

## HYDROXYAPATITE-BASED TPMS SCAFFOLDS FABRICATED BY DIGITAL LIGHT PROCESSING

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### 1 ABSTRACT

Aiming to develop bioceramic scaffolds for bone tissue regeneration, Triply Periodic Minimal Surface (TPMS) structures based on calcium phosphates were explored as potential solutions. Additive Manufacturing (AM) technology Digital Light Processing (DLP) was selected for the fabrication of TPMS Neovius structures, using a commercial hydroxyapatite-based resin. The compressive strength results demonstrated the influence of the sintering temperature, with the maximum strength being attained by the material at 1400°C. Regarding the TPMS, the highest compressive strength (7.24 MPa) was found for Neovius having 50 vol% of ceramic.

### 2 INTRODUCTION

Hydroxyapatite (HAp) is a bioceramic widely employed in biomedical applications, mostly as coating for orthopedic or dental implants [1]. Due to a similar stoichiometry to the bone's mineral component, HAp forms a direct link with the natural bone by generating an apatite layer [2]. This bond is essential for the adsorption of important biomolecules that will then potentiate the necessary steps for bone regeneration such as increased vascularization and stem cell proliferation [2,3]. For this purpose, the porosity in HAp ceramics is fundamental for enhanced degradation, as dense HAp has a negligible solubility in the biological environment, compared to other calcium phosphates [3]. TPMS are structures that bring an interesting tradeoff between porosity and mechanical performance, being defined by continuous surfaces that enclose mathematically defined open spaces [4]. Traditional methods for ceramic scaffolds fabrication are unsuitable for TPMS structures manufacturing due to their complexity. AM enabled the freedom of design needed to manufacture custom-made TPMS ceramics for bone implants. DLP, an AM technology, enables the manufacture of these ceramic TPMS aiming tissue engineering applications [2].

### 3 METHODOLOGY

A commercial HAp-based resin, Bison Osteolite (Tethon, USA) was used as the feedstock. Neovius TPMS structures with distinct volumetric ratios: 40% → Neovius\_40 and 50% → Neovius\_50, were modeled in nTop software (Version 5.8.2, nTopology, USA) with mid-surface offsets of -0.05 and -0.0025, respectively. To optimize the debinding step in the printed samples, DTA/TG analysis was performed. The impact of sintering temperature on the compressive strength of the material was evaluated using 10 printed dense cubes (5x5x5 mm<sup>3</sup>) and four different sintering temperatures (1100°C, 1200°C, 1300°C and 1400°C) during 2h. The crystallographic composition of the sintered samples was analyzed by XRD. The best performing temperature was selected for the sintering of the Neovius scaffolds and subsequent analysis.

### 4 RESULTS AND DISCUSSION

Figure 1 shows the microstructure acquired in a green ceramic body and the element identification by EDS. The XRD analyses (Figure 2) done also in a green body, revealed the presence of wollastonite, in addition to HAp. EDS mapping, also presented in Figure 1, suggests that the two distinctive particles, spherical and elongated, correspond to HAp and wollastonite, respectively. Even though the resin is not exclusively composed by HAp, the presence of wollastonite is not deleterious, as this calcium silicate is also employed in biomedical applications [5].

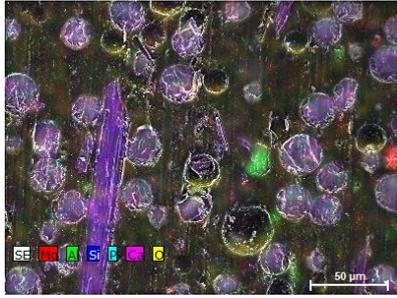


Figure 1 - Micrograph of a green part and element identification

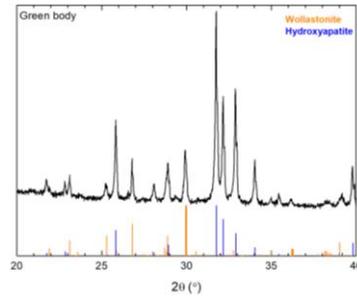


Figure 2 - Diffractogram of a green printed part.

Figure 3 a) shows the compressive strength of bulk specimens, sintered at different temperatures. These results demonstrate that the sintering temperature has a significant impact on the compressive strength of the material. Furthermore, sintering at 1400°C resulted in the highest compressive strength, with a 446% increase when compared to the ones sintered at 1300°C. Hence, 1400°C sintering temperature was selected for the Neovius scaffolds. Figure 3b) shows the compressive strength obtained for the two TPMS groups, displaying very distinctive compressive strengths, due to the different volumetric ratios. The results obtained by Neovius\_50 are above many of the reported values for similar structured ceramics found in literature [6,7] making them promising for bone implants under higher loading conditions.

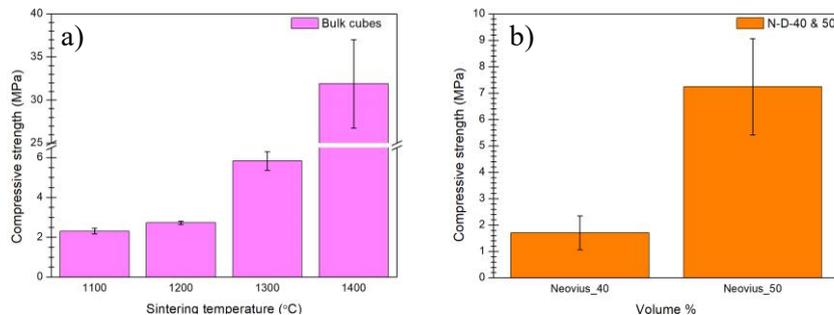


Figure 3. Compressive strength of a) bulk ceramics sintered at different temperatures and b) TPMS structures sintered at 1400°C.

## 5 ACKNOWLEDGEMENTS

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## 6 REFERENCES

- [1] B. Ratner, A. Hoffman, F. Schown, and J. Lemons, *Biomaterials Science: An Introduction to Materials in Medicine*, Third Edit. Academic Press, 2013.
- [2] H. Budharaju *et al.*, “Ceramic materials for 3D printing of biomimetic bone scaffolds - Current state-of-the-art & future perspectives,” *Mater. Des.*, vol. 231, p. 112064, 2023.
- [3] E. Fiume, G. Magnaterra, A. Rahdar, E. Verné, and F. Baino, “Hydroxyapatite for biomedical applications: A short overview,” *Ceramics*, vol. 4, no. 4, pp. 542–563, 2021.
- [4] S. C. Kapfer, S. T. Hyde, K. Mecke, C. H. Arns, and G. E. Schröder-Turk, “Minimal surface scaffold designs for tissue engineering,” *Biomaterials*, vol. 32, no. 29, pp. 6875–6882, 2011.
- [5] L. A. Núñez-Rodríguez, M. A. Encinas-Romero, A. Gómez-Álvarez, J. L. Valenzuela-García, and G. C. Tiburcio-Munive, “Evaluation of Bioactive Properties of  $\alpha$  and  $\beta$  Wollastonite Bioceramics Soaked in a Simulated Body Fluid,” *J. Biomater. Nanobiotechnol.*, vol. 09, no. 03, pp. 263–276, 2018.
- [6] A. Cucuruz, C. D. Ghițulică, G. Voicu, C. A. Bogdan, V. Dochiu, and R. C. Popescu, “Investigation of Porous Ceramic Structures Based on Hydroxyapatite and Wollastonite with Potential Applications in the Field of Tissue Engineering,” *Ceramics*, vol. 6, no. 4, pp. 2333–2351, 2023.
- [7] S. Kunjalukkal Padmanabhan, F. Gervaso, M. Carrozzo, F. Scalera, A. Sannino, and A. Licciulli, “Wollastonite/hydroxyapatite scaffolds with improved mechanical, bioactive and biodegradable properties for bone tissue engineering,” *Ceram. Int.*, vol. 39, no. 1, pp. 619–627, 2013.