

EVALUATION OF 4D PRINTED PLA AND 3D PRINTED PLA/HA FOR BONE TISSUE ENGINEERING

C. MASTALERZ¹, I. VROMAN¹, P. MILLET¹, X. COQUERET², M. DUBUS³, H. KERDOUDJ³, S. ALIX¹

1 : Université de Reims Champagne-Ardenne, ITheMM EA 7548, Campus Moulin de la Housse, 51100 Reims, France, conrad.mastalerz@univ-reims.fr, isabelle.vroman@univ-reims.fr, pierre.millet@univ-reims.fr, sebastien.alix@univ-reims.fr

2 : Université de Reims Champagne-Ardenne, ICMR UMR CNRS 7312, Campus Moulin de la Housse, 51100 Reims, France, xavier.coqueret@univ-reims.fr

3 : Université de Reims Champagne Ardenne, BIOS EA 4691, 51097 Reims, France, marie.dubus@hotmail.com, halima.kerdoudj@univ-reims.fr

Introduction

Additive manufacturing possessed many benefits such as allowing printing object with controlled porosity and high precision in a short time. This process could be used for medical applications, especially for bone tissue engineering [1]. Bone tissue engineering aimed for the regeneration or replacement of bone tissue damaged by disease or injuries. Scaffolds could be manufactured by 3D printing for bone regenerative applications. However, these biomaterials must be in agreement with established specifications containing necessary properties such as biocompatibility and biodegradability. One group of biomaterial-based scaffolds for bone tissue engineering is polymers. Polyesters are commonly used in medical applications due to their biocompatibility with controlled degradation rate. Polyesters with addition of inorganic filler such as hydroxyapatite (HA), main inorganic components of bone, form a biocomposite material with improved mechanical properties and bioactivity [2]. Polylactic acid (PLA) was used as polymer matrix due to his excellent mechanical properties and thermal properties.

In addition, scaffolds of biocomposite could be designed for the regeneration of bone tissue using additive manufacturing. These scaffolds should be porous in order to promote cell adhesion and proliferation [3]. Pore size greatly affected osteogenic properties and the biodegradation rate. However, the biodegradation rate of these scaffolds cannot be spatially controlled. In this case, 4D printing process is a good way to control this aspect by applying structural modifications on materials with an external stimulus [4], such as electron beam radiation, and change the shape of scaffolds in time via chain-scission/crosslinking reaction. Thereby, molecular weight and crystallinity of polymers are greatly affected by the radiation treatment, allowing to control the bioresorption rate.

In the first place, the influence of an external stimulus such as electron beam irradiation was evaluated on thermal and mechanical properties on PLA. Thus, 4D printed PLA was beforehand studied before starting the manufacturing of biocomposites. Then, PLA/HA scaffolds were elaborated and analyzed in order to determine maximum filler ratio possible and the impact of HA particles addition on thermal, mechanical and structural properties. Biological properties were also evaluated.

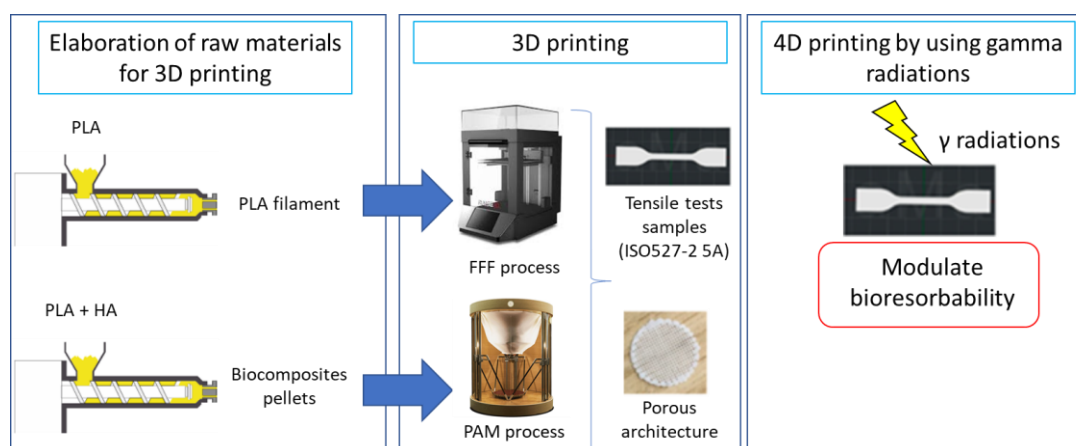


Figure 1. Summary of the process for developing and shaping 3D and 4D printed biomaterials

Conclusions

Electron beam irradiations impacted thermal properties such as the glass transition temperature, decreasing with the irradiations due to the decrease in average molecular weight by chain scission process conducting to better chain mobility. The phenomenon of chemocrystallization occurred on PLA, affecting the degree of crystallinity by increasing it. Moreover, the appearance of a second crystalline structure in PLA such as α and α' -form occurred, where the proportion of the α' -form increased with the amount of irradiations. It affected the mechanical properties by decreasing max stress and elongation at break because of lower length of PLA chains.

Concerning manufacturing of biocomposites, high filler ratio decreased thermal degradation properties due to less stable structures of polymer matrices. However, it was made possible to produce biocomposites with a filler ratio of HA up to 60 % (w/w) which could be 3D printed afterward up to 20 % (w/w) in porous architectures for bone tissue engineering applications. Results showed an increase of stiffness with the addition of HA particles as well as the crystallinity. Plus, biological study showed excellent adhesion and proliferation of mesenchymal stem cells after 14 days.

In order to be applied in bone-tissue engineering, the sensitivity to biodegradation could be adapted by modulating the properties and structure of biocomposites using irradiation.

References

- [1] Huawei Q., Additive manufacturing for bone tissue engineering scaffolds, *Materials Today Communications*, vol 24, p. 101024, 2020.
- [2] Zimina A., Biocompatibility and Physico-Chemical Properties of Highly Porous PLA/HA Scaffolds for Bone Reconstruction, *Polymers*, vol 12, p. 2938, 2020.
- [3] Hamlet N., 2020, Porous scaffolds for bone regeneration, *Journal of Science: Advanced Materials and Devices*, 5(1), 2020.
- [4] Tamay D.G., 3D and 4D Printing of Polymers for Tissue Engineering Applications”, *Frontiers in Bioengineering and Biotechnology*, vol 7:164, 2019.