to 4, the reduction of this behavior can be observed, however in Sample 4 it was still evident at the edges, which indicates that an adjustment in the thermal process parameters, PBT or LP, will be necessary (Figure 5 (f) (g) (h)).

At Sample 4, Figure 5 (d), it can be seen a rough and knitted surface. These characteristics corroborates with Wennerberg and Albrektsson (2009) studies which showed the importance of rougher surfaces to accelerate the process of osseointegration and increase the bone-implant interface. Additionally, El Halabi et al. (2011) demonstrated the significance of the implant design to use at cranioplasty.

Figure 6 presents the correlation between the design of Sample 4 and the required PEEK implants, reinforcing the importance of the structure.

Figure 6 - Correlation between the design of Sample 4 design and the required PEEK implants

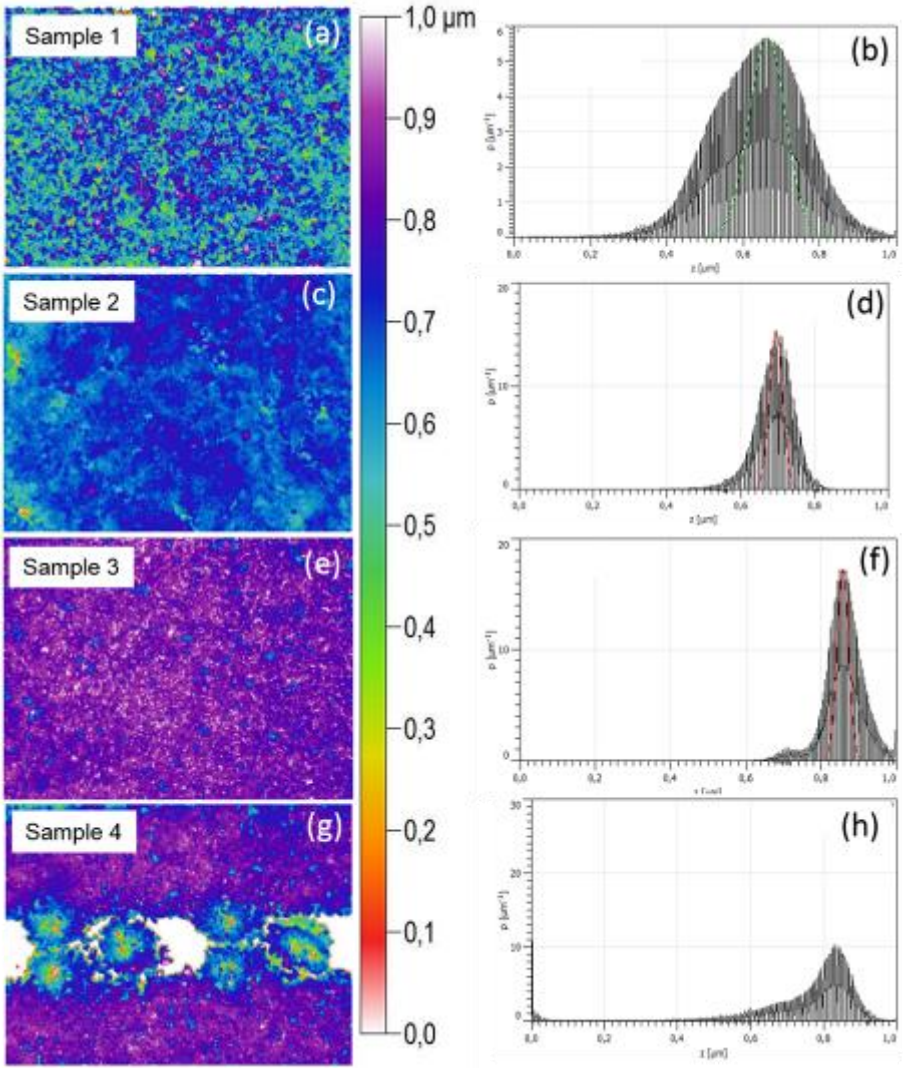


Source: Adapted from El Halabi et al. (2011)

3.2. Roughness of PEEK samples surfaces

Figure 7 shows the surface morphology and the roughness distribution in all samples.

Figure 7 - The surface morphology: (a) Sample 1 (c) Sample 2 (e) Sample 3 (g) Sample 4; Ra distribution: (b) Sample 1 (d) Sample 2 (f) Sample 3 (h) Sample 4



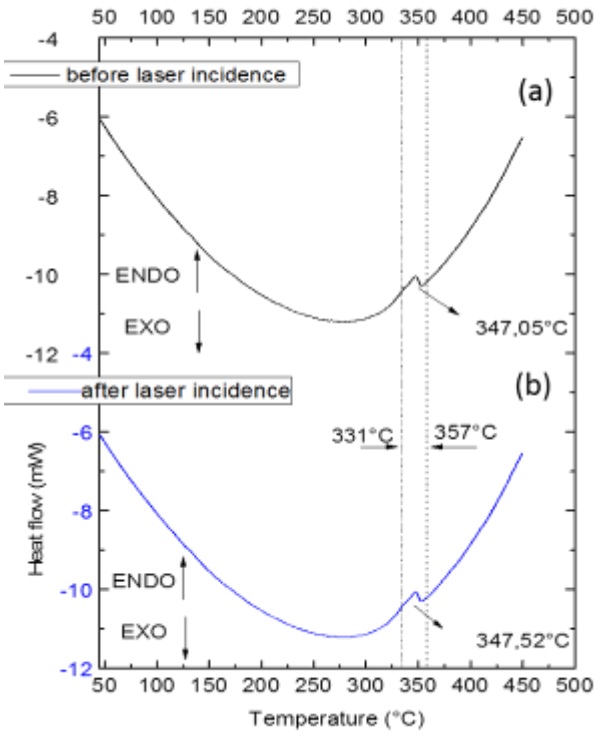
Sample 1 presented the highest roughness and data dispersion, due being the first test (Figure 7b). When comparing the Samples 2 and 3, it was observed an increase in roughness (Figure 7 d and f), especially when a purple color is showed in Figure 7e, which indicates measurements close to 1.0 µm. The roughness analysis of the Sample 4 was impaired by gaps. However, Figure 7g presented in regions of rough surface a color similar to Sample 3, indicating that the choice of the parameters was coherent.

3.3. Influence of thermal conditions on the crystallinity

The Differential Scanning Calorimetry (DSC) analysis was carried out to observe the influence of thermal conditions (LP) at PEEK powder bed and the effects on PEEK Samples.

Figure 8 showed the DSC analysis before and after the laser incidence. During all runnings at SLS bed the PEEK powder was submitted to different process conditions, especially temperature variation. Figure 8 presents the presence of an endothermic peak at 347.05 ºC and 347.52 °C representing the PEEK melt temperature was observed. Lu et al. (2009) emphasized that it is a characteristic behavior of semicrystalline polymers.

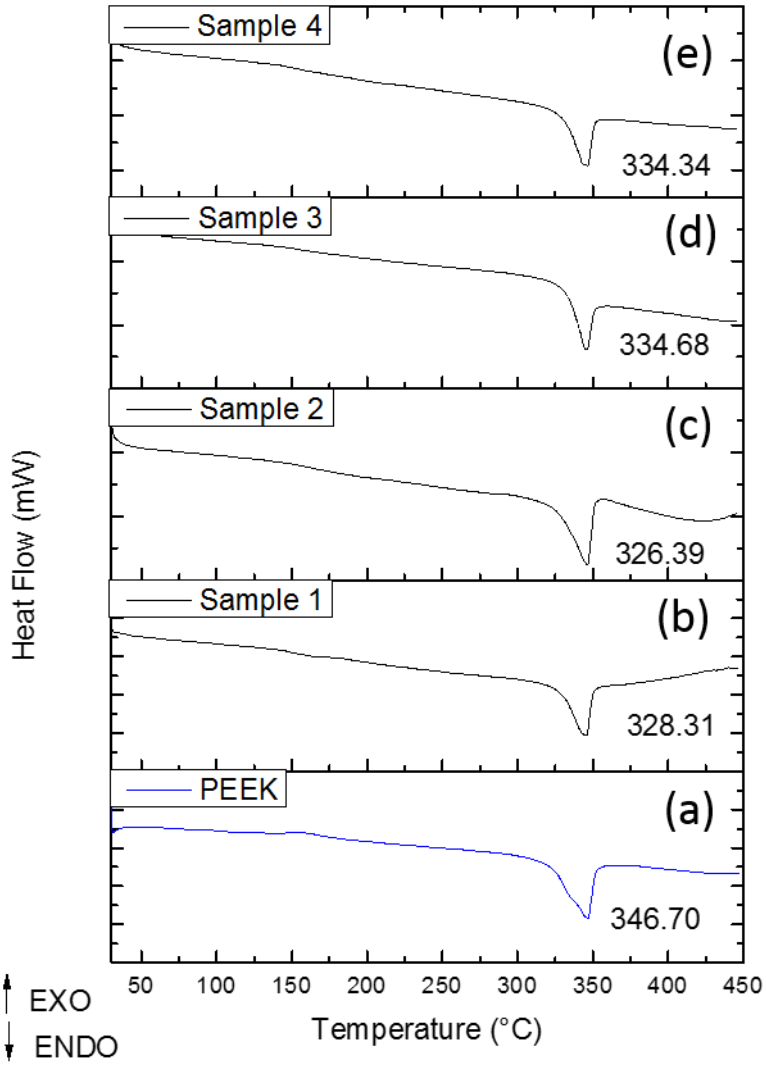
Figure 8 - Differential Scanning Calorimetry (DSC) analysis, (a) before (b) after, the laser incidence



When the crystallinity was calculated it was observed its reduction from 18.05% to 9.46%, if compared before and after the laser incidence. This result indicates that the part bed is submitted to a heating and cooling during several runnings without sufficient time to crystallize the material, influencing the reduction of the final crystallinity in part bed after all steps of this study. This fact was corroborated by Yang et al. (2017), who studied the influence of thermal processing conditions in 3D printing on the PEEK crystallinity.

Figure 9 presents the effects of thermal conditions at PEEK Samples. All samples did not suffer influence by the imposed thermal conditions and all samples melting temperatures were very close to the PEEK melting point.

Figure 9 - Differential Scanning Calorimetry (DSC) analysis, (a) PEEK (b) Sample 1 (c) Sample 2 (d) Sample 3 (e) Sample 4



The crystallinities of samples 1 and 2 were very close, 44.34% and 40.41%, but was increased when comparing samples 3 and 4, from 39.03% to 57.67%. The first step probably occurred because of the insufficient time to recrystallize. Furthermore, the presence of an endothermic peak was observed in all samples.

Thus, it is mainly important to balance the bed temperature and laser power to achieve the melt temperature of the material required to form the 3D structure, however the cooling bed must be slow to allow the material recrystallizing, which may influence directly on the mechanical strength properties of the 3D structure desired. This strength is important especially for cranioplasty. Hanasono et al. (2009) studied craniofacial reconstruction using PEEK made with additive manufacturing and verified that it is important that the 3D structure ownsstrength enough to avoid the compression of pericranial tissues.

4. Conclusions

In this paper, the variation of SLS additive manufacturing technique parameters to fabricate PEEK scaffolds and evaluate their morphology, roughness and the thermal process conditions at crystallinity were studied. The results showed that the resultant morphology has a close relationship to the thermal-dependent parameters of SLS process and that PEEK is potential to be used as biomaterial, specially for cranioplasty due to its high roughness. Moreover, the crystallinity decreased when fast cooling occurred in the SLS bed. The two more sensible process parameters were the PBT (Part Bed Temperature) and LP (Laser Power). However, more detailed tests adjusting the PBT and LP are necessary to reduce the delamination at cross-section scaffold. All experiment demonstrated that SLS method has a huge potential to quick design, control and realize different designs very important for biomedicine and regenerative medicine.

5. Acknowledgments

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