Mechanical properties of ceramic structures based on Triply Periodic Minimal Surface (TPMS) processed by 3D printing

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Abstract. Repairing tissues and organs has been the main goal of surgical procedures. Since the 1990s, the main goal of tissue engineering has been repairation, using porous scaffolds that serve as a three-dimensional template for the initial fixation of cells and subsequent tissue formation both in vitro and in vivo. A scaffold must have specific characteristics of porosity, interconnectivity, surface area, pore volume, surface tortuosity, permeability and mechanical properties, which makes its design, manufacturing and characterization a complex process. Inspired by nature, triply periodic minimal surfaces (TPMS) have emerged as an alternative for the manufacture of porous pieces with design requirements, such as scaffolds for tissue repair. In the present work, we used the technique of 3D printing to obtain ceramic structures with Gyroid, Schwarz Primitive and Schwarz Diamond Surfaces shapes, three TPMS that fulfill the geometric requirements of a bone tissue scaffold. The main objective of this work is to compare the mechanical properties of ceramic pieces of three different forms of TPMS printed in 3D using a commercial ceramic paste. In this way it will be possible to clarify which is the TPMS with appropriate characteristics to construct scaffolds of ceramic materials for bone repair. A dependence of the mechanical properties with the geometry was found being the Primitive Surface which shows the highest mechanical properties.

1. Introduction
The concept of additive manufacturing has expanded the possibilities of manufacturing highly complex parts since its introduction in the 80’s by Charles Hull [1, 2]. Different additive manufacturing techniques have emerged over this time, including stereolithography (SLA), selective laser sintering (SLS) and inkjet printing [3, 4]. However, it has been found that parts manufactured from extrusion-based processes have better mechanical properties and higher density in their microstructure compared to those made from processes based on powder deposition [5].

Due to the emergence of additive manufacturing techniques and the relative ease they provide to construct highly complex parts, their use has been explored in tissue engineering applications such as the design and fabrication of functional scaffolds for repair, regeneration or reconstruction of tissues or organs [6]. The fundamental objective in the design and construction of a scaffold for tissue engineering is to be able to mimic the extracellular matrix (ECM) of the tissue that will be replaced or modified [7]. A mechanically stable environment must be provided to house the necessary cells, growth factors and other biological factors in a porous structure that facilitates
the migration, adhesion, proliferation and vascularization of the growing tissue [8]. In particular, in bone regeneration, the scaffolds must have specific architectural characteristics in order to support the biological and mechanical requirements for the application. The structure of the scaffold plays a fundamental role, since it must have a distribution of interconnected pores and high porosity in order to allow the cellular penetration, vascular growth and a good diffusion of nutrients [9]. It is well known that the porosity percentage of the trabecular bone is in the range of 50% to 90% while the compact bone presents a percentage of porosity less than 10% [10]. Regarding the mechanical properties of spongy bone tissue, it has been found that its maximum compressive strength is between 2 and 12MPa while its Young’s modulus is between 0.02 and 0.5GPa [11].

Modelling of structures for scaffolds represents a challenge because it is necessary to obtain geometries with interconnected pores in a controlled manner. The triply periodic minimal surfaces (TPMS) are interesting geometries in the design of scaffolds since the use of 3D printing became popular [12]. The TPMS have been studied by differential geometry for more than 250 years. One of the pioneers in the study of these surfaces was Lagrange, who postulated that there should be a surface of minimal area having a closed curve as a boundary [13]. The solids that are obtained when thickness has been given to these surfaces constitute a unit cell which has cubic symmetry. The periodic repetition in space of these unit cells form a porous structure whose pores are found interconnected. This is ideal for the design of scaffolds [10].

In the present work the mechanical behavior of three different TPMS processed by 3D printing were compared using a conventional commercial ceramic paste in order to determine which of these geometries is most suitable for the manufacture of scaffolds for bone tissue.

2. Experimental

2.1. Design of triply periodic minimal surfaces

The Triply Periodic Minimal Surfaces (TPMS) selected for comparing their mechanical properties were: Gyroid, Schwarz Primitive Surface and Schwarz Dymond Surface. This TPMS were selected according to their outstanding strength to compression and toughness [14]. These surfaces have interconnected pore circuits. TPMS can be approximated by means of an implicit surface represented by trigonometric combinations of sinusoidal functions [13]. To model these equations, the software MathMod® was used. The unit cell of each TPMS was obtained, which was replicated in three dimensions, 5 times in each XYZ coordinate axis so that the resulting surfaces consisted of 125 unit cells total. From the modelled surfaces, Blender® CAD software was used to impart thickness to these. The solids were designed with a wall thickness of 2.4mm and overall dimensions of $50 \times 50 \times 50 \text{mm}^3$. Table 1 summarizes the equations, surfaces, and modelled solids.

2.2. Printing of the triply periodic minimal surfaces

From the generated models, Slicing Software Cura 3D Printing software version 15.04.2 was used to configure the printing parameters and obtain the G-Code necessary to control the movements of the printer. A layer height of 0.45mm, a density of 100% were determined and the print speed was set between 15 and 25$	ext{mm/s}$ to ensure good print quality.

For printing, a Wasp printer model Delta 20 × 40 was used. A conventional commercial ceramic paste was used for the printing of the chosen minimal surfaces. In order to facilitate the printing process the paste was adjusted with an approximate humidity of 23% to improve its plasticity and viscosity. Since the parts undergo a shrinkage due to drying and heat treatment, a compensation of 8% is made in the dimensions of the models.

The paste was positioned on the feed cylinder of the printer and extruded with a pressure of 101PSI (Approximately, 7Bars). The paste was deposited, following the established design, by means of an extruder with a nozzle of 1.2mm diameter. After print, the pieces were dried at
100°C in a Binder stove until the pieces reached constant weight. Subsequently a heat treatment was carried out at 1050°C for two hours in a furnace Sentro Tech Corp SA 1700X.

Table 1. Equations, surfaces and models of TPMS-based solids designed from trigonometric approximations.

| Schwarz Primitive | Gyroid | Schwarz Diamond |
|-------------------|--------|-----------------|
| $\cos(x) + \cos(y) + \cos(z) = 0$ | $\cos(x)\sin(y) + \cos(y)\sin(z) + \cos(z)\sin(x) = 0$ | $\sin(x)\sin(y)\sin(z) + \sin(x)\cos(y)\cos(z) + \cos(x)\sin(y)\cos(z) + \cos(x)\cos(y)\sin(z) = 0$ |

2.3. Characterization of triply periodic minimal surfaces

Using the software CAD Rhinoceros 5.0, the percentage of porosity of the pieces of the different geometries was determined making the relationship between the obtained pieces and a body of cubic shape completely dense of the same dimensions. For crystalline phase identification, X-Ray Diffraction with a double circle multipurpose Xpert-Pro PANanalytical Radiation Cu-Ka ($\lambda=0.15406\text{nm}$) diffractometer in a range of diffraction of 0-80° ($2\theta$) was used. The printed parts were measured superficially with a Mitutoyo digital caliper with a resolution of 0.01mm and their faces were rectified by means of 400 grid sandpaper to ensure flat-parallel faces and dimensions.

2.4. Mechanical characterization of triply periodic minimal surfaces

The sintered bodies were subjected to the maximum compressive strength test using a Shimadzu universal machine AG-X model. Five tests were performed for each type of geometry at a constant speed of 0.5mm/min with a load cell of 100kN.
3. Results

Figure 1 shows the photographs of the pieces obtained. There are differences in the orientation of the main channels generated by the pores of each of the TPMS. In the Schwarz Primitive the main channels are interlaced perpendicularly and oriented in direction (0 0 1). In the Gyroid, the main channels are oriented in the direction of the diagonals of the cube (1 1 1). In the Diamond the main channels are oriented in direction (1 1 0).

![Figure 1](a) Schwarz Primitive. (b) Gyroid. (c) Schwarz Diamond.

Figure 2 shows the X-Ray diffractograms of the ceramic paste before and after thermal treatment at 1050°C for 120 minutes.

![Figure 2](a) Before thermal treatment. (b) After thermal treatment.

In the paste without thermal treatment, it is possible to recognize illite (I) (2θ=9°, 18° and 20°), kaolinite (K) (2θ=6.3°, 12.5° and 25°) in addition to feldspar (P) (2θ=27.5°) and quartz (Q) (2θ=20.8°, 26.6°, 36.5°, 39°, 50°, and 60°) as main crystalline phases. After calcination the intensity of reflections at 2θ=9° and 2θ=12,5° (illite and kaolinite) decreased as a result of the formation of partially amorphous metakaolinite (broad band between 2θ=5° and 2θ=15°) and mullite (2θ=16.5°, 26.6°, 36.5°, 39°, 50°, and 60°). After firing, signals of illite, kaolinite and
feldspar decreased and finally disappeared leaving quartz, feldspar and mullite (M) as the main crystalline components.

Figure 3 shows the results of the maximum compressive strength of the tested pieces. Table 2 summarizes the data of the calculated porosity of the pieces, the measured porosity, the maximum compressive strength and the Young’s modulus.

![Max Resistance](image)

**Figure 3.** Maximum compressive strength (MPa).

| Table 2. TPMS’s Young modulus. |
|-----------------------------|
| TPMS               | Porosity (%) | Young modulus (MPa) |
|--------------------|--------------|---------------------|
| Schwarz Primitive  | 72.29441 ± 1 \times 10^{-5} | 335.0 |
| Gyroid             | 81.73618 ± 1 \times 10^{-5} | 51.7 |
| Schwarz Diamond    | 78.52382 ± 1 \times 10^{-5} | 238.3 |

The maximum compressive strength of the trabecular bone is in the range of 2 to 12MPa [11]. Of the TPMS tested, Schwarz Primitive and Schwarz Diamond have maximum compression strengths, compatible with those of the bone, being Schwarz Primitive the one with the greatest mechanical resistance (4.7MPa). A direct relationship between the porosity and the mechanical behavior of the parts is evidenced. As the pieces are more porous, the compressive strength and Young’s modulus are smaller. This may be associated with the orientation of the main channels defined by the porosity. In the Schwarz Primitive the direction in which the load is applied in the tests of resistance to compression is parallel to the columns of support of the geometry, whereas in Gyroid and Schwarz Diamond the orientation of the columns that support the load show inclination with respect to the direction of the applied load generating a torque in the walls of the structure. Sintered Ceramic materials containing glass [15] have a good mechanical behavior in the case of compression, however when strain appear as in the case of Gyroid and Schwarz Diamond, the mechanical behavior of the pieces may be affected.

4. Conclusions
It was possible to manufacture ceramic pieces based on TPMS by means of 3D printing. All geometries studied show porosities within the range of those of the trabecular bone. A direct relationship between the percentage of porosity and the mechanical behavior of the studied geometries is evidenced. At lower porosity, greater compressive strength and Young’s modulus. The Schwarz Primitive geometry presented the best mechanical behavior associated with the orientation of the columns that support the load.
References

[1] Gross B C, Erkal J L, Lockwood S Y, Chen C and Spence D M 2014 Evaluation of 3D printing and its potential impact on biotechnology and the chemical sciences Anal. Chem. 86 3240–3253

[2] Bamford R 2013 3D printing in clay building objects in coiled layers Ceramics Monthly 61(2) 60

[3] Wilkinson S and Cope N 2015 3D Printing and sustainable product development green information technology ed Mohammad Dastbaz et. al (Boston: Morgan Kaufmann) chapter 10 pp 161-183

[4] Noguera R, Ljeune M and Chartier T 2005 3D fine scale ceramic components formed by ink-jet prototyping process J. Eur. Ceram. Soc. 25(12) 2055-2059

[5] Thomas A, Kolan K C, Leu M C and Hilmas G E 2017 Freeform extrusion fabrication of titanium fiber reinforced 13–93 bioactive glass scaffolds J. Mech. Behav. Biomed. Mater. 69 153–162

[6] Afshar M, Anaraki A P, Montazerian H and Kadkhodapour J 2016 Additive manufacturing and mechanical characterization of graded porosity scaffolds designed based on triply periodic minimal surface architectures J. Mech. Behav. Biomed. Mater. 62 481–94

[7] Berman B 2012 3-D printing: The new industrial revolution Bussiness Horizons 55(2) 155

[8] Migliaresi C and Motta A 2014 Scaffolds for tissue engineering: Biological design, materials, and fabrication (Singapore: Pan Stanford Publishing Pte. Ltda.)

[9] Rosetl L, Parisi V, Petretta M, Cavallo C, Desando G, Bartolotti I and Grigolo B 2017 Scaffolds for bone tissue engineering: State of the art and new perspectives Materials Science and Engineering: C 78 1246–1262

[10] Fantini M, Curto M and De Crescenzio F 2017 TPMS for interactive modelling of trabecular scaffolds for bone tissue engineering Advances on Mechanics, Design Engineering and Manufacturin (USA: Springer International Publishing) pp 425–35

[11] Velasco M A, Narváez-tovar C A and Garzón-alvarado D A 2015 Design, materials, and mechanobiology of biodegradable scaffolds for bone tissue engineering BioMed Research International 2015(729076) 1-21

[12] Abueidda D W, Bakir M, Abu Al-Rub R K, Bergström J S, Sobh N A and Jasiuk I 2017 Mechanical properties of 3D printed polymeric cellular materials with triply periodic minimal surface architectures Mater. Des. 122 255–267

[13] Sánchez E M 2015 Superficies mínimales. Historia, desarrollo y aplicaciones a otras ciencias (España: Universidad Complutense de Madrid)

[14] Montazerian H, Davoodi E, Asadi-Eydivand M, Kadkhodapour J and Solati-Hashjin M 2017 Porous scaffold internal architecture design based on minimal surfaces: A compromise between permeability and elastic properties Mater. Des. 126 98–114

[15] Zhang Z F, Eckert J and Schulte L 2003 Difference in compressive and tensile fracture mechanisms of Zr59Cu20Al10Ni8Ti3 bulk metallic glass Acta Mater. 51 1167–79