

Processing and characterization of PLA/HA composites reinforced with natural sugarcane powder

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Abstract

In enhancing bone tissue engineering technology, polylactic acid (PLA) composite has been developed as they are biodegradable, renewable, and can be printed. Nevertheless, PLA has a lower mechanical performance due to its brittle nature. The ration of filler that was required in the PLA/hydroxyapatite (HA) biocomposites in this investigation was reinforced by varying ratios of natural sugarcane bagasse (SCB) powder to be applied in fused filament fabrication (FFF) 3D printing processes. PLA/HA/SCB composites with 5, 10 and 15 wt % percent SCB were prepared by solution casting and extrusion of filaments was done on single screw extruder. The filaments that were extruded could then be then easily utilized to come up with samples to be tested using FDM 3D printing. Tensile properties were researched using MTS testing machinery as per ASTM D638 Type V. The findings revealed that the usage of SCB has a great effect on the mechanical behavior of the biocomposites. The presence of solid fillers correspondingly increases the tensile modulus with an increase in the SCB content and therefore, the superior the composite in terms of stiffness the content of rigid fillers. Elongation at the break and tensile strength heavily varied with the load and fiber dispersion with a non-monotonic evolution. Upon comparison of the formulations under study, the PLA/HA/15SCB composite displayed the most desirable mechanical performance, as it concomitantly exhibits enhanced tensile strength, stiffness and ductility. These findings demonstrate that sugarcane bagasse powder can be used as a prospective PLA/HA composite reinforcer, and it can be used to fabricate bone scaffolds based on FDM 3D printing.

1 Introduction

One of the biggest causes of patient morbidity in the past is bone fractures and segmental bone defects which have stunned the economic burden of healthcare systems globally, especially in the orthopedics specialty. Approximately 178 million bone fractures took place in the year 2019 globally- a 33.4 percent increase that had happened since 1990 [1]. These defects and fractures greatly affect the quality of life experienced by the patients, as well as the society, as they add up to the economic burden such as the escalation in healthcare expenses, loss of workforce, and escalating obligation on social services [2]. Metal is the traditional material that has been employed to make the engineered bone tissue and metals are good in mechanical properties. Nonetheless, bone cells do not adhere to metals, and they are stress shielding, nondegradable and incompatible with biology [3,4]. As such, studies have been inclined towards use of inorganic and polymer biocomposites as possible alternatives to metals.

Over the course of recent years, 3D printing transcends the shortcomings of the conventional material processing [7,8]. The development of the particular 3D printing bio-ink may be performed by modulating the ratio parameters of the various materials including the printing performance, mechanical performance and biological activity [9,10]. Fused deposition modeling (FDM) enables printing of several materials, such as ceramics, polymers and composite materials [11]. With the FDM 3D printing technology, the porosity inside the

biomaterials, the size of the pores as well as their interconnectedness can be easily regulated [12,13].

The scaffold needs of critical bone defects must possess great bioactivity capabilities and must have superior mechanical strengths [5]. One of the bio polymers that are used extensively in the FDM process is Polylactic acid (PLA). In the case of the evolution of 3D printing, PLA has become a major consideration because it is easy to work with, the printing temperature should be lower. It is also environmentally friendly because it is made of renewable sources. Despite the reputation, PLA being a brittle material with a limited impact strength PLA has a range of mechanical properties that are rigid and at the same time possessing high strength as well as those that are more flexible [14]. In order to reduce these intrinsic drawbacks and to further modify the mechanical and functional characteristics of PLA, it is progressively being co-reinforced with natural fibers that are less harmful like sugarcane bagasse fibers (SCB), and this would result in the creation of sustainable bio-composites with superior performance.

The bionanocomposites containing 2 wt. % percent sugarcane bagasse nanocellulose yielded a noticeable increase in thermal stability, water resistance and mechanical performance [17]. Calcium phosphate has been very widely used in bone repair owing to its good biological properties [15]. The most stable of all calcium phosphates is hydroxyapatite (HA) which makes it very appropriate in varying medical applications, such as dental restorations and dental implants. Its biocompatibility character of ceramic has been put in wide use in other medical areas especially in bone tissue. HA has been used in the regeneration of hard tissues using its application as a product of composite materials, with its ability to work as a lever because of its spectacular mechanical strength [16]. Its weakness and mechanical weakness have been a challenge though, where it is not applied in many situations.

We examined in this paper the possibility of solvent-casting PLA/HA/SCB biocomposite with different concentration of SCB (5, 10 and 15 wt%) to filament form to be used in FFF-based 3D printing. It was this composite filament that was used in preparing the test specimen in order to study it mechanically.

2 Materials and Methods

2.1 Materials

The grade of PLA (poly-L-lactic acid), 4043D, used in the current study was provided by TAG Plasturgie (No. 188, Southwest Industrial Zone, 28810 Mohammedia, Morocco), whose (Mn) molecular weight is 67 kDa, density is 1.24 g.cm^{-3} , and melting temperature is 145-160 °C. Hydroxyapatite (HA) bioceramic powder was obtained in the company of Sigma-Aldrich (USA). The bagasse of sugarcane was picked at Cosumar Company, Morocco. The solvent used to prepare the solutions through solvent evaporation is analytical-grade chloroform that comes in through Sigma-Aldrich (USA). Sodium hydroxide (NaOH, purity $\geq 98 \%$) was obtained at Sigma-Aldrich (USA) and it was used to pretreat the sugarcane bagasse.

2.2 Preparation of PLA/HA/SCB composite

To pre-treat the sugarcane bagasse first, the pretreatment was carried out as suggested by Juliana Anggano et al. The resultant product was ground by using a grinder (IKA-Werke GmbH & Co. KG, Germany) and this was then sieved to result in a less than 160 μm particle size.

PLA pellets were then dissolved in chloroform under magnetic stirring for 1 h. The weight ratios of 10/5 wt%, 10/10 wt% and 10/ 15 wt% of hydroxyapatite (HA) and sugarcane bagasse (SCB) powders were added gradually to the PLA solution and stirred continuously within 2 h so as to achieve a homogenized dispersion and to avoid agglomeration.

The mixture was poured and left to dry at room temperature over a period of 48 h after which it was cut into small pieces of about 3-5 mm. These were then dried in a vacuum oven (DZF, Huanghua Xingchen Instrument Co., Ltd., China) at 60 °C for 72 h to clear off the solvent. The ready biocomposites were regarded as PLA/HA, PLA/HA/5SCB, PLA/HA/10SCB and PLA/HA/15SCB. The biocomposites of all materials are summed up in Table 1.

Tableau 1 Composition du bio-composite développé avec leur nom

Echantillons	PLA (% en poids)	HA (% en poids)		SCB (% en poids)
PLA/HA/5SCB	85	10		5
PLA/HA/10SCB	80	10		10
PLA/HA/15SCB	75	10		15

2.3 Fabrication de filaments d'impression 3D

The composites were prepared and extruded in manually constructed single-screw filament extruder (Fig. 1). The composite pellets were injected into the extruder in order to obtain the composite filament (Fig. 1). The extruder temperature was adjusted to 160 °C, and the motor speed was adjusted to 20 rpm. The shell diameter of the produced filament was 1.60 mm to 1.80 mm. The extruded filament was picked manually at the die exit where it was left to cool at the room temperature.
An experimental set up of this study is represented in Figure 2.



Figure 1 Laboratory extruder

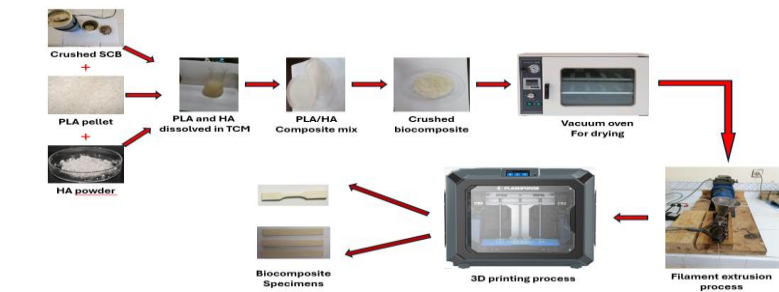


Figure 2 Overview of the workflow, from the synthesis of PLA/HA/SCB composite filament to the fabrication of 3D printed samples

2.4 3D printing of PLA/HA/SCB biocomposite

Preparation of the samples was done on a FlashForge Creator-3 FDM 3D printer. This printer has a dual nozzle extruder employing the nozzle control. Build plate can tolerate a high temperature of 120 °C and extrudes filament at extremely high temperatures up to 320 °C. Adjusted input parameters were used and included extrusion temperature at 215 °C, a build plate temperature at 70 °C, a print speed at 60 mm/min, nozzle diameter at 0.6mm, a layer height of 0.2mm and linear infill. To avoid distortion of the samples in the handling and to maintain good preparation of the sample to be used in material characterization analysis, the samples were cooled after every print to provide a homogeneous distribution of temperature.

2.5 Tensile test

All biocomposite samples to be subjected to tensile testing were prepared as per ASTM D638 Type V. Tensile tests were obtained with the help of the MTS testing machine (model 43) with the 30 kN load cell (see Figure 3). The speed of motion of the cross beam was adjusted to 10 mm/min. The tensile properties stated are the data averages of tensile properties of five samples of each biocomposite value that have been tested.



Figure 3 Tensile test machine

3 Results and Discussion

The tensile strength, tensile modulus and elongation at break were calculated experimentally using the load-tension curves shown in Figure 4. Table 2 summarizes the associated values.

Tableau 2 Tensile properties of samples

Composites	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PLA/HA/5SCB	22.18	0.16	3.73
PLA/HA/10SCB	12.49	0.21	1.79
PLA/HA/15SCB	25.94	0.22	3.73

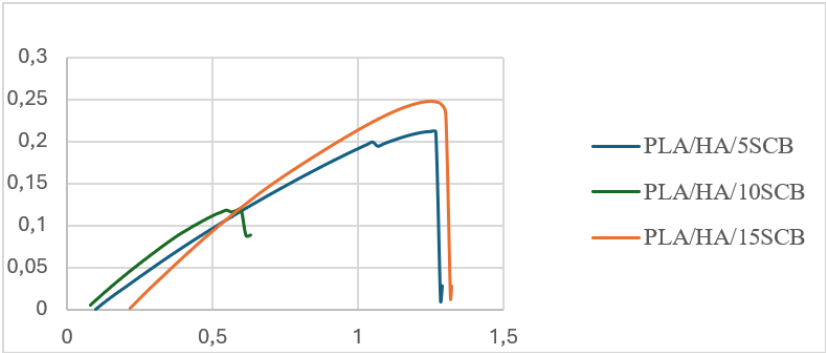


Figure 4 Load v/s extension graph of samples for tensile test.

Generally, the introduction of sugarcane bagasse fibers had considerable effect on the tensile response of PLA/HA biocomposites. The tensile modulus with the percentage of fibers increased, but tensile strength and break elongation were very much varied on the basis of fiber concentration and fiber dispersion; tensile strength and elongation at break was the highest on the PLA/HA/15SCB composite.

4 Conclusion

Here, PLA/HA biocomposites containing various percentages of sugarcane bagasse ground were reinforced and processed into filaments to be utilized in the fused deposition modeling 3D printing (FDM). The solution casting method was used to incorporate homogeneously HA and sugarcane bagasse into the PLA matrix and the resultant filaments showed dimensional stability that is viable to 3D printing. The tensile tests revealed that sugarcane bagasse additions had a negative influence on mechanical properties of the composites. Tensile modulus increased with addition of sugarcane bagasse, which is an increase in stiffness of the natural filler which was inherently rigid and the ceramic phase. The tensile strength and elongation at break were directly proportional to the content of the sugarcane bagasse. An intermediate level of fiber content produced an early failure, which could possibly be attributed to inadequate interfacial bonding or because of agglomeration of the fibers. It has been found that the PLA/HA/15SCB composite showed the highest mechanical performance, which suggests the most appropriate compromise between the effectiveness of the reinforcement and the homogeneity of the matrix. In general, the findings indicate that the sugarcane bagasse powder could be employed as a natural and strong reinforcement of PLA/HA biocomposites to 3D-print the bone in 3D printing. Flexural behavior, microstructural analysis and biological performance will be considered in future work in order to further assess the appropriateness of these materials in bone tissue engineering.

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