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Development of Composites of PLA Filled with Different Amounts of Rice Husk Fibers for Fused Deposition Modeling

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ABSTRACT

Poly(lactic acid) (PLA) has been used as a matrix material to produce composites with natural fibers, which present several advantages, being one of them the addition of value to agricultural waste. Thus, this study aims to develop a PLA 3D filament with the incorporation of a waste agriculture product (rice husk (RH)). For that, RH fibers were prepared, and PLA was loaded up to 20% RH. The filaments were obtained by extrusion. Finally, samples were produced by fused deposition modeling (FDM). The fibers and filaments' density and thermal stability (TGA) were determined, and their chemical structure changes due to alkali treatment were accessed by Fourier Transform Infrared Spectroscopy (FTIR). Printability tests were performed, and printed samples were characterized in terms of density, water absorption, and mechanical behavior (compression, tensile, and flexural tests). The results showed that the alkali treatment changed the chemical structure of RH fibers and TGA showed that the filaments did not degrade significantly until 250°C. The best printability was achieved with 5% of HR content and was the one that showed the lowest mechanical properties reduction. Overall, the present work showed that RH fibers can be successfully used as a filler in PLA filaments for FDM.

摘要

聚乳酸 (PLA) 已被用作基质材料, 以生产天然纤维复合材料, 其具有几个优点, 其中之一是对农业废弃物的增值。因此, 本研究旨在开发 PLA 3D 细丝, 并将其与废弃农产品 (稻壳 (RH)) 结合。为此, 制备 RH 纤维, 并将 PLA 加载至 20% RH。通过挤出获得长丝。最后, 通过熔融沉积模型 (FDM) 制作样品。测定了纤维和长丝的密度和热稳定性 (TGA), 并通过傅里叶变换红外光谱 (FTIR) 分析了碱处理引起的化学结构变化。进行了可印刷性测试, 并根据密度、吸水率和机械性能 (压缩、拉伸和弯曲测试) 对印刷样品进行了表征。结果表明, 碱处理改变了 RH 纤维的化学结构, TGA 表明, 直到 250°C, 纤维才发生显著降解。HR 含量为 5% 时可获得最佳的印刷性, 并且是机械性能降低最低的印刷性。总之, 研究表明 RH 纤维可以成功地用作 FDM 用 PLA 长丝的填料。

KEYWORDS

Rice husk; natural fiber-filled polymer; additive manufacturing; PLA; mechanical properties; composites

关键词

稻壳; 天然纤维填充聚合物; 增材制造; 机械性能; 复合材料

1. Introduction

Petroleum-based polymers are well known for releasing significant amounts of greenhouse gases into the atmosphere during their production and being a nonrenewable resource for manufacturing goods

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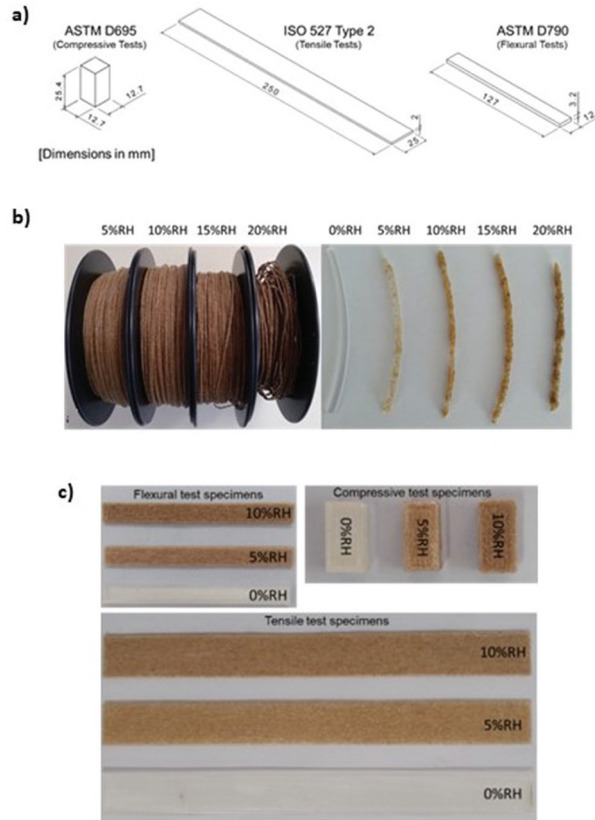


Figure 1. a) Mechanical properties test specimens modeled in Dassault 3D experience; b) Composite filament spools and filaments produced; c) Printed specimens.

(Gholampour and Ozbakkaloglu 2020). As a potential substitute for traditional fossil fuel-based polymers, biopolymers are being more considered and Polylactic Acid (PLA), one of the most researched biopolymers, is already used for plastic film bottles, packaging, and biodegradable medical devices (Ramengmawii et al. 2019). In addition, PLA has been extensively used as a matrix material to produce composites with natural fibers (Ilyas et al. 2021, 2022). Along with biopolymers, natural fibers are emerging as a filler/reinforcement for polymer composites due to their availability, biodegradability, low cost, and eco-friendliness (Ramengmawii et al. 2019). Natural fiber-filled composites are already a reality, widely used in the automotive industry, mainly in panels and insulation (Karthi et al. 2019). Nevertheless, there are still some drawbacks in the composites filled with natural fibers used in the automotive industry since they are not fully biodegradable, present low glass transition temperature (e.g., PLA shows $T_g \approx 55^\circ\text{C}$), and the thermal stability of the majority of natural fibers is below 200°C (Balla et al. 2019).

On the other hand, the use of PLA has increased drastically in the 3D printing area, also known as additive manufacturing (AM), which is a promising technology that has been growing at a fast pace and, according to experts, will continue to grow through 2025 (Panda et al. 2016). AM, mainly fused deposition modeling (FDM), is being used in both the industrial and personal fields, the latter mainly because this process does not require elaborate assemblies, have low energy consumption, and most of the 3D printers are cheap, allowing easy access to a 3D printer and freely downloaded models from the internet (Mazzanti, Malagutti, and Mollica 2019). Other advantages have also been identified such as

the reduction of tooling, production of more complex geometries and possibility of reduction of the number of parts in one component (Aida et al. 2021; Azlin et al. 2022).

As a feedstock material for AM, PLA has attracted much attention from academic researchers because of its complete biodegradability (Liu et al. 2019). Researchers have also begun adding plant fibers to PLA in order to produce a variety of composite filaments for FDM. Adding natural fibers as a filler in biopolymeric materials for FDM can reduce filaments' cost and improve their degradability. In addition, it confers the AM part a natural wood feeling, that with adequate marketing, can lead to the idea that AM products can be produced from renewable resources and have pleasing aesthetics (Liu et al. 2019; Ramengmawii et al. 2019). Moreover, natural fibers as a filler in FDM filaments provide a sustainable lifecycle for 3D printed products since these fibers are waste products coming from industry or agriculture, which are often produced locally (Mazzanti, Malagutti, and Mollica 2019). Moreover, they are less abrasive (than mineral ones) and increase the overall life span and efficiency of processing equipment (Balla et al. 2019). Due to numerous challenges related to inherent characteristics of natural fibers, such as thermal stability, hydrophilicity, inhomogeneity in filler dispersion and creation of voids during processing, there are few studies in the literature addressing FDM with natural fiber composites (NFC) (Balla et al. 2020; Liu et al. 2019; Mazzanti, Malagutti, and Mollica 2019).

Concerning the production of filament, fiber pre-treatment is important for producing plant fiber composite filaments for 3D printing and is decisive in filament printability. The pre-treatment allows to remove undesirable fiber constituents, increase the surface roughness of the fibers, separate individual fibers from bundles, change the chemical nature of the fiber surface, and decrease the hydrophilicity of the fibers (Ilyas et al. 2022). Among the different chemical treatments available for natural fibers that have been reported in the literature, alkali treatment is the most used because it is very effective in surface modification and is economic (Cordeiro, Gouveia, and Jacob John 2011; Jamadi et al. 2021; Koohestani et al. 2019; Saidah, Endah Susilowati, and Nofendri 2019; Xue, Tabil, and Panigrahi 2007). Alkali treatment is a process where fibers are subjected to a strong base solution to disrupt hydrogen bonds in the network structure, with resultant changes in the dimensions and morphology of the fibers and their mechanical performance (Koohestani et al. 2019; Xue, Tabil, and Panigrahi 2007). This treatment removes lignin, wax, oils, and depolymerizes the fiber cell wall (Kabir et al. 2012). Hemicellulose, which is very sensitive to alkali solutions, is removed in variable amounts (depending on time exposure to NaOH solution), increasing the number of cellulose crystallites exposed in the fiber surface (Mohanty, Misra, and Drzal 2001). When hemicelluloses are removed, the interfibrillar region decreases its density and rigidity, making the fibrils more able to rearrange themselves in the direction of mechanical loads (Mohanty, Misra, and Drzal 2001).

Among the rice producing countries in Europe, Portugal occupies the fourth place with a production of around 185,000 tons per year, leading to high amounts of rice husk (RH) residues. Thus, the aim of this work is to present a possible added value for such waste material through its incorporation into a 3D printed polylactic acid (PLA) filament. For this, PLA loaded with different amounts of rice husk fibers (0%, 5%, 10%, 15%, and 20% wt.%) was produced by FDM. Rice husk fibers were prepared, sieved, alkali-treated, dried, and blended with PLA to extrude AM filaments. Regarding the characterization of the fibers and filaments, density and thermal stability were determined, and Fourier Transform Infrared Spectroscopy (FTIR) was carried out to analyze the chemical structure change due to alkali treatment. The produced extrudates (circular cross-section filaments) were subjected to printability tests, and the printed specimens were analyzed by density and water absorption measurements and mechanical testing (compression, tensile, and flexural tests). Moreover, the density and thermal stability of all filament blends were determined. Finally, Scanning Electron Microscopy (SEM) imaging was used to study fracture surfaces of tensile and flexural tested specimens.

2. Materials and methods

2.1. Materials

The materials used in this work for all NFFP filament compounds were PLA (Ingeo™ Biopolymer 4043D, RepRap PT, Portugal) and rice husks (RH) (Alcácer do Sal, Portugal).

Distilled and deionized (DD) water (obtained from a Millipore system) and an aqueous solution of 5% wt. NaOH (MERCK, 99%) were used for the alkali treatment.

2.2. Methods

2.2.1. Fiber preparation and treatment

The RH used in this work were obtained from the rice milling dehusking stage. The first step of fiber preparation was to separate the husks from all undesirable fibers, grains, and impurities by a settling process during 2 h. The supernatant material (mainly RH) was removed and dried in an oven (Binder® ED115, Binder, Germany) for 12 h. After drying, the RH was sieved (2 mm mesh) to remove some remaining impurities, obtaining only RH. After that, RH was ground to obtain a powder with dimensions less than 0.5 mm. All categorized fibers were conserved in the convection drying oven at 50°C to prevent moisture absorption before alkali treatment. The alkali treatment was performed by immersing the RH in a 5% wt. NaOH solution with a weight ratio of 1:10 for 6 h at room temperature. After, the RH fibers were rinsed in DD water until it reached a $\text{pH} \approx 7$. Then, the fibers were filtered and dried in an oven (Binder® ED115, Binder, Germany) for 12 h at 60°C.

2.2.2. Filament extrusion

The PLA 4043D pellets were first dried at 80°C for 4 h in a drying oven and then blended with RH to achieve formulations with 5, 10, 15, and 20 wt.% RH. These were processed using a single screw 3Devo® composer 450 desktop extruder (United Kingdom), with a fixed extrusion temperature profile of 175°C/180°C/190°C/180°C and a screw speed of 4 rpm. The obtained extrudates were circular cross-section filaments with 1.75 mm of diameter.

2.2.3. 3D printing of specimens

Specimens for tensile, compressive, and flexural tests were printed on a Prusa® i3 Hephestos 3D Printer (Czech Republic). Specimens' geometries followed the standards presented in [Figure 1a](#) and the.stl files were created on the Dassault 3D experience® platform. The .gcode files with printing profiles were programmed on Simplify 3D®. All specimens were printed in a flat position without a heated bed, and the printing parameters used in all prints were layer height (0.4 mm), shells (2), printing velocity (1800 mm/min), and nozzle temperature (220°C). All samples were printed with an infill direction coincident with the test direction for all samples.

2.2.4. Density

The density of printed parts, filaments, and PLA pellets were determined by Archimedes principle, using an analytical balance (A&D® GR-200-EC, Reagecon, United Kingdom). RH density values were obtained in a pycnometer (Quantachrome® Ultrapycnometer 1000, Quantachrome Instruments, USA). Five measurements were done for each sample.

2.2.5. Water absorption

Water absorption (WA) of printed parts was calculated according to equation 1, using samples with a volume of $10 \times 10 \times 2 \text{ (mm}^3\text{)}$ trimmed from ISO 527 90° printed specimens. The samples were weighed using an A&D® EK-1200 $\text{g} \times 0.1 \text{ g}$ compact balance before and after being immersed in distilled water for 24 h at room temperature. From each printed blend, five samples were analyzed.

$$WA = \frac{W1 - W_o}{W_o} \times 100 \quad (1)$$

where W_o is the initial weight of the sample (after drying for 24 h at 40°C) and $W1$ is the weight of the sample after 24 h in distilled water.

2.2.6. Scanning electron microscopy (SEM)

SEM images from fracture surfaces were acquired in a Hitachi® S-2400 scanning electron microscope (Japan) using an acceleration voltage of 20kV and a magnification ranging from 20 to 400 ×. Before observation, the samples were previously coated with Au-Pd alloy.

2.2.7. Fourier transform infrared spectroscopy (FTIR)

The chemical composition of RH before and after NaOH treatment was obtained using a Spectrum Two FTIR spectrometer (Perkin Elmer®, Waltham, MA, USA) equipped with a diamond crystal ATR accessory (model UATR Two). The spectra were obtained from eight scans with a resolution of 4 cm⁻¹ and normalized using the OriginPro 8.5 software. Measurements were done in triplicate.

2.2.8. Thermogravimetric analysis (TGA)

All materials were analyzed under a nitrogen atmosphere (200 mL/min) using a Hitachi® STA7200 Thermal Analysis System equipment, at a temperature increase rate of 10°C/min (until 600°C). The TGA resulting thermograms, as well as the derivative curves (DTG) were obtained for the filaments and treated RH. The analysis was carried out in triplicate in each case.

2.2.9. Mechanical tests

Tensile tests were performed in an Impact® E-Series – TS 300 servo-hydraulic UTM (Portugal), equipped with a load cell of ±50kN and an axial extensometer with a nominal length of 50 mm. All tests were conducted at 2 mm/min, following the standard ISO 527–4. Values for Young's modulus, yield stress, ultimate tensile stress (UTS) and elongation at break were determined. Compressive tests were conducted in an Instron® 1342 servo hydraulic UTM (USA) equipped with a ± 250kN load cell and a stroke of ±75 mm. Tests were performed at 1.3 mm/min, according to the standard ASTM D695. The displacement was 25% of the sample height (6.35 mm), and the data from tests were acquired with National Instruments® Labview® 7 express software. Values for Young's modulus and yield stress were determined. Flexural tests were performed on the same equipment as the tensile tests. All the tests were conducted at 5 mm/min following the standard ASTM D790, and rotatable supports for the test

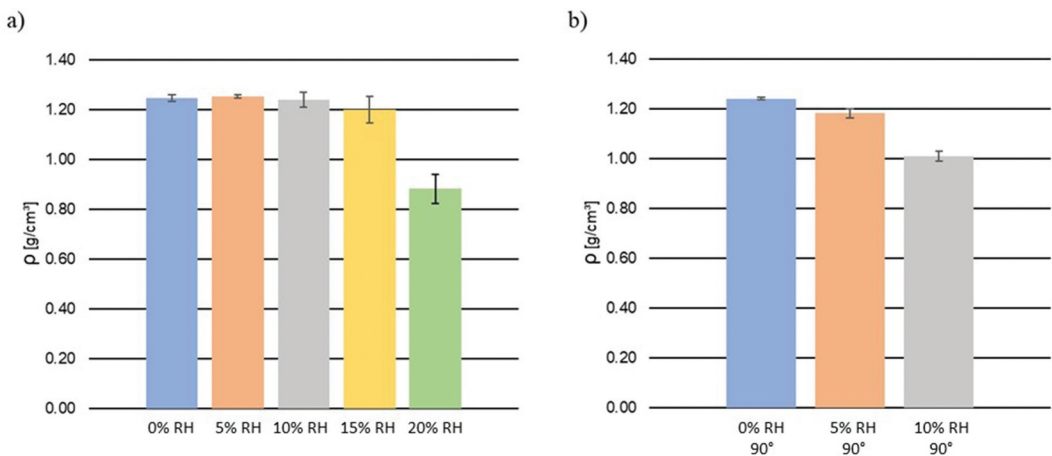


Figure 2. a) filament densities [g/cm³]; b). Densities [g/cm³] of printed specimens for compressive tests.

specimens were used, with a span of 60 mm. The flexural modulus and the maximum flexural stress were determined. For each mechanical test, five samples were used.

2.2.10. Statistical analysis

Excel Statistical Tools were used to perform the statistical analysis. Shapiro–Wilk test was performed to verify the normality of the results. ANOVA (one-way analysis of variance) and t-Student test was applied to compare three or more and two independent groups, respectively. The level of significance chosen was 0.05.

3. Results

3.1. Filament and printability

The obtained filaments are presented in Figure 1b. The maximum amount of fiber content that was possible to integrate in the extruded filament was 20% RH. The incorporation of fiber increased the filament roughness and diameter variation. The fiber agglomeration induced high diameter variation for the filaments of 10%, 15%, and 20% RH content. Issues in printability were found for the 10% RH, 15% RH, and 20% RH filaments. The 15% RH and 20% RH blends revealed to be too brittle to hold the forces applied by the extruder feeder pulley. The 10% RH blend had constant nozzle clogging (even at temperatures above 220°C) and showed a tendency to fracture before the extruder pulley. The 5% RH filament, which had few diameter variations, showed no nozzle clogging or other significant issues. 0% RH filament printability was similar to the average commercial PLA filament printability. Some produced specimens are shown in Figure 1c.

3.2. Density

The results showed that the density of the RH is higher than that of the PLA 4043 pellets ($p < .05$). The value determined for the PLA pellets agrees with the density value provided by the technical datasheet of 4043D grade ($\approx 1.24 \text{ g/cm}^3$). For the RH, the density value was $\approx 1.65 \text{ g/cm}^3$. Filaments (Figure 2a) revealed a statistically significant decrease in density for fiber content above 15% ($p < .05$). When comparing the filaments with the printed samples (Figure 2b), the samples showed a significant density reduction for 5% and 10% RH content ($p < .05$).

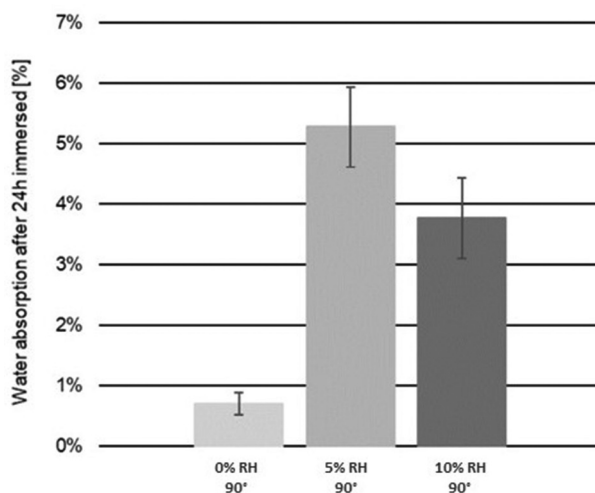


Figure 3. Water absorption after 24 h immersion.

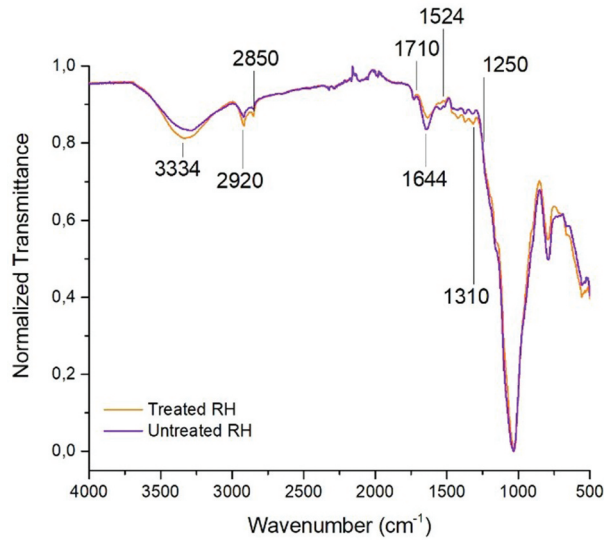


Figure 4. FTIR spectra of raw and alkali-treated fibers.

Table 1. RH (treated and untreated) FTIR band assignment.

Range [cm^{-1}]	Wavenumber [cm^{-1}] labeled on graph	Group
3550–3200	3334	OH stretching (strong)
3000–2840	2920	C-H stretching (medium)
3000–2840	2850	C-H stretching (medium)
1720–1706	1710	C=O stretching (medium)
1662–1626	1644	C=C stretching (medium)
1560–1510	1524	C=O stretching (medium)
1310–1250	1310	C-O stretching (medium)
1310–1250	1250	C-O stretching (medium)

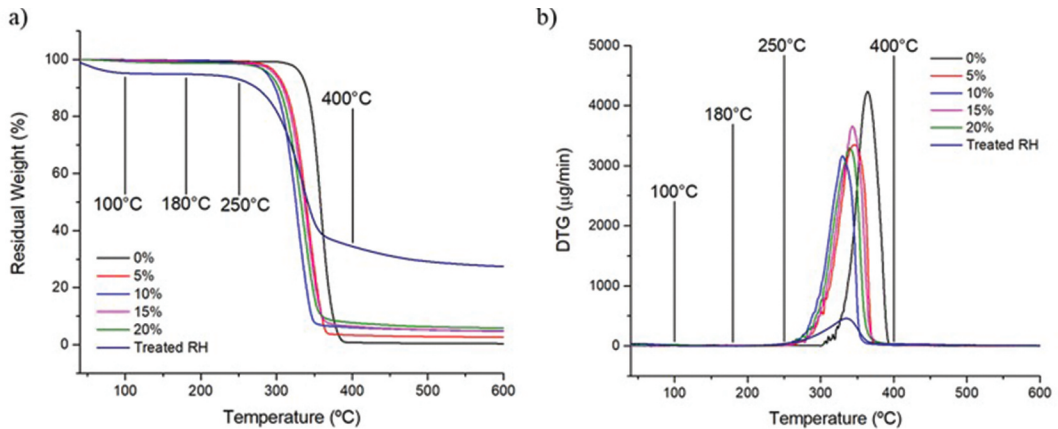


Figure 5. a) TGA thermograms of the filaments and treated RH; b) DTG thermograms of the filaments and treated RH.

3.3. Water absorption

The water absorption is shown in Figure 3. The samples revealed that water absorption is more prevalent in the printed parts with RH content than those with only PLA. Moreover, 5% RH content printed parts had higher water absorption than the 10% RH ones ($p < .05$).

3.4. Ftir analysis of treated and untreated RH fibers

The FTIR spectrum for the treated and untreated RH is depicted in Figure 4. FTIR analysis shows several chemical changes induced by the alkali treatment. The primary changes concern to the wavenumber ranges typical of -OH, C-H, C-O, and C=O bond vibrations. The significant peaks labeled on the spectra of Figure 4 and their respective band assignment are detailed in Table 1. The peaks of alkali-treated RH located at 3334 cm^{-1} , 2920 cm^{-1} , 2850 cm^{-1} , and 1310 cm^{-1} show an increased intensity compared to the untreated RH. These peaks correspond to the stretching frequencies of -OH, C-H, and C-O bonds, respectively. Peaks located at 1710 cm^{-1} , 1644 cm^{-1} , and 1524 cm^{-1} , which are representative of C=O and C=C groups stretching, on the contrary, are shown to decrease in intensity. The shoulder near the 1250 cm^{-1} frequency, coincident with C-O bond stretching, disappeared after alkali treatment. The spectra of both samples showed evidence of the presence of moisture, revealed by the wide band at 3334 cm^{-1} and 1644 cm^{-1} .

Table 2. Mechanical test results.

	Sample					
	0% RH		5% RH		10% RH	
	Mean	SD	Mean	SD	Mean	SD
Tensile tests (ISO 527-4 Type 2)						
UTS [MPa]	57.44	± 1.66	37.08	± 1.67	30.81	± 2.94
Yield stress [MPa]	46.59	± 1.67	32.82	± 1.48	25.50	± 3.82
Elongation at break [%]	4.91	± 2.37	2.45	± 0.11	2.56	± 0.18
E [GPa]	3.33	± 0.06	2.60	± 0.07	2.54	± 0.12
Compressive tests (ASTM D695)						
Yield stress [MPa]	83.98	± 2.33	74.79	± 2.92	44.01	± 0.06
E [GPa]	2.69	± 0.06	2.11	± 0.10	1.34	± 0.06
Flexural tests (ASTM D790)						
Maximum flexural stress [MPa]	109.05	± 3.93	70.43	± 0.84	69.28	± 4.74
Flexural modulus [MPa]	3590.14	± 164.90	2386.94	± 82.99	2754.70	± 216.65

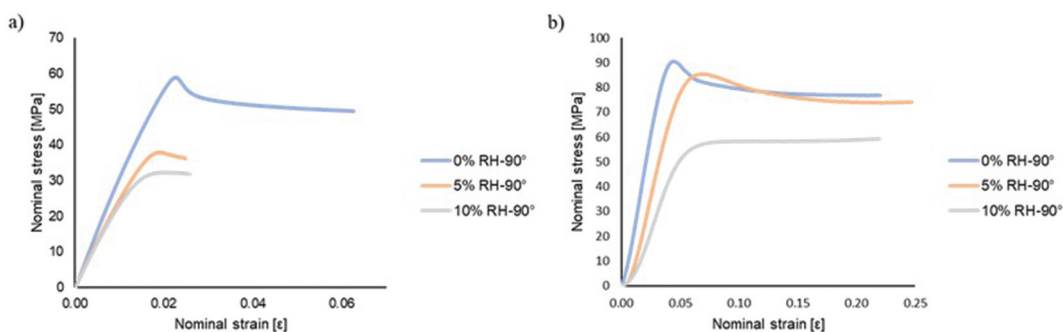


Figure 6. a) Typical tensile stress-strain curves; b) Typical compressive stress-strain curves of neat PLA and RH filled PLA composite printed parts.

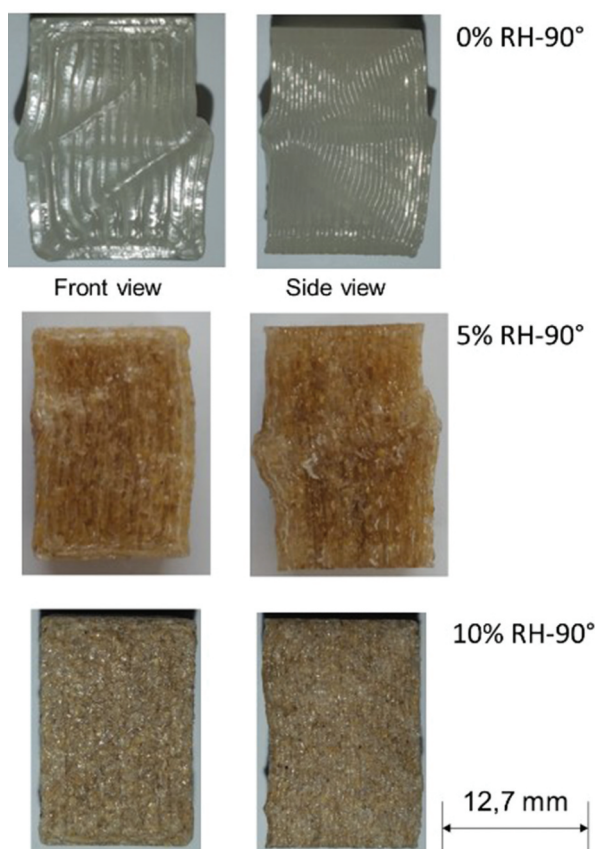


Figure 7. Compressed specimens.

3.5. Thermal stability of filaments and RH fibers

TGA (Figure 5a) shows four relevant intervals where different stages of thermal degradation occur for the filaments and alkali-treated RH. The range until 100°C shows some weight loss for the alkali-treated RH, possibly due to the evaporation of moisture present in these samples, corroborating the findings from FTIR spectroscopy. Between 180°C and 250°C, there is also some weight loss for the treated RH. However, it is between 250°C and 400°C that all analyzed samples, RH, neat PLA, and composite filaments exhibit a drastic weight loss, corresponding to a strong thermal degradation. The DTG graphs (Figure 5b) also show intense peaks for all tested materials in this temperature range. Although neat PLA filaments are the ones with higher degradation temperature (363°C), the residual weight at 600°C clearly increases with the content of RH in the RH filled PLA composite filaments, which might be due to the presence of residues from the RH particles. Indeed, the DTG shows a weak peak for the RH, and it is also noticeable in the TGA thermogram that RH still has 30% of residual weight above the 400°C when compared with the filaments. These results clearly reveal the presence of RH within the PLA matrix of the composites, and their remaining after thermal degradation of the PLA matrix, providing higher thermal resistance to the composites above 400°C.

3.6. Mechanical properties

Tensile tests (Table 2) revealed that adding RH fibers to PLA negatively affected the tensile strength of the printed parts. Figure 6a shows the typical tensile stress-strain curves. It was observed that the neat

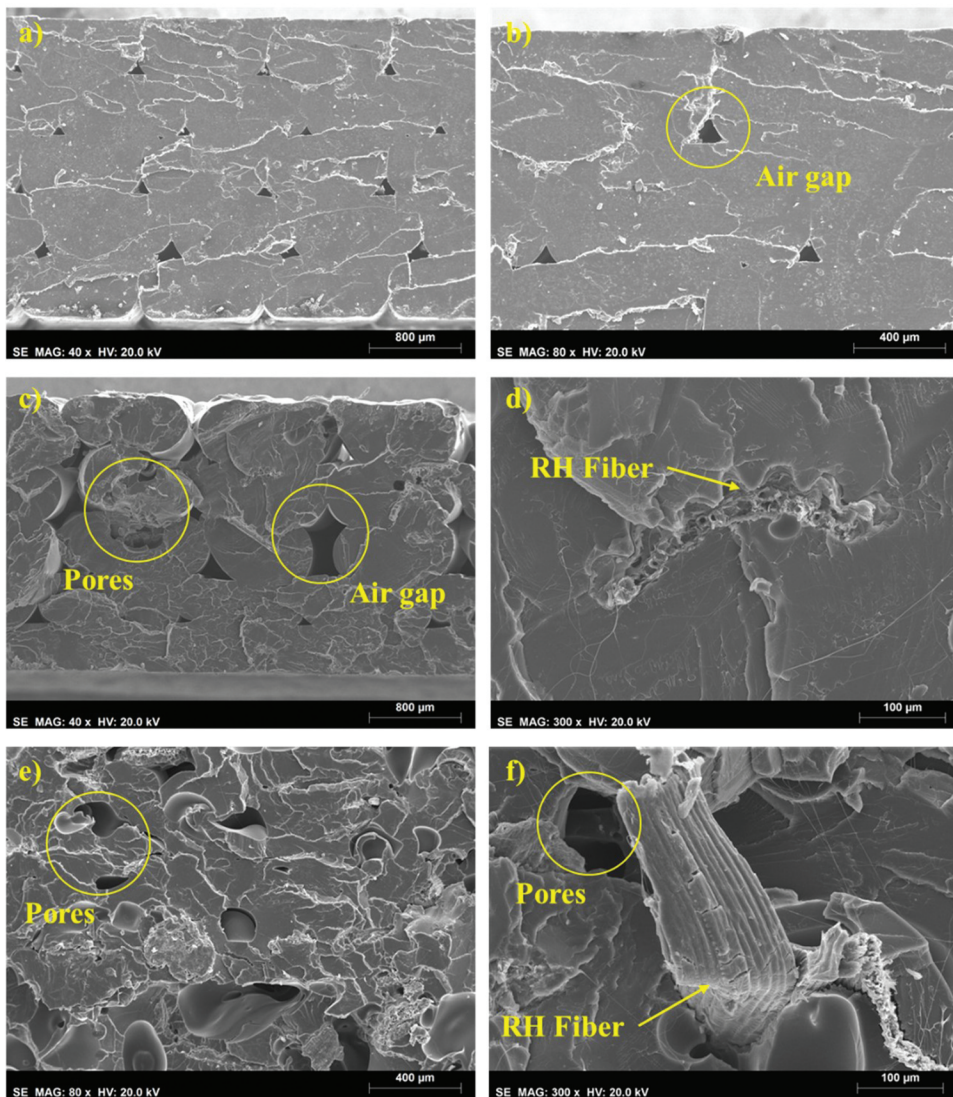


Figure 8. Tensile tested fracture surfaces SEM images of the printed parts for: a) 0% RH; b) Detail from 0% RH; c) 5% RH; d) Detail from 5% RH; e) 10% RH; f) Detail from 10% RH.

PLA shows a higher mechanical performance than the composite specimens. Neat PLA also has a larger elongation at fracture and a higher Young's modulus ($p < .05$).

Results from the mechanical behavior of printed parts under compressive forces are presented in [Table 2](#). The neat PLA led to the highest yield stress and Young's modulus values ($p < .05$), showing that adding fibers to filaments does not improve the compressive strength. Typical compressive stress-strain curves ([Figure 6b](#)) show two distinct behaviors. Both 0% RH and 5% RH showed failure due to shear stress, showing sliding planes at 45° ([Figure 7](#)). The 10% RH specimens ([Figure 7](#)) suffered plastic deformation after yielding without structural failure.

The flexural test results are depicted in [Table 2](#). The results revealed that the presence of RH does not improve the flexural strength of the printed parts. The 5% RH and 10% RH had almost the same maximum flexural strength ($p = .62$), but the flexural modulus for the 10% RH was higher than for the 5% RH ($p = .02$).

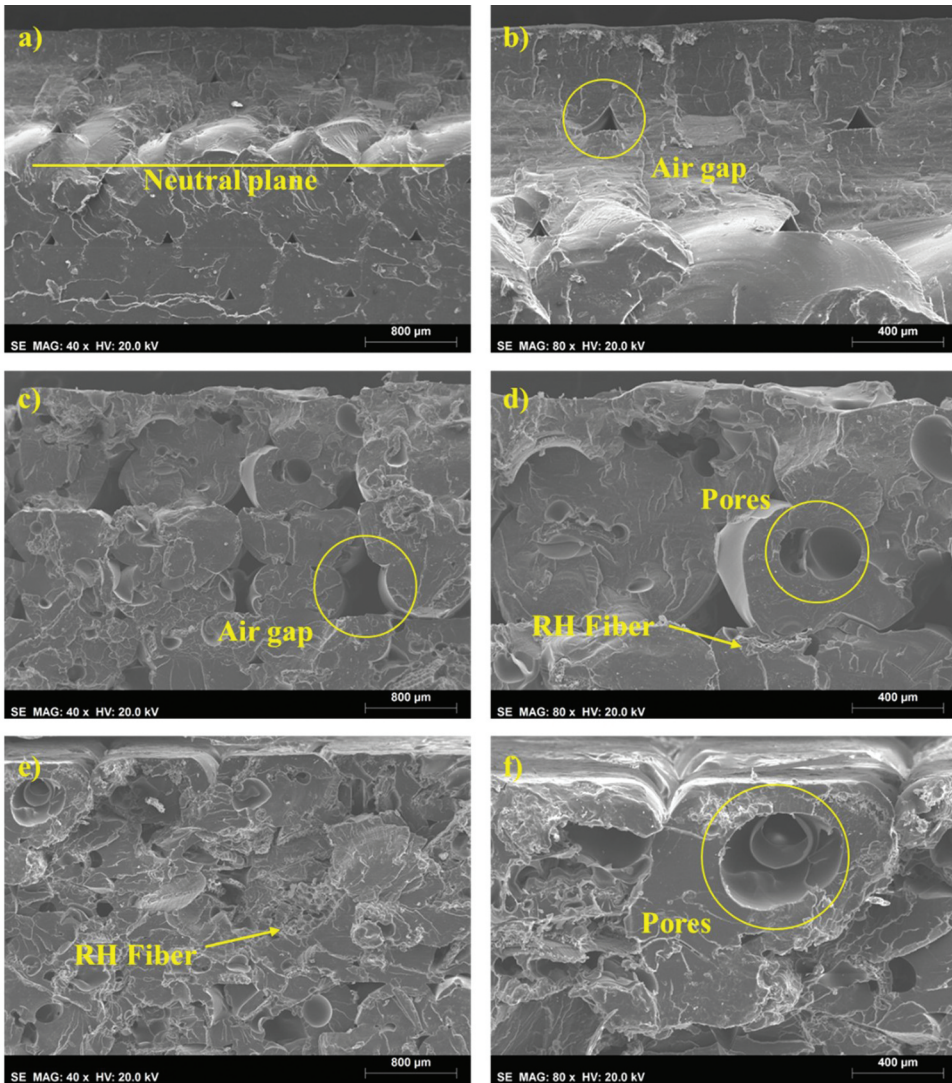


Figure 9. Flexural tested fracture surfaces SEM images of the printed parts for: a) 0% RH; b) Detail from 0%; c) 5% RH; d) Detail from 5% RH; e) 10% RH; f) Detail from 10% RH.

3.7. Sem images of fractured surfaces

SEM images of tensile test fractured surfaces (Figure 8) show different textures for each blend. 0% RH specimen has visible air gaps between layers with no detectable porosities at the scale of the images (Figure 8b). Composite specimens reveal an increased porosity along with the increase of fiber content (Figures 8c and 8e) and uneven air gaps between layers for both blends. The PLA matrix still has a brittle fracture texture and random fractured RH fibers are detectable on the fractured surface of 5% RH and 10% RH specimens (Figures 8d and 8f). Furthermore, RH fibers show reasonably good adhesion to the matrix. The SEM image of Figure 9a shows the distinct texture of a fracture by a flexural load in a 0% RH specimen. Above the neutral plane, the texture is from the compressed side and below from the tensile side. Figures 9a and 9b show intermeshed airgaps between layers for the 0% RH sample. Textures from the 5% RH (Figure 9c; Figure 9d) and 10% RH (Figure 9e; Figure 9f)

fracture surfaces show poor layer adhesion, under extrusion and severe porosities, along with uneven fiber distribution on the matrix.

4. Discussion

4.1. Alkali treatment

Modifications of the RH chemical structure were found to occur with the alkali treatment. Comparing the FTIR spectra of raw and alkali-treated RH (Figure 4), there is evidence of relevant chemical modifications in lignocellulosic fibers. The peaks corresponding to a change in intensity after the alkali-treatment (Table 1) are on the vibrational frequency ranges of OH, C-H, C=O, and C=C groups, which are associated with cellulose, hemicellulose, and lignin components, as well as water absorption (Benítez-Guerrero et al. 2017; Johar, Ahmad, and Dufresne 2012; Kathirselvam et al. 2019; Sepe et al. 2018; Tran, Bénétzet, and Bergeret 2014). The broad peak found at $\approx 3334\text{ cm}^{-1}$ is related to OH bond stretching which is attributed to hydroxyl groups of cellulose, and eventually some moisture present in the material (Balaji and Nagarajan 2017; Kathirselvam et al. 2019; Kim et al. 2018; Long et al. 2019). An increase in this peak's intensity, observed for the alkali-treated RH, may indicate an increase in cellulose fraction after treatment (Kathirselvam et al. 2019). The peaks at $\approx 2920\text{ cm}^{-1}$ and $\approx 2850\text{ cm}^{-1}$ are in the range of C-H bond stretching, characteristic of cellulose, and hemicellulose (Kathirselvam et al. 2019; Kim et al. 2018). Their increase in intensity due to the treatment may express, as well, the cellulose content increase for the treated fibers. A hemicellulose fraction increase, linked to peaks on the $\approx 2920\text{ cm}^{-1}$ and $\approx 2850\text{ cm}^{-1}$ wavenumbers, is unlikely in this analysis. Moreover, several authors referred that peaks on the C-O and C=O stretching wavenumbers are related to hemicellulose (Long et al. 2019; Sepe et al. 2018), namely at $\approx 1710\text{ cm}^{-1}$ (C=O stretching) and a shoulder at $\approx 1250\text{ cm}^{-1}$ (C-O stretching), and these are shown to decrease in intensity (Figure 4). Thus, the hemicellulose fraction may have decreased due to alkali treatment, which is in accordance with what was reported in the studies of Long *et al.* (Long et al. 2019) and Benítez-Guerrero *et al.* (Benítez-Guerrero et al. 2017). Regarding the lignin fraction, evidence for its reduction was found after treatment due to a decrease in the intensity peak at 1524 cm^{-1} . Sanjay *et al.* (Sanjay et al. 2018) attributed this decrease to the presence of aromatic rings in the lignin structure. The lignin content reduction can be complemented by the observations of Tran *et al.* (Tran, Bénétzet, and Bergeret 2014), where the shifting of the broad peak located at $\approx 3334\text{ cm}^{-1}$ toward a higher wavenumber was attributed to lignin fraction variations. Water absorption may have decreased in treated fibers, indicated by the decrease in intensity of the peak located at $\approx 1644\text{ cm}^{-1}$. Some authors correlated hemicellulose in the band at $\approx 1637\text{ cm}^{-1}$ and 1663 cm^{-1} , where the dissolution of hemicellulose can be masked by the assumption of water absorption decrease (Balaji and Nagarajan 2017; Benítez-Guerrero et al. 2017; Johar, Ahmad, and Dufresne 2012; Kathirselvam et al. 2019; Tran, Bénétzet, and Bergeret 2014). Nonetheless, the TGA (Figure 5b) thermogram for the treated RH reveals a loss in weight of $\approx 2\%$ in the temperature interval between 40°C and 100°C , coincident with moisture evaporation.

There is strong evidence that alkali treatment was effective in this work since FTIR analysis suggests that the fraction of cellulose increased and NaOH dissolved some hemicellulose and lignin. Affinity with water absorption may have decreased due to alkali treatment.

4.2. Effect of fibers in filament printability

Filaments with 0%, 5%, and 10% in RH content were printable. However, the 10% RH content filament led to constant nozzle clogging and showed a tendency to fracture while subjected to the feeding process of the extruder. The filaments of 15% and 20% in RH content showed no suitability for 3D printing. Effects of fiber content on 3D printing were evident and could be related to the heterogeneity of the filaments and poor distribution of fibers in the matrix. The increment of fiber content increased the filament diameter and roundness variation. Xiao *et al.* (Xiao et al. 2019) also identified

inconsistencies in filament diameter and roundness as potential causes of nozzle clogging. Kariz *et al.* (Kariz *et al.* 2018) reached the same conclusion: in a study with wood particles and PLA, they found that nozzle clogging was attributed to filament diameter variations and blends with higher content of wood particles. Since the printable filament blends used in the present work had their density values (Figure 2a) almost unaffected by the fiber content, there is no significant correlation between filament density and nozzle clogging. The same results on filament density were obtained by Kariz *et al.* (Kariz *et al.* 2018), where the density of wood/PLA filaments remained with low variation for fiber contents of 0%, 10%, and 20%. The density of RH filaments was most affected by fiber contents of 15% and 20%. Considering that those were the unprintable filaments, density values can be correlated with the lack of stiffness obtained in these filaments and further unstable behavior for a proper feeding process of the extruder.

The thermal stability of the neat PLA was affected by the fiber content. Analyzing the DTG peaks (Figure 5b), 0% RH filament had a maximum mass loss rate at $\approx 363^{\circ}\text{C}$, followed by the 5% RH ($\approx 346^{\circ}\text{C}$), 15% RH ($\approx 343^{\circ}\text{C}$), 20% RH ($\approx 340^{\circ}\text{C}$), and 10% RH ($\approx 330^{\circ}\text{C}$). The 10% RH showed a higher mass-loss rate than the 15% RH and 20% RH, which is probably related to the poor or heterogeneous fiber distribution within the matrix. The percentage of the residual weight with temperature increase (TGA thermogram from Figure 5a) was higher for the 0% RH until $\approx 375^{\circ}\text{C}$, and at higher temperatures the composite filaments kept a higher residual weight. This fact was reported by Kathirselvam *et al.* (2019): the higher residual weight of composite materials was attributed to waxes and some lignin portions in the fibers, which have a final thermal degradation stage between 280°C and 500°C or the composite filaments, the primary weight loss started at $\approx 250^{\circ}\text{C}$ and for the neat PLA filament at $\approx 290^{\circ}\text{C}$. By comparing these temperatures with the treated RH thermal degradation profile, where a weight-loss stage was verified between 180°C and 250°C (hemicelluloses decomposition (Morales *et al.* 2021)), there is evidence that fibers were more thermally stable within the PLA matrix. Regarding the chemical bonding between the treated RH and PLA, Tran, Bénézet, and Bergeret (2014) reported that a good chemical bonding between RH and the PLA matrix affects the thermal degradation temperature of the fibers. Moreover, in their study, the maximum mass loss rate (DTG) peak determined for alkali-treated RH was at 336°C , the same value obtained in this work. However, it is not clear, from the FTIR spectra, that chemical bonding has occurred between fibers and the PLA matrix.

The composite printable filaments (5% RH and 10% RH) and their primary weight-loss stage temperature ($\approx 250^{\circ}\text{C}$) indicated that alkali-treated RH is suitable for use as a filler in polymeric matrices, at operating temperatures of less than 250°C , without significant thermal degradation. Considering that in this work, the nozzle temperature used was 220°C , filaments were processed at a safe temperature concerning the thermal degradation of fibers.

4.3. Properties of 3D printed parts

4.3.1. Density and water absorption

The density of composite-printed samples (Figure 2b) revealed a significant decrease compared to the filaments (Figure 2a). The 5% RH and 10% RH printed samples showed a density decrease of 15% and 19%, respectively. Since raw fibers have a higher density ($\approx 1.6\text{ g/cm}^3$) than PLA ($\approx 1.24\text{ g/cm}^3$), printing defects might be the primary cause of the density decrease. Most printing defects were under extrusion (Figure 8c) and pores with spherical and elliptical shape (Figure 8f). The under extrusion defects are strongly related to filament diameter variation, which is in agreement with Kariz *et al.* (2018) and Xiao *et al.* (2019). Pores are related to water vapor released from the fibers when printing at 220°C , which was observed by Balla *et al.* (2020) and Hachem *et al.* (2019).

The water absorption and density of printed parts were negatively affected by adding RH fibers to PLA. Water absorption (Figure 3) was higher for the 5% RH than for the 10% RH samples, which may relate to the uneven fiber distribution along the filament and thus, on the printed part. Furthermore, printing defects inside the part may have contributed to voids that were additional spaces for water.

Thus, although the results indicate that the composites had higher water absorption than neat PLA, the differences between water absorption on the 5% RH and 10% RH can be related to printing defects.

4.3.2. Mechanical properties

The tensile strength values obtained for the 0% RH specimens (57 MPa) and Young's modulus (3.33 GPa) were similar to the ones reported by Kariz et al. (2018). These authors obtained a tensile strength of 55 MPa and a Young's modulus of 3.27 GPa for printed parts with a very similar PLA grade (IngeoTM 2003D) to the one used in this work. The composite samples had a decrease of tensile strength, elongation at break and Young's modulus. This decrease is associated with the under extrusion and pore defects. A decrease in the tensile mechanical properties was also reported in several works using polymer-based materials loaded with rice husk (Morales et al. 2021; Tsou et al. 2019), wood (Guo et al. 2018; Yubo et al. 2017), cork (Daver et al. 2018), bamboo fiber (Long et al. 2019) and Kraft pine lignin (Eleni, Koumoulos, and Charitidis 2017). The brittleness added due to fiber content was also reported by Xiao et al. (2019). For compressive tests, results showed that the fiber content negatively affects the yield stress and compressive modulus. The 5%vRH printed samples presented a failure behavior that is in agreement with results from Mazzanti, Malagutti, and Mollica (2019), where buckling of layers is the primary mechanism of part failure. Flexural tests showed no enhancement of mechanical properties on bending by adding fibers. The high number of pores and under extrusion issues on the composite samples visible in SEM images of Figure 9 were the primary causes of mechanical strength decrease under bending of composite parts.

5. Conclusions

The objective of this work was to incorporate different amounts (0%, 5%, 10%, 15%, and 20% wt.%) of rice husk (RH), a waste agriculture product, into a PLA 3D filament. The thermal behavior of filaments and the chemical effects of alkali treatment on the fibers were studied. Printability tests were carried out, and the printable filaments were used to produce samples by FDM, which were then subjected to mechanical characterization (tensile, compressive, and flexural tests). This study allowed concluding that the alkali treatment changed the chemical structure of RH fibers, showing that hemicellulose and lignin content of fibers decreased. TGA results showed that the obtained filaments can be used in FDM under operating temperatures of 250°C, without significant thermal degradation. The maximum amount that could be introduced into the PLA filament was 20% RH. However, it is impossible to produce samples by FDM with filaments containing loads higher than 10% RH. The best printability was achieved for filaments with 5% RH, showing no nozzle clogging or fractures during the 3D printing process. It was observed that the quality of printed parts in terms of mechanical strength and density were severely affected by the filament diameter variation, leading to under extrusion defects. Overall, RH fibers can be successfully used as a filler in PLA. In addition, it offers an alternative for 3D printing filament that can be used for prototype manufacturing and development of several types of products where adequate esthetics is one of the main requirements (e.g., furniture, decor market).

Highlights

- *The addition of rice husk fiber leads to a reduction of the mechanical properties.*
- *Rice husk fiber alkali treatment results in reduction of hemicellulose and lignin content.*
- *Rice husk filled PLA filaments for additive manufacturing were obtained with fiber amounts between 5 and 20 wt.*

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