3D PRINTED PLA-BASED BLENDS WITH IMPROVED INTERLAYER BONDING

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ABSTRACT
In order to optimise interlayer bonding and structural integrity of structures produced by Fused Filament Fabrication (FFF), commercial grades of high-molecular weight poly (lactic acid) (PLA) and PLA-based blends were comparatively assessed in terms of their mechanical properties. Tensile specimens were fabricated, in order to study the mechanical properties of the different PLA compositions and FFF processing profiles. An experimental protocol was defined in order to eliminate common structural defects introduced during FFF processing. Fractographic analysis of specimens produced by different settings was conducted, in order to provide feedback on the selection of process parameters that result in improved structural integrity, such as layer height and path width. Subsequently, fabrication of the different PLA formulations was conducted, for comparative assessment of their mechanical properties, inter-fiber and inter-layer bonding. SEM fractographic analysis indicated an improvement on interlayer bonding and reduction of inter-fiber voids in different PLA formulations, that is in accordance with stress-strain curves exhibiting an increase in Young modulus and Ultimate Tensile Strength (UTS) [1-7].

INTRODUCTION
Three dimensional (3D) printing processes are integrated manufacturing technologies that manufacture objects layer by layer. Fused Filament Fabrication (FFF) is a 3D printing process that deposits layers by using a continuous thermoplastic filament which is melted in the extruder of the 3D printer in order to form the object [8]. Thermoplastic PLA based filaments are common materials in FFF applications due to their low shrinkage, high tensile strength and high Young modulus [9,10]. Nevertheless, PLA based filaments display some drawbacks such as low heat resistance, brittleness and low processability that can lead to FFF processing problems. There is a need to evaluate PLA based filaments in terms of their strength and fracture characteristics in order to be employed on demanding applications and thus in industry. Printability assessment of the FFF structures arise complications, due to the different factors that affect strength and quality of the parts, that are also in correlation with the multiple process parameters of Computer Aided Manufacturing software (CAM), machine performance and material properties [12]. PLA grades and PLA-based binary blends were prepared and comparatively assessed in terms of their mechanical properties in order to optimise interlayer bonding and structural integrity of FFF structures.

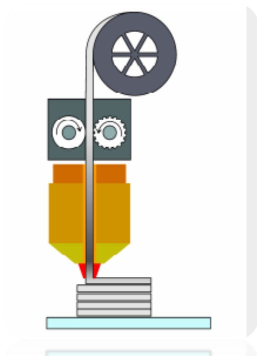
***Figure 1**. Schematic representation of the FFF process [11].*

MATERIAL AND METHODOLOGY
Commercial grades of high-molecular weight poly (lactic acid) (PLA) named Ingeo™ 3D850 and Ingeo™ 3052D were purchased by Natureworks in pellet forms. Ingeo™ 3D850 is a heat resistant PLA grade for extrusion processing, developed for manufacturing 3D printer monofilaments that

was selected as the main PLA grade for the binary blends. Ingeo 3052D is a high flow injection molding grade that was employed to tailor viscosity. Ecovio IS1335 is a mineral-filled compound of PLA/PBAT that was purchased from BASF in order to improve thermal stability and also Bio-flex 3D Clear is a high flow PLA/ PHA compound that was purchased from Fkur in order to improve ductility of the binary blends. Binary blends of different PLA compositions with Ingeo 3D850 were prepared for filament production. The content of 3052D, ecovio IS1335 and Bio-flex 3D Clear for filament production was defined at 20 wt.% [4:1] as it is presented in Table 1, in order to comparatively assess different 3D850 binary blends. Subsequently tensile specimens of PLA grade 3D850 were fabricated with different process parameters such as combinations of layer height and path width that are supported by a 0.2mm diameter nozzle, in order to improve interlayer and interfiber bonding of FFF structures. Nevertheless, tensile testing and SEM fractographic analysis was conducted, to evaluate mechanical properties and structural integrity of the FFF specimens.

Table 1. *Compositions of four different 3D850 based binary blends.*

Binary blends	Compositions (%)
3D850-3052D	[4:1]
3D850-ecovio IS1335	[4:1]
3D850- Bio-flex 3D Clear	[4:1]

TENSILE TESTING PROTOCOL

The experimental protocol for 3D printed tensile specimens fabrication was based on a scaled down version of ASTM D638 Standard Type I with 36 x 8 x 2mm gauge section. For each material, five specimens were fabricated (Figure 3). In order to avoid possible variations of the print-head positional accuracy in XYZ working space, tensile specimens were fabricated in the same position and orientation on the platform, after precise levelling and calibration of the FFF system. Fabrication of the specimens was conducted with 100% infill density in order to eliminate possible errors from G-code generation. Specimens were fabricated by a repeated sequence of layers (type A and B) and under the same environmental conditions. Tensile testing was carried out under the same conditions as the bulk material specimens at a room temperature, with crosshead speed of 2 mm/min. Before FFF processing, vacuum-pre drying of the filaments was conducted at 50°C for 24 h. The fractured surfaces of tensile specimens were sputter-coated with a thin layer of gold before SEM observation.

Figure 2. Tensile specimens successfully fractured in gauge section.

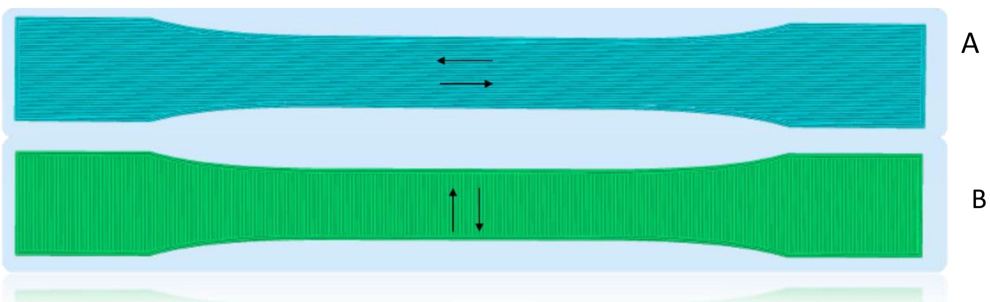

Figure 3. *Simulation of the selected toolpath for XY tensile specimen fabrication (FFF) on Simplify3D.*

PRINTER SETTINGS

In order to define the most suitable parameters for tensile specimen fabrication, a preliminary assessment of different combinations of layer height and path width was conducted for 3D850 material. Two representative combinations of layer height and path 0.18mm/0.25mm and 0.1 mm/0.2 mm (here abbreviated as P1 and P2 combinations) are presented in Figure 6a and 6b. Combination P1, consisting of fibers with the highest height and width supported by 0.2mm diameter nozzle, is referred as an example of reduced interlayer bonding, while P2 refers to fibers with decreased cross section, presenting an improved interlayer bonding and structural integrity. Subsequently specimens with 3D850 binary blends were fabricated with P2 combination of layer height and path width, in order to comparatively assess mechanical properties of different materials. All specimens were printed by Raise 3D Pro 2 Plus FFF system. Design of the specimens was conducted in Fusion 360 CAD software and imported in. stl format. Subsequently a g.code file was created with Simplify3D v4.0 software. FFF specimens were printed with process parameters in Table 2.

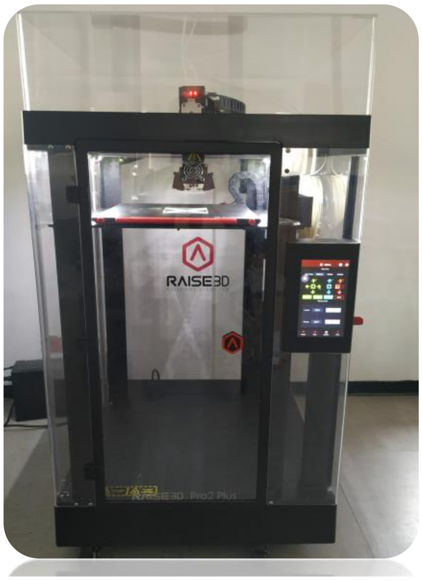

Figure 4. *3D printer Raise 3D Pro Plus 2, where tensile specimens fabrication was conducted.*

Table 2*. Process parameters for tensile specimen fabrication.*

Process parameters	Values
Nozzle diameter	0.2mm
Temperature	205^{0}C
Infill density	100%
Heated bed platform	Off
Speed	40mm/s
Cooling	Off/room temperature
Fill pattern	Rectilinear
Bottom/Top solid layer	0
Outline perimeter shells	3
layer height/Path width	0.18mm/0.25mm, 0.1/0.2mm

RESULTS AND DISCUSSION

According to the stress-strain curves of 3D850 specimens fabricated with P1 and P2 combinations (Figure 6c), an improvement on structural integrity was observed on specimens fabricated by P2, resulting in % increase in UTS. Results from fractographic analysis on the fractured surface of the specimens are in accordance with the stress strain curves, indicating an improvement of inter-fiber welding and a decrease of inter-fiber voids. Comparative assessment of tensile specimens produced by 3D850 and binary blend of 3D850-3052D indicate that the addition of 3052D and the associated viscosity reduction has a positive effect in UTS and inter-fiber gap reduction, however no significant effect in elongation at break (Figure 7a&b). Binary blend of 3D850-ecovio exhibited a more brittle behavior, with a % increase in Young modulus and % reduction of elongation at break (Figure 8).These results are also in accordance with SEM image (Figure 7c), where a decrease of interlayer bonding can be observed in comparison with the other blends. Last but not least, binary blend of 3D850-Bioflex presented the best performance in terms of mechanical properties and welding quality, with a % increase in UTS and % increase in elongation (Figure 8). SEM image also confirms the improvement of interlayer and inter-fiber bonding and decrease of inter-fiber voids (Figure 7d).

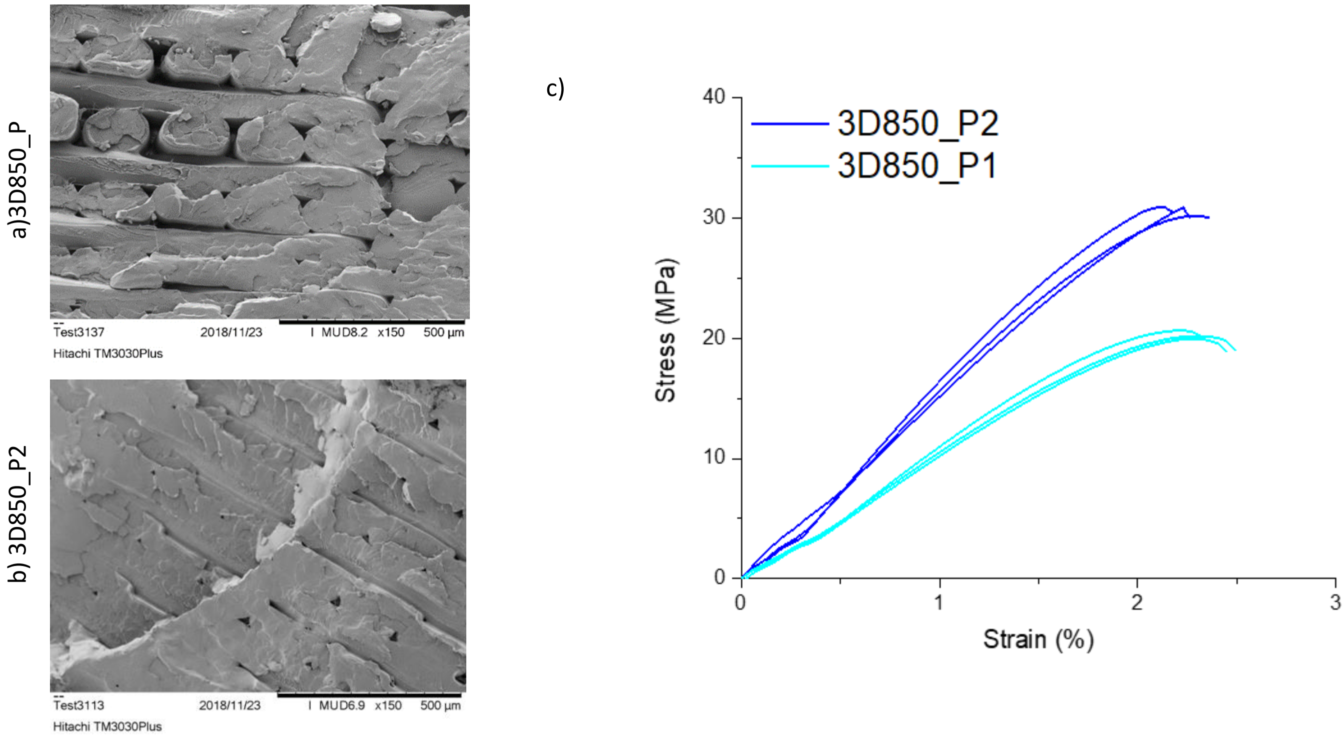

Figure 5. *a-b) SEM images of the fracture surface from the specimens fabricated with P1 and P2 combinations respectively c)Stress-strain curves of PLA grade 3D850 fabricated with P1 and P2 (FFF specimens-3 indicative examples per material).*

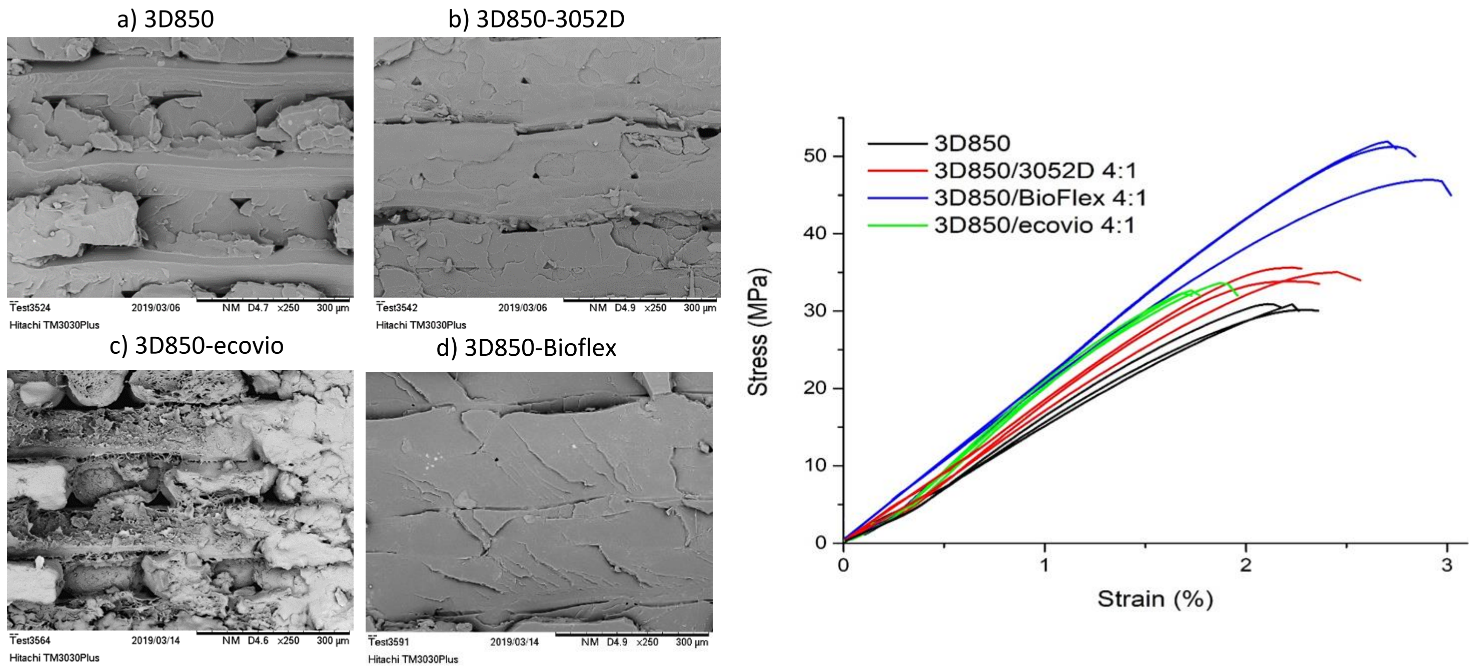

Figure 7*. a-d)SEM images of the fracture surfaces from the specimens fabricated with 3D850, 3D850-3052D, 3D850-ecovio, 3D850-Bioflex. e)Stress-strain curves of 3D850, 3D850-3052D, 3D850-Bioflex, 3D850-ecovio blends (FFF specimen-3 indicative examples per material).*

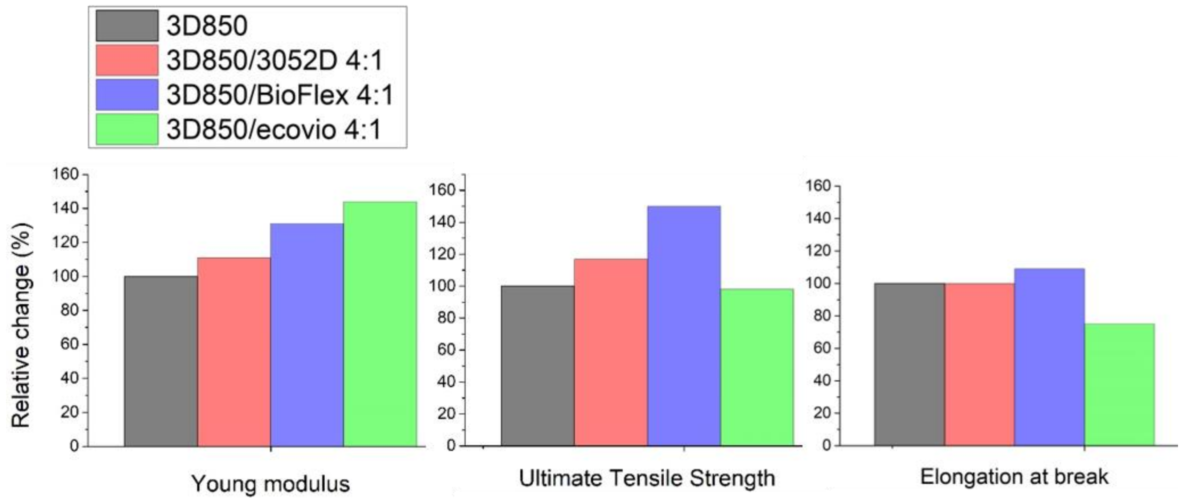

Figure 8. *Relative change of mechanical properties of 3D850 in binary blends. Comparison of average values from five tensile specimens.*

CONCLUSIONS

Commercial grades of high-molecular weight PLA-based blends were comparatively assessed in terms of structural integrity and inter-fiber bonding of FFF structures. A protocol for specimen FFF fabrication, testing and fractographic analysis was established for material comparison. An improvement on interlayer bonding and structural integrity was achieved by the suitable combination of layer height and path width supported by 0.2mm diameter nozzle. Reduction of voids among individual fibers and further improvement of interfiber welding was observed by 3D850-BioFlex and 3D850-3052D blends, while 3D850-ecovio blend presented a more brittle behavior. Binary blends of 3D850-Bioflex presented best performance on mechanical properties with highest Young modulus, UTS and elongation at break.

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