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DOCTORAL SCHOOL OF MATERIALS SCIENCE
AND ENGINEERING
DEPARTMENT OF METAL MATERIALS SCIENCE,
PHYSICAL METALLURGY



ABSTRACT OF DOCTORAL THESIS

MAKING CUSTOMIZED PROSTHETIC COMPONENTS THROUGH ADDITIVE PRODUCTION

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BUCHAREST

2023

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Acknowledgements

The author would like to thank in this way all those who have contributed in particular to the completion of the doctoral thesis.

Deep gratitude and thanks to university professor Iulian Vasile Antoniac, the scientific supervisor, for the guidance during the research, being constantly by his side with proposals and indications in the theoretical and experimental substantiation of the thesis as well as in its final elaboration.

In particular, I would like to thank the official referees: Prof. Dr. Eng. Corneliu Munteanu, Prof. Dr. Eng. Lucian Gruionu, Conf. Dr. Eng. Cosmin Cotruț for the honor of agreeing to evaluate this thesis of doctorate and to Prof. Dr. Eng. Augustin Semenescu for the honor of accepting the position of president of the evaluation committee.

Special thanks for the advice received and for the trust and support given in the completion and support of the doctoral thesis, Professor Florin Miculescu and S.L. Dr. Eng. Robert Ciocoiu.

For the help given in carrying out the experiments, thanks to the members of the Department of Metallic Materials Science, Physical Metallurgy, namely Professor Marian Miculescu, S.L. Dr. Eng. Octavian Trante, S.L. Dr. Eng. Ana Iulia Bița, and all the other colleagues whose help I enjoyed during the realization of the thesis doctorate.

Thanks to fellow PhD students and friends who encouraged and supported me.

Last but not least, warm thanks to the family that was with me during the whole period of the elaboration of the paper.

Alexandrescu Dragoș - Vivi

INTRODUCTION

Production or additive manufacturing is in full technical and technological development and starting from the simple acceptance of transposing a virtual model into a physical model with only a visualization role, in 30 years it has moved to make models functional and components with series production, with a structural role. This production method is implemented in all industrial fields due to its advantages: the possibility of obtaining a finished product with a particularly complex geometry, with minimal material consumption and high production speed. The medical field does not back down from this trend of adopting additive manufacturing which brings a major advantage considering complex, organic, and patient-specific geometries. Predominantly used in the creation of landmarks, models, and surgical guides, most of them with a visual role, with the development of new additive manufacturing processes there is a migration towards the creation of functional landmarks (prostheses, orthoses, components of assemblies) capable of withstanding demands comparable to those made by classical methods.

The opportunity for this research derives from the need to make customized components in a fast, efficient manner, with low material consumption and at a low price. The application considered is that of prosthetic cups attached to limbs that have undergone amputations, a component that connects the complex, organic geometry of the anatomical structure with a component with a simple geometry that takes over the functional role of the limb.

The classic method of making these cups involves making a mold using the reminiscence of the patient's limb, usually using alginate, making a positive plaster mold that is used to make the cup by successively depositing fiberglass fabrics impregnated, usually with resin epoxy.

This classical method can be replaced by digitization, design, and additive manufacturing of the cup. Establishing such a technological flow involves the implementation of digitization processes of the member's reminiscence and the use of the digitized model as a template and tool in the design stage to create the customized model, which is then transferred to an additive manufacturing facility to create the finished product.

The actuality of the research consists of the implementation and association of some methods that are in full development, digitization, and additive production, with the aim of creating personalized products for use in the medical field.

Although additive manufacturing has seen a spectacular development recently, the main limitation of this method is brought by the materials used, predominantly of a polymeric nature, due to the low costs of production facilities, metal and ceramic materials being less used due to the high costs of production facilities.

Choosing a material for an additive manufacturing application requires a double evaluation, first in terms of the characteristics required for the application and second in terms of the physico-chemical characteristics required to be used in the additive manufacturing facility. Now there are polymer materials devoted to additive production, limited in number, which show slight variations by making some composites by adding elements with a reinforcing or functional role, and less by structural changes at the level of molecular bonds. The realization of new polymers for additive manufacturing proves to be particularly difficult, but the improvement of some characteristics of the produced benchmark can be achieved by its post-processing.

A new element of this work is the establishment of a set of thermal processing parameters, a proposed procedure for improving the mechanical characteristics of the landmarks.

The second element of novelty is the association of additive production with classic production processes, the aim being to improve mechanical characteristics.

Through the purpose of the research, that of establishing a technological flow to produce

customized prosthetic components, an interdisciplinary approach is called for, which requires design knowledge, mechanical elements, and, mainly, those specific to materials science applied in their characterization.

To achieve the proposed goal, a study of the specialized literature was carried out, regarding additive manufacturing, with an emphasis on applications in the medical field. A presentation of additive manufacturing processes, both for general use and those specific to the medical field, is presented, highlighting their advantages and limitations, aspects that facilitated the choice of a process for the implementation of the experimental program. The experimental program is structured in such a way as to cover the main aspects of the production flow of the custom prosthetic cup.

Experimental research begins with a study on the possibility of digitizing an amputated limb, using two approaches that require minimal investment: photogrammetry and direct scanning. Through the comparative analysis of the two methods, the advantages and disadvantages of the two methods are highlighted in the context of the application, and for a fast production direct scanning is the simpler and more efficient procedure, although it loses the dimensional accuracy that photogrammetry presents. Obtaining the digitized object involves a series of data conversion operations in the form of a cloud of points in a CAD file, where the relationships between the points are described by means of equations. Basically, that cloud of points is used to define, through regression, the equations of curves, planes, and surfaces, using specific algorithms for specialized applications. The reconstruction in CAD format of the digitized object allows it to be used as a template and even a tool for the subsequent design operations of the customized prosthetic element, more precisely the prosthesis cup. Once designed, the cup is exported from the CAD application to the specific program of the additive manufacturing facility, where the production parameterization is carried out, depending on the available process.

The choice of material is the last step in the experimental program, polylactic acid being considered, for reasons of availability, cost, and the cost of the additive production facility, the one by extrusion, used in this research. The availability of a varied range of shapes, colours, and even composite (polylactic acid matrix with the addition of an element with a structural or functional role) made it necessary to carry out research on the mechanical behavior of the landmarks made of this type of filament, using a simple filament and two filaments, one with added silver and one with added copper, with an antibacterial role. The mechanical behavior of the filament with the addition of silver proved to be unsatisfactory for the application, the decision being to use the filament of polylactic acid with the addition of copper nanoparticles, with a content of 1% by weight. This decision represented a compromise, giving up mechanical performance in favour of the antimicrobial effect brought about by the presence of copper.

The subsequent improvement of the mechanical behavior was attempted by the thermal processing of the landmarks and the association of additive manufacturing, used to create an outer perimeter (a "shell" of the finished landmark), in which epoxy resin was infiltrated and it was also used to reinforce with a fibre composite of glass in an epoxy resin matrix.

The mechanical characterization carried out through tensile, compression, and bending tests made it possible to identify the failure mode of each material and opened the opportunity to further improve the assembly by adding additional structures in the additive manufacturing step to increase the contact surface with the epoxy resin and ensure a uniform distribution of stresses.

The results obtained in the current research allow, to a large extent, to establish the key steps in the production flow of a customized prosthetic component, through additive manufacturing: For digitalization, the faster, simpler, but dimensionally accurate method is direct scanning, and as material for additive production, polylactic acid is required, the addition of copper

conferring antimicrobial properties to the component. In the case of internal components that are mechanically stressed, post-processing by infiltration with epoxy resin is recommended.

The characterization methods used in the research are established for materials science, starting from optical microscopy, stereomicroscopy, scanning electron microscopy, used to characterize the surface of produced landmarks and fracture surfaces. Fourier transform infrared spectroscopy was used to evaluate possible variations in the structure of the polymers. The wetting of the surface was evaluated using the contact angle method, and the mechanical characteristics were evaluated by tensile, compression and Shore D hardness tests. The results obtained from the characterizations were processed and compared statistically to formulate conclusions.

The results obtained in this research were partially disseminated by publishing two articles in ISI indexed journals and by presenting three papers in international scientific communications.

CHAPTER 1

The current state of research on the use of additive manufacturing in the medical field

1.1. General considerations regarding additive manufacturing

Additive manufacturing (AM) is growing rapidly and represents an innovative and versatile technology [1]. "Additive manufacturing" is the official terminology, first defined in ASTM F2792, and "three-dimensional (3D) printing" [2]. Initially, the terminology used for this production method was that of "rapid prototyping" (RP - Rapid Prototyping) which uses different processes to quickly create a component or a system. According to ASTM [3], the terminology of "rapid prototyping" is not adequate to describe the process, since the components are obtained through an additive approach, and lately the components can be obtained directly by this method, let alone prototypes. The new terminology adopted is that of "additive manufacturing" (AM - Additive Manufacturing). The basic principle of additive manufacturing consists in the fact that a model generated by computer-aided design (CAD - Computer Aided Design) can be manufactured directly, without a design of a technological flow, practically describing a method of production of components by adding material, layer upon layer. In this way, components, or systems with static and/or mobile elements, already assembled, can be obtained.

Due to its advantages, additive manufacturing is used in most areas of strategic and economic importance.

The spread and field of use of benchmarks obtained by additive manufacturing are illustrated in Fig. 1.1.



Fig. 1.1. The main areas of use of benchmarks obtained by additive manufacturing [5]

1.2. Classification of additive production processes

Achieving a classification of the processes involved in additive manufacturing, there are many approaches, but the most used is the one through the prism of basic technology: the use of LASER, the technology of printing, extrusion, etc., although it can generate some confusion

regarding the classification of a method or the division into two distinct classes of methods with similar principles.

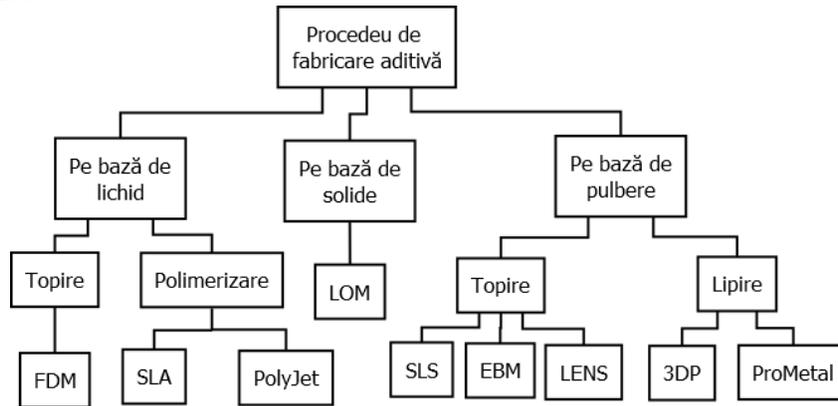
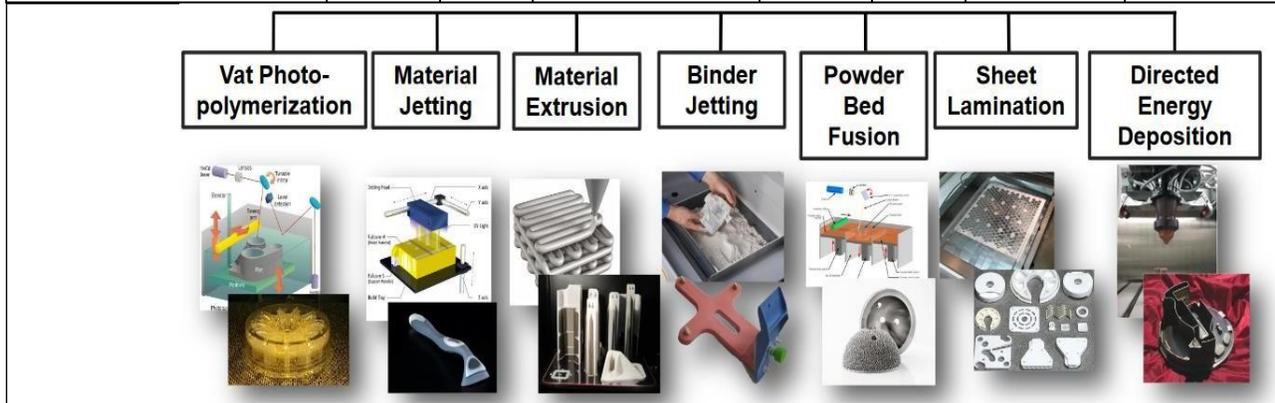


Fig. 1.3. Classification of additive manufacturing methods according to the material and its transformations

In table 1.1. associations of material classes with additive manufacturing processes were made.

Table 1.1 Materials usable for additive manufacturing processes [10,11]

	Light curing in the vat	Material spraying	Material extrusion	Spraying of binder	Fusion powder support	Fusion powder support	Directed beam deposition
Polymers, mixture of polymers	X	X	X	X	X	X	
Composite	X	X		X	X		
Metals		X		X	X	X	X
Ceramics	X			X	X		
Paper						X	



CHAPTER 2

General objectives and methodology of experimental research

2.1. The objectives of the doctoral thesis

The experimental studies carried out in this doctoral thesis started from a concrete clinical case, namely a male patient, a former performance athlete, who suffered a car accident after which bilateral amputation of the lower limbs was performed.

Bilateral amputation significantly increases the metabolic demands of walking compared with unilateral amputation and requires specialized rehabilitation and prosthetic provision to

maximize potential mobility. The rehabilitation program for bilateral transfemoral amputations lasts up to 18 months.

The abutment (sometimes called the residual limb) plays an important role in transmitting forces from the body to the prosthetic limb. Therefore, the ideal abutment should be of adequate length to accommodate the prosthetic equipment, with soft tissues appropriately shaped to support what can sometimes be very high forces and sometimes multiples of the patient's body weight. The healed abutment should be of adequate length to fit the prosthesis with sufficient stability. Correct abutment length is important to incorporate the necessary prosthetic components. It is understandable that the trauma abutment may not meet perfect surgical criteria when attempting surgical salvage, but it is desirable to aim for as optimal a length as possible. However, length should not be preserved at all costs, as the prosthetic components must be able to fit into the potential space between the end of the abutment and where the foot, in the case of the lower limb, or the terminal device, in the case of the upper limb, is to be positioned. Sufficient soft tissue coverage is achieved by good myodesis or myoplasty in case of diaphyseal amputation. A good quality, healed, non-adherent and pain-free scar will allow the patient to engage in rehabilitation with a prosthesis in due time. The muscles of the sectioned abutment atrophy over time, so enough muscle must be preserved at the time of surgery. However, excessive redundant soft tissue is a significant problem in the fabrication of the prosthetic limb, as well as limiting modes of prosthesis suspension, such as suction suspension. The risk of skin infection is also increased due to excessive soft tissue invagination. During medical rehabilitation, the amputee is evaluated for a permanent prosthesis and appropriate goals are established. Comorbidities that may cause insufficient cardiorespiratory function, neurological conditions that cause physical and cognitive deficits are carefully analysed, as they may have an impact on gait. For patients with bilateral transfemoral amputations, shortened prostheses are used to determine the patient's ability to progress to a standard full-length prosthesis. The patient's height is much lower with these specialized prostheses, which makes the patient's center of gravity lower, resulting in better balance and stability in gait training. After the prosthesis, the amputee will continue rehabilitation, often for several months, with the goal of independently putting on and taking off the prosthetic limb, re-educating walking, and progressing to maximum independence in daily activities and mobility.

A concrete picture of the clinical case is presented in the following figure.



Fig. 2.1. Clinical image of the bilateral lower limb amputation used in the study

One year after the accident, during which he is recovering medically, he has bilateral prosthetics. Prosthetic cups are customized using the classic method of taking the mold from the prosthetic abutment, obtaining appropriate external prostheses for each limb, and the re-education of walking with their help and crutches begins. According to the poor conditions of the muscles of the trunk and upper limbs, the patient suffers a rupture of the supraspinatus muscle, he is forced

to interrupt the medical rehabilitation and re-education of walking, in favor of the medical recovery of the affected muscle. Due to syncopes during medical recovery and frequent fluctuations in weight and muscle tone, he is often forced to order prosthetic cups adapted to the current situation of the prosthetic abutments, which involves the consumption of time and money. Another aspect specific to the case, is the fact that the patient was left with neuropathies following the amputation surgery, which leads to additional difficulties in making prosthetic cups through the classic execution technology and in their effective use, due to the appearance of pain when the abutment contacts the prosthetic component.

2.2. Experimental research methodology

To achieve an optimized and simplified technological flow for the creation of a customized prosthetic component, all stages were taken into account starting from the digitization of the abutment, the design of the cup using the digitized abutment and the simulation of obtaining it through additive manufacturing. Once the work sequence and parameters were established, the research direction focused on the analysis and improvement of the mechanical performance of the finished product by adding post-processing stages of the benchmarks obtained through additive manufacturing. In the following paragraphs, the infrastructure, software applications, materials, equipment used, and the way of work undertaken in the implementation of the experimental program are presented.

1. Digitizing the abutment

For the digitization of the abutment, **two** economically efficient **methods** that do not require an expensive infrastructure were considered. For the application of the first method, the digitization of the abutment by **photogrammetry**, the equipment used was a camera with a 10MP resolution, with the help of which snapshots were taken of a plaster cast obtained by the kindness of a company producing prosthetic cups. The second digitization method was **by direct scanning**, using a low-resolution scanner with a proprietary software application (Skannect). In this application, a file in *.stl format was generated and later processed in the Meshmixer program to remove unnecessary elements (image background, the support on which the mold was located, etc.).

2. Designing the cup

For the design of the cup and the samples used for the tests carried out in this work, a series of software applications were used, in association, that allow processing, reconstruction, and CAD design using a *.stl file as a guide.

3. The selection of materials and the achievement of milestones through additive manufacturing.

An analysis presented in detail in the respective chapter justifies the choice of polylactic acid (PLA) as the base material for making components through additive manufacturing, alongside the FDM production method. For this study, **3 types of PLA-based filaments were considered, two containing silver and copper particles, respectively, to confer antimicrobial properties, and a commercial polylactic acid filament.** A Sigma BCN3D 3D printer with a dual extrusion system and a working volume of 210x197x210mm was used to make the landmarks. The materials used in the post-processing steps were a 2:1 epoxy resin and the glass fiber was in the form of short, interconnected fibers (ply).

4. Materials characterization methods

For the characterization of the materials obtained, the following were used:

- mechanical tests, Walter + Bai LFB300 universal testing machine, equipped with devices for performing tensile, compression and bending tests
- stereomicroscope Olympus SZX7 with the related program QuickPHOTO MICRO3.2

- optical microscope Olympus BX51
- JASCO 6200 FT-IR infrared spectrometer with ATR Golden Gate
- installation for measuring the contact angle DSA30, KRUESS
- scanning electron microscope Philips XL 30 ESEM TMP
- analytical balance with 4 decimal places
- manual Shore D durometer

2.3. Materials, methods of analysis, and equipment used in the experimental program

Materials used in the experimental program

Additive manufacturing methods are very varied and include methods using material extrusion, vat photopolymerization, powder bed fusion, material spraying, binder spraying, beam deposition, 3D microprinting, and lamination. Each method includes different material deposition processes that use the same principle, and a large number of possibilities makes it necessary to choose the appropriate method for the destination that meets the following criteria: adequate mechanical characteristics, fast production, low costs, elimination of post-processing steps, on as much as possible and the level of staff training.

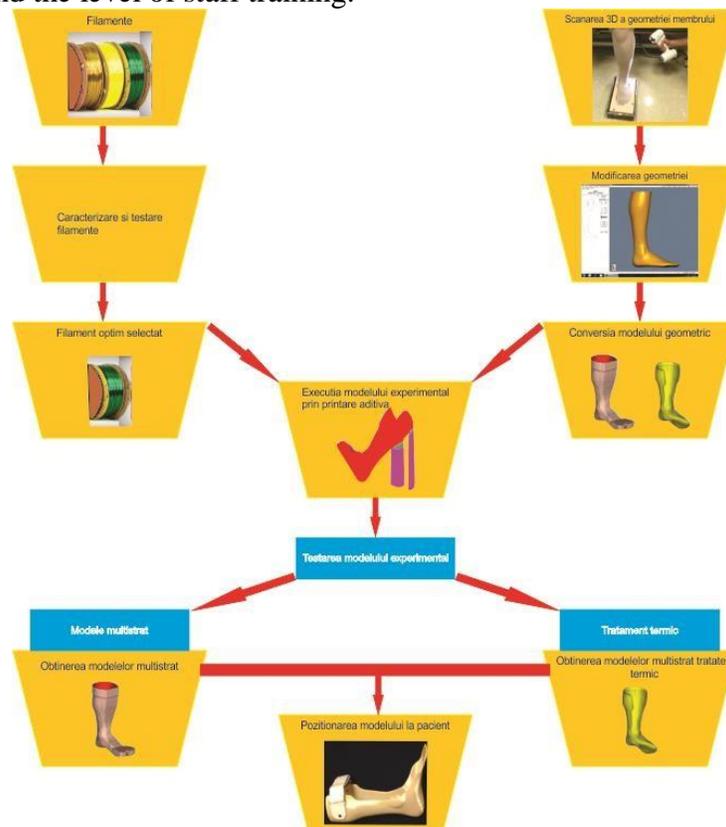


Fig. 2.6. Synthetic representation of the experimental work program of the doctoral thesis

An analysis carried out in consultation with a medical device manufacturer identified the material extrusion method (FDM - Fused Deposition Modeling) as the most convenient due to the following considerations:

- the additive manufacturing facility has a much lower purchase price compared to the other methods, maintenance is much easier and economically efficient
- the materials are available at a reasonable price, and it is also possible to choose the colour (an important criterion for the customer)
- the production speed is reasonable and can be easily increased by using several facilities

simultaneously and dividing the model into components

- the training of the personnel operating the additive manufacturing facility through material extrusion is minimal, with only familiarization with the interface being necessary
- the mechanical characteristics of the finished landmark are suitable for use
- post-processing steps can only be reduced to surface finishing by grinding/polishing

Once the additive manufacturing method is established, that through material extrusion, the material selection would be the next aspect to be established. Most additive manufacturing facilities considered semi-professional or professional that use the principle of material extrusion can reach working temperatures of a maximum of 300°C, so the selection of polymer materials is restricted to those thermoplastic polymers that reach the liquid phase up to this temperature. As options for the considered application would be polylactic acid (PLA), poly-acrylic-butadiene-styrene (ABS) or thermoplastic polyurethane (TPU).

To make a prosthetic cup, in addition to the mechanical characteristics, the possibility of conferring antimicrobial properties on the surface was taken into account, these properties being ensured by the addition of silver or copper particles in the commercially available filaments.

Consequently, for the selection of the material for making the prosthetic cup, three types of filaments were considered:

- polylactic acid filament without any addition, commercially available,
- polylactic acid filament with added silver particles, commercially available,
- polylactic acid filament with the addition of copper particles, commercially available.

CHAPTER 3

Experimental research on the digitization and design of some landmarks in the medical field

Obtaining a traditional custom cup involves obtaining a mold of the patient's abutment and using it as a mold. The steps involved involve obtaining the negative of the abutment, using an alginate, filling it with plaster/gypsum to obtain the positive, and using it to make the cup, by layering resin-impregnated fabrics or thermoforming thermoplastic polymers. This sequence of operations requires a long duration, several days, and a consumption of material that raises the price considerably. The elimination of these steps can be achieved by digitizing the abutment using methods involving medical imaging, direct reconstruction by taking measurements, or an indirect reconstruction using the scanning of the abutment. The use of medical imaging, using computed tomography images, would be the most indicated method for accurate reconstruction, but the associated costs and exposure of the patient to X-rays recommend it as a last resort. Direct reconstruction, by measurement, is feasible, but requires a relatively long time to perform the measurements and discomfort for the patient, forced to adopt unnatural positions. The accuracy of the reconstruction is mainly dictated by the quality of the abutment measurements. The methods that involve scanning using industrial scanners, due to their large dimensions, involve a rather high cost for the purchase of such a device. However, the accuracy of the reconstruction becomes comparable to that achieved using medical imaging. Another method, little used in medicine, is that of digitization by means of photogrammetry, a method intensively used in geography, topography and even in archaeology. In this research, two digitization methods were used: by photogrammetry and by direct scanning, using a low-resolution scanner with a low purchase price.

3.1. Digitization by photogrammetry

The process used for digitization by photogrammetry involves, in the first phase, the recording in digital photographic form, from several angles, of the object targeted for digitization [164-167]. The recorded images are aligned and processed with the help of dedicated programs

to obtain a *.STL file that can be used further in the design. A positive of an abutment showing an amputation in the first third of the femur was used for digitalization by photogrammetry. This method was used to verify the applicability of the method without creating discomfort to the patient. This abutment, shown in Fig. 3.1, was photographically recorded from several perspectives. Since the quality of the reconstruction depends on the number and accuracy of the recorded images, the working procedure adopted involved the recording of the abutment by rotating it by 10° and the digital photographic recording from three angles to the half-height of the abutment.

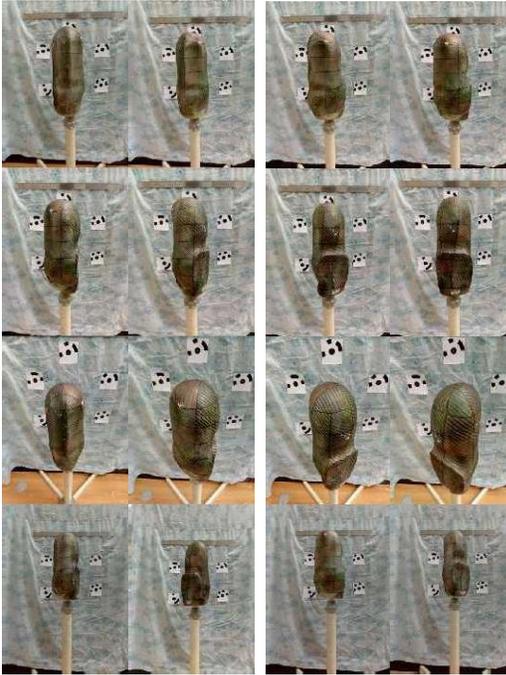


Fig. 3.1. Selection of images representing the abutment used for digitization

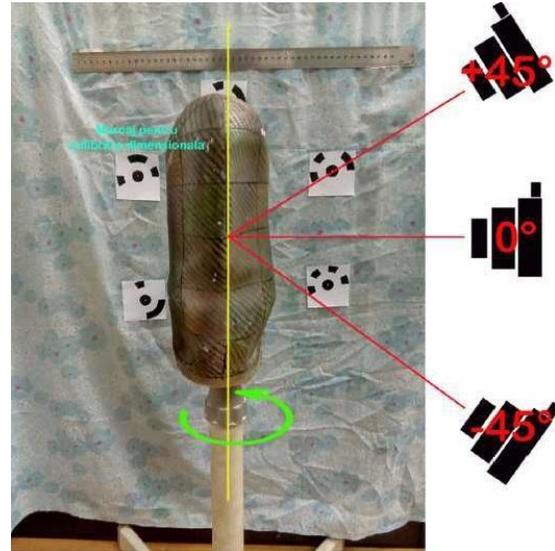


Fig. 3.2. Sketch showing the mode of photographic recording

The first recording was made at 0° , the second at $+45^\circ$ and the third at -45° , details indicated in the sketch in Fig. 3.2. A total of 108 digital photographs were obtained. The digital photographs were imported into a digital reconstruction program, the chosen one to be Agisoft Metashape which offered a trial period of the application for 29 days. The first stage was the alignment of the photographs according to the automated performed by the program. In the second stage, the point cloud (Dense Point Cloud) was created in which the program identifies, aligns and assigns coordinates (x,y,z) to the points in the 2D images. Once the point cloud is built, it is possible to edit it, by removing some points/areas that are not of interest for the reconstruction, such as background details. Once the unnecessary details were removed, we moved on to the last, and most computationally intensive, point cloud discretization.



*Fig. 3.5. The abutment digitized by photogrammetry. Different views from the *.STL file.*

In this last stage the points in coordinates (x,y,z) are used for the construction of triangles and the establishment of normal vectors to these triangles, the network thus obtained can be exported in a *.STL format file that will be used later in the programs CAD for cup design. Details regarding the content of the *.STL file can be seen in fig. 3.5, the digitized abutment being presented from several perspectives. The process of digitization by photogrammetry does not prove to be complex, being easy to implement and the associated costs being low: a digital camera and the license of a reconstruction program, although there are freeware variants, the options present in them are quite limited.

3.2. Digitization by direct scanning

To obtain a file in which 3D coordinates can be obtained for the points that define an object, it is necessary to use a scanner that works by contact, a probe attached to a computerized arm or a transducer makes contact with the physical object and records the coordinates (x,y, z) of the contact point. The necessary equipment turns out to be very expensive, the alternative being a low-resolution scanner, mostly used in digitizing characters/objects intended for computer games. Despite the low resolution, this device proves to be very useful in scanning medium to large sized objects. Using such a scanner and the associated program the used abutment was scanned by rotating the scanner around it until the program indicated a sufficient number of points to be able to perform the reconstruction, details indicated schematically in Fig. 3.6. The procedure proves to be fast, the accuracy of the reconstruction being conditioned, mainly, by the dexterity of the operator in scanning. The learning curve is very smooth, after 2-3 attempts the reconstruction quality is very good.

Through the two chosen methods, photogrammetry and direct scanning with a low-resolution scanner, a digitization of the objects can be achieved. Through photogrammetry, the digitization of small objects can generate some difficulties, requiring the use of macro lenses for the camera, while direct scanning in the configuration used in this work can be used to digitize objects of sizes close to 5cm. In Fig. 3.7 shows the content of the *.STL file obtained by direct scanning.

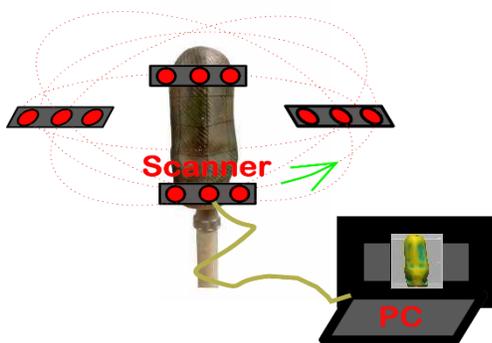
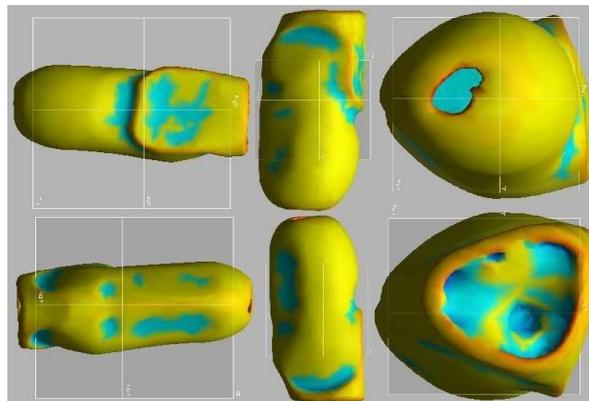


Fig. 3.6. Sketch showing direct scan mode



*Fig. 3.7. Abutment digitized by direct scanning. Different views from the *.STL file.*

The use of macro lenses in photogrammetry eliminates dimensional restrictions, while direct scanning of objects smaller than 5cm requires special, expensive scanners. Regarding the resolution of digitized objects, an assessment can be made by the number of captured details, which is reflected in the file size. *.STL obtained. By photogrammetry, the average file size for this application is about 210113.7 ± 2086.3 KB, and in the case of direct scanning with the reduced resolution scanner 897.7 ± 1.2 KB, 234.01 times smaller, which involves a small amount of

information. However, the higher the number of points, the more computing power is required, and for an application of the indicated dimensions, the direct scan version also provides a sufficient number of points for the reconstruction to provide the information needed for cup customization.

CHAPTER 4

Obtaining and characterization of experimental materials used for additive manufacturing

Additive manufacturing methods are very varied and include methods using material extrusion, vat photopolymerization, powder bed fusion, material spraying, binder spraying, beam deposition, 3D microprinting, and lamination. Each method includes different material deposition processes that use the same principle, and a large number of possibilities makes it necessary to choose the appropriate method for the destination that meets the following criteria: adequate mechanical characteristics, fast production, low costs, elimination of post-processing steps, on as much as possible and the level of staff training. An analysis carried out in consultation with a medical device manufacturer identified the material extrusion method (FDM

- Fused Deposition Modeling) as the most convenient due to the following considerations: 1. the additive manufacturing facility has a much lower purchase price compared to the other methods, maintenance is much easier and economically efficient; 2. the materials are available at a reasonable price, it being also possible to choose the colour (an important criterion for the customer); 3. the production speed is reasonable and can be easily increased by the simultaneous use of several facilities and the division of the model into components; 4. the training of the staff operating the additive production facility through material extrusion is minimal, only familiarization with the interface being necessary; 5. the mechanical characteristics of the finished part are suitable for use; 6. post-processing steps can be reduced to just surface finishing by grinding/polishing. Once the additive manufacturing method is established, that through material extrusion, the material selection would be the next aspect to be established. Most additive manufacturing facilities considered semi-professional or professional that use the principle of material extrusion can reach working temperatures of a maximum of 300°C, so the selection of polymer materials is restricted to those thermoplastic polymers that reach the liquid phase up to this temperature. As options for the considered application would be polylactic acid (PLA), polyacrylic-butadiene-styrene (ABS) or thermoplastic polyurethane (TPU). The table below compares the main characteristics for each class of polymers. Considering the characteristics in table 4.1, the choice of polylactic acid (PLA) meets the needs from the mechanical point of view, and the purchase price/kg is the lowest at the moment. Considering the biocompatibility and the fact that it is a biodegradable polymer under certain conditions, a series of filaments with different types of reinforcements or additions of particles with the role of functionalization are available on the market.

Table 4.1 Characteristics of polymers usable for additive manufacturing [170]

Polymer / Characteristics	PLA	ABS	TPU
Shore D hardness	48 -87	68-103	12-79
The modulus of elasticity (GPa)	0,5 - 10	0,7 - 6,10	0,003-0,870
Mechanical resistance (MPa)	0,2 - 300	2,6 - 75	4-73
Melting temperature (°C)	90 - 220	180-310	100-230

To make a prosthetic cup, in addition to the mechanical characteristics, the possibility of conferring antimicrobial properties on the surface was taken into account, these properties being ensured by the addition of silver or copper particles in the commercially available filaments. Consequently, for the selection of the material for making the prosthetic cup, three types of

filaments were considered: polylactic acid filament without any addition, commercially available, polylactic acid filament with the addition of silver particles, commercially available, and a filament of polylactic acid with the addition of copper particles also commercially available. In order to establish the mechanical behavior of these filaments, material samples were purchased that were used to make some cylindrical specimens that were tested in compression to observe the mechanical behavior and analyze the influence of the addition of particles.

4.1. Determination of compressive strength and hardness of experimental materials

Cylindrical specimens obtained by additive manufacturing (material extrusion method - FDM) using a Sigma BCN3D FDM additive manufacturing facility were used for the compression test. The structure of the specimens was identical for all, using a degree of filling of 50% and the same production direction so that the stress during the compression test was applied perpendicular to the direction of layer deposition. The parameters used for production (temperatures and speeds) followed the indications specified by the filament manufacturer. 5 samples were made for each type of filament, the three types of filaments being coded PLA for the commercial polylactic acid filament, PLA+Ag, for the polylactic acid filament with the addition of 1% silver nanoparticles, and PLA+Cu for the filament with the addition of copper nanoparticles. After the compression tests, the recordings were taken and processed to obtain the stress-strain curves and determine the parameters of interest, the modulus of elasticity and the yield strength in compression.

Comparative analysis of the mechanical behavior

In fig. 4.4. a representative selection of stress-strain curves is presented for the comparison of the mechanical behavior of the specimens made from the three types of filaments.

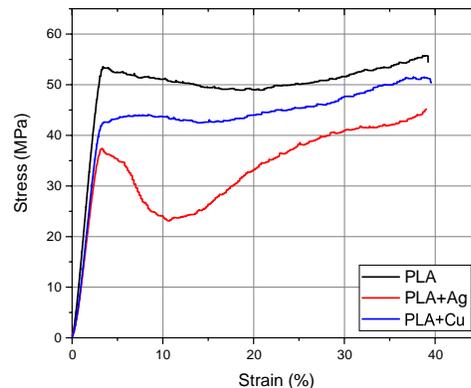


Fig. 4.4. Selection of representative curves for specimens made from the three types of filaments

Regarding the mechanical behavior of the specimens. the fragile behavior of the samples made of PLA+Ag can be observed, in their case. the outer perimeter (the number of layers on the outside of the specimen) yields relatively quickly, while the specimens made of PLA and PLA+Cu show significant plastic deformations, the outer perimeter does not yield catastrophically. In fig. 4.5 shows, comparatively, the average values of the modulus of elasticity and yield strength for the benchmarks obtained from the three types of filaments.

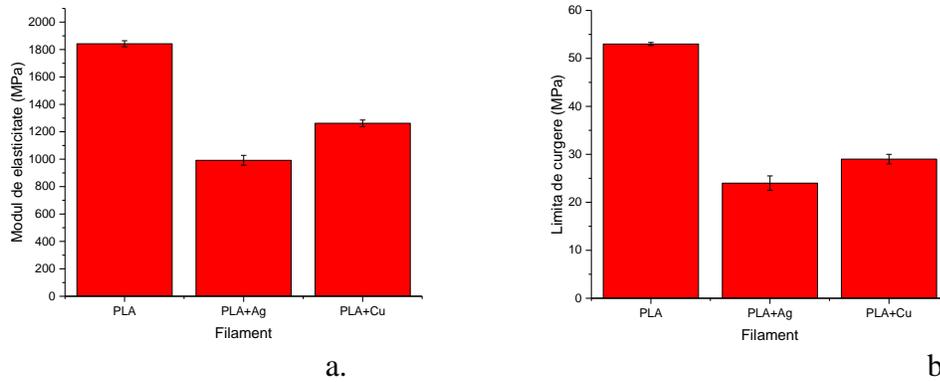


Fig. 4.5. Comparisons of mechanical characteristics, average values of a. modulus of elasticity and b. yield strength

4.2. Morpho-compositional analysis of PLA-based filaments used for additive manufacturing

The first investigation was carried out by scanning electron microscopy (SEM) on the filament, on a broken surface, showing the aspects of the broken surfaces of the three filaments. In the case of the particle-free filament, at high magnifications, micro-pores resulting from the manufacturing process can be observed, along with the typical aspects of a brittle fracture of the investigated sample. In the case of the filament with the addition of copper particles, the presence of copper particles uniformly dispersed in the polymer matrix is observed on the breaking surface. It should be noted that, compared to the silver filament, these particles do not have dimensions of the order of micrometres, thus reducing the probability of particle agglomeration in the region of the extrusion hole.

Through scanning electron microscopy, the surfaces of some landmarks obtained through additive manufacturing using the FDM method were also studied, the aspects are indicated in Fig. 4.12. - 4.14. for one landmark obtained from each type of filament.

In the case of the surface of the landmark that used the PLA filament, in Fig. 4.12. a. the successive layers resulting from the deposition process are observed, and some debris also resulting during production is observed. The interface between the layers has good continuity, as can be seen in Fig. 4.12.c, and e., the adhesion between the layers is a key factor in the good mechanical behavior of the landmark. In Fig. 4.13. the surface aspects of a landmark obtained using polylactic acid filament with copper particles are shown. The filament with copper particles has copper particles uniformly distributed over the surface, Fig. 4.13.a., but the thickness of successive layers shows a clear variation. In the interface region of the layers, the presence of copper particles can be observed, Fig. 4.13.d., their presence reducing the adhesion between the layers and, inherently, the mechanical behavior of the landmark. The interface area, Fig. 4.13.e. and f., show some discontinuities.

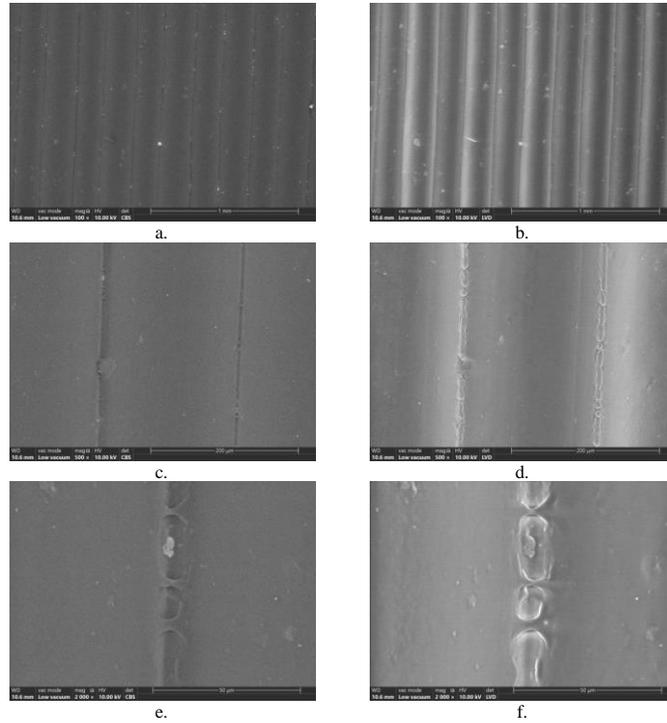


Fig. 4.12. Scanning electron microscopy micrographs of the surface of a trace made of commercial polylactic acid filament, backscattered electron (a,c,e) and secondary electron (b,d,f) images

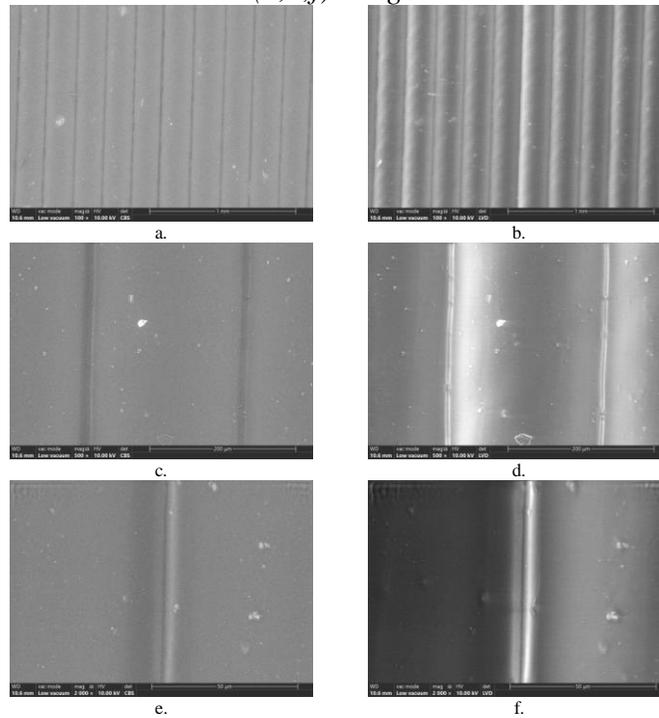


Fig. 4.13. Scanning electron microscopy micrographs of the surface of a trace made of polylactic acid filament with copper particles, backscattered electron (a.,c.,e.) and secondary electron (b.,d.,f.) images

The analysis performed on a landmark obtained from the polylactic acid filament with the addition of silver particles is shown in Fig. 4.14.

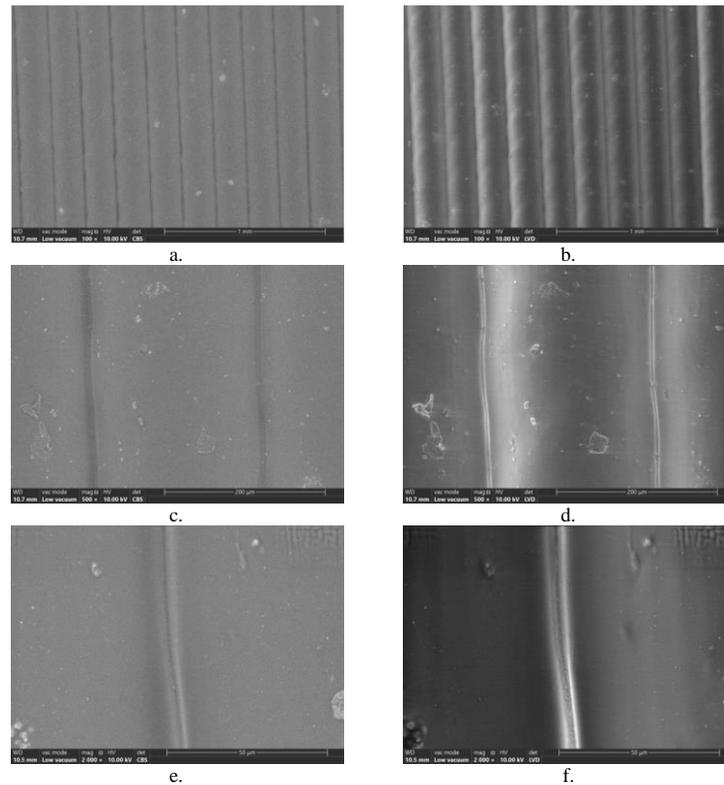


Fig. 4.14. Scanning electron microscopy micrographs of the surface of a marker made of polylactic acid filament with silver particles, backscattered electron (a.,c.,e.) and secondary electron images (b.,d.,f.)

In the case of the landmark obtained with this filament, layers of variable thickness can be distinguished, Fig. 4.14. a. and b., clusters of silver particles appearing on the surface, Fig. 4.14. c.-f. Discontinuities are found in the contact region between two successive layers, the layers having areas where there is no contact between them, which induces a significant decrease in mechanical characteristics and an increase in anisotropy. This preliminary analysis suggests that the addition of particles induces a variation in layer thickness and the appearance of particle agglomerations. In the case of the filament without particles, at high magnifications, micro-pores resulting from the manufacturing process can be observed, and in the case of filaments with particles, particles of micrometric size, of polyhedral shape, randomly dispersed in the polylactic acid matrix can be distinguished [171]. Through the agglomeration of the particles, a blockage of the extruder hole can be achieved, which has as a consequence a variation of the layer thickness, and with variable layer thicknesses, the adhesion between the layers is incomplete, and the integrity of the structure suffers in the sense of a decrease in mechanical characteristics and an increase in anisotropy. The inference made on the variation of the thickness of the layers was tested by a procedure described below.

Measuring the thickness of successive layers

To evaluate the thickness of the successive layers deposited during additive manufacturing, a series of measurements were made on SEM micrographs obtained on the surfaces of the 3 benchmarks. The protocol consisted of measuring layer thicknesses at equal distances, an example

of analysis being shown in Fig. 4.15., 7 successive layers being analyzed, 12 thickness measurements being performed on each layer.

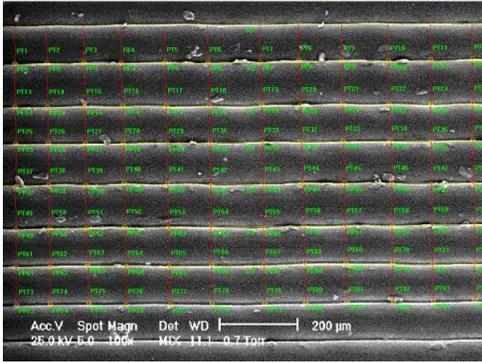


Fig. 4.15. Exemplification of the measurement procedure for layer thicknesses

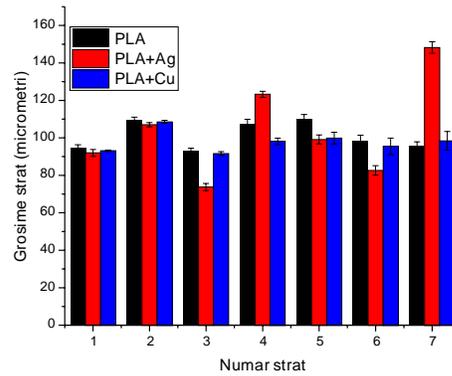


Fig. 4.16. Average layer thicknesses for landmarks obtained using the two types of filaments

The results obtained after the measurements were processed statistically, in Fig. 4.16. being presented, comparatively, the average values of the thicknesses for the measured layers. In the case of all benchmarks, there is a variation in layer thickness, but in the case of benchmarks with added silver, there is a more pronounced variation in layer thickness, in the case of this benchmark, the highest and also the lowest average thickness in the analysis is recorded. It is possible to appreciate, globally, the central tendency and the spread of the thickness of the investigated layers. It is found that in the case of using the PLA filament, layers with a more uniform thickness were obtained than in the case of using the other two types of filaments. The addition of copper induces a slight increase in the layer thickness and there is also a tendency to increase the variation of the thickness, which is noted by the increase in the spread of the measured values. Although the average layer thickness is in the area of the PLA and PLA+Cu benchmarks, the benchmarks made from the polylactic acid filament with the addition of silver show the greatest variability in the layer thickness, an aspect noted by the very large scatter of the measured thicknesses. This variability is assumed to be due to silver particles blocking the nozzle by agglomeration, an inference previously indicated from scanning electron microscopy analysis.

In the case of the surface of the landmark that used the PLA filament, successive layers resulting from the deposition process can be observed, and some debris also resulting during production can be observed. The interface between the layers has good continuity, the adhesion between the layers is a key factor in the good mechanical behavior of the landmark [171 - 179]. The particulate filament has particles uniformly distributed over the surface, but the thickness of the successive layers shows a clear variation. In the interface region of the layers, the presence of some particles can be observed, their presence reducing the adhesion between the layers and, inherently, the mechanical behavior of the landmark [180-186]. The interface area shows some discontinuities.

4.3. Determination of the structure of PLA-based filaments used for additive manufacturing by Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) investigations were performed on the three types of filaments, the superimposed spectra being shown in Fig. 4.18. The FTIR spectra of the investigated samples show the characteristic bands of the semi-crystalline PLA polymer. Between $2850-3000\text{ cm}^{-1}$ maxima are found for the bands due to the symmetric and asymmetric stretching (valence) vibrations of the -C-H bonds from the methyl (CH₃) groups, respectively the stretching vibrations of the -C-H bonds from the methine (CH) groups; At 1750 cm^{-1} appear the

bands due to the stretching vibrations of the -C=O bonds from the carbonyl groups, and between $1350\text{-}1460\text{ cm}^{-1}$ appear the bands due to the deformation vibrations of the -C-H bonds from the methyl and methine groups; At 1182 cm^{-1} and 1078 cm^{-1} appear the bands due to the symmetric and asymmetric stretching vibrations of the -C-O- bonds in the ester groups; The bands at $\sim 866\text{ cm}^{-1}$ and $\sim 753\text{ cm}^{-1}$ can be attributed to the amorphous and crystalline phases of PLA, respectively.

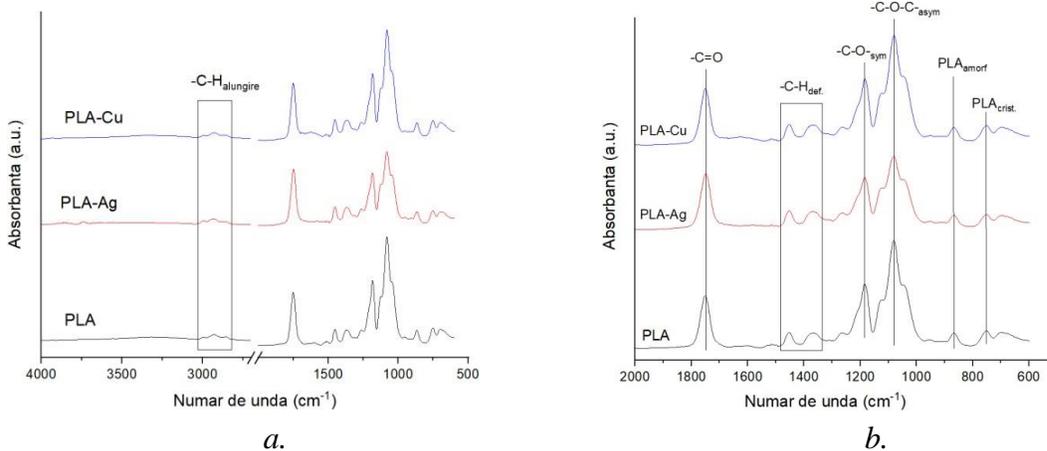


Fig. 4.18. FTIR spectra for the two types of filaments: (a) full spectrum; (b) detail of the $2000\text{--}500\text{ cm}^{-1}$

Polylactic acid (PLA) is a biodegradable semi-crystalline polyester widely used in the biomedical field [179, 183, 186].

4.4. Investigations on the surface wettability of experimental materials

Characterization of surface wettability was performed by the contact angle method, a drop of water was deposited on the surface of each landmark obtained by additive manufacturing, and the contact angle was measured using the specific program of the device. The determinations were repeated 5 times for each benchmark. The average values of the contact angles indicate that the surface is hydrophilic, its value is less than 90° . The addition of particles slightly lowers the value of the contact angle, emphasizing the hydrophilic nature of the surface, but considering that the analysed surface is the one resulting directly from the additive manufacturing process, a number of factors can influence this behavior: the roughness of the surface, determined mainly by the thicknesses of successive layers deposited by the installation, associated with the existence of particles on the surface, along with the proportions of constituents on the surface.

4.5. Selection of the optimal material for obtaining customized prosthetic cups through additive manufacturing

For the realization of the prosthetic cup components through additive manufacturing, 3 types of materials were considered, following the analysis, two were eliminated due to the cost and unsatisfactory mechanical characteristics for the application. The polymer of choice is polylactic acid (PLA) due to its advantages in terms of availability, price, processing parameters and mechanical characteristics. In order to improve the surface characteristics, the induction of an antimicrobial effect, two types of polylactic acid-based filaments were considered in which copper nanoparticles and silver nanoparticles were introduced, respectively. A comparative analysis of the mechanical behavior of some landmarks made of the two types of filaments and a conventional filament indicated a decrease of the mechanical characteristics following the addition of particles with an antimicrobial effect. In order to identify the cause of the decrease in

mechanical characteristics, a comparative analysis of filaments with particles compared to conventional PLA filament was carried out, following the structure of the unprocessed filament and the landmarks obtained by additive manufacturing through scanning electron microscopy (SEM) and infrared spectroscopy with Fourier transform (FTIR), as well as wettability and Shore-D hardness investigations. This analysis led to the conclusion that the presence of particles in the filament produces a considerable variation of the layer thickness and can modify the adhesion characteristics between the layers, thus the mechanical characteristics are influenced in the direction of their decrease. As a result of the obtained experimental results, it was decided to continue using PLA filament reinforced with copper (Cu) nanoparticles as the optimal material for the execution and testing of the experimental models obtained through additive manufacturing.

CHAPTER 5

Execution and testing of custom prosthetic cup functional designs

5.1. The execution of the experimental model and testing in a simulated environment

Since additive manufacturing components get in touch with the skin, prolonged exposure to human sweat could alter the structure and consequently the mechanical characteristics of the material. To evaluate the mechanical behavior following exposure to artificial perspiration, an immersion test was performed on some cylindrical samples (dimensions 25 x 12 mm) made by additive manufacturing, the FDM method, in artificial perspiration, the container used had a special construction, to ensure complete immersion of the specimens. Artificial perspiration followed the composition indicated by BS/EN 1811/2011, in one liter of distilled water 1g of lactic acid, 1g of urea, and 5g of salt (NaCl) were dissolved. Sets of 5 samples were extracted at 14, 28, 42, 56, and 70 days, measured, and weighed, the Shore-D hardness was determined were later tested in compression, the results of these determinations being later centralized, processed, and compared with the values obtained by investigating non-immersed samples, considered as a reference.

5.1.1. Assessment of mass loss

After removing the cylindrical specimens from the container, they were dried on filter paper and weighed using an electronic balance with an accuracy of 4 decimal places. Each specimen was weighed, the value shown is the arithmetic mean for each set. The evaluation of mass loss according to the number of days of immersion shows an increase in weight after 14 days of immersion, after which this value enters a plateau until 58 days, after which it registers a further increase. It can be stated, following an ANOVA analysis, that the variation in weight is generated by the duration of immersion, the mechanism involved being absorption, however, increased absorption cannot be eliminated in the context of rough surfaces [189-195].

5.1.2. Determination of compressive strength and hardness

The specimens were tested in compression using the universal testing machine on which the compression device was mounted. All test parameters were kept constants for all sets of specimens tested. The coding of these samples includes the symbol G followed by an order number and an indicator indicating the duration of immersion (0 - no immersion, reference samples). The stress-strain curves are presented for the reference samples, which show a fragile mechanical behavior, their failure occurring at strains of 5-10%. A considerable scattering of the results is also noted, this being caused, according to previous studies, by the variability of the

thicknesses of the layers that make up the benchmarks obtained through additive manufacturing. The stress-strain curves obtained from the compression test of the samples immersed in artificial perspiration for 14 days are presented. The mechanical behavior still remains brittle, with low deformations, but the breaking strain tends to increase compared to the reference ones. The stress-strain-in-compression curves obtained after testing the samples immersed for 28 days in artificial perspiration are presented. Compared to the previous sets, there is a smaller spread of the results, the behavior being again fragile. However, the strain at break is greater. The stress-strain curves of the samples immersed for 42 days in artificial perspiration are presented. The mechanical behavior is still fragile, they yield to reduced deformations. The mechanical behavior of the specimens immersed for 56 days in artificial sweat is observed, the brittle behavior is again observed. The stress-strain curves are presented for the samples kept for the longest time in artificial sweating, 70 days. The mechanical behavior is fragile, the samples yield to small deformations. In fig. 5.8. a selection of stress-strain curves is presented with the purpose of evaluating, comparatively, the mechanical behavior of the samples according to the duration of maintenance in artificial sweating.

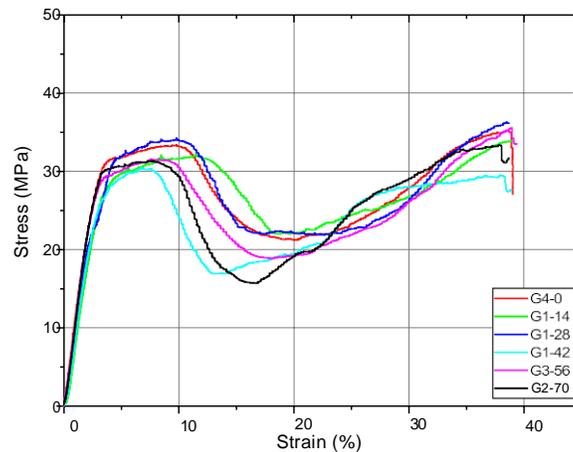


Fig. 5.8. Selection of stress-strain curves in compression to appreciate, comparatively, the mechanical behavior.

Analysing, comparatively, the mechanical behavior of the samples, a slight tendency to improve the plasticity is found during the first 28 days of immersion, after which this parameter starts to decrease again. These slight changes can be attributed to the elimination of internal stresses in the material and a possible plasticizing effect of the liquid in which the immersion was carried out. From the point of view of the mechanical characteristics, the values of the modulus of elasticity and of the yield strength were determined for the sets of specimens, the results being interpreted using the calculated average values. In Fig. 5.9. the variation of the modulus of elasticity according to the duration of immersion in artificial sweat is presented graphically. The value of the modulus of elasticity apparently does not seem to be influenced by the duration of immersion, but, considering the variability of the results, the analysis of variance test, ANOVA, was used. considering the duration of immersion as treatment. The test was performed at a confidence level $\alpha=0.05$, the test result indicated that, statistically, there is no treatment-induced variation (immersion in artificial sweat). The variability of results arises due to structural inhomogeneities. Regarding the variation of the yield strength values according to the immersion duration, it is shown graphically in Fig. 5.10. A slight increase is apparently observed after an immersion period of 14 days, followed by a decrease, at 28 days the values start to increase again reaching a maximum value in the set of specimens with the longest

immersion duration, 70 days. To check whether the variation is indeed produced by immersion, the analysis of variance test was again used. At the same confidence level $\alpha=0.05$, the result of the ANOVA test indicates that the variability in the results cannot be attributed to the treatment.

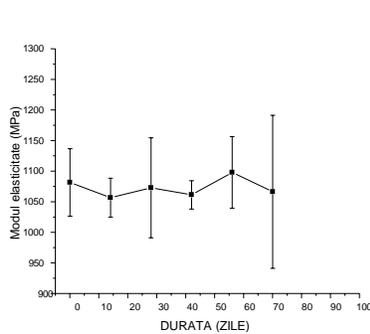


Fig. 5.9. The evolution of the modulus of elasticity according to the duration of immersion

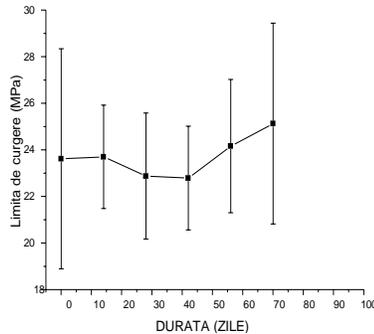


Fig. 5.10. The evolution of the yield strength according to the duration of immersion

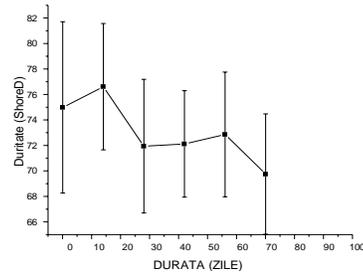


Fig. 5.11. The evolution of the Shore - D hardness according to the duration of immersion in artificial

Shore-D hardness was determined experimentally using a hand-operated Shore-D durometer following the specifications of the ASTM D2240/2010 standard. 5 determinations/samples were performed, on the flat surfaces, the values being subsequently averaged for each set of samples. The evolution of the average value of the shore hardness - D according to the duration of immersion in artificial sweat indicates an initial increase in the Shore hardness - D after 14 days of immersion, subsequently, the values fall below the initial value and remain at a plateau up to 70 days of immersion when a new downward trend appears. The increase in hardness recorded at 14 days of immersion is assumed to be caused by a relaxation of the internal stresses induced during the additive manufacturing of the specimens. Once these stresses are removed, the specimens also change their dimensions, the hardness begins to decrease, the ANOVA test indicates that the treatment, immersion in artificial sweat, is responsible for this variation in results [196 - 203].

In conclusion, because of the analysis of the variation of the mechanical characteristics of polylactic acid with the addition of copper nanoparticles immersed in artificial sweat, it was found that the landmarks obtained by using such a filament retain their mechanical characteristics, which recommends it for the application - obviously, taking - the limitations of the experiment are taken into account.

5.2. Thermal processing of experimental benchmarks

The purpose of this study was to establish the appropriate temperature and duration to ensure the set of mechanical characteristics required for the application. It involves the implementation of a programmed experiment-type analysis that takes into account two influencing factors, the heating temperature and the holding time, on the response factor, the value of the flow limit.

The implemented program consisted in performing thermal processing at temperatures of 120°C, 140°C, 160°C and 180°C with a holding time of 3h. Depending on the results obtained after the first stage, when extending the holding time to 6h, the temperatures taken in the samples processed at 180°C the initial dimensions. The samples used were parallelepipedal in shape, the CAD project having a side of 10mm, the printing method is indicated in the following paragraphs. The material used for 3D printing was the poly(lactic acid) filament with copper particles mounted on the BCN3D SIGMA 3D printer equipped with a nozzle diameter of

0.40mm and an extrusion multiplier of 1.00. Following the filament manufacturer's instructions, the printing temperature was 220°C and the temperature of the printer's heated bed was 80°C to ensure better component adhesion throughout printing. This sequence of layers was chosen to obtain a structure with anisotropy in two directions, parallel and perpendicular to the printing direction. The specimens obtained in this way were thermally processed, using an electric furnace in which a steel sheet box was inserted, in which sodium chloride powder was inserted, the specimens being positioned in this assembly. The use of sodium chloride powder has multiple roles: on the one hand, it provides a dimensional constraint blocking the excessive deformation of the samples, it ensures shielding from direct thermal radiation, and allows uniform heating of the samples. To carry out the study, 6 samples were used for each state, these being divided, depending on the orientation with respect to the printing direction, into 3 oriented parallel and 3 perpendicular to them. The coding of the specimens used calls for the symbology indicated in table 1, together with an order number and the indication of the symbolized test direction || (for orientation parallel to the print direction) and ⊥ (for orientation perpendicular to the print direction).

5.3. Mechanical testing and fractographic analysis of thermally processed experimental benchmarks

The thermally processed samples were tested in compression using the Walter+Bai LFV300 universal testing machine, the test being controlled at a travel speed of 5mm/min. Following the centralization of the obtained results, the conducted study can facilitate the choice of a combination of parameters for thermal processing so that the most favourable mechanical characteristics for the application can be obtained. The first finding was the change in the malleability of the tested samples: with the increase in the processing temperature, a decrease in malleability was observed, the samples passed from a malleable behavior, with significant plastic deformations, to a brittle one, as can be seen in fig. 5.23 which shows an overlay of a selection of compression stress-strain curves for selected specimens from each set.

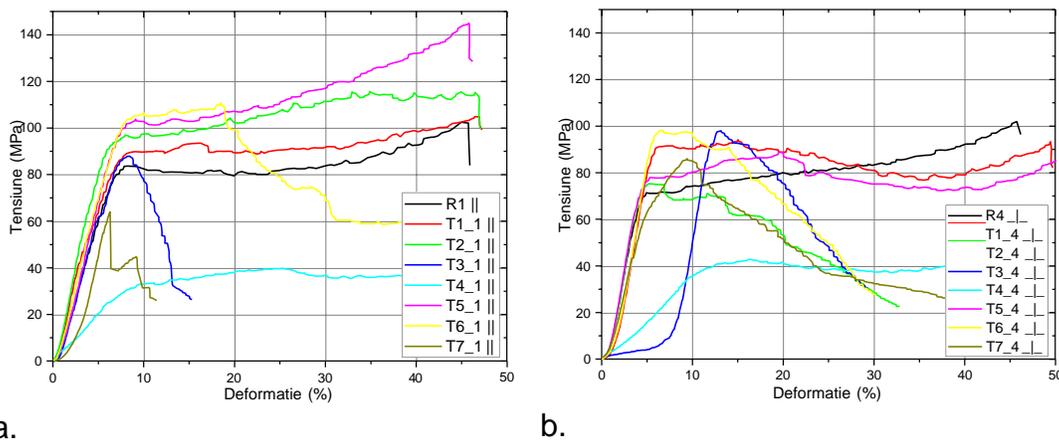


Fig. 5.23. Selection of compressive stress-strain curves for reference and heat-treated specimens-oriented a. parallel and b. perpendicular to the printing direction

Fractographic analysis

The mechanical behavior of the samples can be explained primarily by the structure generated by the sequence of printing layers and their failure mode, analysis carried out with the help of a stereomicroscope. The fractographic analysis performed on the samples tested in compression is presented in Fig. 5.24. In the case of the reference samples "R" tested in a direction parallel to the printing direction, a significant barrelling is observed, the constituent layers begin to deform strongly, as can be seen in Fig. 5.24.a. The specimens tested in the perpendicular direction show a different failure mode, mainly through the delamination of the

layers and their yielding in bending stress, as can be seen in Fig. 5.24.b and c. By applying thermal processing, a reduction in the malleability of the material is observed, the T1 samples, oriented perpendicularly, yield through delamination, Fig. 5.24. e and f, while the parallel- oriented specimens show a failure suggesting a bending stress of the outer layers, Fig. 5.24. d. Increasing the holding temperature to 140°C, specimen T2, retain a similar failure mode to that of specimen T1, in Fig. 5.24. g – i, observing details suggestive of brittle fracture and delamination. By processing at 160°C, in the T3 specimens, a better cohesion of the inner layers of the specimens is found (similar to the sintering of metallic materials), the fracture surface indicating a typical brittle appearance with mixed stress modes, as observed in previous figures (Fig. 5.24. j – l). By processing at 180°C the details in the fracture surface suggest a structure, in volume, with fully fused layers Fig. 5.24. m - o, similar to that of a part obtained directly by injection of the polymer. The fracture surface shows typical brittle fracture aspects, with aspects similar to those of cleavage fracture in metallic materials. However, the outer region has a porous structure, prone to failure.

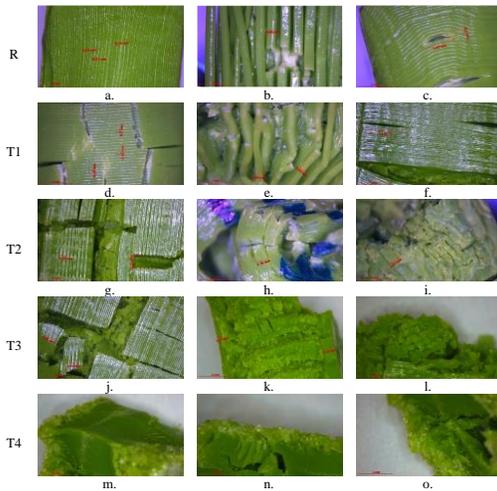


Fig. 5.24. The appearance of the fracture surfaces for the thermally processed samples (3h time)

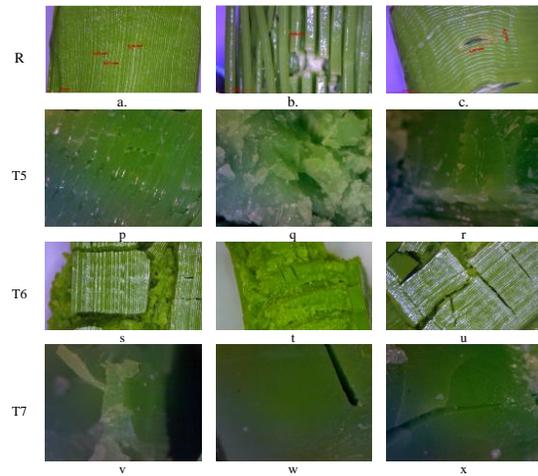


Fig. 5.24 The appearance of the fracture surfaces for the thermally processed samples (6h time)

With the increase of the processing temperature, good cohesion is found between the inner layers of the material, but the main mode of failure consists of the failure of the outer layers, either those of the outer perimeter or those of the solid layers, depending on the orientation. The improvement of the cohesion between these outer layers and the inner filling ones would lead to a significant increase in mechanical characteristics. In order to investigate the influence of temperature and holding time along with the orientation of the specimens on the mechanical characteristics, a series of graphs were built to follow their evolution. In the case of a holding time of 3h, regardless of the orientation, an increase in the value is observed with the increase of the processing temperature until the temperature of 160°C is reached, followed by a steep decrease to lower values compared to the initial ones. In the case of a holding time of 6h, an initial increase in the value of the modulus of elasticity is observed, following a holding at a temperature of 120°C, followed by a continuous decrease of the values with the increase of the holding temperature. The holding time of 6h would lend itself to holding at a maximum of 120°C to obtain superior elasticity characteristics. Analysing the variation of the value of the elastic limit as a function of the temperature and the duration of processing and orientation, it is found that the samples maintained for 3h suggest a slight increase in the value with the increase of the processing temperature for the parallel oriented samples, up to the temperature of 160°C, followed by a drastic decrease. The

perpendicularly oriented specimens show a more pronounced increase in values at a holding of 120°C, followed by a less significant increase up to a temperature of 160°C. At 180°C the same drastic decrease in the characteristic occurs. In the case of a holding time of 6h, a more significant increase in the average values of the elastic limit was found, regardless of the orientation of the samples. For the parallel-oriented samples, the significant increase is found when maintaining at 120°C, followed by a decline in the values with the increase in temperature. For the perpendicularly oriented specimens, the increase occurs gradually, the most significant being the one obtained after holding at 140°C, at 160°C the decline appears. Investigating the variation of the yield strength according to the three parameters, temperature and holding time, alongside of orientation, a variation is found indicating a slight increase in the value with the increase in temperature for the samples maintained for 3h, up to a maximum of 160°C, followed by a decline in the value. The most significant increase in value was observed following a hold at 160°C. In the case of specimens with a holding time of 6h, in the case of a parallel orientation, the increase in the value of the yield point appears gradually, up to 140°C, followed by a decline. In the case of a perpendicular orientation, the most important increase is observed at a holding time of 120°C, after which the decline of the values is observed. Also taking into account the anisotropy of the material obtained by 3D printing, a study was carried out in order to analyse its improvement or worsening according to the two thermal processing parameters, the duration and the holding temperature during the thermal processing. An anisotropy coefficient (C.A.) was thus defined as a ratio of the characteristics studied in one direction to the other direction.

With the increase of the processing temperature, good cohesion is found between the inner layers of the material, but the main mode of failure consists of the failure of the outer layers, either those of the outer perimeter or those of the solid layers, depending on the orientation. The improvement of the cohesion between these outer layers and the inner filling ones would lead to a significant increase in mechanical characteristics. In order to investigate the influence of temperature and holding time along with the orientation of the specimens on the mechanical characteristics, a series of graphs were built to follow their evolution. In the case of a holding time of 3h, regardless of the orientation, an increase in the value is observed with the increase of the processing temperature until the temperature of 160°C is reached, followed by a steep decrease to lower values compared to the initial ones. In the case of a holding time of 6h, an initial increase in the value of the modulus of elasticity is observed, following a holding at a temperature of 120°C, followed by a continuous decrease of the values with the increase of the holding temperature. The holding time of 6h would lend itself to holding at a maximum of 120°C to obtain superior elasticity characteristics. Analysing the variation of the value of the elastic limit as a function of the temperature and the duration of processing and orientation, it is found that the samples maintained for 3h suggest a slight increase in the value with the increase of the processing temperature for the parallel oriented samples, up to the temperature of 160°C, followed by a drastic decrease. The perpendicularly oriented specimens show a more pronounced increase in values at a holding of 120°C, followed by a less significant increase up to a temperature of 160°C. At 180°C the same drastic decrease in the characteristic occurs. In the case of a holding time of 6h, a more significant increase in the average values of the elastic limit was found, regardless of the orientation of the samples. For the parallel-oriented samples, a significant increase is found when maintaining at 120°C, followed by a decline in the values with the increase in temperature. For the perpendicularly oriented specimens, the increase occurs gradually, the most significant being the one obtained after holding at 140°C, at 160°C the decline appears. Investigating the variation of the yield strength according to the three parameters, temperature and holding time, alongside orientation, a variation is found indicating a slight increase in the value with the increase in temperature for the samples maintained for 3h, up to a maximum of 160°C, followed by a decline in the value. The most

significant increase in value was observed following a hold at 160°C. In the case of specimens with a holding time of 6h, in the case of a parallel orientation, the increase in the value of the yield point appears gradually, up to 140°C, followed by a decline. In the case of a perpendicular orientation, the most important increase is observed at a holding time of 120°C, after which the decline of the values is observed. Also taking into account the anisotropy of the material obtained by 3D printing, a study was carried out in order to analyze its improvement or worsening according to the two thermal processing parameters, the duration and the holding temperature during the thermal processing. An anisotropy coefficient (C.A.) was thus defined as a ratio of the characteristics studied in one direction to the other direction, according to equation (1).

5.4. Design of functional models of the customized multi-layer prosthetic cup

Designing the model of a custom prosthetic cup filled with epoxy resin

Aiming to improve the mechanical characteristics of the material used to make the custom cup, the first method chosen is that by which the cup is designed similar to a mold, 3D printed, and filled with epoxy resin through a hole machined in the upper region. Starting from the previously designed model, a series of operations were performed that allowed obtaining a shell-type model, presented, in different perspectives, in Fig. 5.44. A circular hole was designed and cut in the upper region of the cup to introduce the liquid epoxy resin into the 3D-printed shell model. After curing the epoxy resin the custom cup can be used as such, the outer layer obtained by 3D printing is not removed, also benefiting from the antibacterial properties of the copper embedded in the PLA filament.

Design of custom prosthetic cup model filled with fiberglass and epoxy resin

In order to increase the mechanical performance of the material intended for the customized cup, the use of a glass fibre composite + epoxy resin to fill a shell obtained by 3D printing was also taken into account, a concept similar to that of the previous situation. The ability to use a composite to fill a 3D printed shell model may involve pre-mixing the fiberglass, in the form of short fibers, with the epoxy resin and injecting the mixture into the mold. however, the application of this procedure requires specialized equipment, and the mechanical characteristics would be slightly inferior to a composite made of the mat (agglomeration of glass fibres in the form of a carpet) impregnated with epoxy resin (Fig. 5.44). The second reinforcement option can be done manually, without special equipment, but it is necessary to modify the filling form, in this case, it is designed from two components that join after reinforcement. The cup previously obtained in the Autodesk Inventor CAD program was divided into two components that can be 3D printed separately and, after reinforcement, joined to obtain the finished product. The appearance of the two components, in CAD format, can be seen in the following figures (Fig. 5.45 and Fig. 5.46.).



Fig. 5.44. The constructive version of the cup for filling with epoxy resin



Fig. 5.45. Cup components for epoxy resin and fiberglass mat filling variant - First component (interior)

Fig. 5.46. Cup components for epoxy resin and fiberglass mat filling variant - Second component (external)

Making these components turns out to be a relatively easy procedure once the basic model of the custom cup is obtained using the previously digitized abutment.

5.5. Execution and testing of mechanical properties of functional designs of multilayer custom prosthetic cup

To evaluate the mechanical behavior of the materials in the case of traction, compression, and bending stresses, 5 samples were made for each set of determinations with specific geometries and dimensions and in accordance with the standards. The tests were carried out using the Walter+Bai LFV 300 universal testing machine on which, depending on the nature of the test, the necessary devices to apply the stress were mounted. In these determinations, the samples were obtained directly through additive manufacturing, 3D printing using an installation using the FDM principle and tested as such, without post-processing. The second set of samples was thermally processed, after being obtained by additive manufacturing, using the parameters established following the previous study, heating to 160°C and holding for 3h. The third set was obtained by combining additive manufacturing with classical methods: through additive manufacturing, the outer shape of the specimen (shell) was obtained, later infiltrated with epoxy resin, and the last set of specimens was obtained similarly, using additive manufacturing to obtain the geometry exterior of the specimen, subsequently using epoxy resin and a glass fiber mat with random orientation. Each set consisted of a number of 5 samples, the symbol "X" indicating the order number of the sample, X=1..5.

Comparative analysis of the results

E1. The tensile test

The appearance of the curves indicates a brittle behavior for all the sets of specimens investigated, the plastic deformation is negligible. In the case of the PE and PFS samples, a change in the slope is observed, which indicates a change in the stress distribution in the sample: in the case of the PE samples (infiltrated with epoxy resin), a good adhesion between the epoxy resin and the polylactic acid can be appreciated, while the addition of glass fiber produces an effect contrary to expectations by decreasing stiffness and mechanical strength. This can be explained by the incompatibility of the mechanical characteristics of the materials involved: polylactic acid, epoxy resin, and glass fiber which generates an uneven distribution of stresses and deformations in the material, the failure being observed at the interfaces polylactic acid - epoxy resin and epoxy resin - fiberglass. The elimination of incompatibilities of characteristics could be compensated by modifying the surfaces, more precisely by creating additional geometries in the outer perimeter of polylactic acid that would ensure the increase of the lateral surface, which would result in improved adhesion and uniform distribution of stresses and deformations throughout the volume. Thermal processing induces an increased fragility of the material by unevenly changing the contact surfaces between the layers. An optimization of the thermal processing procedure would considerably improve the obtained surface. Regarding the mechanical characteristics obtained. It is found that the highest modulus of elasticity occurs in the PE set, followed by the P3D, and PTT sets and the lowest values appear in the PFS set. In the present situation, the modulus of elasticity can no longer be seen in the classical sense, as a measure of the strength of the inter-atomic bond, but rather as a measure of the cohesion between interfaces that can be extrapolated to the mode of distribution of stresses and implicitly deformations of material. In this case, a deviation from the established variation for the modulus of elasticity is found. The PE set shows the highest mechanical strength value, followed by the P3D set, but there is an inversion between the PTT set and the PFS set, with the PFS set showing a higher mechanical strength than the PTT set. The explanation of the change in the hierarchy can be explained by taking into account also the elongations at break. In terms of elongation at break, the PFS set presents the highest value, followed by the PE set, the P3D set and the PTT set. By associating the mechanical strength with the elongation at break, the mode of distribution of stresses and deformations in the material can be inferred: the presence of the glass fiber in the form of a mat (random distribution of short fibers) allows a greater elongation through slight reorientations and alignments of the fibers, practically the stress it is initially taken up by the glass fiber. In the case of uniaxial tensile stresses, the use of materials made by combining additive manufacturing with epoxy resin infiltration would be the most appropriate processing route to obtain superior mechanical characteristics.

E2. The compression test

Specimens obtained by additive manufacturing (P3D) along with those obtained by 3D printing and thermal processing show a particularly brittle behavior, while specimens obtained by post-processing with epoxy resin (PE) and epoxy resin reinforced with glass fiber (PFS)) shows an improvement in brittle behavior, becoming more malleable. By thermal processing the value of the modulus of elasticity increases, the PTT specimens reaching an average value of approximately 3000MPa, 500MPa more than the P3D specimens. Post-processing leads to a decrease in the modulus of elasticity, the lowest being observed in the case of the samples from the PE set, followed by the PFS set. The compressive strength shows a decrease in the order of P3D, PTT, PFS and PE. The obtained results are somewhat contrary to expectations, but their

variation is mainly explained by the distribution mode of stresses and strains in the specimen, since we cannot consider the specimen as being made of a homogeneous and isotropic material, but rather as an assembly of materials. During the compression request, it is mostly taken over by the outer perimeter of the specimen, being later transmitted to the internal elements. In order to improve this way of transmitting the stress in the case of post-processed specimens, internal structures can be designed to distribute the stresses more evenly.

E3. The bending test

Representative curves were superimposed for the samples obtained by additive manufacturing without post-processing (P3D4), heat-processed (PTT1), infiltrated with epoxy resin (PE5) and those reinforced with glass fiber and epoxy resin (PFS5). A brittle behavior is observed in the case of samples infiltrated with epoxy resin and those thermally processed, it improves to some extent in the case of those obtained directly by additive manufacturing, without post-processing, as well as those reinforced with glass fiber and epoxy resin. In terms of mechanical characteristics, comparison is made using modulus of elasticity and flexural strength. The value of the modulus of elasticity shows a spectacular increase in the case of samples infiltrated with epoxy resin, reaching values of approximately 15GPa, followed, by a considerable difference, by the thermally processed ones, reaching a value around 6GPa. Reinforcement using glass fiber does not show high bending stiffness, the modulus of elasticity reaching values of approximately 4GPa, approximately double those obtained directly by additive manufacturing, which have a modulus of elasticity of approximately 2GPa. This variation can be explained mainly by the way the stresses are transferred in the material, the samples infiltrated with epoxy resin and thermally processed result in a compact material, in which the stress distribution is more uniform than in the case of the samples obtained directly by additive manufacturing or by reinforcement with fiberglass: in this situation we can use the analogy of a layered composite, the strength of the specimen being mainly dictated by the interlaminar shear strength. The flexural strength is similar to the modulus of elasticity: the epoxy resin-infiltrated specimens show the highest values, around 200MPa, and the heat-treated and glass fiber reinforced specimens have a flexural strength of around 75MPa. The lowest value is again observed in the case of samples obtained by additive manufacturing, without post-processing, the bending strength having an average value of approximately 50MPa.

Conclusions

Regarding the mechanical behavior of the materials proposed to improve the performance of the product, improvements can be found depending on the type of applied demand. In tensile stress, infiltration with epoxy resin proves to have higher stiffness and superior mechanical strength, while in compressive stress, thermal processing increases stiffness and provides satisfactory mechanical strength. In the case of a mixed stress, that of bending, the samples infiltrated with epoxy resin show the highest values of the elastic modulus and the best bending resistance. In all situations, the mechanical performance of the proposed materials depends mainly on the way of distribution of tension and deformations during loading. **Practically, in the case of infiltration with epoxy resin, the structure closest to that of an isotropic material is obtained, a tendency that can also be appreciated in the case of thermal processing, but to a lesser extent. Additive production generates, as a consequence of the manufacturing process, an accentuated anisotropy of the product, and reinforcing with layers of fiberglass does not improve it in any way. Another option would be to arm the matrix with short, randomly oriented fibers, a direction that will be pursued in further research. The main conclusion of this mechanical behavior study is that infiltration with epoxy resin provides the best**

mechanical characteristics for the considered application, being, at the same time, the simplest and most efficient production method.

CHAPTER 6

Conclusions, original contributions and future development perspectives

6.1. Conclusions

From the analysis of this doctoral thesis, the following general conclusions and assessments can be drawn:

- Regarding the materials used in additive manufacturing, the evolution is spectacular: the first additive manufacturing technologies were developed to use existing materials, designed for processing by other methods, nowadays materials are designed to adapt to the requirements for additive manufacturing. Starting from the photo-polymerizable resins used at the beginning that allowed obtaining fragile and dimensionally inaccurate models, at the moment polymeric, metallic, ceramic or composite materials are optimized to obtain high production speeds, dimensional accuracy, resistance, and good resolution;
- Additive production is closely related to information technology, directly through the facilities used, but also indirectly through the technology required for processing;
- Additive manufacturing technology makes it possible to anatomically customize the device or some components of the medical device;
- Image processing remains a problem that limits the expansion of additive manufacturing applications in the medical field through the prism of geometric and dimensional accuracy;
- The implementation of additive manufacturing in the medical field is difficult due to the strict requirements imposed by the standards and laws that regulate this field;
- In the case of artificial limb prostheses, those that are anatomically adapted bring increased comfort to the patient due to superior aesthetics and functionality;
- Through additive manufacturing, anatomically adapted prosthetic components can be made, with appropriate mechanical properties and controllable in the production stage, with a high degree of complexity: joints, joints, sensors and effectors can be included in the product that can be obtained in one stage;
- Medical devices obtained through additive manufacturing are lighter, they can have property gradients, and can reach a lower production cost by eliminating material losses;
- The difficulties of implementing additive manufacturing come from the need for personnel training, the high cost of the system and the unsatisfactory mechanical characteristics from the limited number of materials available for the production method;
- Digitization of objects for their subsequent printing can be done by photogrammetry and direct scanning, with a low-resolution scanner. Through photogrammetry, the digitization of small objects can generate some difficulties, requiring the use of macro lenses for the camera, while direct scanning in the configuration used in this work can be used to digitize objects close to 5cm in size. Photogrammetry would have an advantage in terms of dimensional accuracy, repeatability, and reproducibility, but the process requires operator experience in dimensional calibration, whereas direct scanning is relatively simple and does not require advanced technical knowledge on the part of the operator;
- For the execution of prosthetic components, it is recommended to use the material extrusion process (FDM, Fused Deposition Modeling) considering the low costs of the installation, the cost of the raw material, its availability and variety, and the mechanical characteristics of the parts made;

- For the realization of the components of a prosthetic cup through additive production, it is appreciated that polylactic acid (PLA) presents clear advantages due to its availability, low price, processing and post-processing parameters, mechanical characteristics, and compatibility with living tissues;
- Additive production generates, as a consequence of the manufacturing process, a pronounced anisotropy of the product;
- Thermal processing of 3D printed components has a significant influence on mechanical characteristics and behavior;
- The improvement of the mechanical behavior of the landmarks is possible through the post-processing of the landmarks produced by additive manufacturing, either by thermal processing of the landmarks or by their reinforcement;
- By tensile, compression, and bending tests of parts obtained by additive manufacturing without post-processing, parts obtained by additive manufacturing and thermally processed, parts obtained by additive manufacturing infiltrated with epoxy resin and parts obtained by additive manufacturing and reinforced with epoxy resin and glass fiber it was tried to establish the most convenient method of improving the mechanical characteristics.
- In the case of additive manufacturing, feature anisotropy poses great problems in predicting the behavior over time due to the way stresses and strains are distributed, while post-processing greatly reduces this aspect.

6.2. Original contributions

The researches carried out brought a series of novel contributions through the original results obtained and through their theoretical interpretation. The original contributions will be presented in the following together with the most important results obtained. The thesis aimed to establish the stages of a technological flow for the creation of customized prosthetic components, in a fast, cheap way and that would cause minimal discomfort to the patient, because the classic method of creating prosthetic components today proves to be ineffective, lasting, expensive, with high material consumption and with considerable discomfort for the patient by obtaining the mold. The implementation of object digitization and additive manufacturing technologies eliminates the material consumption for making a mold and the positive of the targeted component by directly obtaining a model three-dimensional that can be used as a template for design and later transferred to the additive manufacturing facility that is capable of providing the finished or near-finished product. The duration of the entire procedure can be considerably shortened, the digitization of the body part being a process that takes place in a few minutes, the design can be done in a few hours, and the physical realization of the project, depending on the complexity and the chosen realization method, can be realized between 4-36 hours.

The experimental program investigated, in the first phase, the digitization stage of the part of the body targeted in this study, the rest of the lower limb after amputation. Using a positive obtained from a prosthetics manufacturer it was digitized by two methods, photogrammetry and direct scanning using a low-resolution scanner. These methods were chosen because they involve minimal equipment costs: for photogrammetry, a camera with a good resolution and a personal computer with a dedicated program are required, and in the case of direct scanning, a specialized sensor with a low acquisition cost and a personal computer. Digitization, in the case of both methods, was achieved by using images taken from the physical model and associated through different algorithms to create a cloud of points, a file in *.STL format.

To verify the repeatability and reproducibility of the digitization procedures, a

dimensional analysis was used, by comparing the digitized model repeatedly, by each method. The results of the study indicate that photogrammetry would have an advantage in terms of dimensional accuracy, repeatability, and reproducibility, but the process requires operator experience in dimensional calibration, while direct scanning is relatively simple and does not require advanced technical knowledge from the operator. Once the scanned model was obtained, in the form of an *.STL file, it was necessary to convert it into a format supported by CAD programs. The *.STL file has in its structure the coordinates (x,y,z) and the normal for each point, therefore most CAD programs (which use equations) cannot work with such files. Consequently, the CAD reconstruction of the *.STL file was resorted to using the scanned data as a template and, with the help of a specialized program, the object was reconstructed in a format accepted by CAD programs. The reconstructed solid was used as a template and tool to design the custom cup, made in the same CAD program. Once the project has been completed, it is exported in *.STL format to be manipulated by the slicer, the specific program of the additive manufacturing facility, a program that translates the project's elevations into coordinates for moving the additive manufacturing facility to create the physical object. In order to make the prosthetic component, an initial study was carried out taking into account polylactic acid (PLA), poly-acrylic-butadiene-styrene (ABS), and thermoplastic polyurethane (TPU), the working parameters, the mechanical characteristics, and the price imposing polylactic acid as the more suitable for the desired application, a custom prosthetic component. The antimicrobial effect obtained by the addition of different elements was considered desirable for this application, so a comparative study was carried out on some benchmarks made of simple polylactic acid, polylactic acid with the addition of silver nanoparticles (1% weight), and the addition of copper nanoparticles (1% by weight). The study focused on the evaluation of the mechanical behavior of some benchmarks obtained from these three filaments, through the compression test. The results of the tests indicated that the addition of nanoparticles, either copper or silver, tended to decrease the mechanical characteristics of the benchmarks compared to those of plain polylactic acid. The simple polylactic acid markers presented the best mechanical characteristics, followed by those with copper addition and the weakest were those with silver nanoparticle addition.

In order to identify the failure mechanism, a comparative study was carried out between the benchmarks made of simple polylactic acid and those with added silver (which presented the weakest characteristics) and with added copper. By scanning electron microscopy, optical microscopy and Fourier transform infrared spectroscopy, the cause of the decrease in mechanical characteristics by the addition of silver nanoparticles was identified: structural changes of the polymer were not observed by FT-IR, instead the variation of successive layers thickness and poor adhesion of which is the main factor in the unsatisfactory mechanical behavior of polylactic acid and silver landmarks. Agglomeration of nanoparticles in the area of the printer extrusion orifice and modification of liquid phase polymer flow were inferred. Among the three types of filaments, the polylactic acid filament with the addition of copper nanoparticles (1% weight) was chosen, achieving a compromise between mechanical performance and the antimicrobial character desired for the application. Considering the contact with the skin and the exposure of the component to biological fluids, sweat, in this case, an immersion test was also performed to evaluate the variation of the mechanical characteristics. Landmarks were printed that were immersed in artificial transpiration and mechanically characterized for different periods of time, a maximum duration in the case of the experiment of 10 weeks. The obtained results indicate a slight decrease in the mechanical characteristics following immersion in artificial perspiration, but the observed decrease is insignificant for the intended application. The experiment confirmed

the maintenance of a high safety factor even after prolonged contact with sweat.

A third direction of research addressed in this work was the improvement of the mechanical behavior of the landmarks, the chosen method being the post-processing of the landmarks produced by additive manufacturing. Two main directions were approached: thermal processing of landmarks and an association of additive production with classic production methods: the creation of an external perimeter through additive production and its infiltration with epoxy resin, a first variant, and the creation of an external perimeter that will be reinforced by a composite consisting of epoxy matrix coppered with short, interconnected fiberglass.

Regarding the thermal processing of the benchmarks, it was decided to approach a programmed experiment to establish the parameters of thermal processing, temperature, and time. Mechanical characteristics determined by compression test were chosen as the response factor. Thermal processing was performed in an electric furnace using a NaCl enclosure into which the 3D printed landmarks were inserted using a combination of temperatures and holding times, with temperatures chosen to range from 120 - 180°C and holding times ranging from 3 - 6 hours. Following the mechanical characterization by compression test and the performance of fractographic investigations on the yielded points, it was found that the variation of the processing parameters results in a significant variation on the mechanical characteristics. The parameters that ensured the best results were the holding temperature of 160°C and the holding time of 3h. By combining these parameters, a considerable reduction of anisotropy was found, practically the value of the ratio approaching 1 and the increase of the modulus of elasticity at the highest values. As a result of the thermal processing, a dimensional change of the parts was also observed, in the plane parallel to the production direction, contractions of approximately 2% were observed, while in the perpendicular direction, an expansion of almost 4% was observed. At the same time, through thermal processing, a change in the surface energy estimated by the contact angle method was also found, its value increasing in direct association with the temperature and holding time. These changes are mainly due to the changes that occur at the surface level, through the superficial melting of the successive layers of polymer and the modification of the roughness.

The association of additive production with classical methods does not imply, in any way, the modification of the surface characteristics of the polymer, consequently in this case the mechanical behavior of the landmarks was evaluated. By tensile, compression and bending tests of parts obtained by additive manufacturing without post-processing, parts obtained by additive manufacturing and thermally processed, parts obtained by additive manufacturing infiltrated with epoxy resin and parts obtained by additive manufacturing and reinforced with epoxy resin and glass fiber, an attempt was made to establish the most convenient method of improving the mechanical characteristics. In the case of additive manufacturing feature anisotropy poses great problems in predicting the behavior over time due to the way the stresses and strains are distributed, while post-processing greatly reduces this aspect. In the case of the three types of demands, strongly different behaviors were found for the 4 types of samples tested, making it difficult to choose a method. When tested in tension, the samples infiltrated with epoxy resin showed the best characteristics, followed by those obtained directly through additive manufacturing, those reinforced with glass fiber being in the third position, and the weakest characteristics in tension being identified to the thermally processed samples. When tested in compression, the samples obtained by additive manufacturing and the thermally processed ones show the best characteristics, infiltration with epoxy resin and glass fiber reinforcement ensure inferior characteristics. In terms of bending strength, infiltration with epoxy resin presents the best mechanical characteristics. These results, associated with the analysis of the fracture surfaces, indicate that the mode of stress distribution in the landmark plays a crucial role in the mechanical performance. The benchmarks

obtained by combining additive manufacturing and classical methods show an inefficient transfer of stresses between the component made by additive manufacturing and the one added by post-processing. The advantage of additive manufacturing is that it allows the creation of support structures that increase the contact surface and allow a more uniform distribution of stresses as a whole. Through the results obtained, the use of external perimeters made through additive manufacturing that present scaffolding to increase the contact surface and their infiltration with epoxy resin represents an innovative, cheap and fast solution for the creation of customized prosthetic components.

The proposed flow to produce customized prosthetic components is easy to implement, economically efficient and ensures high productivity, and the proposed materials and production methods lead to the production of components in an efficient manner by reducing material consumption and manufacturing time, obtaining products with controllable characteristics and even migrating to fully biodegradable materials. Following the analysis of the variation of the mechanical characteristics of polylactic acid with the addition of copper nanoparticles immersed in artificial sweat, it was found that the benchmarks obtained by using such a filament retain their mechanical characteristics, which recommends it for the application - obviously, taking into account limitations of the experiment

It is mentioned that the experimental part was mainly carried out in the laboratories of the Department of Metallic Materials Science and Physical Metallurgy, Faculty of Materials Science and Engineering, Polytechnic University of Bucharest, although experimental determinations were also carried out in other laboratories. Far from claiming to exhaust the theoretical and experimental research in the field of making customized prosthetic components through additive manufacturing, the paper makes an important theoretical and practical contribution, at the same time opening new horizons for future research in this field.

6.3. Future development perspectives

This Ph.D. thesis has prospects for further development in several directions. Thus, it is possible to expand the studies on the potential modification of the surface properties of the printed landmarks, with the help of nanostructured coatings, and to follow the evolution of the degraded surfaces from the point of view of the compounds that are formed depending on the simulated test environments used. Further research can be developed on the improvement of the post-processing methods of the printed landmarks or the use of carbon nanotubes or graphenes, as well as the embedding in the deposited layers of substances with a protective role for the patient's skin. Obviously, it is possible to expand research on biofunctionality testing on specific models. Last but not least, new materials and new production flows can be developed and studied for the execution of customized prosthetic components.

List of published scientific papers

Papers published in ISI-indexed journals::

1. Alexandrescu, D., Antoniac, I., Olteanu, C., Anghel, L., Sarbu, N., Ciocoiu, R., Scutariu M.M., Surlari, Z., Ioanid, N., Stefanescu, V., Influence of thermal processing for 3D printed components, *Materiale Plastice*, 58, 4, 250-260, 2021, DOI: 10.37358/MP.21.4.5550
2. Alexandrescu, D., Vasilescu, M., Sfat, C., Tabaras, D., Gheorghita, D., Antoniac, I., Ciocoiu, R., A study on 3D printed components surface made of PLA with silver particles, *University Politehnica of Bucharest Scientific Bulletin Series B - Chemistry and Materials Science*, 83, 2, 303-312, 2021

Papers presented in scientific communications:

1. Alexandrescu, D., Ciocoiu, R., Turcu, R., Popescu, D., Streza, A., Stere, A., Miculescu, M., Antoniac, I., Immersion of 3D printed PLA parts in artificial sweat - changes in mechanical properties, 9th International Conference “Biomaterials, Tissue Engineering & Medical Devices” BIOMMEDD, July 20-22th, 2022, Bucharest (Romania).
2. Alexandrescu, D., Antoniac, I., Ciocoiu, R., Stere, A., Robu, A., Combining additive manufacturing with conventional production methods to obtain new materials for prosthetic cups, 9th International Conference “Biomaterials, Tissue Engineering & Medical Devices” BIOMMEDD, July 20-22th, 2022, Bucharest (Romania).
3. Bololoi, R., Ciocoiu, R., Tecu, C., Gradinaru, V., Manea, A., Alexandrescu, D., Antoniac, I., Physical 3D spine model created from DICOM images, International Conference BIOREMEDI2019. September 26-28th, 2019, Craiova (Romania).

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