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Parameter settings of the PEEK and PPSU filaments production with the ceramic component

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Abstract. The aim of the work is to determine suitable settings of filament production parameters for medical applications from materials PEEK and PPSU alone, as well as with a 10wt% of the ceramic components Hydroxyapatite (HA) and Tricalcium Phosphate (TCP) admixture. Filaments were made using the Filament Maker machine (3devo, The Netherlands). The filaments were manufactured according to the requirements for usage in the FDM technology with a nominal diameter of 1.75 mm. The diameter of the filaments was measured with an optical sensor and analyzed using DevoVision software (3devo, The Netherlands). The analysis of the filament diameters was carried out using descriptive statistics in order to determine quality of the filaments. The analysis of the produced filament diameter from the materials PEEK, PEEK + HA/ TCP , PPSU and PPSU + HA/ TCP demonstrated that the measured values of the diameters of the filaments from the nominal value (1.75 mm) showed minimal deviations, as well as the fact that the limit values were not exceeded (1.85 mm; 1.65 mm) and thus it is possible to state that the manufactured filaments meet the required quality for use in FDM technology. A microscopic analysis was also carried out on the manufactured filaments in order to determine the distribution of the ceramic component in the manufactured filaments. An Olympus GX71 inverted metallographic microscope with an Olympus DP12 camera was used for the purpose of expertise. The total number of examined samples was n = 40, while 10 samples from each filament were selected from random areas. Microscopic analysis of the produced filaments showed a uniform distribution of the ceramic component in the composite filaments, which means that the manufacturing process does not affect the distribution of the ceramic component in the filament.

Introduction

Fused Deposition Modeling (FDM) technology is part of additive manufacturing technology, which is gaining more and more use in various areas such as e.g. automotive production, cosmonautics or medical applications [1,2,3]. Statistical data indicate that the use of this technology in the field of medicine was at the level of 0.973%, but forecasts indicate that by year 2026 this share of use in the given sector will be at the level of 18.2% [4]. This fact creates new questions and requirements for the material side in the form of the production of new and high-quality filaments.

High demands are placed on the group of materials intended for medical applications in the form of biocompatibility. Polyetheretherketone (PEEK) and polyphenylsulfone (PPSU) can also be included in this group of biomaterials. PEEK is characterized by resistance to hydrolysis, high temperatures, wear and has good mechanical properties [5,6]. PPSU is characterized by high glass transition temperatures, high mechanical strength and stiffness, good chemical, hydrolytic and dimensional stability [7,8]. Based on these properties, PEEK and PPSU materials turn out to be suitable candidates for the replacement of biological structures in the form of bone. Another very important parameter is osseointegration between the biomaterial and the biological structure in the form of bone. Due to the fact that PEEK itself does not have a biological activity for the process of osteonitration, it is necessary to create composite materials using Hydroxyapatite (HA) [9]. One such study is by the authors Senatov et al. [10] where they investigated the osseointegration level of scaffolds made of PEEK material with an admixture of HA in a cranial defect in mice. The results of the study show that scaffolds made of PEEK material with an admixture of HA demonstrated a higher level of osseointegration than pure PEEK scaffolds. A similar study by Durham et al. [11] investigated HA coating on PEEK implants in a rabbit model. Animals were studied in two groups of 9 for observation 6 or 18 weeks after surgery. The results of the study demonstrated that heat-treated HA coatings showed improved implant fixation as well as higher bone regeneration and bone-implant contact area compared to uncoated PEEK.

The aim of the subject study was to produce filaments with a diameter of 1.75 mm from the materials of pure PEEK and PPSU as well as variants with an admixture of a ceramic component in the form of HA and TCP that will meet the required production standards. The relevant analyzes in the form of the analysis of the diameter of the filament as well as the distribution of HA and TCP in composite materials represent the basic parameters of the quality of the manufactured filament. The output is to produce filaments that can be used in the 3D printing process and subsequently in pre-clinical studies.

Materials and methodology

Material characteristics

Single-component medical materials PEEK and PPSU as well as composite medical materials PEEK + HA/TCP and PPSU + HA/TCP were used for the production of filaments. All materials were in pellet form (see Fig. 1). In the composite material PEEK + HA/TCP, the mass ratio of the individual components was 80% PEEK, HA 10% and TCP 10%. In the composite material PPSU + HA/TCP, the mass ratio of the individual components was PPSU 80%, HA 10% and TCP 10%.

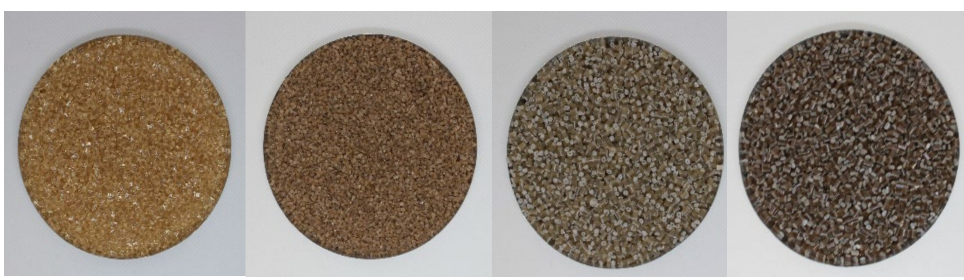


Fig. 1 Pellet form of materials for extrusion (A: pure PPSU ; B: pure PEEK ; C: PPSU + HA/TCP ; D: PEEK + HA/TCP)

Production of filaments

Filaments were produced from the materials described above on a Filament Maker Composer 450 (3devo, The Netherlands), which contains 4 heating zones. The entire production process consisted of 4 stages. In the initial stage, the Filament Maker was heated and cleaned at temperatures from 180 to 300 °C using HDPE and Devoclean Purge Mid cleaning materials. After cleaning, the filament production process continued with the 2nd stage where the filament production parameters were set (see Table 1). In the third stage of filament production, the diameter of the filament was recorded, which was determined to be 1.75 mm. The filament diameter was recorded via an optical sensor with an accuracy of ± 43 µm. After producing a sufficient amount of individual filaments, the process continued with stage 4 where the device was cooled and cleaned. The cooling of the device was up to a temperature of 180 °C with Devoclean Purge Mid and HDPE cleaning materials.

Table. 1 Basic settings for the production of PEEK filaments; PPSU; PEEK + HA/TCP; PPSU + HA/TCP

PEEK		**PEEK + HA/ TCP**	
Filament diameter	1,75 mm	Filament diameter	1,75 mm
Heat zone 1	390 °C	Heat zone 1	380 °C
Heat zone 2	390 °C	Heat zone 2	380 °C
Heat zone 3	385 °C	Heat zone 3	380 °C
Heat zone 4	375 °C	Heat zone 4	390 °C
RPM	4,5	RPM	3
Fan percentage	100 %	Fan percentage	100 %
PPSU		**PPSU + HA/ TCP**	
Filament diameter	1,75 mm	Filament diameter	1,75 mm
Heat zone 1	344 °C	Heat zone 1	344 °C
Heat zone 2	347 °C	Heat zone 2	347 °C
Heat zone 3	347 °C	Heat zone 3	347 °C
Heat zone 4	347 °C	Heat zone 4	347 °C
RPM	5	RPM	5
Fan percentage	72 %	Fan percentage	73 %

Microscopic analysis

Microscopic analysis was carried out using light and electron microscopy in order to quantitatively describe the distribution of the ceramic component. The total number of investigated samples was n = 40, while 10 samples were created from random areas from each filament produced. Before the analysis, the samples were prepared in dentacryl, sanded with sandpaper with a grain size of 200, 400, 600 and 800 μm. For the purposes of expertise, the experimental technique of light microscopy was used on the Olympus GX71 metallographic microscope with the Olympus DP12 camera. The details of the microstructure were checked by scanning electron microscopy on a Jeol JSM 7000F device in the mode of secondary electrons - SEI, which obtained detailed information about the morphology of ceramic particles and their distribution in the polymer filament matrix. Backscattered electron imaging - BSE provided information on the distribution of elements in the sample by atomic number. Areas in which elements with a higher atomic number are present are lighter in this display, on the other hand, areas formed by elements with a lower atomic number are shown as darker. A necessary condition for the analyzes of polymer matrix pellet samples was to ensure an electrically conductive surface of the preparation with each polymer matrix pellet. Before observation in the electron microscope, a layer of gold was deposited on all analyzed samples.

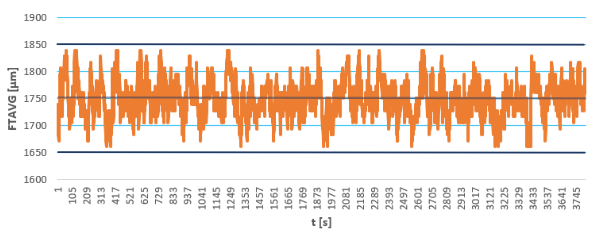
Statistical evaluation

The analysis of the diameter of the filaments was evaluated using descriptive statistics, while the following parameters were evaluated: diameter (x), standard deviation (SD), max./min. value, range (R), variance (Var(x)), kurtosis (K) and skewness (S_{KP}). Parameter K is an indicator of the distribution of measured data in the file. If its value is greater than 0, then the distribution is more peaked, and thus most recorded filament diameters approach the arithmetic mean.

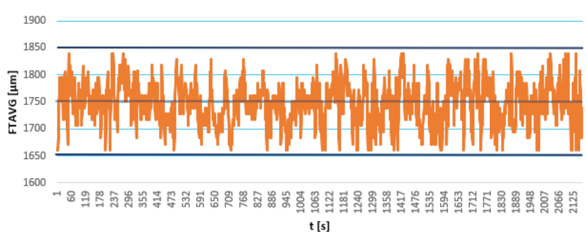
Results

During the production of filaments from the given materials, the limit values of the diameter of the filament were set at 1.85 mm (upper limit) and 1.65 mm (lower limit). As a reference value for the diameter of the filament, a value of 1.75 mm was set. In Fig. 2 it is possible to see the graphs of the measured diameters of the produced filaments, where it is shown that these limit values of the diameters were not exceeded during the production process of the filaments. The average value for the produced filaments from the PEEK material was at the level of 1.747 ± 0.039 mm, for the PEEK + HA/TCP material at a value of 1.7473 ± 0.038 mm, for the PPSU material at 1.749 ± 0.039 mm and for the PPSU + HA/TCP material at a value of 1.749 ± 0.032 mm.

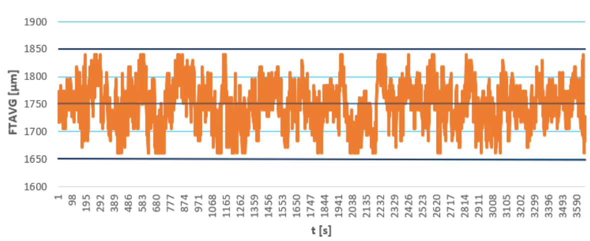
The SKP parameter evaluates the manufactured filaments from the point of view of the uniform distribution of the measured diameters of the filaments ($S_{KP} = 0$). If $S_{KP} > 0$, then smaller values prevail in the statistical set of measured filament diameters and the filament is thinner than the nominal value (1.75 mm). Conversely, if $S_{KP} < 0$, then higher values prevail in the statistical set of measured filament diameters and the filament is thicker than the nominal value. This indicator for the filament made of PEEK material had a value of $S_{KP} = 0.11$, which means that the filament is somewhat thinner than the nominal value. However, this minor deviation is not significant and does not affect the 3D printing process. The opposite effect was observed with other filaments. The S_{KP} parameter showed negative values (PEEK + HA/TCP = -0.04 ; PPSU = -0.06 ; PPSU + HA/TCP = -0.04) which indicates that more higher values than the calculated arithmetic mean were detected in the statistical set of measured averages. It is possible to state that with these filaments there are places with a larger diameter than the calculated arithmetic mean in the individual statistical files. However, these values represent minimal deviations from a uniform distribution, which can be considered insignificant. Other parameters can be seen in Fig. 2.



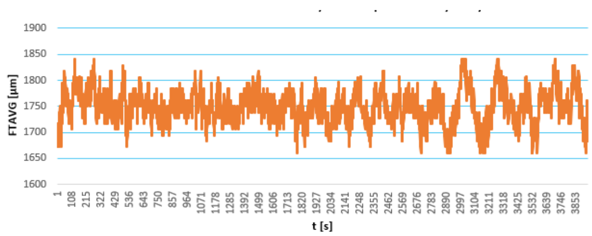
PEEK	
x = 1,747	R = 0,179
SD = 0,039	Var(x) = 1143,2
Max. = 1,84	K = 0,01
Min. = 1,661	S_{KP} = 0,11



PEEK + HA/TCP	
x = 1,7473	R = 0,179
SD = 0,038	Var(x) = 1504,1
Max. = 1,84	K = -0,43
Min. = 1,661	S_{KP} = -0,04



PPSU	
x = 1,749	R = 0,179
SD = 0,039	Var(x) = 1526,3
Max. = 1,84	K = -0,45
Min. = 1,661	S_{KP} = -0,06



PPSU + HA/TCP	
x = 1,749	R = 0,179
SD = 0,032	Var(x) = 1049,93
Max. = 1,84	K = 0,12
Min. = 1,661	S_{KP} = -0,04

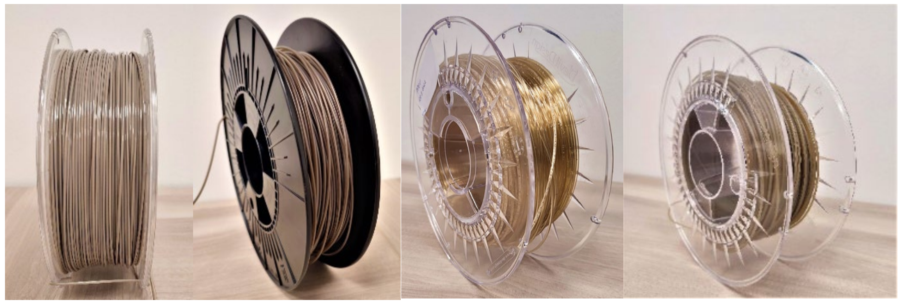


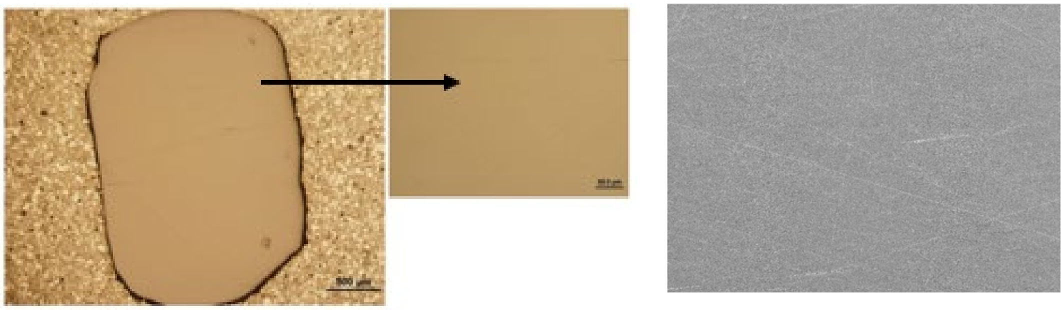
Fig. 2 Analysis of filament diameter of produced filaments using descriptive statistics (A: PEEK ; B: PEEK + HA/TCP ; C: PPSU ; D: PPSU + HA/TCP

Microscopic analysis

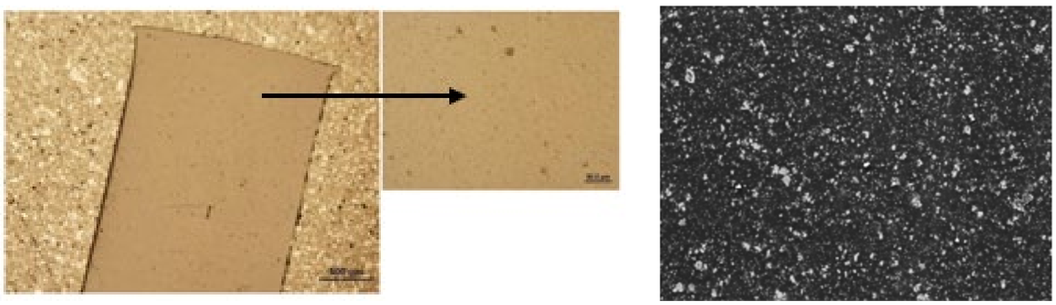
Fig. 3 shows the outputs in the form of light and electron microscopy for manufactured filaments from the materials PEEK, PEEK + HA/TCP, PPSU as well as PPSU + HA/TCP. During the evaluation of samples from PEEK filament, defects of the polymer matrix were not detected, and no filler was found in the matrix. In the EDX spectrum, the distribution of oxygen and carbon was visible in the entire section of the examined samples.

No defects in the integrity of the polymer matrix were observed during the evaluation of the produced filament made of PEEK + HA/TCP material. On the samples, it was possible to observe parts of the HA and TCP filler with a size of 1 to 2 µm (globular shape). The distribution of calcium and silicon was visible in the EDX spectrum. This distribution in the polymer matrix in the form of filler and clusters dispersed evenly, while all particles of the filler were well fixed in the polymer matrix. When evaluating the samples from the produced filament from the PPSU material, it was ensured that there is no filler in the polymer matrix in the entire observed detail. However, the presence of microscopic cracks in the form of bubbles was detected. Furthermore, only small scratches after sanding were observed in the close-up. In the EDX spectrum, a uniform distribution of oxygen and carbon was visible throughout the section. Samples made from PPSU + HA/TCP filament demonstrated by microscopic analysis that no defects in the integrity of the polymer matrix were detected. Irregular parts of the filler with a size of 1 to 2 µm (globular shape) were observed in the samples. The distribution of calcium and silicon was visible in the EDX spectrum, which in this case represents the HA and TCP components. This distribution was uniform in the section of the experimental sample.

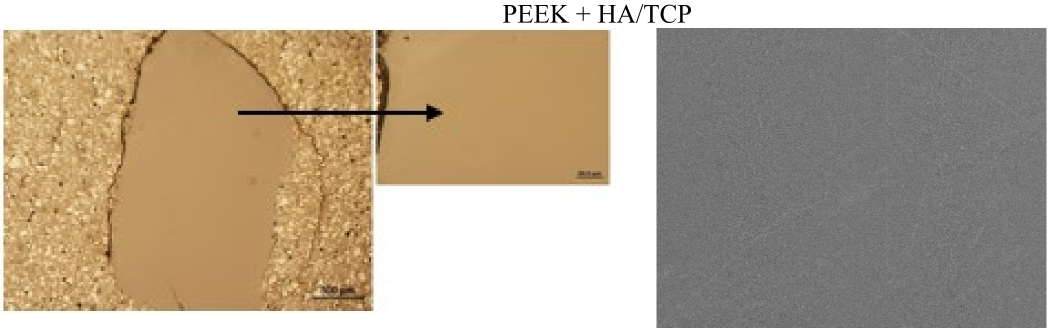
Overall, it can be concluded that in the case of composite filaments made of PEEK + HA/TCP and PPSU + HA/TCP, there is a uniform distribution of calcium and silicon in the sections of the experimental samples, and therefore the filaments are considered homogeneous.



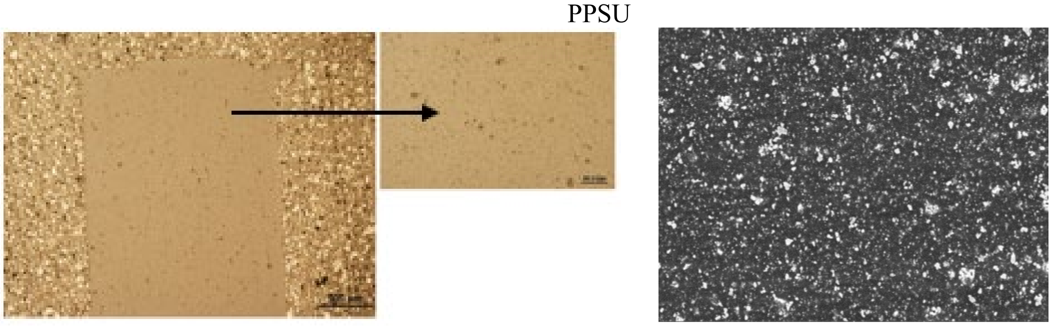
PEEK



PEEK + HA/TCP



PPSU



PPSU + HA/TCP

Fig. 3 Microscopic analysis of PEEK, PEEK + HA/TCP, PPSU and PPSU + HA/TCP materials

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Summary

Filaments made from the materials PEEK, PPSU, PEEK + HA/TCP and PPSU + HA/TCP meet the given regulations in the form of a diameter of 1.75 mm, as well as the homogeneity of the distribution of individual components in the case of composite materials in the form of PEEK + HA/TCP and PPSU + HA/TCP. Analysis of the diameter of the subject filaments showed minimal differences from the nominal value of the filament diameter of 1.75 mm. Microscopic analysis showed minimal clusters in the composite materials, which are considered insignificant and therefore it can be concluded that the produced filaments are homogeneous at the selected production parameters.

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