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Methodology and Subsequent Analysis of Polymer Filament Production from PEEK Material With a Ceramic Admixture

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Abstract: The aim of the presented article is to describe the process of filaments production from the material of pure PEEK as well as from PEEK mixed with the ceramic component HA and TCP and subsequently its analysis. The analysis of the filament consisted in the analysis of the diameter of the produced filament, the distribution of the ceramic component in the produced filament, as well as the biological test of cytotoxicity after the extrusion process. In the analysis of the filament diameter, descriptive statistics were used to detect the thickness of the entire filament produced. Electron microscopy using SM and SEM modes was used to analyse the distribution of the ceramic component in the produced filament. The cytotoxicity biological assay was performed using the L929 cell line according to ISO 1099-5. The results of the filament diameter analysis show average values of pure PEEK of 1.7501 ± 0.032 mm and for PEEK with a ceramic component of 1.7503 ± 0.041 mm. Analysis of the distribution of the ceramic component showed irregular filler particles with a size of 1 to 2 μm in the produced filament. EDX analysis showed a distribution of calcium and silicon in the filament. The cytotoxicity assay showed higher values from the reference value using 100% and 75% extraction. From the presented analyses of the produced filament, it can be stated that the diameter of the filament meets the required quality for the 3D printing process. In terms of ceramic component distribution analysis, smaller clumps were detected but these clumps were evenly distributed in all samples. The cytotoxicity test showed that the extrusion process did not affect the cytotoxicity of the produced filament.

Keywords: PEEK, TCP, HA, filament, extrusion

1. Introduction

Additive technology is increasingly used in industrial production [1, 2, 3, 4]. One of them is Fused Deposition Modeling (FDM) technology, which uses plastic filaments made of polyetheretherketone (PEEK) in the printing process, which are subject to high demands in terms of its production process and material composition [5, 6, 7]. This area is also devoted to the professional public, where the material characteristics and subsequently their mechanical properties are examined using various admixtures, either carbon fibres [8], glass fibres [9], or ceramic component [10]. A study by S.M. Tang [11] describes the mechanical behaviour of a ceramic component in the form of Hydroxyapatite (HA) in PEEK. The samples were divided into individual groups, each group having a different proportion of HA in the ratios of 5%, 10%, 20%, 30% and 40%. These groups of specimens were subjected to stress fatigue in a controlled load mode. The results of tensile tests showed that the tensile stiffness of HA / PEEK composites increased with increasing percentage of HA. However, as the percentage of HA increased, the tensile strength decreased. The author further states that all

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samples survived the cyclic loading at 50% tensile strength, indicating that the combination of HA and PEEK materials is a promising composite in terms of material fatigue for biomedical applications. Another study dealing with the issue of impurities in PEEK is from Wang et al. [12] Where the preparation of PEEK composite fibres with carbon (CF) and glass fibre (GF) reinforcement and their complex evaluation of properties for 3D printing is described. The weight fraction of carbon and glass fibres was 5%, 10% and 15%. The mechanical results in this work suggest that the addition of CF / GF to PEEK can significantly increase the tensile and flexural strength at the expense of ductility. The lower fibre content contributes to improving the surface quality and reducing the porosity of the printed CF / GF-PEEK. All these composite polymeric materials contain two or more materials that have different temperature and viscous properties [13, 14, 15, 16]. This effect can cause different filament diameters, which ultimately affects the 3D printing process itself.

The present work describes the process of production of medical filaments from the material of pure PEEK and PEEK with an admixture of a ceramic component in the form of HA and Tricalcium phosphate (TCP). Part of the work is also the analysis of the basic parameter in the form of the diameter of the filament, which is evaluated by descriptive statistics.

2. Filament production process and analysis methodology

Two materials were used in the production of filaments: pure PEEK (Grade: LUVOCOM 3F PEEK 9581 NT) and a mixture of PEEK with ceramics (PEEK-80% / TCP-10% / HA-10%, Grade: SOLVAY - ZENIVA ZA-500) (Fig. 1). The filament production process was performed on 3Devo machines (Netherlands) (Fig. 2).

2.1. Preparation of pellets

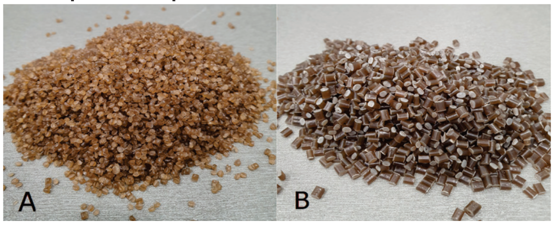


Figure 1: Pellets: (A) pure PEEK. (B) PEEK with ceramics admixture.

Both PEEK variants of the material were supplied in the form of pellets (Fig. 1), protected from moisture and light by an opaque vacuum package with 13485 certificate of production. Nevertheless, the materials underwent a drying process in a 3Devo, Netherland's dryer. Drying was performed at the temperature of 150°C for 3 hours. The same drying procedure was chosen for both variants of material. The rotating blades of the apparatus mix the material during the drying process, evenly distributing the heat radiated by the dryer. The drying process was chosen to eliminate moisture in the materials.

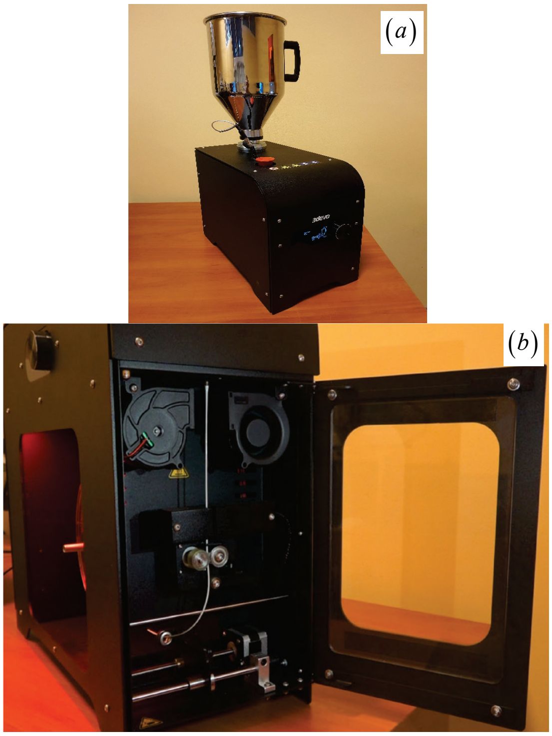


Figure 2: AirID polymer dryer (a), Material extrusion by filament maker 3Devo (b).

2.2. Filament extrusion

Extrusion was performed on a Filament maker (Precision series) device. The device was put in the air-conditioned room, to maintain a constant temperature of 18°C. First, it was necessary to find a suitable starting temperature. For pure PEEK as well as PEEK with ceramic admixture was chosen same initial temperatures at all four filament maker heaters (400°C). This temperature was based on the knowledge of the PEEK material melting point, increased by 50°C to achieve a thinner mixture [17].

Given that information and large temperature range (15-400°C) for these materials, it necessary to use transit material. So, as transit materials were used:

- *HDPE – temperature range 180-280°C,*
- *Devoclean MidTemp - temperature range 180-320°C,*
- *Devoclean HighTemp - temperature range 320-420°C.*

By gradually increasing the temperatures, we reached the required 400°C. Both pure PEEK and PEEK with ceramics do not burn at those temperatures, but they are not rigid.

The filament maker works on the principle of moving the molten material with a sliding screw towards the nozzle. After being placed in the hopper, the pellets are gradually heated by heating elements # 4, # 3, # 2 # 1. When extruding the material, we followed the manufacturer's recommended motor current consumption, which is 2100mA. During extrusion, other important parameters were also adjusted: the sliding screw RPM and cooling by appropriate fans. Visual inspection of the filament was very important. The aim was to achieve an optimal and constant viscosity and detect air bubbles and impurities inside the produced filament. With the suitable settings of the device, our goal was a filament with a diameter of 1.75 mm. The final combinations of parameters are summarized in Tab. 1,2. After stabilizing the filament flow, extruded fibre was placed in a sensor that measures its diameter. The filament was then wound into a spool. A graph showing the filament thickness can be seen in Graph. 1,2. Sampling frequency was 1 second.

Table 1: Machine settings – pure PEEK.

Heater number	*#4*	*#3*	*#2*	*#1*		*Screw RPM (round per minute)*	4
Real temperature [°C]	371	383	385	391		*Fan output [%]*	80
Set temperature [°C]	372	385	385	390		*Laboratory temperature [°C]*	18,5

Graph 1: Extruded filament diameter over time - pure PEEK, output from the produced filament.

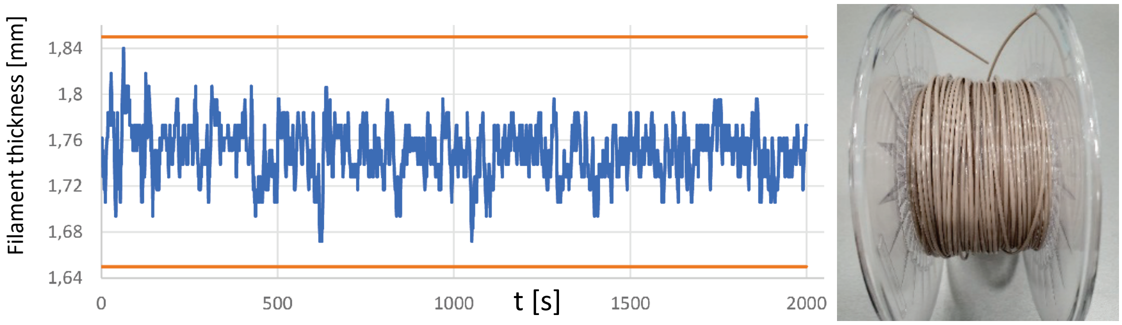
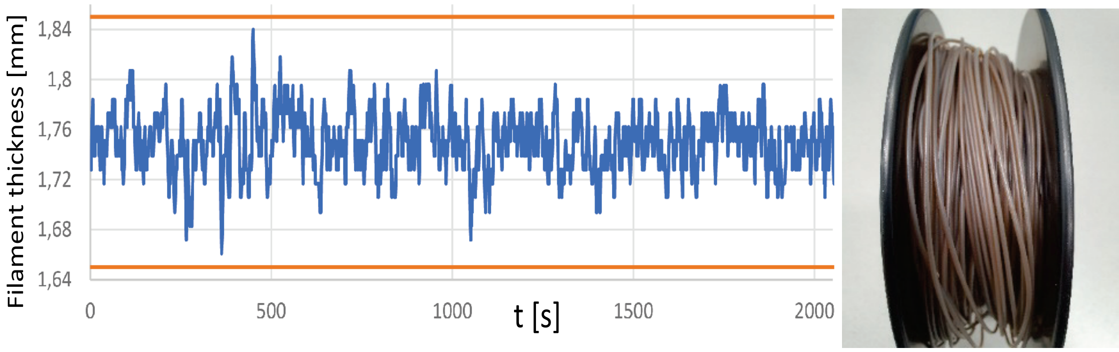


Table 2: Machine settings – PEEK-80%/TCP-10%/HA-10%.

Heater number	*#4*	*#3*	*#2*	*#1*		*Screw RPM (round per minute)*	4
Real temperature [°C]	422	397	399	399		*Fan output [%]*	100
Set temperature [°C]	420	400	400	400		*Laboratory temperature [°C]*	18

Graph 2: Extruded filament diameter over time - PEEK-80%/TCP-10%/HA-10%, output from the produced filament.



2.3. Distribution control of ceramic admixture

The aim of this part was to quantify the distribution of the ceramic component in the PEEK material. In this case, an electron microscope (Jeol JSM 7000F) in the secondary electron mode (SEI) was used for detailed microstructures, thanks to which detailed information on the morphology of the ceramic parts and their distribution in the polymer filament matrix was obtained. Samples were selected at random from the produced filament, while the shape of the individual components was in the form of granules. The total number of samples was set at 10 pieces. Prior to the microscopic analysis itself, the samples were prepared in dentacryl, sanded with 240, 400, 600 and 800 µm sandpaper, polished with diamond paste and finally rinsed with benzylalcohol.

2.4. Cytotoxicity test

The aim of cytotoxicity test was to determine the level of cytotoxicity after the extrusion process and to quantify the findings. Extracts were prepared by placing sterile samples in MEM + 5% FBS + ATB medium. The defined ratio was 0.2 g / ml. The temperature in this case was 37°C, with shaking 120 RPM. The extraction was set at 24 hours. Cell seeding was performed through a 96-well arrangement. The L929 cell line (1 * 105 cells * ml^{-1}) was used. MEM + 10% FBS was used as medium. The incubation time was 24 hours. All these procedures were performed according to ISO 10993-5. The total number of samples was set at 6 pieces, while their selection from the produced filament was random. The shape of the sample was pelleted.

3. Analysis of filament

3.1. Analysis of filament diameter

The aim of this section was to present the complete production process of filaments from materials: pure PEEK and PEEK with a composite ceramic admixture. During the production of filaments, an effort was made to create a filament with a diameter of 1.75 mm with small geometric deviation of diameter. However, many variables played a role in this process such as laboratory temperature or limiting factors of the machine. The constant room temperature ensured rapid cooling of the extruded fibre. In the production of high-temperature polymeric materials, the laboratory temperature 18°C was chosen, which is suitable due to the high temperature difference between the extruded filament and the laboratory. Appropriate cooling fans also contributed to the cooling of the filament. For this reason, there were no large changes in the thickness of the filament for pure PEEK or PEEK mixed with ceramic materials. In Tab. 3 is shown numerical evaluation of results.

From Tab. 3 is clear that using the determined combination of machine parameters and ambient temperature, it is possible to produce a printing fibre with a relatively small deviation in the diameter of the filament (approx. ± 0.04 mm).

Another important parameter to creating a good quality filament is extrusion [18]. If the device (filament maker) is to extrude the same amount of material all the time, it is necessary that the motor of the device maintains a constant speed of the sliding screw. From our observation we can say that the set speed tended to fluctuate (4 ± 0.3 RPM) in both materials. Differences in the set and real temperatures of the heating elements also contributed to the instability of the filament diameter (see Tab. 1,2).

From the findings (suitable machine parameters for extrusion of new materials), it was found that higher temperatures of heaters than pure PEEK were required for PEEK with ceramics. The resulting temperatures are on average 23.25°C higher per heater. We attribute this phenomenon to 20% of the presence of ceramics, which is characterized by lower thermal conductivity than PEEK [17,19]. The heaters must develop higher temperatures to heat all the material in the machine chamber.

3.2. Distribution analysis control of ceramic admixture

The aim of this part was to quantitatively evaluate the distribution of the filler in the produced filaments made of pure PEEK and PEEK materials with an admixture of a ceramic component in the

Table 3: Analysis of filament diameter.

Pure PEEK		***PEEK + Ceramics***	
Overall average of diameter [mm]	1.750074	Overall average of diameter [mm]	1.750357
Standard Deviation [mm]	0.032854	Standard Deviation [mm]	0.041204
Max / Min average value [mm]	1.840/1.675	Max / Min diameter value [mm]	1.843/1.662

form of TCP and HA in a weight ratio of 10%. The total number of experimental ones was determined to be 10, and their shape was pelleted. No defects in the integrity of the polymer pellet matrix were observed in any of the samples. EDX analysis of the samples detected an even distribution of carbon and oxygen throughout the sample section. This result can be attributed to the fact that it was a one-component material in the form of pure PEEK and thus it can be stated that during the extrusion process the production of filaments no contamination of the produced filament took place. In Fig. 3 you can see the examined sample of pure PEEK in SE as well as SEM mode where it is possible to see that the given sample does not contain any filler in the form of added material.

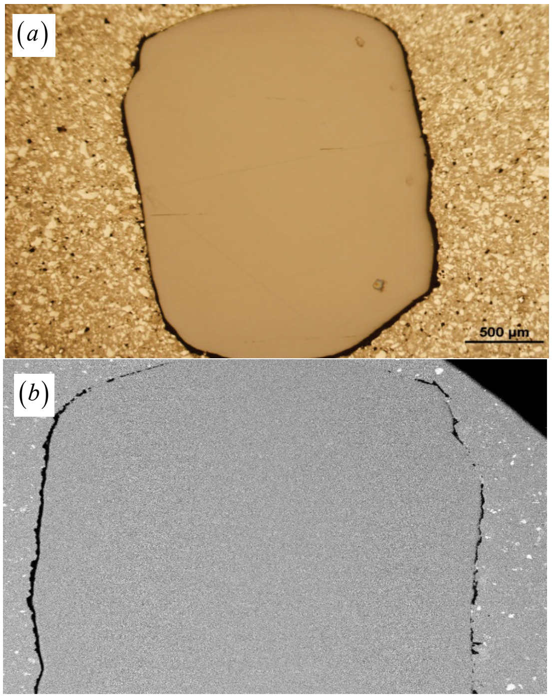


Figure 3: Pure PEEK - (a) SM mode, (b) SEM mode.

No defects in the integrity of the samples were detected during the analysis of the PEEK samples with the ceramic component. The analysis showed irregular filler particles with a size of 1 to 2 µm. The local filler particles formed clusters of globulite shape. The individual aggregates of filler particles were up to 10 µm in size. In the polymer matrix, the filler particles as well as the aggregates of filler particles were dispersed evenly, the filler particles were well fixed in the polymer matrix of the pellets. EDX analysis showed a calcium and silicon distribution, which corresponded to the distribution of globulite particles and agglomerates. For this reason, it can be said that the detection of calcium and silicon represents added components in the form of HA and TCP. In Fig. 4 it is possible to observe a sample made of PEEK with an admixture of ceramics in the SM and SEM modes. From the individual modes it is possible to observe clusters of filler in the form of HA and TCP materials in the form of white dots.

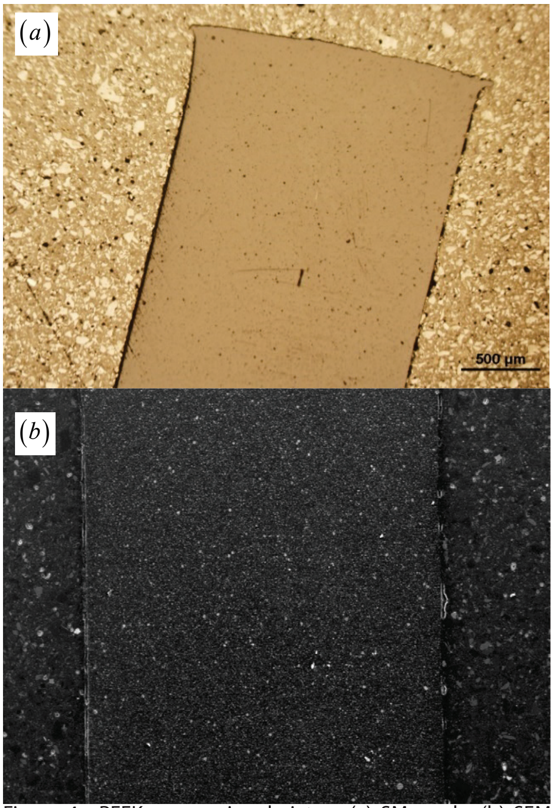


Figure 4: PEEK + ceramic admixture (a) SM mode, (b) SEM mode.

3.3. Analysis of cytotoxicity test

Visual inspection of the cytotoxicity test showed a corresponding increase in the number of cells after culturing for 24 hours in all 6 samples, either for pure PEEK or with ceramic admixture. Cells after culturing with the extract are morphologically comparable to unaffected cells. Graph 1 shows the metabolic activity of L929 cells at 100% and 75% extract. The reference value was considered to be 70%. It is clear that for pure PEEK material these values were at 86% at 100% extraction and at 88% at 75% extraction, indicating that the reference value was exceeded by 16% at 100% extraction and by 18% at 75% extraction. It follows that the extrusion process during the production of filaments is not cytotoxic to the material. A similar effect was observed when evaluating the PEEK material with the ceramic component, with a value of 89% for the 100% extract. A value of 90% was recorded for 75% of the extract. When comparing the achieved values with the reference value, a difference was recorded in the 100% extract at the level of 18% and in the 75% extract by 20%. From the above differences, it can be stated that no cytotoxicity occurred during the extrusion of the production of the filament from the PEEK material with the admixture of a ceramic component.

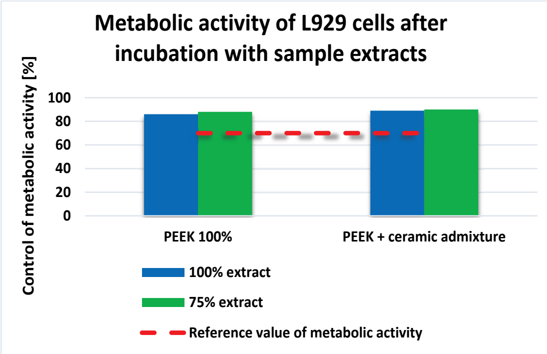


Figure 5: Comparison of the metabolic activity of cells in the materials of pure PEEK and PEEK with the admixture of a ceramic component versus the reference value of the cytotoxicity test.

4. Discussion

The output of the present study deals with the production of filaments from pure PEEK and PEEK materials with an admixture of a ceramic component, both filaments were produced with a diameter of sufficient accuracy (PEEK = 1.7501 ± 0.03 mm; PEEK + ceramic component = 1.7504 ± 0.04 mm). According to Herianto [20], this filament parameter is crucial for 3D printing because if the diameter is reduced, the extrusion process will reduce the amount of material required so that the fibre does not reach the end of the nozzle. If the diameter is increased, the 3D printing process will show an excess amount of material, which can degrade the resulting model or the extruder itself will become clogged. Several parameters [21, 22, 23] affect the correct filament diameter, including temperature, extrusion rate, cooling of the extruded material, and winding.

A study by Goldbang et al. [24] describes the production and nanocomposite of PEEK in combination with tungsten disulfide for additive production: simultaneous improvement of processing characteristics and material properties. The production temperature of this filament was around 395°C, which almost corresponds to our temperature range to produce filament from PEEK + ceramic component. However, the flow of molten material did not have the same viscous properties compared to pure PEEK. This may be due to the higher viscosity of the added particles in the material. This fact is also confirmed by a study by Afir et al. [25] where it describes the production of PEEK fibre with 1% and 3% by weight of CNTs. The study showed that the processing of the PEEK melt with 1% by weight of CNT had good viscous properties during production, however, the PEEK melt with 3% by weight of CNT had higher viscosity properties, which ultimately affects the extrusion process itself. Another parameter that can affect the filament diameter is the RPM. This issue is described by the team of authors Ponsar et al. [26] his study Fluctuations of the hot extrusion process from the melt and their influence on the attributes of fibres and 3D printing. They concluded that the increasing screw speed resulted in a lower material pressure due to the smaller volume of material in the cylinder of the device and thus the lower shear stress. However, with increasing screw speed, the IQR pressure of the material also increases, which also affects the diameter deviation. This fact correlates with our results since in our case we used a small RPM which resulted in filaments with a standard deviation of 0.03284 for pure PEEK and 0.041204 for PEEK with a ceramic component at a nominal value of 1.75 mm.

5. Conclusion

Our study shows that the described methodology can produce a medically high-quality filament from pure PEEK and PEEK mixed with ceramic mixtures homogeneously distributed in the filament. However, different quality control steps must be set up, i.e. ensuring production stability. Most printing fibre manufacturers use a tolerance of ± 0.05 mm in fibre production. It looks like a small number, but we must not forget that this type of deviation can increase / decrease the expected flow by 11.4% at its extreme values [27]. The next step in the ongoing development will be the 3D printing of experimental samples and the subsequent description of the mechanical properties of the materials. It should be noted here that even a processing method has a significant effect on the resulting mechanical properties [28]. Electron microscopy analysis showed an even distribution of the ceramic component along the entire length of the fibre produced, which means that the phenomenon known as sifting segregation did not occur (the horizontal extrusion process agglomerates ceramic particles at the bottom of the extruder chamber). The suitability of using FDM 3D printing technology is also questionable, just for the content of the ceramic component. A study by Chang et al. [29] dealt with the production of biocompatible PCL / HA composite filaments for 3D printing of bone scaffolds using FDM technology. Using 30% by weight of ceramic component (HA), the filament was unsuitable for use in FDM due to its brittleness. This is a matter of great concern for our variant of the PEEK/TCP/HA material, which contains a total of 20% of the ceramic component. It has also been shown that the extrusion process of the fibre extrusion did not affect its biological properties, in particular its cytotoxicity. Based on the previous information, it can be said that the newly formed material composed of polymer and ceramic component is, using the same production methodology and equipment, a possible candidate for future biomedical applications.

Acknowledgments

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