Fabrication of 3D Printed Hybrid Scaffolds with Dielectric and Piezoelectric Behaviour

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***Abstract* —**Hydroxyapatite (HAp - $Ca_{10}(PO_4)_6(OH)_2$), is the major component of bones and teeth and is characterized with high biocompatibility and osteoconductivity. Furthermore, HAp polarizes and displays intrinsic piezoelectric behavior, by accumulating electric charge in response to mechanical stress. This behavior is attributed to the asymmetric collagen molecules that are produced by the sliding of collagen filaments in ionic solutions. The electric potentials created in the, under stress, bone are related to the transference of mechanical signals to the cells, a process, which affects the bones regrowth. Hence, it is rather obvious, why the medical scientific community exhibits big interest in piezoelectric materials.

Combination of the bioactive properties of HAp with those of a piezoelectric and high dielectric constant ferroelectric material, such as barium titanate ($BaTiO_3$), which is considered an active dielectric, due to its ability to polarize in the absence of an external electric field is of great importance in the field of bone filling materials. For applications where high charging is required, polymer matrix composite materials with bioactive ceramic fillers can be used. The new 3D printing technology enables the construction of scaffolds with specific geometric characteristics, such as the shape, size and total volume of the pores.

This research has focused on the fabrication of scaffolds through the Fused Filament Fabrication (FFF) technique which applies on the heated extrusion of thermoplastic polymers in the shape of a filament. Polylactic acid (PLA) and polycaprolactone (PCL) are semicrystalline biodegradable hydrophobic thermoplastics, widely used in 3D printing for the development of new biocompatible bone implants. The combination of the last two materials to a copolymer provides the required abilities for tissue engineering applications, such as being environmentally friendly, non-toxic, biocompatible, and biodegradable. It has been noted that most cells adhere and grow faster on PLA surfaces containing bioactive ceramics, such as HAp, than on pure PLA surfaces. Furthermore, the addition HAp increases osteoconductivity and induces bone growth.

The present study includes: a) Synthesis and characterization of nanosized hydroxyapatite crystals, b) Fabrication of composite PLA based filaments containing HAp and $BaTiO_3$, c) Construction of scaffolds using the FFF 3D printing technology, d) Study of thermal, dielectric and piezoelectric behaviour of the constructed scaffolds.

The results shown that nanosized HAp with a needle-like morphology, was prepared using the precipitation method from aqueous solution. Composite PLA filaments containing HAp and $BaTiO_3$ were brittle and therefore PCL was used as plasticizer. Filaments containing 70% PLA, 30% PCL, 10 phr HAp and 10 phr $BaTiO_3$ showed excellent extrusion properties. 3D scaffolds with dimensions of 2.5x2.5x0.5mm were constructed successfully using the above composition. Dielectric and piezoelectric measurements revealed that composite PLA/PCL scaffolds containing HAp and $BaTiO_3$, have enhanced dielectric and piezoelectric properties in comparison with pure PLA/PCL specimens making these materials good candidates for tissue engineering applications.

***Keywords* —** 3D printing, hybrid composites, scaffolds, hydroxyapatite/barium titanate

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