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A STUDY ON 3D PRINTED COMPONENT'S SURFACE MADE OF PLA WITH SILVER PARTICLES

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This study was aimed to observe, by comparison with conventional PLA, if embedding of silver particles can alter the printed parts surface characteristics. The studies performed include scanning electron microscopy and image analysis, Fourier transform infrared spectroscopy and surface wetting on 3D printed samples made of commercial and PLA with silver particles added for antibacterial properties. According to the results it was observed that by silver particle addition an uneven layer thickness in the structure of the part occurs and no noticeable changes in surface morphology and chemistry.

Keywords: 3D printing, antibacterial PLA, silver particles, surface morphology

1. Introduction

Research in the field on various production technologies has shown that 3D printing is an optimal, fast, and easy method of producing prototypes or products. Due to these advantages, 3D printing has been quickly used in the medical field, as it allows the production [1, 2]. This is done by depositing successive layers of material, computer-assisted, starting from a digital model. In 3D printing there are common terms that define the thickness, density and quality of the product, such as [3, 4]:

- infill represents the density of the interior, which has the appearance of a honeycomb, not being a solid, compact body. The higher the density, the higher the strength of the print.
- shells represent the walls of the object and refer to how many times the outline of the drawing is redone. These "shells" represent the outside of the printed object.
- the print resolution represents the height of a deposited layer, measured in microns. To obtain a very good resolution and implicitly to obtain a smooth surface, it is printed in very thin layers.

3D printing is a simple and relatively fast method of translating a physical object from a virtual environment into reality.

This technology appeared in 1980 when the Japanese doctor Hideo Kodama developed the first patent for rapid prototyping. In the 3D printing process, there are several procedures [5]:

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I. The classical procedure has 3 stages:

- Obtaining in DICOM format (Digital Imaging and Communication in Medicine) medical data by CT (computer tomography) or MRI (nuclear magnetic resonance) in order to obtain the model to be printed, which is processed using CAD techniques (Computer-aided Design) and CAM (Computer-aided Manufacturing);
- Convert DICOM files to STL (Standard Tessellation Language) through the data segmentation process automatically, manually or by combining the two involving voxel clustering (volume element) in the region of interest (ROI). This process, using various algorithms, generates the CAD / CAM model.
- Printing the object.

This method is very useful when a permanent component is made to the patient, requiring a single radiation exposure. In case of manufacture of temporary elements or that change periodically this method is not viable because for each change made the patient is exposed to radiation [5].

II. The alternative procedure is used in the case of projecting for example a prosthetic cup, following an amputation, which involves making several cups, intermediate, until the final one. In this case, to obtain the digitized image, the CAM model is done by:

a. Photogrammetry that involves photographing the prosthetic abutment from different angles and its three-dimensional reconstruction, by processing the images obtained with the help of special programs that generate an STL file. It is a seemingly cheap and handy method, but it requires multiple and advanced interventions from the operator to remedy the defects. The accuracy of the data obtained by photogrammetry is quite low compared to 3D scanning [6].

b. Scanning of the prosthetic abutment with the help of an infrared scanner, which allows the digitization of the obtained image and to obtain the CAM model. The scanner must be adapted to the given requirements, depending on the size or complexity of the object which needs to be scanned. 3D scanning offers detail and dimensional accuracy, as well as a much faster data processing speed [7].

This alternative procedure has 4 stages:

- Digitization of the abutment which is done with the 3D scanner and with the help of a program the data obtained is converted into STL file.
- Design of the prosthetic cup with the help of the CAD Program.
- Choosing 3D printing parameters depending on the type of filament. In this case using PLA, the working temperature will be 210 ° C [8];
- Printing the prosthetic cup and checking the dimensions, by testing by the patient. If there is a need for adjustment, it will be done with metallographic paper.

From what can be seen, the alternative method is faster, with a high fidelity. The design and execution time are much shorter, and the patient should not be irradiated. Under these conditions, the price of producing the prosthetic cup is also diminished.

With the advent of various 3D printing techniques and types of printers with a very high resolution, there was a need to use different thermoplastic materials. There is a wide range of polymers used in 3D printing and among the most used are ABS (acrylonitrile-butadiene-styrene) and PLA (polylactic acid) [9].

PLA (polylactic acid) is a biphasic, environmentally friendly, biocompatible, and biodegradable polymer. Compared to petroleum-based polymers, it is made from renewable raw materials such as corn starch, sugar cane, wheat, and rice. It is based on lactic acid, which is obtained by the bacterial fermentation process, especially corn starch. It has good mechanical characteristics, is fireproof, has thermoplastic processing capacity and a low production price [10]. Due to its biocompatibility, it was quickly adopted in the medical field. PLA is widely used in various medical applications such as surgical implants, tissue culture, resorbable surgical sutures, wound closure, and controlled delivery systems. PLA produced from renewable resources are linear aliphatic thermoplastics, which is easily biodegradable by hydrolytic and enzymatic routes. More importantly, PLA is a synthetic immunologically inert polymer and for this reason, it was chosen in the present study for the design of an engineering scaffold tissue composition [11].

In many studies, the PLA is recommended to be used as a biomaterial for obtaining different implants but is was also demonstrated that the simple PLA did not show effective in vitro results against E. coli and S.aureus bacteria. Also, polylactic acid (PLA) has low elastic modulus and tensile strength and lack of bactericidal capacity. For this reason, in the last period, nanomaterials with antibacterial activity have been intensively studied. In the field of nanotechnology, significant advances have been made that have offered new perspectives on antimicrobial agents and have led to the development of functional nanomaterials with unique chemical and physical properties [12].

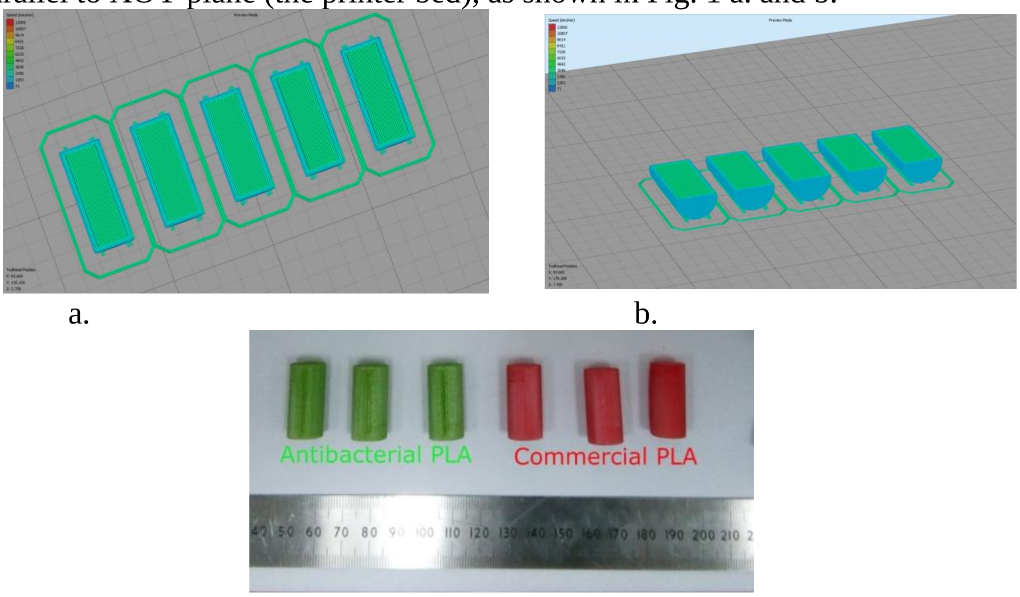
Antibacterial agents such as silver, copper, zinc, and zinc oxide nanoparticles can reduce the attachment and viability of microbes on the surfaces of biomaterials used for implants [13].

The first notes on the antimicrobial activity of silver were recorded by Herodotus, who shows that the king of Persia, when he went to war, boiled, and stored water in silver vessels [14]. In the 19th century, in 1869, the first record of this effect was given by Victor Felix Raulin (1819 - 1905) professor of geology, mineralogy and botanical studies at the University of Bordeaux. He noticed that Aspergillus niger, a fungus that causes "black mold" disease on certain fruits and vegetables, could not grow in silver pots [15]. Recent studies proved that silver nanoparticles (AgNPs) have inhibitory and bactericidal effects, as they have the ability to interact with bacteria that destroy their membrane, cross the body of the microbe and create intracellular damage [16,17]. Thus, Ag has the ability to attack bacteria and studies have shown that its antibacterial activity against E.coli is 86%, and for S.aureus over 98%. In addition, Ag not only offers antimicrobial protection but also the addition of Ag nanoparticles in PLA leads to a drastic increase in its elastic modulus, improves its mechanical properties, and also offers much greater thermal stability [18, 19].

2. Materials and methods

The study comprised two PLA based filaments denoted as commercial PLA (a common use filament for 3D printing) and antibacterial PLA (a PLA filament with embedded silver particles for antibacterial purpose), from Stratasys.

The bulk filaments were studied by scanning electron microscopy (SEM) to observe the structure and silver particle shape, size, and distribution in the antibacterial filament. Both filaments were used in 3D printing of cylindrical samples as shown in Fig. 1.c using a BCN3D Sigma 3D printer using same parameters: the heating temperature for the nozzle was set at 210°C and for the bed at 60°C with an extrusion multiplier of 1.00. The sample infill was set as 100%. The samples were oriented in such way that the long axis of the sample is parallel to XOY plane (the printer bed), as shown in Fig. 1 a. and b.



a. b.

c.

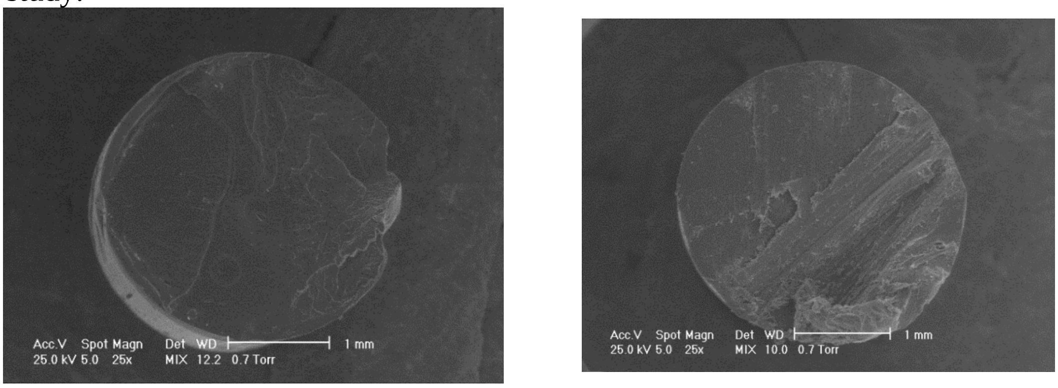
Fig. 1: The samples used in the study showing a. and b. printing direction and infill and c. the 3D printed samples

The 3D printed samples were studied by SEM with a Philips XL 30 ESEM TMP microscope and image analysis was performed on the micrographs using Image-Pro Plus (Media Cybernetics) and J MicroVision. Fourier Transform Infrared Spectroscopy (FTIR) in attenuated total reflectance mode was performed on a JASCO 6200 with ATR Golden Gate spectrometer. The contact angle measurements were performed using the Kruess Drop Shape Analyzer DSA100 on as printed and polished sample surface.

3. Results and discussion

I. SEM study and image analysis

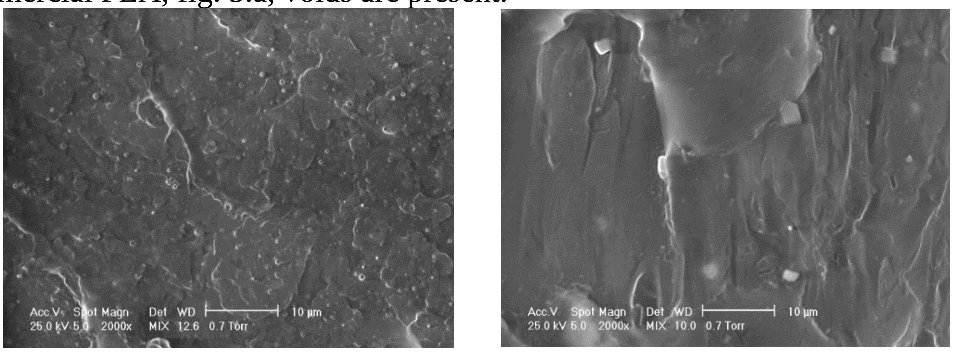
The first SEM studies were performed directly on the cross-section of PLA filaments, Fig. 2 shows the fracture surface of the filaments as prepared for the study.



a. b.

Fig. 2: SEM images shown the fracture surface of the as received a. commercial and b. antibacterial PLA filament

At higher magnifications, the Ag particles are easily distinguished in fig. 3.b with angular shape and uniformly dispersed in the PLA matrix. In the commercial PLA, fig. 3.a, voids are present.

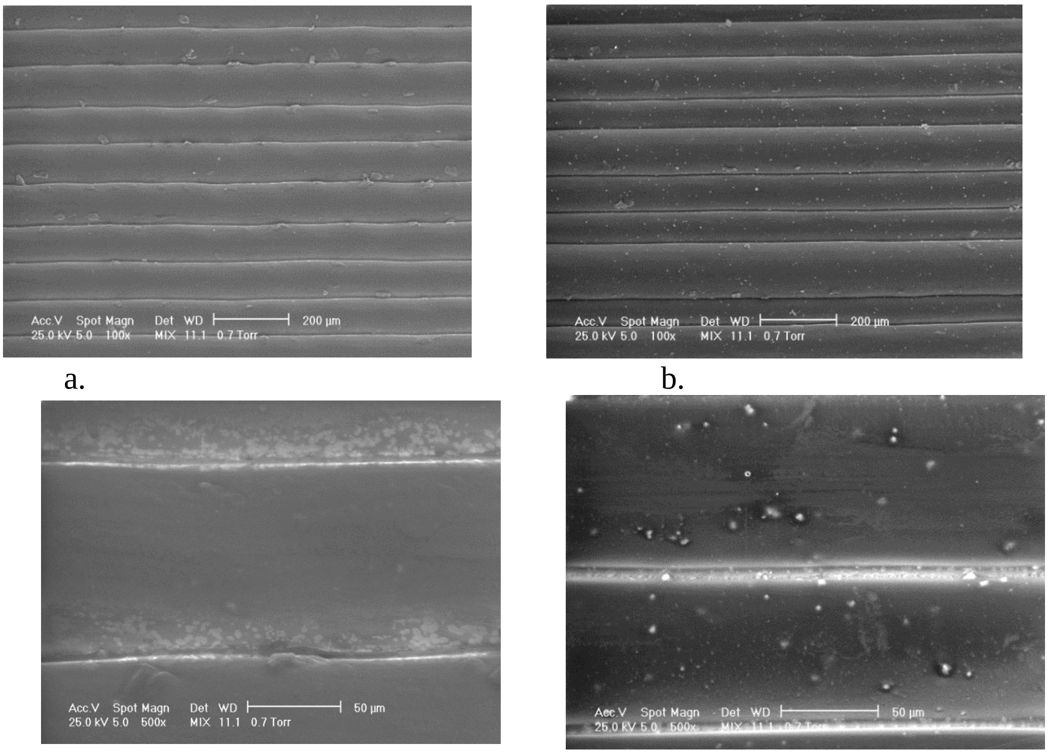


a. b.

Fig. 3 SEM images shown the detail on the fracture surface showing a. voids in the commercial and b. angular particles in the antibacterial PLA filament

On 5 images like 3.b the Feret diameter (the average value over many orientations of the distance between two parallel tangents on opposite sides of randomly oriented particles) was determined to be 5.23±0.88µm.

Post printing the samples were also studied by SEM, in Fig. 4 the results are shown.

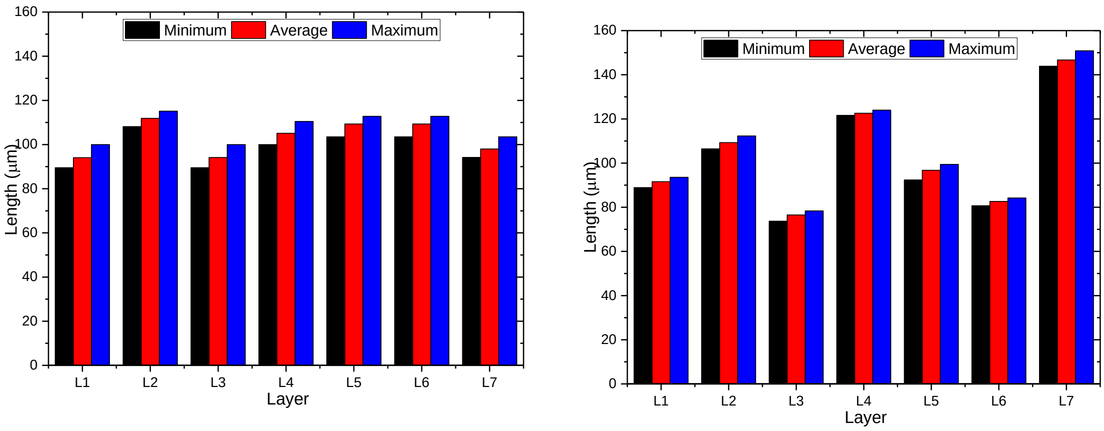


c. d.

Fig. 4 SEM images shown the aspect of layers of 3D printed materials on the a., c. commercial and b., d. antibacterial PLA

In fig. 4. a. and b. the layers of the printed parts can be observed, with a smooth surface and debris and on the antibacterial PLA surface (Fig. 4.b. and d.) angular particles are present. By performing an image analysis on the SEM micrographs, it was determined that the antibacterial particles occupy a 6.33±0.59% of the investigated area.

On SEM micrographs layer width measurements were performed on 7 consecutive layers using an automated procedure: thresholds were set for each layer boundaries and length measurements were performed. In Fig. 5 a length distribution of the minimum, average and maximum layer width is presented.



a. b.

Fig. 5 Layer width distribution in a. commercial and b. antibacterial PLA printed samples

In the commercial PLA samples the layer widths do not show a strong variation, a mean thickness value of 101.27±7.46μm was computed, while for the antibacterial PLA samples the layer widths vary in a more pronounced manner, a mean layer thickness of 103.74±25.41μm being computed.

Although the mean values are similar, the data spread suggests that an uneven flow of molten polymer occurs in the antibacterial PLA.

II. FTIR studies

To observe if any interaction between silver particles and the matrix in the antibacterial PLA occurs FTIR experiments were performed on samples obtained from both specimens. The results are presented by comparison in Fig. 6.

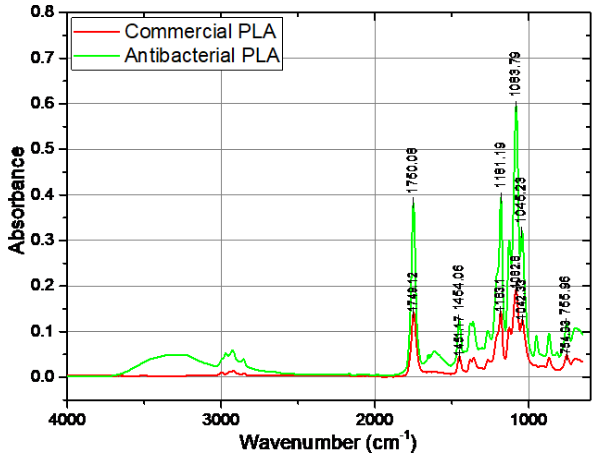


Fig. 6 Comparison of commercial and antibacterial PLA FTIR spectra

In Fig. 6 the peaks appearing at approximately 1750 cm^{-1} and 1180 cm^{-1} correspond to "C=O" and "C-O-C" stretching of the PLA [*J.P. Mofokeng, A. S. Luyt, T. Tabi, J. Kovacs, Comparison of injection molded, natural fiber-reinforced composites with PP and PLA as matrices, Journal of Thermoplastic Composite Materials, 25(8) 927-948, DOI: 10.1177/0892705711423291] and a new peak appeared in the antibacterial PLA at approximately 1650 cm^{-1} that corresponds to a bending of "O-H" [*] that can be attributed to absorbed water.

From the FTIR analysis no interactions between antibacterial particles and the matrix were inferred, aside that the antibacterial PLA appears to absorb water more than the commercial PLA.

III. Contact angle measurements

Contact angle measurements were performed on a surface obtained as 3D printed denoted with "N" and a polished surface denoted "P". On the surface 50µL distilled water drops were deposited using the DSA100 and the contact angle measured using the specific software. The experiment was repeated 9 times for each sample. In Fig. 6 the results are depicted, for comparison, as box-plots.

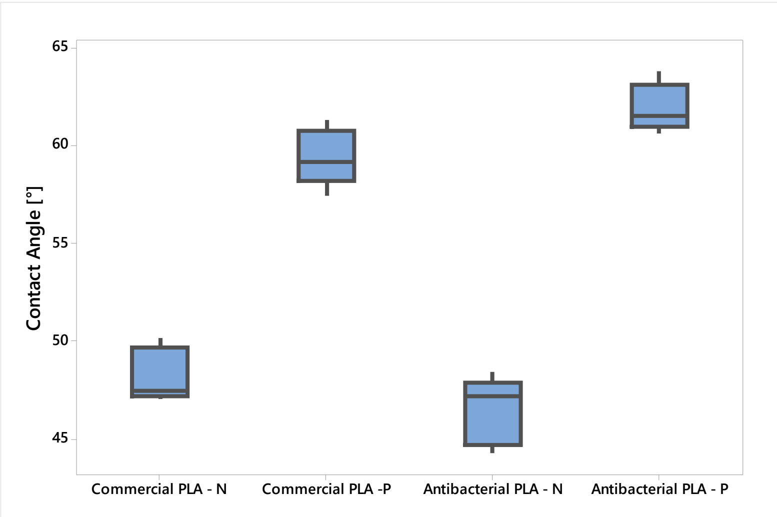


Fig. 6 Box-plots showing the results of contact angle measurement

Analyzing the results, it was found that on unprocessed surface for the commercial PLA the average contact angle value was 48.18±1.29° while for the antibacterial PLA 46.58±1.59°. Polishing the surface, the hydrophobic behavior of the surface was enhanced, the commercial PLA averaged at 59±1.38° and the antibacterial PLA at 61±1.16°.

By statistically comparing the means at α=0.05 it was concluded that there is no statistical significant difference between the average values: the average contact angle value on the as printed surface of the commercial PLA can be considered equal to the one on the antibacterial PLA, as well as on the polished surface.

The antibacterial particles embedded in the PLA did not alter the surface chemistry in as much to produce a noticeable effect.

4. Conclusion

The aim of the study was to determine the printing behavior of antibacterial PLA filament in comparison to a commercial one. Following image analysis results it was observed that the printed layer thickness of the antibacterial PLA varied strongly and it is believed because of silver particles clutter in the nozzle which alters melted polymer flow.

Post FTIR analysis no interactions between antibacterial particles and the matrix were observed. By the occurrence of a peak that corresponds to a bending of "O-H" at approximately 1650 cm^{-1} which was attributed to absorbed water it was concluded that the antibacterial PLA absorbs more moisture from the atmosphere than the commercial one.

Surface wetting was found to be similar for both the commercial and antibacterial PLA, the contact angles with water as wetting agent did not vary. An increase of the contact angle value was obtained by polishing the surface of the sample. Following this study, it was concluded that, in order to obtain a uniform layer width, printing parameters should be optimized when particle reinforced filaments are used.

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