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## Production of biomedical filaments

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**Abstract:** In this study we try to produce biomedical polymers that have never been produced in such a proportion of materials. These fibers are intended for biomedical use in the future. All necessary parameters were recorded during production. Medically certified materials in the form of granules were used for production. The production took place on a filamentmaker Composer 450 from the company 3Devo, where 3 types of polymers PLA, PHB and thermoplastic starch were used. PLA is widely used in 3D applications because it is one of the most comfortable material that can be easily processed with FDM without the use of important vapor technologies. However, it is necessary to solve its solution thermal and high degradation rate during the stability of fiber production. A 25 percent amount of plasticizer in the first type of filament and a 30 percent amount of plasticizer in the second type of filament were added to the polymers.

**Keywords:** Additive technology FDM, filament, PLA, PHB

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### 1. Introduction

Thermoplastic-based fibers used in additive technologies are produced using plastic extrusion machines called fiber extruders or filament mashers. These extrusion systems work with the logic of mixing raw plastic granules and other additives in a mechanical mixer and subsequently transporting the formed composite granules through a hopper to the nozzle side of the heater by means of a screw shaft. These sophisticated devices can be found in various companies engaged in mass production. At the Department of Biomedical Engineering and Measurement, we managed to produce filaments with optimal properties. These manufactured filaments are intended for use in the biomedical field in the future. In the production process, we made a number of attempts to optimize the parameters. We used equipment from the company 3Devo. When using the filament in additive technologies, it is essential that it meets the requirements necessary for quality 3D printing and subsequent application in a medical environment. In this study, we managed to optimize all the necessary parameters for successful 3D printing. The diameter of the produced filaments must be in the range from 1.65 mm to 1.85 mm. This is important so that the filament does not jam in the nozzle.



## 2. Filament production and printing using FDM technology

The production of medical filaments is a production process divided into several steps. The first step is to obtain the material in the form of granules, which are then dried in a dryer. After drying, it is possible to proceed to the production itself. After the production of the filament, storage under suitable temperature conditions is important to prevent moisture degradation. The filament produced in this way is suitable for 3D printing of objects using FDM technology. FDM additive technology is the process of applying molten material to a heated flat table surface in layers. The fibrous material enters the heated nozzle via a feeder (Figure 1). This additive production technology is becoming more widespread due to the advantages of the thermoplastic material used. Due to the simple principle and low need for equipment, the cost of 3D printing using the FDM method is lower than with other additive technologies.

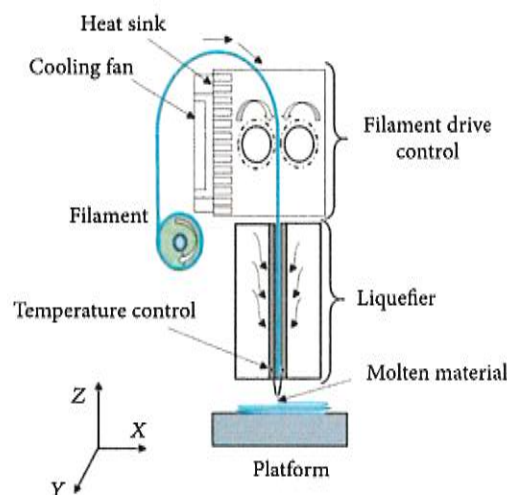


Figure.1. FDM 3D printing technology [5].

### 2.1. Preparation and drying of granulate in a dryer

To prevent the biodegradation process, the filament material was vacuumed in an opaque package. This material was supplied in the form of granules. Nevertheless, we dried the material in a dryer from 3devo (Figure 2). The drying temperature was set at 160 °C for 180 minutes.

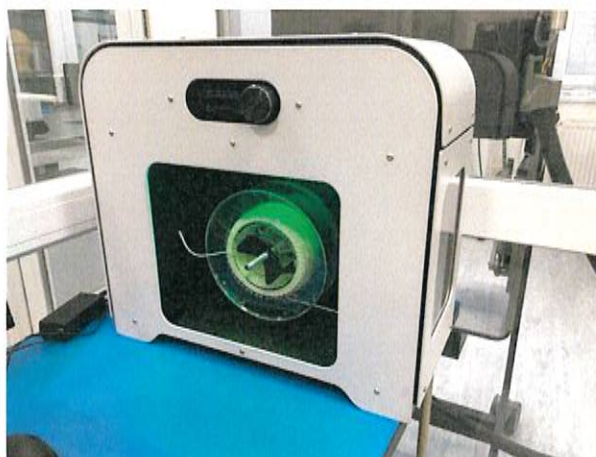


Figure.2. Granulate drying.



## 2.2. Filament extrusion

The filaments were produced on a 3devo filament maker Composer 450 under ideal conditions in an air-conditioned room at 18 ° C (Figure 3).



**Figure.3.** Filamentmaker Composer 450.

After cleaning the device, we poured the granulate into the hopper (Figure 4). In the production of the first medical filament with a 25% amount of plasticizer, we set the melting temperature to 170 ° C on 4th heater and to 171 ° C on other heaters. In the production of the second filament with a 30% amount of plasticizer, we set the temperature on first heater to 156 ° C, on second heater the temperature was 166 ° C, on third 155 ° C and on the last 4 heating element 150 ° C. We achieved these temperatures by combining knowledge about the melting temperature of PLA / PHB materials. After stabilizing the filament flow, we placed the extruded fiber in a sensor that measured the diameter of the filament. By monitoring and optimizing all production parameters, the filament was wound into a spool. The filament production parameters are summarized in Table 1 and Table 2. We managed to maintain the optimal filament diameter as can be seen in (Figure 5) and (Figure 6).



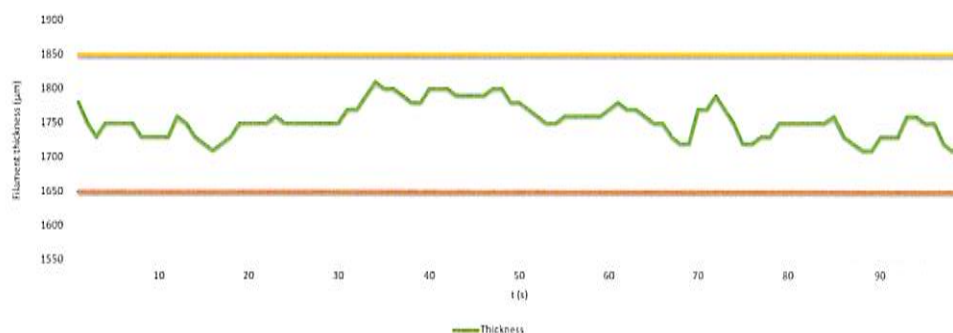
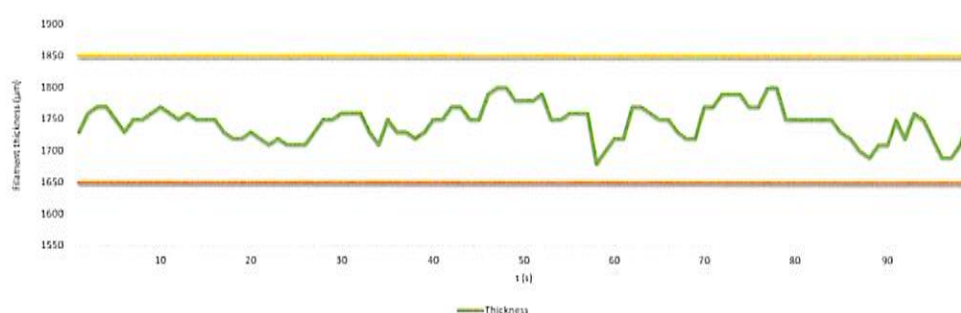
**Figure.4.** Granulate poured into a hopper.

**Table 1.** Production parameters of the first filament with 25% amount of plasticizer.

HEATING ELEMENT	4	3	2	1
REAL TEMPERATURE	170°C	170°C	172°C	171°C
SET TEMPERATURE	170°C	171°C	171°C	171°C
SET TEMPERATURE	2.0 RPM			
FAN PERFORMANCE	80%			

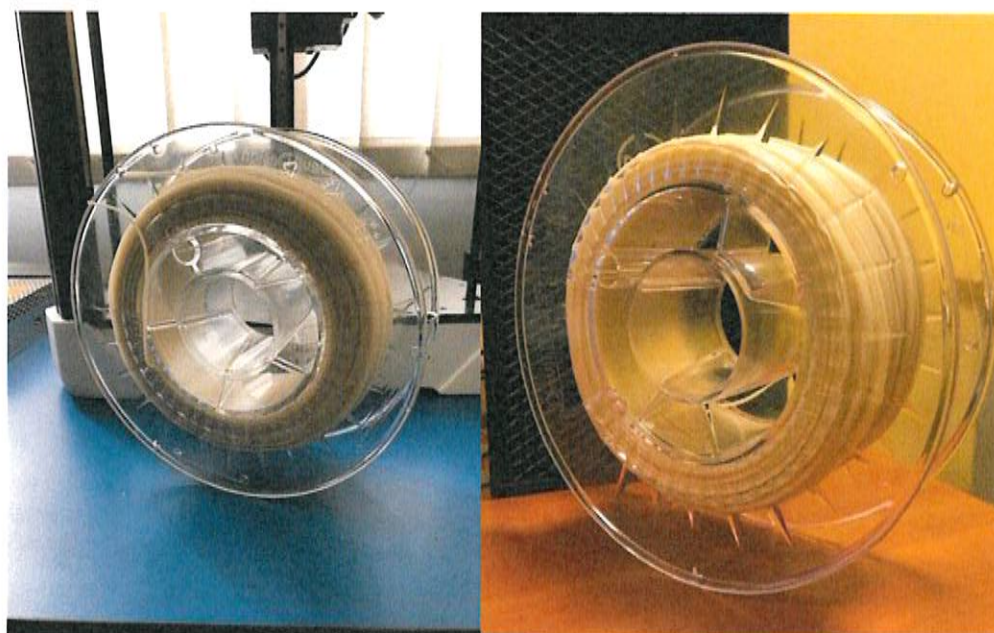
**Table 2.** Production parameters of the second filament with 30% amount of plasticizer.

HEATING ELEMENT	4	3	2	1
REAL TEMPERATURE	150°C	154°C	165°C	171°C
SET TEMPERATURE	150°C	155°C	166°C	156°C
SET TEMPERATURE	4.3 RPM			
FAN PERFORMANCE	100%			

**Figure.5.** Graph of the filament diameter with 25% of plasticizer per time (t).**Figure.6.** Graph of the filament diameter with 25% of plasticizer per time (t).

The diameters of both filaments were in the optimal range of 1.75 mm. The filament with 25% plasticizer weighed 410.13 g (Figure 7a) and the filament with 30% plasticizer weighed 556.82 g (Figure 7b).





**Figure 7a.** Finished filament with 25% plasticizer, **Figure 7b.** Finished filament with 30% plasticizer.

### 3. Conclusion

The mentioned scientific study brings new knowledge in the field of materials engineering and is a theoretical output of the production of filaments that will be used in the field of medical applications. Both filaments were extruded from PLA / PHB / thermoplastic starch granules with the addition of 25% plasticizer in the first type of filament and with 30% addition of plasticizer in the second type of filament. The most important condition regarding the diameter of the filament was met and the individual filaments correspond to the stated tolerance and have a constant diameter of 1.75 mm along their entire length. With the help of the Composer 450 from 3devo, located in the Department of Biomedical Engineering and Measurement, results have been achieved that have significant benefits in the production, testing and use of medically certified materials. The future of research lies in destructive and non-destructive testing of extruded samples using FDM technology. We managed to describe additive technology in detail in the introductory chapter of this scientific article.

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# Methodology of sample preparation for testing the adhesiveness of metal-ceramic dental prostheses

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**Abstract:** The present study aims to determine the methodology of sample preparation for testing the adhesion of metal-ceramic dental prostheses. The first part describes the design of the shape of samples for CAD software and their subsequent production using 3D printing and CNC milling. Subsequently, the procedure of applying the ceramic component to the prepared metal-based samples is described in detail. In the next part, the study focuses on the standardization of sample testing and the determination of indentation testing methodology.

**Key words:** ceramic; adhesivity; CoCr sample, Ti sample, zirconium

## 1. Introduction

Over the last five decades, the development of biological materials has advanced significantly and visibly improved the durability and quality of dental prostheses. Each biomaterial has its specific chemical, physical, mechanical and biological properties, which are important especially for the behaviour and the resulting effect of the implant.

The forces that act on the teeth vary depending on what type of food is chewed. The force applied to one tooth is also different to the total force between all the contacting teeth during chewing. The maximum bite force ranges from 500 N to 700 N. [1]. These high forces are thought to be a decisive factor in the friction of the tooth surfaces and the abrasiveness of the tooth surface [2].

The chewing of an individual is influenced by various factors that manifest themselves throughout life. Such basic factors include the following: age (low, high), food status (mushy, hard), pathology (bruxism).

Bruxism often results in physical damage to the enamel or altered chewing muscle function. Since muscles are the main generators of chewing force, a change in their function may be reflected in the value of the maximum bite force (MBF). According to a study [1], patients who regularly train their masticatory muscles can develop more bite force over the time.

Several studies describe the various factors and influences that can cause an increase in the value of the maximum bite force. Such examined factors include the sex of the individual, where the anatomical differences of the individuals as well as the average of the muscle fiber thickness and the incidence of bruxism in the given individuals were examined. [2-8]

The role of dental materials used in dental prosthetics is to supplement defect of hard tissue in the oral cavity with removable and fixed dental prostheses. They are part of the human body and participate in one of the most important activities of food processing - chewing.

In the oral cavity, dental materials are constantly exposed to body fluids and the strength of the masticatory muscles. These forces act on the teeth, producing various reactions leading to deformation, which can impair durability over the time.

Prosthetic materials that are used in dental must meet strict criteria such as mechanical properties, biocompatibility, wear resistance, high corrosion resistance, osseointegration, non-toxicity and long fatigue life. [9] [10].

Based on these findings, the present study is focused on the elaboration of a sample preparation methodology, which will be used to the test adhesivity of metal-ceramic dental materials.

## 2. Material and methods

The present study aims to develop a methodology for the preparation of samples intended for testing adhesivity of materials used to produce metal-ceramic dental prostheses.

### 2.1 Methodology of sample production

The methodology of production specimens includes proposition of adequate shapes and dimensions, material selection, production of three-dimensional objects in the shape of boards using a 3D printer (Mlab Cusing R (GE Additive, USA) and CNC milling machine Ceramill Motion 2 (Amann Girrbach, Germany), their grinding, cleaning and manual application ceramics and related configuration of suitable kiln parameters and additional cleaning of samples.

#### 2.1.1. Design of samples

The test specimen was modelled in SolidWorks 2018 3D CAD software (SolidWorks Corporation, USA). Based on ASTM C1624 (Standard Test Method for Adhesive Strength and Mechanical Damage of Ceramic Coatings Using Quantitative Single Point Scratch Testing), which explains in detail the scratch test principles along with limitations, applicability to various coatings, terminology, methodology, sample and equipment requirements, calibration, test procedure or even specific calculations, a rectangular shape of the test sample was selected. The frontal plane in which the model was selected was selected in the software. Subsequently, a "Central Rectangular" was selected from the toolbar and modelled with a page size of 20 mm x 20 mm. The "Add by extrusion" function was used to select a body thickness of 3 mm. The resulting model was exported to .stl format, which can be imported into software for 3D printing and CNC milling. [11].

#### 2.1.2. Production of samples

Three types of test materials were chosen to produce samples. The first material is cobalt-chromium powder Starbond Easy CoCr Powder (Scheffner Dental, Germany). The second group is Rematitan CL (Dentaurum, Germany) formed by TiAl and Vanadium. The last group is ceramics with zirconium base Ceramill Zolid HT + white. 5 pieces of test samples are produced from each group of materials.

The Mlab Cusing R 3D printer was used to prepare test samples from the CoCr and Ti bases. This 3D printer works using the SLM (Selective laser melting) method. The produced samples were prepared for further processing.

The last group is different, it does not have a metal base, but a ceramic one, the production of which is different. Five samples of zircon material with the required shape with dimensions of 20x20x3 mm were made on a 5-axis Ceramill Motion 2 milling machine. The advantage of this material is the fact that it is not necessary to apply surface ceramics as in the case of metal bases. The advantage of using zirconium is the combination of its high mechanical properties (flexural strength is around 1100 MPa +/- 150 MPa) and aesthetic properties (high translucency and transparency).

### 2.1.3. Ceramic application to test specimens

The first step before applying the ceramic was to sand the sample to ensure a homogeneous surface. The samples were cleaned with distilled steam and dried with compressed air. In the first step, a layer of Ceram Bond powder mixed with the liquid was applied to the CoCr and Ti sample with a brush to form a homogeneous mass. The application of this layer is important in order to create a mechanical and chemical bond between the metal base and the ceramic. These samples were placed in a kiln and the desired program given by the manufacturer was selected. The whole firing process took place in a vacuum and was divided into four basic phases:

- 1. 550°C, holding temperature (evaporation H<sub>2</sub>O),
- 2. 600°- 980°C, temperature rise 55°C/min,
- 3. 980°C, burning,
- 4. gradual cooling.



**Figure 1.** Samples after firing the first layer of Ceram Bond [own processing]

It took about 15 minutes to burn the first layer. After firing, each sample had to be steam cleaned and dried. Subsequently, it was possible to apply the second layer - opaque. The opaque is a cover layer for covering the metal to prevent the metal part from shining through the ceramic part. The powdered opaque was mixed with distilled water to the desired consistency and a thin uniform layer was again applied with a brush. After application, the structure was placed in the furnace and the firing process with individual phases was repeated.

The third applied layer was already ceramics. The ceramic powder specially designed for the CoCr substrate was mixed with the modelling fluid. The light pink slurry was then brushed onto the metal samples from centre to edge. Again, 4 phases of firing followed.

After the samples had cooled, it was again necessary to steam clean the surface and then dry it so that the last layer of ceramic could be applied. The process was repeated. When applying the ceramic, it was necessary to consider the contraction of the ceramic, which after firing reaches a value of up to 10% compared to the unfired mass. The firing lasted approximately 27 minutes. Figure 2 shows the final visualization of the samples prepared for testing by mechanical tests.





**Figure 2.** CoCr samples after last firing [own processing]

The procedure for Ti samples was the same as for CoCr samples, but a different type of ceramic (GC Initial, USA) was used, which is used to work with titanium.

Ceramics were not applied to the group of zircon samples, because zircon is a ceramic, therefore it has excellent mechanical and aesthetic properties, which are like ceramics applied to a metal substrate.

## 2.2. Standardization of sample testing

Several standards are set to ensure relevant results of biotribology studies. Standards such as ISO, ASTM, and others regulate and define a specific biotribological wear test to mimic various real-time conditions. ISO standards define the solution of procedures, methods of measurement, calibration and validation. This defines in detail the test parameters such as applied load, ambient temperature, movement speed, number of cycles, sample sizes and shapes and others. Table.7 shows information about ISO standards.

**Tab 1.** ISO standards for nano-indentation [12]

Name of the standard	Title	Year of publication	Subject
ISO 14577-1	Hardness and material penetration test (part 1)	2002 (modified in 2015)	Describes the test method
ISO 14577-2	Hardness and material penetration test (part 2)	2002 (modified in 2015)	Describes the procedures for verification and calibration of testing machines
ISO 14577-3	Hardness and material penetration test (part 3)	2002 modified in 2015)	Describes the calibration of reference blocks
ISO 14577-4	Hardness and material penetration test (part 4)	2007 (modified in 2016)	Describes the penetration of coatings and thin films

Nano-indentation is a universal technique that is widely used to characterize the mechanical response of materials. This is a technique in which scratches are smaller than 200nm (based on ISO 14577-1). Thin coatings have a thickness of the order of a few microns, so the conventional embossing method is not suitable for obtaining mechanical and tribological properties. It requires destruction and large dimensions of materials, which is economically unprofitable [12].

An optimal combination of metal and ceramic is required for a long-term clinical result. Separation of the ceramic from the metal is unacceptable to the patient and requires a redesign. The rate of reconstruction of metal-ceramic crowns is about 5-8% [13] [14]. Based on the specification of the American Dental Association 38 (2000) and the ISO 9793: 2012 standard, the strength of metal-ceramic dental prostheses is set at a minimum of 25 MPa. The mechanism of bonding of metal and ceramic is the result of chemical bonding, mechanical bonding, compressive and Van der Waals forces. Chemical bonding is the

most important bonding mechanism that occurs when firing ceramics. The most important factors influencing the quality of the chemical bond include temperature [ $^{\circ}\text{C}$ ], time [min], number of burns [n] and atmospheric pressure [kPa] [15-22]. Studies have shown that a slight change in the number and firing temperature of opaque layers will increase the strength of metal-ceramic dental prostheses. [23] To support the bonding of the layers, McLean recommends firing the opaque layer at a temperature  $20^{\circ}\text{C}$  higher than the production temperature for firing ceramics [24] [25].

### 2.3. Indentation testing methodology

#### „Pin on disc“

The tribological properties of the applied layers can be measured at the IPR SAS in Košice. The CSM THT high temperature tribometer in a "pin on disc" configuration will be used for the measurement. Mechanical properties such as Young's modulus and hardness will be investigated. Tribological pathways will be examined with a Neox Plu optical microscope (Sensofar, Spain).

All three types of materials (CoCr, Ti and Zr) will be tested. There will be two samples from each material. One sample from each type of material will be tested with a friction force of 5 N, the other with a friction force of 10 N. A zirconia pin with a diameter of 5 mm is used as the friction body. Measurements will be performed in air, at a temperature of  $37^{\circ}\text{C}$ . Humidity will be 90%, which corresponds to a humid environment in the oral cavity. All layers will be analyzed at a constant rotation speed of 180 mm / s, which corresponds to 100 revolutions per minute with a wheel diameter of 35 mm. The length of the test track will be 200 m.

#### Scratch test

The Bruker UMT 3 universal tribometer is used to measure mechanical properties such as adhesion, delamination and hardness. As it has a wider load range than the CSM THT high temperature tribometer, tests up to 1000 N can be performed. The effect of the applied load on coefficient of friction and wear of the layer.

Again, three types of materials (CoCr, Ti and Zr) covered with a ceramic layer will be tested. Samples are polished before testing. The polished surfaces of the samples will be arbitrarily divided into three fields resp. areas (left part of the sample, middle part and right part of the sample) (Figure 3) in order to avoid scratching on already existing scratches and to allow more tests to be performed on one sample.

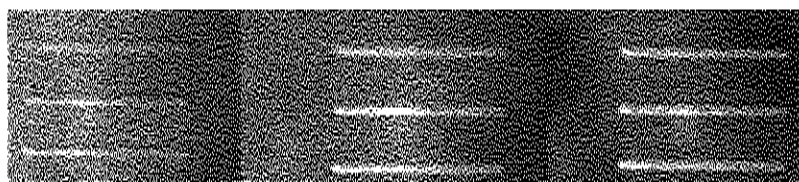


Figure 3. Breakdown of samples shown under a microscope

Nine different loads of 30 N, 50 N, 60 N, 80 N, 100 N, 120 N, 150 N, 180 N and 200 N with a constant loading force are selected. Thus, three samples from each type of material will be examined. A Vickers diamond indenter with a four-walled pyramid tip with an apex angle of  $136^{\circ}$  is selected for the study. The device is configured to perform a reciprocating motion at a speed of 10 mm / s. It will be tested under lubricated conditions with an ambient temperature of  $37^{\circ}\text{C}$ . The effect of the applied load on the coefficient of friction and wear of the layers will be investigated. For this purpose, all layers will be analyzed under nine different loads.

### 3. Discussion

As part of the theoretical research, the horizon of ceramic coatings has broadened and hardness test strategies have been identified. The purpose of the present study was to investigate the wear resistance of dental ceramic samples. The basic material of these coatings was metals and zirconium. The microstructure of the applied ceramic layers was formed by hard anchored particles. The particle properties determine the overall properties of the coating. A study of the wear mechanisms of the applied metal-ceramic layers has shown that, depending on the method of wear and the properties of the particles of applied ceramic, wear occurs preferentially in some structural samples. Therefore, attention was focused on determining the individual properties of the samples using nano-indentor tests, which allow to determine their basic mechanical properties - hardness and modulus of elasticity. Their mutual  $E/H$  ratio characterizes the elastic-plastic properties of the evaluated materials. Knowledge of these basic mechanical characteristics not only makes it possible to directly predict their resistance to wear and brittle failure, but is also necessary to determine other material constants, such as resistance to crack propagation evaluated by the method of measuring indentation fracture toughness.

### 4. Conclusion

The present study focuses on the design of a sample production methodology for testing the adhesiveness of metal-ceramic dental prostheses and on determining the most suitable methods for testing the samples themselves.

For the purposes of this study, three types of materials were selected, namely titanium, cobalt-chromium and zirconium. Metal samples were made on a Mlab Cusing R 3D printer (Concept Laser Inc., USA), zirconia were milled on a 5-axis Ceramill Motion 2 milling machine (Amann Girrbach, Germany). Layers of ceramics were applied to the metal substrates, which were applied by hand with a brush in the form of several layers so that the final thickness was in the range of 1 mm - 1.5 mm. The samples were fired in kilns at high temperatures under vacuum. Subsequently, a methodology of mechanical tests using "pin-on-disk" and "scratch test" methods was developed.

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**Conflicts of Interest:** The authors declare no conflict of interest

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# Scheme of methodology of magnesium powder preparation for 3D printing

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**Abstract:** Magnesium alloys are very attractive as biodegradable implant materials. This work deals with the preparation of a methodology for the production of magnesium powder with the aim of an amorphous structure for additive production. The powder is prepared on the basis of magnesium, calcium and zinc with the possible addition of yttrium to increase mechanical properties. The powder production itself consists of a suitable ratio of elements, chamber pressures and melting temperature. Based on the obtained data, it has not yet been possible to determine a suitable combination of individual parts in order to achieve a positive result. Achieving the required results is also hampered by the lack of professional literature in the field. The work explains the methodology of magnesium powder preparation.

**Keywords:** magnesium alloys, biodegradation, additive manufacturing

## 1. Introduction

Magnesium (Mg) as a metal with low weight, mechanical properties similar to bone tissue, importance in biological processes of the human body and degradation in the living organism is suitable for the production of biocompatible, biodegradable and osteoconductive implants in orthopedic or cardiovascular applications. In contrast to the titanium alloys used so far, the application of magnesium alloys is much more suitable.

## 2. Usage of magnesium

Biodegradable implants are the focus of the industry and have faced increasing interest in recent years. The main reason for the development of biodegradable implants is precisely their degradability in the physiological environment (the words "degradability" and "corrosion" have similar meanings but are used in the context of in vivo or in vitro). The advantage provided by this class of material is that the clinical function of the permanent implant is achievable and if successfully completed, the implant will disintegrate if it is no longer needed. Another of the main advantages of biodegradable implants is the elimination of the subsequent operation to remove the implant after sufficient tissue healing as with permanent implants. Thus, it means reducing or eliminating lifelong problems caused by permanent implants such as prolonged endothelial dysfunction, permanent physical irritation, and chronic local inflammatory reactions. Nevertheless, polymeric materials have a dominant position in current medical applications, but magnesium, iron and zinc based alloys have been introduced as more advantageous biodegradable materials for load-bearing and loaded implants due to their first-class combination of strength and toughness over polymers. [1]

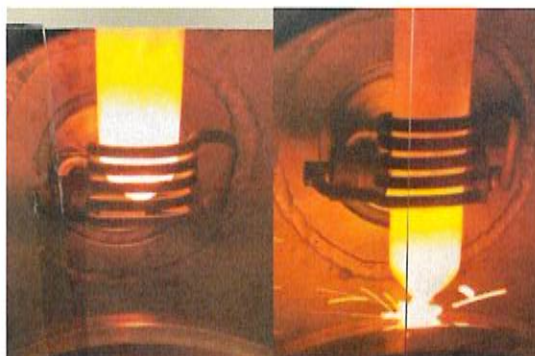
### 3. Methodology of powder preparation

The surface energy of magnesium powder is high due to the small particle size. As a result, Mg powder oxidizes easily and is difficult to deposit in layers. Therefore, alloying is usually used to reduce the sensitivity to oxidation. Some common non-toxic alloying elements include calcium, zinc and manganese. These elements affect the obtained grain structure, strength and heat resistance of magnesium. [2]

The prepared alloys contain magnesium, calcium and zinc. Yttrium 2%, 4%, 6% was gradually added at the expense of magnesium to increase the mechanical properties.

At present, the amorphous structure of the alloy  $Mg_{66}Zn_{30}Ca_4$ ,  $Mg_{64}Zn_{30}Ca_4Y_2$ ,  $Mg_{62}Zn_{30}Ca_4Y_4$ ,  $Mg_{60}Zn_{30}Ca_4Y_6$  is being prepared at the Institute of Materials Research of the Slovak Academy of Sciences.

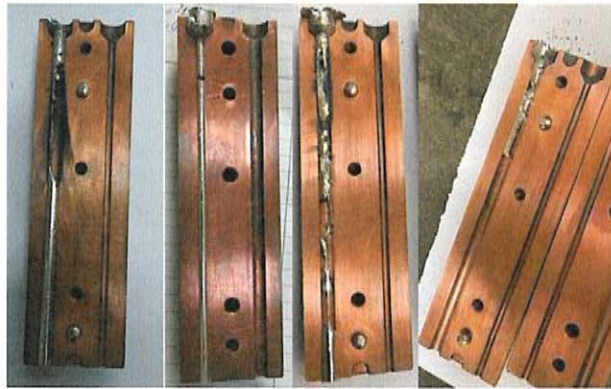
First, the proportions of the elements to the weight of 5g are weighed. Initially, only  $Mg_{66}Zn_{30}Ca_4$  was used but the samples were very fragile. Therefore, yttrium was added to increase the mechanical properties. The firing process was also modified, because before that only the melting point of all the elements present was reached and fired, but now it remains at a temperature of about 12-15 min. Initially, the elements are weighed, pressed and placed in a graphite tube. It is operated at the Melt Spinner SC plant (Edmund Bühler GmbH, Germany) where a high vacuum is gradually generated by means of an argon overpressure.



**Figure 1.** Melt Spinner; left-heating the tube, right-firing the contents of the tube under argon pressure

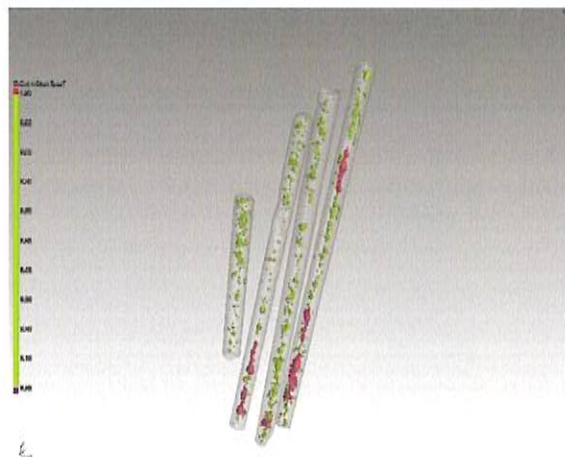
Initially, a pre-vacuum is created using a rotary pump and a second time it is pulled with a  $5 \cdot 10^{-2}$  millibar high vacuum turbomolecular pump. When the chamber is ready, the insert is lowered to be in a coil where it is gradually heated up to 600 degrees Celsius to homogenize the entire contents of the graphite tube (Figure 1). At a temperature of 600 degrees, it is held for about 15 minutes. The insert is then fired under argon pressure as the tube is lowered. The copper mold into which it is cast is cooled by water. It is cast at a temperature of 730-740 degrees.





**Figure 2.** Cast samples  $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$

The goal is to create a solid rod with an amorphous structure (Figure 2). Samples were monitored with a ZEISS METROTOM 1500 non-destructive industrial tomograph (Carl Zeiss, Germany) (Figure 3). The Carl Zeiss meter enables non-destructive non-contact measurement of components in their entire volume by applying X-rays. Using computed tomography (CT), we get a comprehensive view of the part from any side and in any section. The point cloud representing the volume of the part is obtained from the number of X-rays taken to measure the part as it rotates about the vertical axis. In the process of generating a point cloud, the images are analyzed and in the resolution given by the high accuracy of the system, each point is assigned exact coordinates in space and its intensity, which corresponds to the density of the part material. [3]



**Figure 3.** CT scan ( $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$ ); green color is defects smaller than  $1\text{mm}^3$ , pink color - defects larger than  $1\text{mm}^3$

From figure 3, it is possible to state a high presence of defects along the entire length of the cast bar. Mechanical testing on such samples would not be relevant as the result would be affected by input defects. The samples that were formed had a high porosity, so exhausts were made in the copper mold so that the bubbles could be released during the casting process.



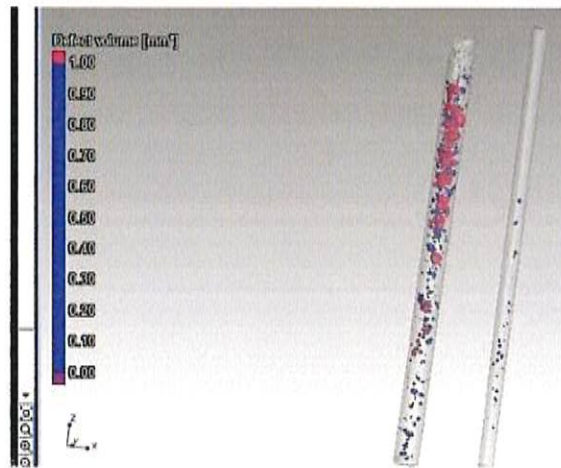


Figure 4. CT scan ( $Mg_{66}Zn_{30}Ca_4$ ) after casting with exhausts with lower porosity

For 5 mm diameter the porosity is 7.63%, for 3 mm 0.345%, the porosity of the sample was reduced (Figure 4).

#### 4. Further testing

The produced samples will then be subjected to several tests. Among the first will be a mechanical pressure test. The samples for the pressure test will be adjusted to a size ratio of 1: 2, with a diameter of 3mm and a length of 6mm. The pressure test will take place on a Tiratest 2300 (Tira GmbH, Germany), which will monitor the maximum rupture force, of which the ultimate strength and the assumed yield strength. The goal is to get the strength limit  $R_m$  higher than 550 MPa, because according to Wang and the team (Figure 5), they reached strength strengths of up to 600 MPa with similar alloys. [4.5]

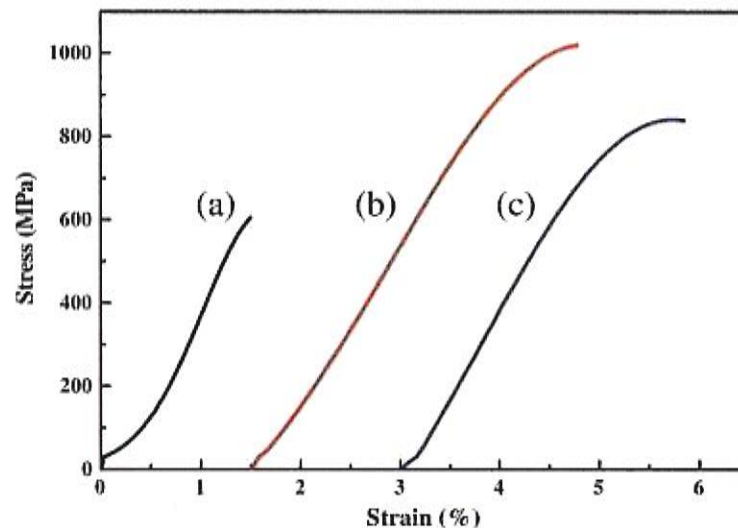


Figure 5. Deformation stress curves between alloy bars (a)  $Mg_{66}Zn_{28}Ca_4Y_1$ , (b)  $Mg_{66}Zn_{27}Ca_4Y_1$  and (c)  $Mg_{66}Zn_{25}Ca_4Y_3$  with a diameter of 1.5 mm when compressed at room temperature. [4]

At the same time, the samples will be subjected to biodegradation. Half of the tested samples will be surface treated with chitosan, which should slow down the degradation. The other half will be uncoated, all samples will be soaked in Hank's solution (Hank's solution is an example of an artificial solution that is standardly used for corrosion testing in laboratory conditions) for 45 days, when weighed every 15 days, taken by industrial

tomograph so that the course of degradation is clear and at the same time the pH is equalized to 7.4 before re-immersion. The samples in the tubes will be at a stable temperature of 36 ° C to simulate body temperature and will be placed on a shaker that will simulate the movement of body fluids. [6]

## 5. Conclusions

Magnesium as a newly discovered material for implantation provides a very promising future in the field of regenerative medicine. However, the complexity of its processing slows down the development in additive production. This article deals with the preparation of magnesium alloys, with a view to the future possibility of implantation, so that they are suitable for processing by additive technology.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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# Methodology of degradation assessment of polymeric materials

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**Abstract:** The presented study deals with the definition of biomaterials and the degree of biocompatibility, which is important in the interaction of the organism with a foreign entity. Furthermore, the process of biodegradation of materials to which any material implanted in a living organism is subjected is developed. Since one of the conditions for the introduction of new biomaterials into clinical practice is a series of in vivo and in vitro testing, the authors collective focused on the in vitro method, where a methodology for assessing the biodegradation of polymeric materials was proposed. The choice of polymeric materials was not random, but purposeful due to the increasing use in implantology because of their excellent mechanical properties, easy availability, and cheap manufacturability.

**Key words:** biodegradation, testing methodology, polymer materials

## 1. Introduction

An integral part of modern medicine is an intensive connection with the field of implantology. Since ancient times, people have tried to replace damaged tissues or missing parts of the human body with available natural materials such as wood or animal skin. However, over time, synthetic materials began to come to the fore, which were characterized by better mechanical properties, increased functionality, and the ability to better withstand degradation processes. Subsequently, the interest of scientists in the field of regenerative medicine, cell biology, tissue engineering, biomedical engineering, etc., focused on the development of bioresorbable materials, which would support the growth of new living cells and thus initiate increased regeneration of the human body to the point where the damaged tissue or segment in the living organism was completely replaced. As a result of the biodegradation taking place in the human body, the material would decompose into bioabsorbable particles upon termination of its function, thus achieving a state where reoperation of the damaged part would no longer be necessary due to implant failure and thus increase patient comfort itself. However, in order to achieve such bold goals, it is necessary to know to a sufficient extent how biodegradation affects the mechanical-physical-chemical properties of given materials over time. These results can be achieved by a series of tests using the in vitro method, which is also the subject of the research of the present work [1].

## 2. Biomaterials and their interaction with the human body

According to the author Kulinets, biomaterial can be defined as material that comes into contact with a living organism in order to perform the desired function. Because biomaterials can be created from a wide range of solids, liquids, and gels, the definition itself has changed over the years to demonstrate the current state.

At present, biomaterials can be divided into three basic groups:

- Synthetic materials (metals, polymers, ceramics, composites)

- Natural materials (plant origin, animal origin)
- Polysynthetic or hybrid materials

Because medicine uses biomaterials to treat, augment, or replace organs and tissues, it is essential that the material meets clinical, manufacturing, and economic requirements. In order to achieve the desired result, chemical, physical, biological, and mechanical requirements are considered in the selection of a suitable material. The material must not undergo spontaneous degradation during implantation, must not cause allergic and inflammatory reactions, nor must it be non-radioactive, non-carcinogenic and non-toxic [1]. All of these requirements determine the degree of biocompatibility of the material, which is crucial because, when a tissue is injured, an immediate healing reaction occurs in the body by flooding the damaged area with blood. The soluble fibrinogen contained in the blood converts to fibrin and forms a blood clot that promotes platelet adhesion. Subsequently, monocytes aggregate, which differentiate into macrophages, which absorb foreign microbes and cells, thus cleaning up the site of injury. The blood clot is transformed into vascularized granulation tissue by fibroblasts and endothelial cells, which is gradually replaced by the extracellular matrix (ECM). The degree of ECM remodeling depends on the extent and location of the injury, where the result is either a total regeneration of the tissue structure or the formation of different types of scar tissue. When any material is implanted in an organism, a process called a foreign body reaction occurs in the human body (Figure 1). Immediately after implantation, non-specific adsorption of proteins occurs on the surface of the implant. The paradox is that this phenomenon never occurs during natural physiological wound healing. Due to the excessive adsorption of individual cells, inflammatory processes are triggered at the implantation site, resulting in the formation of multinucleated cells surrounding the implant. The final stage is the complete isolation of the implant by avascular, collagen tissue [2].

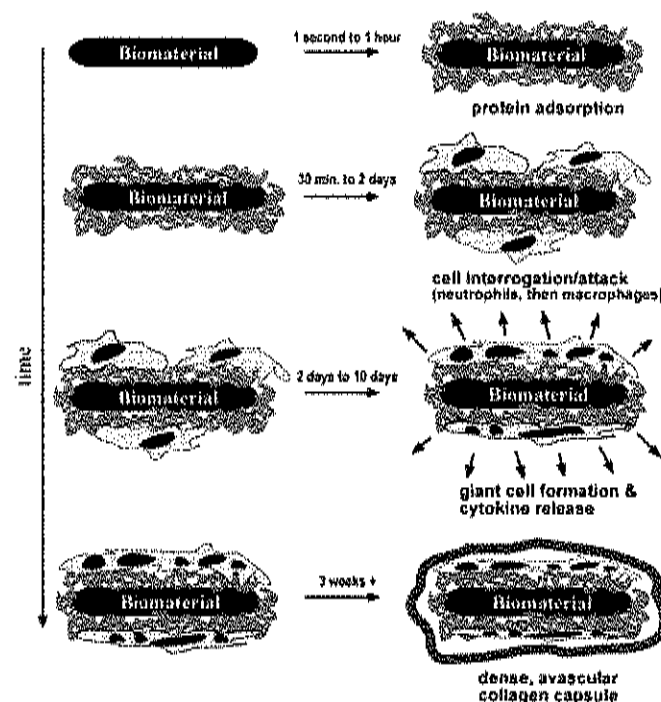


Figure 1. The organism reaction to a foreign entity [2]

### 3. Degradation of materials and their testing in vivo and in vitro



Degradation can be defined as an irreversible process in which the structure of a given material changes permanently over a period of time. In the case of components implanted in living tissue, this term is called biodegradation. In the process of biodegradation, organic and inorganic substances are decomposed into simpler and more easily degradable compounds with the help of living organisms [3]. Experts in the field of surgery, therapeutic medicine and biomedical engineering are increasingly looking at the process of biodegradation as a targeted phenomenon, which brings with it a wide range of usability. Examples are biomaterials that are implanted in the human body for the gradual release of drugs, in the case of tissue engineering these are porous structures on which living cells are deposited. Such a scaffold provides the body with a suitable environment for the damaged tissue to regenerate to such an extent that the porous structure is no longer needed. Controlled biodegradation by the immune response results in gradual degradation of the scaffold without intoxication of the body [4-6].

### 3.1 Possibilities of biodegradation

When implementing any material into clinical practice, the material must be subjected to a series of tests, which are performed using two methods, *in vivo* and *in vitro*.

The *in vivo* method is based on the principle of monitoring changes in the implanted material that take place directly in the living organism, for example animal models, in the case of clinical studies humans [7].

The *in vitro* method is performed under laboratory conditions in which the environment of the living organism is simulated in the presence or absence of cellular structures, while the interaction of the material with the solution is monitored. It should be added that in order to obtain the most relevant results, it is necessary to subject the investigated material to both test methods [8].

## 4. Design of the methodology for biodegradation of polymeric materials *in vitro*

In the presented work, we focused on the evaluation of polymeric materials *in vitro* due to the fact that they are widely used in the field of implantology because they are easily manufactured in various forms and their composition is similar to those found in living organisms.

The design of the *in vitro* methodology was preceded by research of scientific publications in the field of biodegradation of polymeric materials, which is listed in Table 1.

**Table 1. Overview of scientific biodegradation studies**

Material	Degradation solution	Time of degradation	Authors collective
PCL	PBS solution + lipase	28 days	Neumann et al., 2019 [9]
PHB/HA	Suspended growth medium	30 days	Senatov et al., 2017 [10]
PLA	SBF solution	8 months	Guo et al., 2017 [11]
PLA/PCL	PBS solution	4 weeks	Navarro-Baena et al., 2016 [12]
PLA/BG	PBS solution	6 months	Vergnol et al., 2015 [13]
PLA/PEG	SBF solution	8 weeks	Barbeck et al., 2017 [14]
PLA/BG	SBF solution	600 days	Blaker et al., 2011 [15]
PCL	PBS solution + NaOH	6 weeks	Lam et al., 2008 [16]
PLA/PHB	PBS solution	12 months	Freier et al., 2002 [17]

The first step in evaluating polymeric materials *in vitro* is to select the material to be tested and determine a suitable biodegradation method.

Accelerated in vitro biodegradation, in which the test material is exposed to more demanding conditions, which can be induced by accelerating the flow in a mechanical mixer, by increasing the ambient temperature as well as by changing the pH. The advantage of this method is the delivery of results in a short period of time, which ultimately leads to a reduction in the cost of the testing itself. The disadvantage is the need to verify the relevance of the results by standard non-accelerated testing [18].

Natural biodegradation simulates real processes that take place in the body after implantation of the material. Both of these methods are included in the European standard ISO 10993-13, which specifies values such as pH, ambient temperature, duration of the experiment, etc. [19].

The second step is to select a biodegradation medium that depends on the selected material and its solubility. The difference between the individual solutions lies in their composition, speed of action and in the properties themselves. The following media are used for biodegradation experiments.

The saline solution, which contains 9 grams of NaCl dissolved in 1 liter of water, reaches an almost identical osmolality value with the blood plasma, which has a value of 287 mOsm/kg. For this reason, it is widely used in molecular biology, cell biology and medicine, where it is infused in dehydration or serves as a solvent for various drugs [6].

Phosphate-buffered saline (PBS) can be defined as an aqueous salt solution containing compounds such as potassium dihydrogen phosphate, sodium hydrogen phosphate, sodium chloride or potassium chloride. Due to the correct salt concentrations and stable pH, it is one of the most widely used solutions in the field of biodegradation [13].

Simulated body fluid (SBF), while maintaining physiological temperature and constant pH, is able to reach the osmolality value of blood plasma, similar to physiological solution. It is used to evaluate the bioactivity of the material because it contains a large amount of calcium and phosphate ions, which cause spontaneous growth of bone cells on the surface of the biomaterial. [15]

Hank's solution (HS) consists of inorganic salts that are rich in bicarbonate ions supplemented with glucose. It is used in cell culture media because it maintains a physiological pH of 7-7.4, which is necessary for proper cell growth [6].

The third step is the preparation of test samples. In the case of polymeric materials, based on a review of the scientific literature, it is appropriate to use additive technology, i.e., 3D printing, to produce samples. Based on the prepared samples, the duration of the experiment, the ambient temperature and the required pH values are determined. As it is necessary to ensure constant conditions throughout the biodegradation assessment, regular monitoring of these conditions is necessary to achieve relevant results.

The fourth step is to insert the test samples into the individual solutions. Prior to self-storage, samples must be weighed, and this process repeated at each condition check.

The fifth step is to evaluate the results obtained. Biodegradation can be assessed based on changes in the weight of individual samples. From these data, the absorption of the samples and the weight loss of the samples can then be calculated. The absorption analysis of the samples provides important information regarding the hydrophilic nature of the test material and the weight loss analysis can define the rate of degradation of the samples in each solution. By analyzing pH changes, it is possible to determine which solution showed the most stable pH values during biodegradation. Industrial tomography analysis provides more detailed information regarding changes in sample volume, surface area, and radius compared to a non-degraded sample. The analysis of mechanical stress will make it possible to determine the influence of biodegradation on the mechanical properties of the monitored materials.

## 5. Conclusion

The presented work dealt with the methodology for the evaluation of biodegradation of polymeric materials using the in vitro method. The design was preceded by an overview of scientific publications listed in Table 1, in which the authors monitored the effect

of biodegradation solutions on individual polymeric materials. The aim of this study was to summarize the available information and create a clear background material that will be used for further research and subsequent publications.

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# Methodology of the personalized implants manufacturing process by additive technology

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**Abstract:** Advances in medicine and additive manufacturing have changed the way surgeons use patient data for personalized treatment. Polyetheretherketone (PEEK) is currently mentioned more and more as a suitable biomaterial in the field of cranioplasty. With the development of additive technologies, personalized implants in the field of medicine are appearing more and more often. As a result of examining the reliability of personalized implants using additive technology, it becomes a necessary effort. In this study, the process of production of cranial implants and their optimization was investigated. The results of the study revealed high dimensional accuracy and repeatability of the M220 3D printer using FFF technology and showed acceptable morphological similarity in terms of contour adaptation and continuity. In conclusion, personalized implants should be tested by simulating real situations where the implants are subjected to different external forces in different injuries.

**Keywords:** additive manufacturing 1; cranioplasty 2; patient specific implant 3; fused filament fabrication

## 1. Introduction

Cranioplasty is a surgical reconstruction procedure that restores the physiological functions of the cranium and restores the structure of cranial defects [1-2]. The goal of cranioplasty is also reconstruction from the point of view of aesthetics, which also improves the quality and mental well-being of the patient. Defects in the cranial part of the patient can occur with decompressive craniectomies, which can lead to cranial infections, head injury, or head tumours [3-4]. Currently, great advances in the reconstruction of head defects have been recorded using various CAD / CAM software [5-7] and in parallel using various AM technologies. Using AM technologies and CAD / CAM software, it is relatively easy to design and manufacture personalized implants for a patient with a head defect, and this opens new possibilities for surgeons. There are already studies in this area dealing with the production of biomodels, surgical guides, prosthetic devices [8]. In the field of 3D printing, the most used technology is FFF / FDM technology, which is based on the extrusion of material usually in the form of a filament. Advances in these technologies enable the printing of high-temperature thermoplastics, e.g., PEEK, from which milling implants are commonly made, however, medical-grade PEEK have only recently been used [9-10]. As the use of 3D printing increases, questions are being raised about examining the reliability of the production of personalized implants from PEEK biomaterial [11-

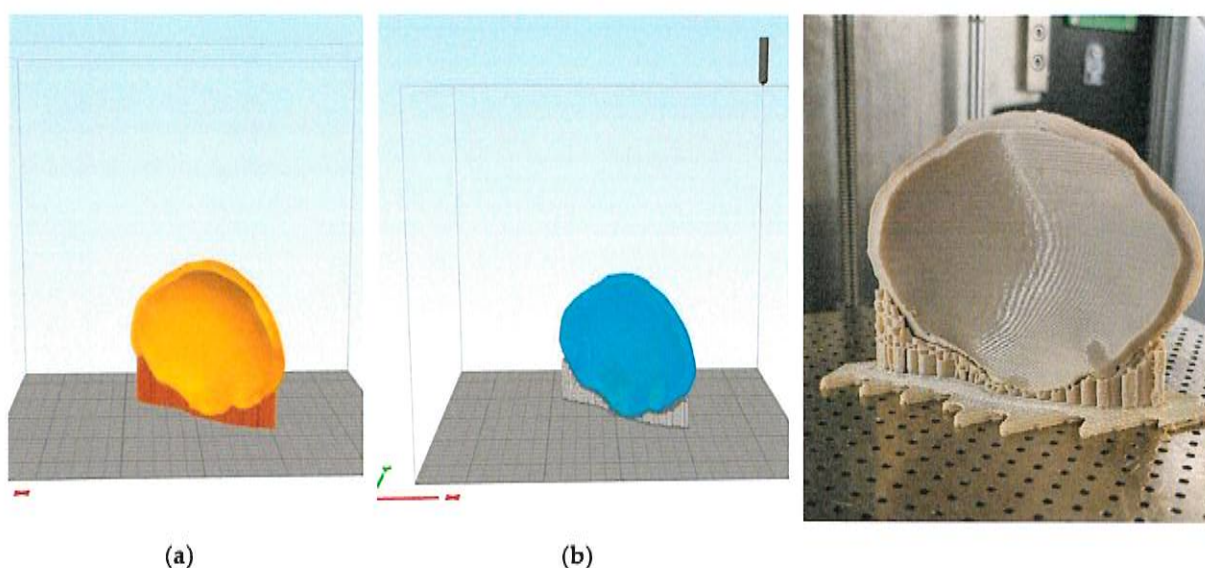
12]. The aim of this study is to provide a methodology for the design and production process of personalized implants using 3D printing.

## 2. Methodology

This study describes the following processes: DICOM data processing in MIMICS software, implant production process using 3D printer M220.

### 2.1 DICOM data processing in MIMICS / 3-matic

M220 3D printers using FDM / FFF technology for PEEK material (Apium, Additive Technologies GmbH, Karlsruhe, Germany) were used to produce a personalized cranial implant. This 3D printer is designed to produce implants used in clean rooms with a constant temperature in the range of 10 - 30 ° C. The personalized implant was made of PEEK material with a filament diameter of 1.75 mm (PEEK 4000, Apium, Additive Technologies GmbH, Karlsruhe, Germany). To achieve the best 3D printing process, the support under the 3D implant model is designed automatically or manually to prevent the implant from deviating during 3D printing. The parameters of the 3D printing process can be found in Tab. 1 and in Tab. 2. After setting up the process in Simplify3D software (Cincinnati, OH, USA) it is necessary to generate a g-code from which the M220 3D printer software can read the parameters of the 3D printing process (Apium Print Control, Apium Additive Technologies GmbH, Karlsruhe, Germany) Fig. 1.



**Figure 1.** Personalized implant extrusion process: (a) Orientation of the implant in the slicing software; (b) Parameter setting and generating a g-code; (c) 3D printed cranial implant.

**Tab. 1** Parameters for the Cranial implant printing process.

Extruder	Infill	Layer
Extruder diameter 0.4 (mm)	Internal Fill Pattern Rectilinear	Primary layer height 0.15 (mm)
	External Fill Pattern Rectilinear	Top solid layers 2
	Infill Percentage 100%	Bottom solid layers 2
	Angle 45°/-45°	Outline 2

**Tab. 2** Parameters for the Cranial implant printing process.

Temperature	Support	Speed (mm/min)
Extruder temperature 485 (°C)	Support infill percentage 40 (%)	Printing speed 1900
Airflow temperature 130-280 (°C)	Support pillar resolution 3 (mm)	

The printing process before the final printing consists of the following quality control steps: (1) filament moisture control; (2) calibration of the plate by software and subsequently manually; (3) nozzle diameter calibration before separate implant printing.

To prevent deformation of the implant during printing, automatic raft generation has been activated and is integrated into the M220 3D printer software (Apium Print Control, Apium Additive Technologies GmbH, Karlsruhe, Germany). Subsequently, the printing process was started, and the production of the cranial implant was completed. To ensure repeatability, each implant must be placed in the middle of the building plate during printing to achieve an even heat distribution in the chamber. After extrusion, the implants and the implant support are separated from the raft using forceps and a chisel.

### 3. Discussion

Over the years, biomaterial PEEK has proven to be a good choice for the reconstruction of craniofacial defects [6,13-14], but at present little is known about implants made using additive technologies. With the advancement of additive technologies, prospects are emerging for personalized implants made of PEEK material manufactured using FDM technology [10-11,15]. The current literature on the geometric and morphological characteristics of personalized implants made from additive technologies is. Although few studies have evaluated the accuracy of cranial defect reconstruction using hospital-made implants, these studies are primarily focused on moulded acrylic prostheses [16-18]. One study focused on the quantitative evaluation of dimensional accuracy of personalized implants made using laser sintering technology in terms of print orientation [19]. In a study by Berrett et al. [19] stated that the transversely (horizontally) manufactured implants



showed the smallest deviation from the planned model. Therefore, due to the working principle of FDM technology, cranial implants were personalized in an axial orientation with minimal support structures. According to our results, our personalized implants have been printed to an acceptable extent in terms of dimensional accuracy for cranioplasty reconstruction procedures. In addition, the dimensional accuracy of the FDM technology indicates that the personalized cranial implants produced using the M220 3D printer had high repeatability with minimal deviations. Irregularities noted in the morphological adaptation of the implant to the contact area of the defect can lead to postoperative complications. The limitations of the study include simplifying the setup of printing processes. In the future, it would be appropriate to test personalized implants by simulating real situations where the implants are subjected to different external forces in different injuries. And analyse internal types of fills by non-destructive inspection, which would help accurately determine the accuracy of internal structures after printing processes.

## 5. Conclusions

In terms of geometric results, personalized cranial implants made using additive technology had high dimensional accuracy and repeatability. In addition, these cranial implants revealed clinically acceptable morphological adaptation and contour continuity. Accordingly, the results of this study are satisfactory with the expectations of the ceramic implant manufacturing process, but the specific attributes have room for further improvement. In the future, these personalized implants need to be tested biomechanically to see if they have sufficient strength for subsequent clinical use.

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# Software support and additive technologies for veterinary applications

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**Abstract:** The purpose of this publication is to describe the process of implementing individual implants for veterinary applications. One of the main points is the description of individual software suitable for such use. The individual software are also compared in terms of their use in the individual implants modeled by them. Another part of the paper is focused on the use of 3D printing technology, also taking into account their use in individual implantology for veterinary applications.

**Keywords:** Individual implant; software; additive production; veterinary

## 1. Introduction

With the gradual introduction of additive technology and rapid prototyping in various industries such as engineering [1], electrical [2] or construction [3], additive manufacturing has also found application in the field of human medicine [4]. The production of individual implants, but also orthotic devices, is expansive and, due to this fact, additive production is gradually finding its place in veterinary applications [5].

An important part of the production of any product produced through additive production is its 3D modelling or 3D design. The production of individual proteinaceous devices using additive technology is a relatively complex process which, as in other industries, cannot be done without knowledge of the individual software and its operation [6] [7]. However, in the case of medical use, whether in human or veterinary applications, design, in addition to the software support itself, cannot be done without the support of appropriate diagnostic and imaging methods. One of the imaging methods used in the design of individual implants is computerized tomography or CT. Data in the form of DICOM are processed into stl. files using appropriate software. (Stereolithography), which can be further modified in these software to create individual 3D models [7] [8]. Another way to obtain this data, for example for the production of individual orthotic prostheses, is to use handheld 3D scanners such as Artec Eva [9]. The principle of data processing is similar to the previous case.

In addition to the production of implants, these software can also be used to plan surgery by printing 3D anatomical models. Surgical planning, especially for personalized hard tissue implants, is based mainly on conventional CT images or MRI images. Thus, for effective preoperative planning of a surgical procedure, its planning on 3D printed models based on CT information is possible. Another way is to simulate such surgery directly with software on a virtual model. However, this requires specific software functions to simulate surgical procedures and to calculate certain parameters such as volume distance and bone density. In the case of procedures requiring individual implants, the implants can be designed on a 3D model. An alternative to this approach is to work directly on a 3D model in a computer [10].



There are several types of software on the market used for 3D product modelling [11]. Some of them are their certifications directly intended for use in human medicine [12]. However, other non-certified software can also be used for this purpose – for example in the field of veterinary applications. This may be software that is freely available or software that requires a valid license to be purchased. In this publication, I will try to describe the software that was used in the design of implants for veterinary applications.

## 2. Overview of softwares

Whether it is the printing of 3D models for the planning of the operation or the design of the individual implant, both processes require the processing of CT or MRI images by specialized software for medical imaging. A powerful software interface is required to accept the inputs of all types or brands of scanners, to facilitate the selection of the anatomical structure made using imaging methods, and to link this information to 3D printing devices.

Surgical simulation on virtual models on a computer requires specific functions of the surgical simulation software and other software packages (CAD, FEA, CFD, etc.) [10]. Equally important is the "separation" of individual tissue types based on their bulk density. For these purposes, but also for design purposes, software such as Mimics or Vesalius 3D are used [25] [26] [27].

In addition to the software mentioned above, there are many other software that can be used to model and design 3D implants. However, not all of them are permitted for use in human medicine. As these are veterinary applications in this case, they can be considered in terms of availability.

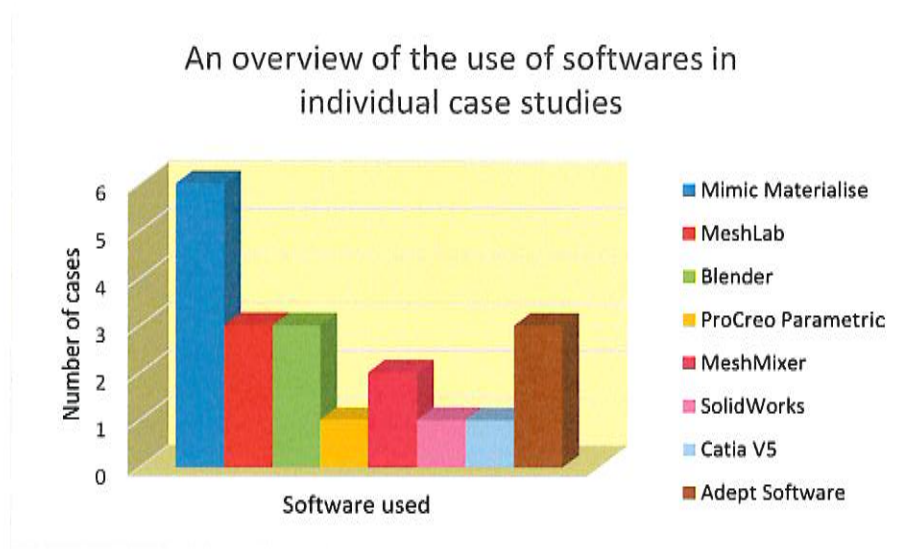
### 2.1. Use of individual software in veterinary practice

In veterinary practice, certified software for human use from Materialize - Mimic is currently one of the most widely used software. This software has been used to a greater extent, especially in modeling implants with more complex geometry. Another advantage of this program was its use in the planning of surgery, which ultimately resulted in the total operating time required for implantation. This time was significantly shortened, which had a positive effect on the overall health and time required for the overall sedation of the animal. Other software used to create the implant included software such as Blender, MeshLab and Mesh-mixer (Autodesk). The first of these were used to model beaks for species such as toucan, goose or parrot. For simpler types of implants, software used in common practice such as SolidWorks and Pro Creo Parametric were used. In some cases, however, it was not quite possible to determine the type of software used to design the implants.

The table below (Tab. 1) provides an overview of the software used along with the type of tissue being replaced. The data from Table 1 were transferred to a graph (Fig. 1), where these software are clearly displayed with respect to their use on a number of cases.

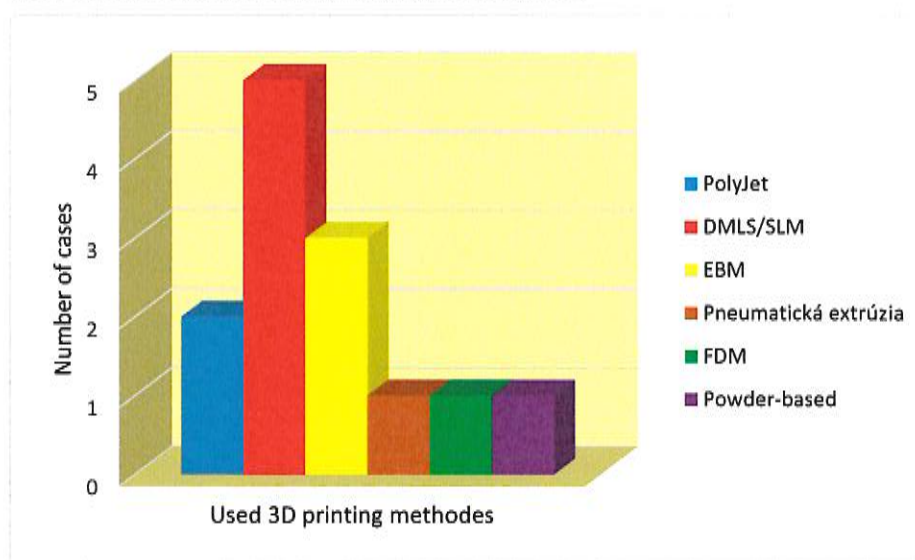
**Table 1.** Summary overview of individual software and methods of 3D printing with regard to the replaced structure

	Replaced tissue	Software used	3D printing method
Birds	Toucan; parrot; house / Beak	MeshLab, Blender Chyba! Nenašiel sa žiaden zdroj odkazov.Chyba! Nenašiel sa žiaden zdroj odkazov. (3x toucan, parrot and goose)	not specified
	Eagle / Beak	SolidWorks Chyba! Nenašiel sa žiaden zdroj odkazov.	not specified
	Bird / Wing	Pro creo Parametric, Meshmixer [28]	PolyJet (Objet) [28]
Cats	Kolenný kĺb	Materialise Mimics Innovation Suite Chyba! Nenašiel sa žiaden zdroj odkazov.	DMLS Chyba! Nenašiel sa žiaden zdroj odkazov.
Turtle	Maxillofacial area (missing 60%)	Materialise Mimics Innovation Suite 3-Matic Chyba! Nenašiel sa žiaden zdroj odkazov.	EBM Chyba! Nenašiel sa žiaden zdroj odkazov.
Dogs	Limb reposition	not specified	EBM Q10plus Chyba! Nenašiel sa žiaden zdroj odkazov.
	Stabilization of the spine	not specified	EBM Q10plus Chyba! Nenašiel sa žiaden zdroj odkazov.
	Skull	3 cases - dogs; skull tumor Materialise Mimics, Materialise 3-matic (+Data processing) Chyba! Nenašiel sa žiaden zdroj odkazov. ADEPT software (+ the cranial plate was designed in) Chyba! Nenašiel sa žiaden zdroj odkazov.	SLM/DMLS Chyba! Nenašiel sa žiaden zdroj odkazov. AM400 (Renishaw) – The Renishaw AM 400 industrial 3D printer Chyba! Nenašiel sa žiaden zdroj odkazov.
	Foreleg - 5 dogs (osteosarcoma)	Catia V5 Chyba! Nenašiel sa žiaden zdroj odkazov.	DMLS - EOSINT M280 (+ Surgical guide; ABS – FDM) Chyba! Nenašiel sa žiaden zdroj odkazov.
	Knee joint	Mimics Materialise SLA-190, 3D Systems (+ full size replica) Chyba! Nenašiel sa žiaden zdroj odkazov.	Z 400 (3D printer) Chyba! Nenašiel sa žiaden zdroj odkazov. Powder – based Chyba! Nenašiel sa žiaden zdroj odkazov.
	Trachea (Two implants, 1 case study)	Meshmixer, Materialise Magics	PolyJet, Pneumatic Extrusion (Bioplotter)



**Figure 1.** Graphical overview of the use of softwares in individual case studies

In addition to the use of individual software, Table 1 also shows the technologies used in 3D printing. In this case, however, it is not entirely possible to box the most used technology as in the case of software. The use of individual types of 3D printing technology depends mainly on the material used. In cases where materials paired with a group of metals were used as the material for the implant, the most used method was the DMLS method resp. SLM. The PolyJet method (Stratassys) was used the most for 3D printing from non-metallic materials, see. graph in Figure 2.



**Figure 2.** Graphic overview of individual 3D printing methods in individual case studies

#### 4. Conclusions

From the above-mentioned graphs, it can be stated that in addition to certified software, it is also possible to use non-certified ones for veterinary practice. Although their percentages are different, they have ultimately served the purpose for which they were used. When using these software, it is important to be aware of the overall geometry and

complexity of the future implant before designing and designing, and to select the appropriate software based on that.

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# Production of filaments and optimization of the 3D printing process for PLA/PHB material with an admixture of a ceramic component

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**Abstract:** The presented work describes the methodology of production and processing of composite filament as a promising material variant with the possibility of use in the biomedical industry. The primary part of the material consists of a polymer mixture containing the following materials: poly (lactic acid) (PLA): 85% by weight, polyhydroxy butyrate (PHB): 15% by weight, tris aminocyclopropenium (TAC): 5% proportion of the total weight of the mixture. The ceramic admixture consists of the following materials: hydroxyapatite (HA) and tricalcium phosphate (TCP), with a content of 10% by weight. Medically certified materials were used in the production. The production took place on the product line of devices and equipment (Filamentmaker, Dryer) from the company 3Devo, the Netherlands. The work includes a list of optimal conditions to produce filament intended for 3D printing, but also the necessary software modifications in the pre-processing phase. The result is a 3D print of an experimental sample using a Deltiq 2 device (Trilab, Czech Republic) designed for mechanical tensile testing.

**Key words:** extrusion; filament production; optimization; ceramics; composite material; 3D printing

## 1. Introduction

3D printing, also known as rapid prototyping or additive manufacturing, describes a process in which a computer-aided design (CAD) product is created by a layered application [1,2]. Unlike conventional manufacturing processes such as injection moulding, 3D printing ushered in an era of design freedom and enabled the rapid production of customized objects with complex geometries [3,4]. One of the main advantages of 3D printing is the ability to directly convert the concept into the final product in a convenient and cost-effective way. 3D printing has been used in industrial design since the 1980s. However, it has only adapted to medical use in the last decade [5,6]. Imaging data from routine computed tomography (CT) or magnetic resonance imaging (MRI) can be converted to a CAD file using a variety of 3D software programs.

While a range of 3D printing techniques have been developed for industrial applications, stereolithography (SLA), multi jet modeling (MJM), selective laser sintering (SLS) and fusion deposition modeling (FDM) are the main technological approaches that have also been explored in a clinical setting [7]. The FDM 3D bioprinting method is a common and simple method of using thermoplastic filaments as a bioprinting material [8]. The fibers are melted in the head of the 3D printer by heating and then used to create 3D structures.

Materials engineering is considered worldwide as a top priority for innovation and technological growth. Synthetic materials (such as PCL, PLA, PEG, PEEK) offer greater advantages over natural materials in that they can be adapted to specific physical properties and have greater uniformity than natural materials [9]. Mixing several materials and

adding additives (ceramics, carbon fiber, glass fiber) can significantly modify the mechanical and biological properties of the composite. When replacing bone tissue, the strength characteristics of a particular bone make it possible to adapt the mechanical properties of the implant by adding a certain percentage of the additive [10].

Both PLA and PHB are biodegradable polyesters and are used in consumer products by several industrial sectors due to their biocompatibility, biodegradability, and sustainability. They have comparable thermal and mechanical properties to conventional polymers, which has aroused great interest in investigating their physical properties for potential medical applications [11]. Attention has focused primarily on use in combination with ceramic additives.

In recent years, many favorable reports have been published on the use of bioactive materials such as HA and TCP as replacements for defective bones or teeth in dental, maxillofacial and orthopedic surgery. From a chemical point of view, they are known to be biocompatible, bioactive (i.e. have the ability to form a direct chemical bond with surrounding tissues), osteoconductive, non-toxic, non-inflammatory and non-immunogenic substances [12]. However, the use of HA-based systems was not entirely satisfactory due to the possible mobilization of free HA particles from the implant site with their possible migration outside the intended area [13]. To overcome these problems, common plastic materials, including poly glycolic and lactic acid (PLGA), PLLA and PCL, have been combined with HA and TCP ( $\alpha$ -TCP,  $\beta$ -TCP) particles to form composite materials [14].

The aim of the work is to describe the methodology of filament production from PLA/PHB materials with ceramic admixture (HA, TCP) by extrusion. The resulting filament is then used for 3D printing of experimental samples. The task was to find the optimal parameters for the production and processing of 3D printing.

## 2. Methodology of printing fiber production

A mixture of PLA/PHB (85/15), TAC (5%) and ceramics was used to produce the target filament. The TAC additive contributes to the softening of the compound. The ceramic component consisted of two materials: TCP and HA (Captal®, UK). Both ceramic materials represented 10% by weight. The particle sizes of the ceramic powder were as follows: TCP (2-6 $\mu$ m), HA (<15 $\mu$ m). The pre-mixed material in the form of pellets was supplied in vacuum packs to prevent the absorption of moisture and impurities. Nevertheless, the pellets had to be dried before extrusion. The material was dried on an Airid Polymer Dryer (3devo, The Netherlands). The drying temperature was set at 45 °C for 4 hours after consultation with the equipment manufacturer. The drying process was performed to remove unwanted moisture during material transport, as the moisture of the material can affect the filament extrusion process itself [15].

### 2.1. Description of extrusion and optimal parameters in filament production

The process of transformation from pellets to fiber suitable for FDM 3D printing took place on a specialized equipment Filamentmaker - Composer series (3devo, The Netherlands), see Figure 1. Prior to extrusion, the equipment was placed in an air-conditioned room with a temperature of 18°C due to temperature adjustment. The device comprises 4 consecutive heating elements (material displacement direction: #4→#3→#2→#1), which gradually heat the material inside the horizontally positioned chamber. The Composer series has a rotating screw with a mixing element at its end. Using this screw, the material is transported from the hopper towards the nozzle of the device. Behind the nozzle is a filament diameter sensor and a traction system for moving the filament towards the spool. The mixing element also contributes to the perfect distribution of ceramics in the material.





Figure 1. Extrusion process using the Filamentmaker - Composer series

Since there was a cleaning material - HDPE material - in the chamber of the device after the last extrusion process, it was necessary to heat the device to temperatures that would melt the material. The temperature of 180°C was set. This temperature was also a suitable starting point for the PLA/PHB/CER material. At these temperatures of heaters, after the pellets were loaded to the hopper, the outlet material appeared to be sufficiently viscous, as evidenced by compliance with the recommended value of the current drawn by the motor (approximately 2000mA). After the time when the HDPE material was completely replaced by the PLA/PHB/CER material, it was necessary to change the device settings based on a visual inspection of the output. Variables that have a significant effect on the extrusion result include ambient temperature, RPM (revolution per minute) and heater elements temperatures. The aim was to stabilize the flow through the nozzle and achieve a constant filament diameter - 1.75 mm. You can see the optimal combination of variables in Table 1.

Table 1. Optimal settings of the device in the production of PLA/PHB material with ceramic admixture

Heating element	#4	#3	#2	#1		Ambient temperature [°C]	18
Set temperature [°C]	154	175	178	176		Fan output	60
Real temperature [°C]	155	175	180	175		RPM [round/min]	3

### 3. Statistical evaluation of the produced filament

We consider the composite printing fiber to be the output of the production process using the determined optimal parameters of the device (see Figure 2, left). Due to the quantitative evaluation of the filament, the device itself has a built-in optical sensor with an accuracy of 43µm. Using an optical sensor, it was possible to observe the course of the filament diameter during the whole extrusion process with a sampling frequency of 1 second. Figure 2 shows the dependence of the measured filament diameter as a function of time.



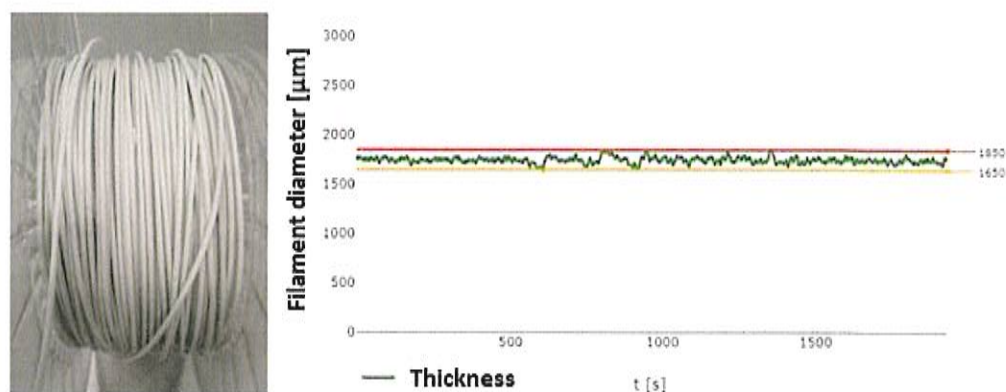


Figure 2. Time course of filament diameter, filament wound on a spool

From the graphical representation of the diameter, it is possible to record the apparent variation of the curve caused by the fluctuation of the material flow. This phenomenon can be attributed to several factors. The speed of the sliding screw tended to fluctuate ( $\pm 0.2$  rpm) throughout the extrusion of the material. The addition in the form of a ceramic component significantly increased the viscosity of the material, making it more difficult for the propulsion system to maintain a constant RPM. Another factor was the deviations of the real temperatures from the values of the temperature of the radiators determined by us, as well as the room temperature. The diameter value was maintained between 1.862 and 1.638 mm. The results of the Filamentmaker, which is not intended for large-scale industrial production, must also be included in the results. For a quantitative description of the average, the record was evaluated using descriptive statistics (see Table 2).

Table 2. Basic characteristics of filament diameter variability

Maximum value [mm]	1.862	Standard deviation [mm]	0.032389
Minimum value [mm]	1.638	Variance [mm <sup>2</sup> ]	0.001049
Average [mm]	1.7493	Skewness of a distribution	0.135248
Variation range [mm]	0.224		

Based on the values proved above, it is proved that with the help of the determined device settings (heater temperatures, RPM, fan output, ...) it is possible to produce a filament with a total average diameter of 1.7493 mm. This data is the result of 1919 partial measurements of the optical sensor. The largest deviation from the required value of 1.75 mm was measured in a unique extreme case, i.e. + 0.112mm. Based on the positive skewness coefficient, we can say that the diameter of the produced filament had for the most part smaller values than the nominal value of 1.75 mm.

#### 4. Optimization of 3D printing using PLA/PHB/CER filament

3D printing of experimental samples took place on a Deltiq 2 device from the manufacturer Trilab (Czech Republic). The mentioned printer works on the principles of FDM technology. Due to the planned mechanical tensile tests, the geometric shape of the computer model was identical to the test specimen given by the standard STN EN ISO 527-2, specifically type 5A (Figure 3). The last step before 3D printing of experimental samples was to find the appropriate software settings that the printer works with. Simplify3D software was used for this purpose. Main compound component, therefore the general configuration for this material was chosen. You can see the basic printing parameters in Table 3.

Table 3. Parameters used in the process of production of experimental samples

Default printing speed [mm/s]	20		Extrusion multiplier	1,4
Retraction speed [mm/s]	25		Coasting distance [mm]	0,2
Infill [%]	100		Top/Bottom solid layers	1
Infill extrusion width [mm]	0,6		Outline/Perimeter shells	1
Extrusion width [mm]	0,4		Internal infill angle offsets [°]	45/-45
Primary layer height [mm]	0,2		Fan output (%)	85

A major change from the general configuration for the PLA material was made in the material flow tuning (Extrusion Multiplier), where the value was changed from 1.0 to 1.4. This step significantly increased our flow, which affected the print quality. The best results were obtained at temperatures: nozzle 215°C, printing bed 70°C (see Figure 3-B). The print head feed speed was reduced to 20 mm/s due to the higher viscosity caused by the ceramic.

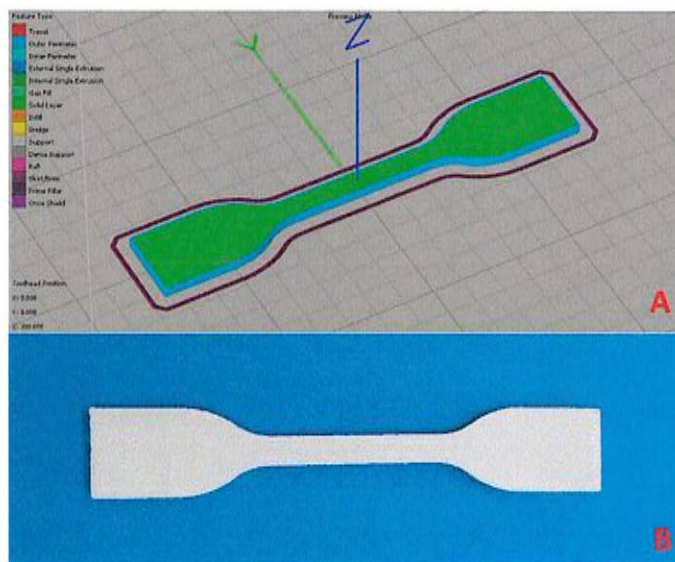


Figure 3. Experimental sample: A-in the Simplify3D software environment, B-after the 3D printing process

## 6. Conclusion

The result of the presented work is a brief description of the production and processing of filament from PLA/PHB/CER composite material. Based on the presented parameters of the extrusion equipment, it is possible to produce a filament with a diameter value of 1.7493 mm. Proof of the correctness of the set parameters is the long-term extrusion process without major diameter deviations. By configuring the 3D printing process in the Simplify3D software, it is possible to print the given experimental samples for mechanical testing, namely tensile tests of sufficient quality.

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Zameranie konferencie:

- Automatizácia, mechatronika a robotika
- Technologické a materiálové inžinierstvo
- Manažment, priemyselné a digitálne inžinierstvo
- Konštrukčné a procesné inžinierstvo
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