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Research article

Investigating mechanical properties of 3D printed polylactic acid / poly-3-hydroxybutyrate composites. Compressive and fatigue performance

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A R T I C L E I N F O

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Material extrusion (MEX)
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A B S T R A C T

The 3D printing technique known as Material Extrusion (MEX) was initially employed for prototyping, but it has evolved to fit applications in mechanical and biomedical industries. Polylactic acid (PLA) stands out as a commonly used polymer for manufacture pieces by MEX, due to its good properties and organic origins. Pursuing renewable and biodegradable thermoplastics has led to the development materials such as composite of PLA with wood fibers and blends with poly-3-hydroxybutyrate (PHB). This study aims to characterize the effect of the most relevant printing parameters on the mechanical properties of a PLA/PHB blend, motivated by the interest to facilitate the use of this type of materials in industrial applications. To achieve it, compressive and fatigue tests were carried out, comparing the results with those obtained in previous studies for pure PLA and PLA-wood composite. Results show that the compressive behavior of PLA/PHB is influenced by the layer height, nozzle diameter and fill density. Its fatigue behavior is mainly determined by the nozzle diameter and the fill density. Moreover, the mechanical performance of PLA/PHB (Young's Modulus of 1.67 GPa, yield Strength of 33.8 MPa and maximum fatigue life of 9711 cycles) is inferior compared to pure PLA and PLA-wood composite. Despite the increase in the biodegradability that PHB introduces into PLA, the findings of this study reveal that there is statistically evidence that it can also hinder the mechanical performance of the base material.

1. Introduction

Additive manufacturing (AM), also known as 3D printing, consists of a group of manufacturing technologies that have revolutionized the modern industry landscape, replacing traditional subtraction methods with layer-by-layer construction techniques [1]. The AM method that has most promoted the use of thermoplastic polymers such as Acrylonitrile Butadiene Styrene (ABS), Polylactic Acid (PLA), Polyethylene Terephthalate Glycol (PETG), Nylon, among others, is defined as Material Extrusion (MEX).

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The MEX techniques are processes that use layers of a material superimposed from a digital design, creating a final physical model by adding extruded material. The final characteristics of the part derive among others, from the printing parameters [2]. Layer height, nozzle diameter, printing velocity, and printing orientation, are some of them that might influence the bonds between filaments of the same layer (intralayer) and within layers (interlayer), contributing to the anisotropy of the printed piece [3,4]. For these reasons, it is key to define the perfect combination of these parameters taking into account the final working conditions of the part.

The current state of the art focuses on the chemical and mechanical characterization of some materials used in the MEX process, most with biodegradability problems. With the aim of reducing the environmental impact of these materials, polymers such as PLA are being reinvented and Polyhydroxyalkanoates (PHAs) are making their way onto the market. Made from living organisms, PLA is in fact presented as an ecologically based polymer widely used in MEX [5,6]. Besides, PHAs are biobased and biodegradable polyesters often defined as bioplastics [7]. Like PLA, PHAs are produced by certain microorganisms as a product of carbon assimilation, from glucose or starch [8]. Furthermore, the matrices generated from certain types of PHA are biocompatible in nature, thus being attractive for biomedical applications [9]. For example, the porosity present in them is used in regenerative medicine, creating bone implants [10–13].

Nowadays it is possible to find filaments based on a combination of PLA and PHA, with improved characteristics. On the one hand, PHAs guarantee better biodegradability [14,15], in addition to being considered an alternative to chemical products derived from petroleum [16]. On the other hand, PLA assures good processability on the blend [16,17], resulting in a key piece for the properties and printability of the PLA/PHB compound [18,19]. Although they are affordable in the polymer market, PHB and PLA maintain high production costs, fact that justifies combining them with low-cost materials such as wood fiber [20].

There are different PHAs produced on a commercial scale. These include poly-3-hydroxybutyrate (PHB), poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), and poly-3-hydroxybutyrate-co-3-hydroxyhexanoate (PHBH), among others [16,21]. Fuentes et al. [22], investigated the 3D MEX printability of a series of PLA/PHBV composites. The rheological analysis of the printed samples showed that the mechanical properties were connected to the nozzle temperature and printing velocity. PHB is one of the most used of the PHA family of materials. It is a biodegradable, bio-based, mechanically rigid and brittle polyester that has a narrow thermal window of processability [23]. Even though PLA has a renowned printability, the printability of pure PHB is more complicated and has a small processing range. However, the combination of PLA and PHB generates a compound whose processing is not always easy and the resulting mechanical properties may depend on the correct choice of its percentage in the composition of the new material [24,25], but the biodegradability of the blend is increased. Several authors have suggested the mixture of PLA and PHB as a strategy to address the poor characteristics of PHB and improve the biodegradability of PLA [14,22,26–28].

There are sources showing research on the mechanical properties of PLA/PHB and their comparison with those of pure PLA. Their main results have been related to the mechanical properties in tensile, bending, and impact tests. Almonti et al. [14] tested PLA/PHB samples in tensile, bending and impact tests, observing a modification in the mechanical properties of pure PLA due to the addition of PHB. Mainly, a reduction in the brittleness of PLA and a considerable increase in shock absorption was observed. They also demonstrated an influence of the printing orientation on the results, showing a higher elastic modulus in response to the orientation orthogonal to the print bed. Wang et al. [29] studied the PLA/PHB material observing lower tensile modulus and stresses compared to pure PLA. They associate this loss to the lower intrinsic stiffness of PHB and the rather poor miscibility between PLA and PHB. Pérez-Fonseca et al. [20] demonstrated the positive effect of the combination of PLA and PHB regarding the chemical properties of pure PLA. The results of their work showed significant increases in the crystallinity of PLA with the addition of PHB and wood, especially with the twin-screw extrusion used to manufacture the filament.

Compared to the results found in the literature, a commercial material has been used for this work, when in most of related references used a material obtained ad-hoc at laboratory level is used [14,20,25,30]. That is why it is difficult to use them from an industrial point of view, since they are not commercially available. This is the main novelty presented in this paper. The composition of the material studied (percentages of PLA and PHB in the content) will not be modified in the experimental stage, since the material is provided by a company that manufactures and commercializes it.

This present study focuses on compressive and fatigue tests with the aim of finding the best mechanical parameters for the printed samples, based on their intended applications. The experimental design follows a Taguchi L27 array, involving the layer height, nozzle diameter, fill density, and printing velocity as variable parameters. The studied material is positioned as a more sustainable option compared to PLA. Therefore, a comparison between PLA/PHB and pure PLA is done to assess the mechanical implications of incorporating PHB. Additionally, PLA with wood (PLA-wood) is included in the comparison as another sustainable material alternative to PLA. Notably, all three materials share PLA as their polymer base and are commercially manufactured by the same company. This investigation is motivated by the understanding that introducing copolymers or composites, such as PLA/PHB and PLA-wood, respectively, may lead to changes in mechanical behavior.

The novelty of this paper lies, on the one hand, in the comprehensive mechanical study of properties mentioned above, thereby contributing to the understanding of manufacturing by MEX for users and relevant industries. On the other hand, in the comparison to assess the effect of enhancing the biodegradability of PLA by incorporating copolymers like PLA/PHB and composites like PLA-wood. This study seeks to clarify the mechanical distinctions among these materials and their implications for manufacturing and industrial applications.

2. Material and methods

The characteristic anisotropic formation of printed parts processed through MEX requires a precise choice of printing parameters to guarantee good mechanical properties. Based on the accumulated experience in the manufacture of parts with MEX and the extensive review of publications aimed at low-cost printers, the printing parameters chosen are those that have shown the most direct influence on the mechanical properties. In fact, Layer Height, Nozzle diameter, Fill density and printing velocity play an important role in the formation of intra- and inter-layer bonds that are generated in the deposition of material [3,21,22,31,32]. Compressive and rotating fatigue properties Fig. 1 of the commercial PLA/PHB copolymer from Fillamentum Company (Fillamentum Manufacturing Czech s.r.o., Hulín Czech Republic), catalogued as NonOilen, were studied. To carry out this characterization, a Taguchi L27 experimental design was used for both mechanical tests. On the one hand, compression tests were carried out following the ASTM-D695. The dimensional and geometric specifications of the rotating fatigue machine were used for the fatigue printed parts. All the specimens were 3D printed using a Creality Ender 3 printer (Shenzhen Creality 3D Technology Co., Ltd., Guangdong, China). The methodology for each specific test is outlined in the subsequent section.

The studied PLA/PHB properties differ from those obtained for PLA (Table 1). Thus, it can be noticed the presence of PHB provides certain changes in the general properties of the raw filaments.

2.1. *Design of experiments*

An experimental design with an orthogonal array was used to study the effect of the defined parameters. Therefore, 27 combinations resulted from the DoE (Table 2). In addition, five samples of each configuration were printed and tested to guarantee repeatability. To analyze the statistical influences of the parameters, the Minitab software was used. The remaining parameters, treated as constants, are also defined in Table 2.

2.2. *Compression test*

Compression tests were conducted in accordance with the ASTM-D695 standard utilizing a Zwick/Roell Universal Testing Machine (ZwickRoell GmbH & Co., Ulm, Germany). The tests were executed at a speed of 1.3 mm/min, with a maximum load of 5 kN. During each test, shrinkage and force values were recorded to facilitate the subsequent construction of stress-strain curves. Data processing was carried out using Matlab software to derive the characteristic curve of all specimens. The calculation of the Young's modulus and the yield strength at 0.2 % deformation was then performed based on the obtained stress-strain curves. The specimens were printed in a vertical orientation to achieve constant and defect-free circular cross-sectional areas.

2.3. *Fatigue tests*

To conduct the fatigue tests, the GUNTO WP 140 machine (Gunt Hamburg, Barsbüttel, Germany) equipped with a rotary electric motor capable of maintaining a consistent speed of 2800 rpm, was used. The specimens, designed specifically for this machine, feature a thicker end attached to the motor's side, while the opposing end is fastened to the side where the force is applied (Fig. 1). In order to verify the absence of any thermal contribution to the fatigue failure of the material, the temperature was systematically monitored throughout the test with the PCE-TC3 thermal camera (PCE Holding GmbH, Hamburg, Germany). A force of 8 N was applied, with the objective of reaching the failure of the specimens. The specimens were printed in a horizontal orientation along the X-axis. The generated supports were removed and a post-processing sanding left the surface free of residue, reducing the possible influence on the fatigue test. To address printing challenges arising from the material type and the geometry of the specimens, brim was applied to mitigate the warping effect.

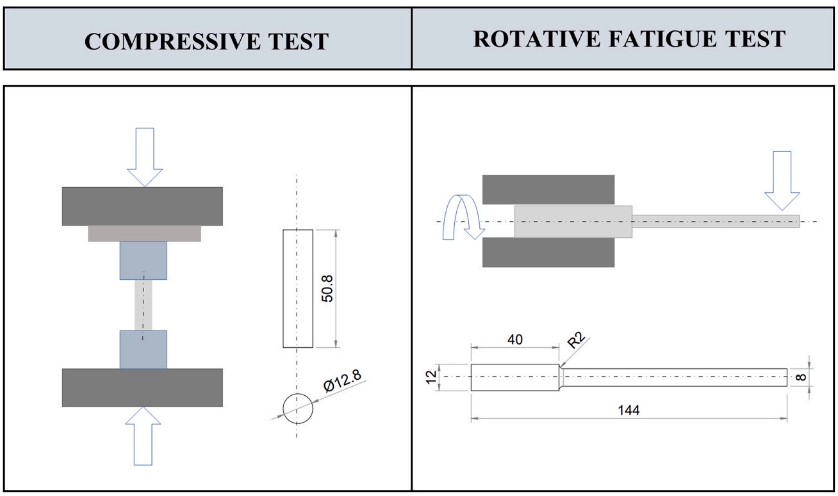

Fig. 1. Left) Universal Testing Machine; standard specimen according to ASTM-D965. Right) Rotating fatigue machine; fatigue specimens (dimensions in mm).

Table 1
Comparison of biodegradable raw filaments' nominal properties [33–35].

Property	PLA	PLA/PHB	PLA-wood
Polymer base	Polylactic acid	PLA/polyhydroxy-butyrate	PLA/wood
Material density [g/cm^3]	1.24	1.20	1.26
Tensile strength [MPa]	60.0	38.6	39
Elongation at break [%]	6.0	7.7	2.0
Young's modulus [MPa]	3600	1900	3200

Table 2
Factors, codes, and levels for the creation of Taguchi L27 design.

Variable parameters	Code	Level		
		1	2	3
Layer height [mm]	A	0.1	0.2	0.3
Nozzle diameter [mm]	B	0.3	0.4	0.5
Fill density [%]	C	25	50	75
Printing velocity [mm/s]	D	25	30	35
Constant parameters		**Value**		
Top layers		2		
Bottom layers		2		
Fill pattern		Tri-Hexagonal		
Printing temperature [°C]		190		
Build plate temperature [°C]		50		
Wall line count		2		

2.4. Materials comparison

In order to assess the difference between PLA, PLA/PHB and PLA-wood, five specimens were printed from PLA and PLA-wood utilizing identical printing parameters, which had previously yielded superior mechanical properties in PLA/PHB. Compression tests were carried out using a Zwick/Roell universal testing machine (ZwickRoell GmbH & Co., Ulm, Germany) according to ASTM-

Table 3
Orthogonal matrix of Taguchi L27 used in the DoE. Results and standard deviation of Young's modulus and yield strength obtained in the PLA/PHB compressive and fatigue test tests.

Combination	Printing parameters				Compressive results		Fatigue results
	Lh [mm]	$\varnothing_e$ [mm]	F% [%]	v_e [mm/s]	Young's modulus [MPa]	Yield strength [MPa]	Lifecycles
1	0.1	0.3	25	25	892 ± 23.9	14.9 ± 0.40	3300 ± 300
2	0.1	0.3	50	30	1270 ± 10.7	23.3 ± 0.60	5000 ± 1000
3	0.1	0.3	75	35	1579 ± 27.2	31.6 ± 0.50	6000 ± 1200
4	0.1	0.4	25	30	960 ± 74.3	15.5 ± 1.4	2800 ± 500
5	0.1	0.4	50	35	1100 ± 104.2	17.7 ± 1.38	4400 ± 700
6	0.1	0.4	75	25	1665 ± 21.6	32.17 ± 0.39	4204 ± 437
7	0.1	0.5	25	35	944 ± 49.15	17.48 ± 0.20	1776 ± 441
8	0.1	0.5	50	25	1391 ± 20.0	25.93 ± 0.57	5239 ± 528
9	0.1	0.5	75	30	1671 ± 12.56	33.78 ± 0.43	6858 ± 790
10	0.2	0.3	25	30	775 ± 13.3	12.74 ± 0.07	1750 ± 91
11	0.2	0.3	50	35	1220 ± 18.8	22.13 ± 0.64	2937 ± 319
12	0.2	0.3	75	25	1516 ± 34.6	29.79 ± 0.58	3159 ± 437
13	0.2	0.4	25	35	984 ± 13.8	16.8 ± 0.20	2600 ± 300
14	0.2	0.4	50	25	1331 ± 10.4	24.7 ± 0.20	3400 ± 400
15	0.2	0.4	75	30	1618 ± 8.8	33.3 ± 0.30	6100 ± 700
16	0.2	0.5	25	25	969 ± 11.9	16.6 ± 0.25	7700 ± 600
17	0.2	0.5	50	30	1305 ± 16.8	25.6 ± 0.14	9500 ± 300
18	0.2	0.5	75	35	1524 ± 12.3	32.7 ± 0.5	7000 ± 400
19	0.3	0.3	25	35	709 ± 103.9	11.40 ± 1.43	2421 ± 547
20	0.3	0.3	50	25	1070 ± 23.2	19.53 ± 0.54	8759 ± 354
21	0.3	0.3	75	30	1475 ± 25.4	28.90 ± 0.35	4996 ± 318
22	0.3	0.4	25	25	888 ± 6.9	15.80 ± 0.23	4679 ± 422
23	0.3	0.4	50	30	1270 ± 16.9	23.92 ± 0.37	5184 ± 710
24	0.3	0.4	75	35	1582 ± 11.9	31.22 ± 0.33	6245 ± 489
25	0.3	0.5	25	30	896 ± 29.9	15.46 ± 0.28	4792 ± 618
26	0.3	0.5	50	35	1200 ± 30.5	24.1 ± 0.61	6400 ± 400
27	0.3	0.5	75	25	1460 ± 9.5	30.9 ± 0.60	9700 ± 1200

D695 and test conditions as described in section 2.2.

3. Results and discussion

The syntheses of the results obtained are reported in this section, distinguishing the two tests carried out. Table 3 contains the results obtained from both study, compression and fatigue tests. The average of the five replicas for each combination is shown as well as their deviation.

3.1. Compression tests

Analyzing the data obtained from the stress–strain curve, the Young's modulus and the yield Strength of all configurations were obtained (Table 3). The best parameter combination results in the one with a Young's modulus of 1670 MPa associated to a yield strength of 33.78 MPa (run number nine). Fig. 2 graphs the main effects by averages of Young's modulus and yield strength, clearly showing the effect of the four printing parameters used. It should be noticed that the fill density has more effect on both properties than the other studied parameters. To quantify the statistical influences, p-values were determined with a significance level of 95 % (Table 4).

Young's modulus measures stiffness or, in other words, the difficulty to deform the bonds at very low stress. Its value is not sensitive to bond energy (quality of bonds), but to the quantity of bonds as well as the initial strength. Therefore, the pores affect significantly the Young's modulus, but not so much the weak necks between layers. As small layer heights and big nozzle diameters leave less pores, these parameters tend to improve the stiffness. The infill percentage is what determines the spaces between deposited filaments (porosity) and therefore it is the parameter with the highest effect.

The yield strength determines the beginning of the plastic deformation and must be more related to the quality of the bonds. As the samples are compressed during the test, the layer height does not have an effect on it. However, the nozzle diameter affects the yield strength, since it determines the number of defects per section unit, and therefore, those defects grow as the specimens are subjected to higher compressive stresses, inducing permanent deformation. Similarly, if there is no material, it is easier to deform the specimen, so the infill percentage is, again, the most significant parameter.

The layer height is not significant, because during the test, the pores tend to close because of fiber deformation. However, this parameter affects the number of weak points that appears between filament's bonds in the vertical direction. For this reason, the interaction between layer height and nozzle diameter is significant. Results on such influence are demonstrated in the study by Mushtaq et al. [31], where the authors show the importance of fill density to optimize the printed PLA.

The nozzle diameter is also clearly significant in printed specimen properties. An increase in the nozzle diameter results in more material being deposited, which leads to an enhancement in strength and an improvement in the surface finish of the printed part [32]. Moreover, Triyono et al. [Triyono_2020] demonstrated that increasing the nozzle provides more density and tensile strength of the printed products.

Besides, layer height has a significant effect only on the Young's modulus. However, it is not statically influent for the yield strength, as during the compressive tests the inter layer bonds are closed by the effect of the applied force. Nevertheless, there is an interaction between the layer height and nozzle diameter that is significant. This is due to the fact that while the layer height determines the number of voids in the vertical axis, the diameter extruder determines the width between them. Therefore, when a smaller diameter is combined with a small value of layer height, a larger number of voids are created. Consequently, the value of the yield strength decreases. With low layer height values and high nozzle diameters, fewer voids are generated, tending to improve Young's modulus. Logically, the filling percentage is the factor that most determines porosity and therefore the one that has the greatest effect. The result is corroborated by the study by Yanping Lui et al. [36] which demonstrated the influence of layer height on the mechanical characteristics of PLA parts. The p-values corresponding to the printing velocity are not significant for Young's modulus and yield strength (Table 4).

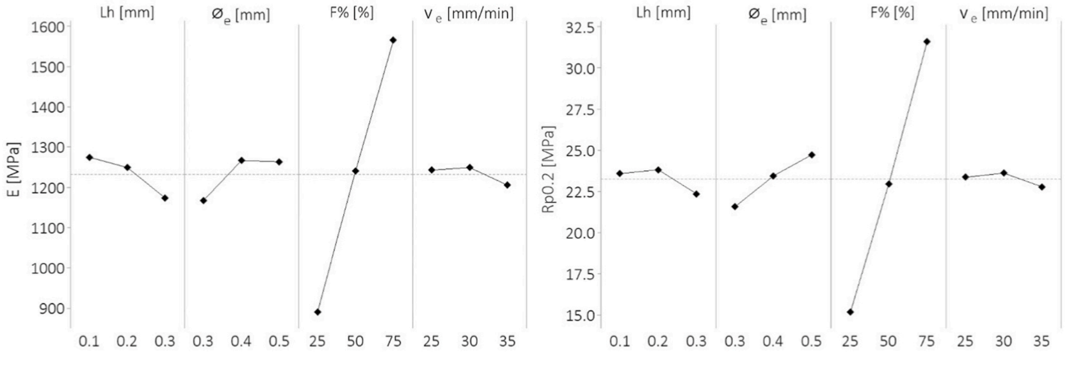

Fig. 2. Main effects of Means for Young's modulus (left) and yield strength (right). Lh – layer height; $\varnothing_e$ – nozzle diameter; F% - fill density; v_e – printing velocity.

Table 4
P-values of factors and interaction for Young's modulus and yield strength.

Factor	p-value	
	Young's modulus	Yield strength
Fill density [%]	0.000	0.000
Nozzle diameter [mm]	0.024	0.004
Layer height [mm]	0.032	0.086
Printing velocity [mm/min]	0.337	0.387
Layer height [mm] * Nozzle diameter [mm]	0.215	0.043
Nozzle diameter [mm] * Fill density [%]	0.332	0.271
Layer height [mm] * Fill density [%]	0.632	0.375

The second-order analysis shows that the interaction of layer height and nozzle diameter reaches a statistical influence on the yield strength with a p-value of 0.043, being on the limit of the significance level. It should be noted that the layer height has been shown to be correlated with the diameter of the nozzle [37].

All these results can be explained if one has in mind that Young's modulus measures stiffness and, therefore, how hard it is to deform the bonds at very low stress. This makes it not sensitive to bond energy (bond quality) but to the quantity and the initial strength. Therefore, the pores affect it to a high extent, but not so much the weak welds between layers. As small layer heights and large nozzle diameters leave fewer pores, they tend to improve it. Logically, the percentage of filling is what most determines the porosity and therefore what has the most effect on the responses.

The yield strength marks the beginning of plastic deformation and may already be more related to the quality of the joints. As we are compressing, the layer height does not affect, since one close the possible defects, but the diameter of the nozzle does, since this gives the number of defects per section, and therefore, those that can grow under compression and induce plastic strain. Similarly, if there is no material, it costs less to deform, and that is why the percentage of filling is the most significant parameter.

The height of the layer is not significant, because we tend to close it, but it does affect the amount of weak points that the joints between filaments have in the vertical direction. For this reason, the interaction between the layer height and nozzle diameter is significant.

3.2. *Fatigue rotating tests*

The specimens had a notch factor due to the change in diameter Fig. 3, which helped to locate the critical section. From the analysis of the breakage temperature done with the thermal camera was determined that there were no significant thermal effects during the tests. The graph in Fig. 3 shows the influence that each of the printing parameters used has on the fatigue rupture of the specimens.

The results show that the layer height of 0.3 mm guarantees higher life cycles, a conclusion that was demonstrated in previous studies [38]. Furthermore, it is evident that the fill density has a high influence on the life cycle of the parts. However, the printing velocity was identified as a less significant parameter compared to those analyzed.

Table 6 shows the p-values obtained by the analysis of variance of means. It can be concluded that the only two statistically significant parameters are the fill density and the nozzle diameter, and both are quite close to the significance threshold. On the contrary, printing velocity and layer height result in a p-value >0.05, which shows that they are not statistically significant.

The interactions of means between the different parameters reveal that none are statistically significant, that is, the interactions between parameters have no influence on the results (Table 5). The best average corresponds to combination 27, which corresponds to the following parameters: 0.3 mm of layer height, 0.5 mm nozzle diameter, 75 % fill density and a velocity of 25 mm/min.

To understand the behavior of the copolymer PLA/PHB, a Wöhler curve was created using the best resulting configuration

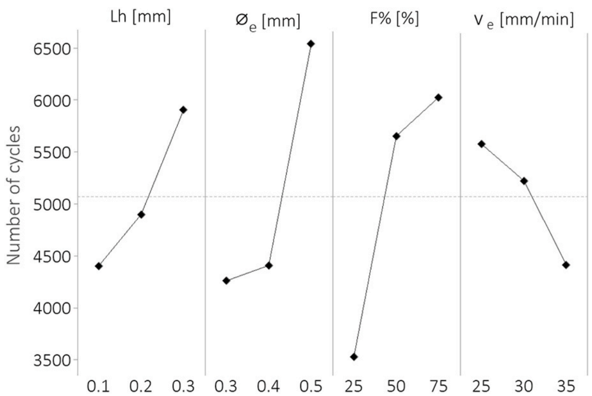

Fig. 3. Graph of main effects by Means of the number of Life Cycles. Lh – layer height; $\varnothing_e$ – nozzle diameter; F% - fill density; v_e – printing velocity.

Table 5
P-values of factors and interaction for life cycles of fatigue tests.

Factor	p-value life cycles
Fill density [%]	0.040
Nozzle diameter [mm]	0.049
Layer height [mm]	0.233
Printing velocity [mm/min]	0.381
Layer height [mm] * Nozzle diameter [mm]	0.186
Nozzle diameter [mm] * Fill density [%]	0.767
Layer height [mm] * Fill density [%]	0.879

Table 6
Compression results on PLA, PLA/PHB and PLA-wood samples.

Property	PLA	PLA/PHB	PLA-wood
Young's modulus [GPa]	2.26 ± 0.04	1.67 ± 0.013	1.31 ± 0.02
Yield strength [MPa]	57.6 ± 1.6	33.8 ± 0.4	22.3 ± 0.3

(combination 27) in section 3.3.2.

3.3. *Materials comparison*

Combining biomaterials to create hybrids with enhanced functions has the potential to overcome the limitation of each material. The choice of the biopolymer considered in this study reflects the importance that is being given to the search for polymers with lower environmental impact, starting from a PLA base [39]. Although PLA is recognized as a thermoplastic with good mechanical properties and is easily processable, it has disadvantages associated with fragility, crystallization and low thermal resistance. The compound based on PLA and PHB is a solution to overcome these drawbacks, and also provides improvements in thermal characteristics [40].

In this work, a comparison between PLA/PHB and pure PLA was conducted to evaluate the mechanical effects of introducing PHB, while comparisons were also made between PLA/PHB and PLA-wood as it provided a sustainable alternative. This analysis sought to clarify any alterations in mechanical properties resulting from the transition of PLA to a more sustainable form, considering that all three materials share the same polymer base. Thus, the subsequent sections compare the obtained results for PLA, PLA/PHB, and PLA-wood to analyze the evolution of their mechanical behavior.

3.3.1. *Compression properties*

Table 6 outlines the mechanical properties acquired for the three materials.

Based on the compression results presented in Table 6 for PLA, PLA/PHB, and PLA-wood samples, several conclusions can be drawn. First, PLA exhibits the highest Young's modulus among the three materials, with a value of 2.26 GPa. PLA/PHB demonstrates a lower Young's modulus compared to PLA, indicating a decrease in stiffness with the addition of PHB, with a value of 1.67 GPa. PLA-wood composite presents inferior mechanical results compared to the other two, so its use should be questioned based on the levels of mechanical stress. The composite, in fact, shows the lowest Young's modulus among the three materials, suggesting a further decrease in stiffness due to the incorporation of wood particles, with a value of 1.31 GPa. Moreover, the same trend can be seen regarding the yield strength. In the final analysis, Fig. 4 compares the three materials object of this study from a stress-strain perspective, where the different behavior exposed in this section is observed.

It can be concluded that the addition of PHB and wood particles to PLA leads to reductions in both Young's modulus and yield strength, suggesting alterations in the mechanical properties of the materials. Specifically, PLA/PHB and PLA-wood composites show

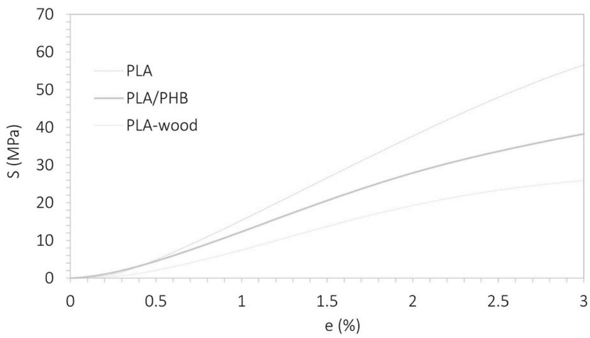

Fig. 4. Comparison of stress-strain curves for the materials studied.

decreased stiffness and reduced ability to withstand deformation compared to pure PLA.

3.3.2. Fatigue properties

Wöhler curves were constructed for each material to compare PLA, PLA/PHB, and PLA-wood. The construction of the Wöhler curves involved using the best configuration for each material. Thus, for the PLA/PHB copolymer, the data was obtained in this present study, while results from previous works developed in our research group were used to graph the Wöhler curves of PLA [42] and PLA-wood [41]. The printing parameters that yielded the best mechanical properties were applied consistently across all materials. A range of different load forces was then excerpted, specifically chosen to cover the entire cycle range from specimen breakage to 10000 cycles. The variability in the applied forces could ensure the precision of the resulting curve. The Wöhler curve is defined by Equation (1).

$$S_f = S_a \cdot (2 \cdot N_f)^{b} \quad (1)$$

with Sf determined as indicated in Equation (2),

$$S_f = \frac{K_t \cdot M_f \cdot \frac{D_{eq}}{2}}{I_x} \quad (2)$$

The constants of the tested samples are detailed in Table 7.

Fig. 5 shows the stress vs cycles-to-failure curves of the three polymers mentioned above allowing the direct comparison of the results. It can be seen that the addition of wood or PHB appears to alter the rate of stress amplitude decay compared to pure PLA, as evidenced by the differences in the exponents of the Wöhler curve equations. However, unlike PLA and PLA-wood, PLA/PHB does not converge towards a constant stress amplitude value as the number of cycles increases, suggesting a different fatigue behavior or fatigue limit for PLA/PHB. This can be attributed to the nature of the additives and their effect on the polymer matrix, as explained below.

The addition of wood to PLA typically does not alter the fundamental polymer structure of PLA. Wood particles primarily act as fillers or reinforcements within the PLA matrix, affecting mechanical properties but not fundamentally changing the polymer itself. In contrast, when PHB is added to PLA, a copolymer is formed. This copolymerization process results in a different molecular structure compared to pure PLA. The introduction of PHB alters the polymer matrix, potentially leading to differences in mechanical behavior, including fatigue properties.

Pure PLA exhibits the highest resistance in terms of fatigue behavior. PLA-wood, containing wood fibers, displays lower properties due to the creation of gaps between layers during the printing process, leading to reduced adhesion and consequent deterioration in mechanical behavior. Ultimately, samples printed with PLA/PHB demonstrate the lowest mechanical properties among the tested materials.

It can be seen that the reduction in mechanical properties compared to the PLA [38,43] is not only reflected in the case of PLA/PHB, but also in the composite of PLA-wood [20,44]. The wood fibers present in the PLA-wood composite seem to act as crack nucleators, so at high amplitudes they significantly reduce fatigue life. On the other hand, at low amplitudes the tendency to propagation dominates, generating the same fatigue limit as PLA (Fig. 4). Also, the PLA/PHB copolymer has lower resistance to all stress amplitudes, to the point that it has no fatigue limit.

Despite the decline in mechanical properties, these materials find utility in applications where high mechanical performance is not a primary concern. Moreover, considering their higher degree of biodegradability compared to PLA, they offer added environmental benefits. For instance, leveraging the biocompatibility of PLA/PHB, it serves as a suitable material for biomedical applications within the field of tissue engineering [44–46].

4. Conclusions

In the present study, the influences of certain printing surfaces such as layer height, nozzle diameter, fill density, and printing velocity on the compression and rotating fatigue performance of PLA/PHB were analyzed through a Taguchi DOE.

The results obtained in the case of the compression study indicate that a combination of a layer height of 0.1 mm, nozzle diameter of 0.5 mm, fill density of 75 %, and a printing velocity of 30 mm/s provides the best results in terms of Young's modulus (1.67 ± 0.01 GPa) and yield strength (33.8 ± 0.4 MPa). This parameter configuration corresponds to a small layer height combined with a large extruder diameter that allow more material to be deposited, reducing the pores between layers and providing a good mechanical response. The layer height is not significant, but it affects the filament bonds in the vertical direction, which justifies the iteration between layer height and nozzle diameter as significantly influential. Furthermore, the most influential parameters were nozzle diameter, and fill density. The fatigue study determines that the best configuration is layer height of 0.3 mm, nozzle diameter of 0.5 mm, fill density of 75 %, and a printing velocity of 25 mm/s, with a lifecycle number of 9700 ± 1200. In this case, the most influential parameters turned out to be the nozzle diameter and the fill density.

When comparing PLA/PHB with pure PLA, the results showed that pure PLA is the most resistant material regarding compression and rotating fatigue tests, while PLA/PHB has the lowest strength. In fact, the mixture with PHB improves resistance to impact and deformation, as mentioned above [29]. In particular, the Young's modulus on PLA/PHB decreased by around 35 % and the yield strength decreased by around 40 %. In addition, in the rotating fatigue tests it was found that the Wöhler curves from both materials had different morphologies due to the fact that PLA/PHB is a copolymer. In all cases, the fatigue resistance of PLA/PHB is lower than pure PLA, although the impact absorption increases and the fragility of PLA is reduced [14]. Regarding the comparison between

Table 7
Constants and applied stress for the Wöhler curve of PLA/PBH.

Proven features		Applied Force [N]	M_{max} [N·mm]	σ_{max} [MPa]
Maximum area [mm^2]	53.75	5	520	17.9
Resistant area [mm^2]	42.36	7	728	25.1
D_{eq} [mm]	7.34	8.5	884	30.5
I_x [mm^4]	142.79	10	1040	35.8
Cantilever samples [mm]	104	11.5	1196	41.2
K_t	1.34	13	1352	46.6

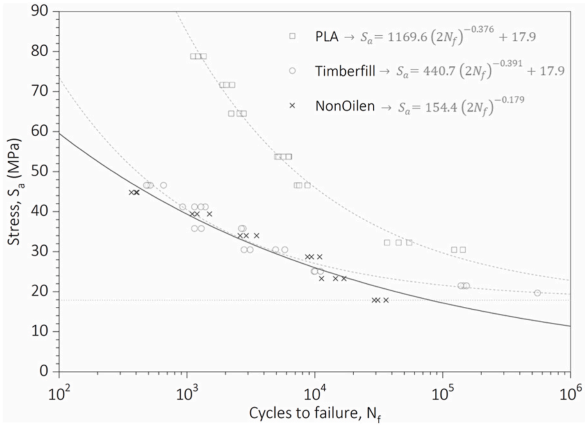

Fig. 5. Wöhler curve for the results obtained in this study and those obtained in the work of [38,41].

PLA/PHB and PLA-wood, PLA/PHB showed better mechanical behavior. The Young's modulus of PLA/PHB is 20 % higher, and the yield strength is 35 % higher. The Wöhler curves morphologies are also different, but in this case, the PLA-wood resisted more cycles before breakage.

Overall, from the results obtained in both tests, it can be concluded that depending on the ultimate application of the samples, the selected printing parameters should be different. The analysis of a commercial material allows the industry to use it in its applications. The best configurations presented are proposed as a guide to obtain a good print quality with this commercial filament and using a low-cost commercial printer.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

CRediT authorship contribution statement

Walter Crupano: Writing – original draft, Software, Investigation, Data curation. **Bàrbara Adrover-Monserrat:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jordi Llumà:** Writing – review & editing, Validation, Software, Methodology, Formal analysis, Conceptualization. **Ramón Jerez-Mesa:** Writing – review & editing, Visualization, Methodology, Formal analysis. **J. Antonio Travieso-Rodriguez:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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