



A New Preparation Method for 3D Bio-composite Filament Manufacturing: a Study on the Effects of Ball Milling on the Cohesion/Adhesion of an Agave tequilana Bagasse/PLA Pellet Mixture

Mathias Salignon¹ · Simon Gray² · Timothy Rose² · Adriana Encinas-Oropesa¹ 

Received: 22 March 2022 / Accepted: 28 November 2022 / Published online: 20 December 2022
© The Author(s) 2022

Abstract

This study created a composite polymer for 3D printing from agave by-product using mechanical alloying process. The cold milling technique used by the ball mill is a standard procedure to homogenize metallic mixtures. This paper reports results from a series of laboratory tests to create a homogeneous mixture that could be extruded into a printable filament mixture of agave bagasse fibres and PLA pellets by using the kinetic energy of a ball mill. PLA and agave bagasse mixtures in this study were ground several times using this principle; steel and ceramic balls were used to grind them. The results of the study showed that this principle can be effective on a polymer-based mixture; indeed, an adhesion between the pellets and the agave bagasse fibres was obtained. The results showed the different parameters that influence the mixture quality as the milling time, the ball material, the number of balls, the mixture concentration and the rotational speed. Optical and ESEM/EDX analyses have confirmed our expectations about cohesion between fibres pulverized in powder and pellet adhesion, where powder accumulation on all the surfaces was detected. The absence of powder penetration in the pellets allowed us to explain the losses obtained during the process and to find new solutions to reduce them. Proof-of-concept parts were 3D printed with agave bagasse/PLA filaments. Their printed quality can be compared to that of commercial filaments. These results offer new perspectives to reuse agricultural by-products to create composite filament with a chemical-free manufacturing process.

Keywords Post-harvesting waste · Agave bagasse reuse · Cold milling · Biomaterials · Sustainable additive manufacturing · Circular economy

✉ Adriana Encinas-Oropesa
a.encinas-oropesa@cranfield.ac.uk

¹ School of Water, Environmental and Energy, Cranfield University, Cranfield MK43 0AL, Bedfordshire, UK

² School of Transport, Aerospace and Manufacturing, Cranfield University, Bedford MK43 0AL, Bedfordshire, UK

Introduction

Polymer 3D printing is used to create a large array of parts using materials derived from petroleum such as acrylonitrile butadiene styrene (ABS) or from biological polymers such as polylactic acid (PLA). PLA offers a very good opportunity for development as it is a 100% natural material that is widely used in this industry. However, the challenge of proposing new materials from natural materials for 3D printing is a very interesting gamble because it allows other sectors to be developed, for example, bespoke 3D components and products applicable in aerospace, automotive, healthcare, biomedical, construction, culinary and textile sectors. Furthermore, the use of natural materials for 3D printing has the potential to increase compliance with zero waste and circular economy guidelines in these sectors [1–3].

An abundant plant molecule present in biomass is cellulose [4]. The blending of cellulose with PLA was made possible thanks to the principle of controlled and stabilized emulsion known as “Pickering emulsion”. It consists of introducing some fibre solvent droplets into oil, water and cellulose mixture to make them miscible. The outcome of the study was the creation of a bio-composite filament created from plant molecules that added value to an abundant by-product and is likely to offer better mechanical characteristics [5]. Other studies have been carried out following the same emulsion scheme by chemical process [6], where the emulsion allows the control of porosity in a bi-material after mixing and demonstrated the possibility of printing with a porous material. Currently, research relies on improving the methods for fusing continuous fibres with the composite matrix [7].

The recovery of agricultural waste contributes to guaranty resource efficiency, sustainable production and consumption and the reduction of negative environmental impact [8]. A large body of research has been conducted to reuse and recycle agricultural resources; e.g. coconut shell-clay composite can be used as inexpensive alternative composite for treatment of wastewater contaminated with phenol and 4-notrophenol [9], the application of an isolated fungus to replace chemicals used in detergent industries [10]. The agave-tequilana bagasse originating from Mexico is found in significant quantities as a by-product from the beverages industry. Production of Tequila beverage involves milling of thousands of “cooked” agave plant hearts. This action liberates agave syrup which is then fermented and distilled to make the beverage. The milling process accounts for the majority of this industry’s vastly fibrous by-product, i.e. agave bagasse. It is estimated to exceed 300,000 t annually [11]. New waste regulations, make its effective management an urgent problem for the sector.

To date, possible routes for valorisation and upcycling of agave bagasse have demonstrated the viability and versatility of this by-product. This includes bagasse reuse to produce bio-fuel [12], activated carbons [13], adobes reinforced with agave fibres [14], MDF boards [15], nutraceutical compounds [16], other valuable biochemical compounds [17] and bagasse-based composites [18]. Agave leaves have also been used to obtain fibres by mechanical extraction [19]. More recent studies have demonstrated the potential of using this by-product as a reinforcement in polypropylene automotive composites [20] and in PLA for non-structural automotive components as well as consumer goods [21]. However, fibre compatibility through surface treatments is often used to improve the interfacial bonding, ease the compounding and improve the resulting properties for natural fibre-based composites [22–25].

From the environmental point of view, this work explores the cold grinding of solid compounds using mechanical alloying method (MAM), currently used in the aeronautical industry [26], as an alternative chemical-free filament elaboration process. This study

evaluates whether it is legitimate to think that the MAM ball mill is suitable to obtain a homogeneous mixture with two materials initially immiscible by cold grinding, namely a mixture composed of PLA pellets and Agave bagasse fibres (ABF) to create an industrial quality 3D printing filament with a simple manufacturing process. In terms of social-economic aspect, the ultimate challenge would be to allow the agave based spirit producers to add value to their agave bagasse by-product thus diverting the need for landfill disposal.

The proposed process is following 4 phases, the fibre treatment, the mixture milling in pellets, the extrusion into a filament and the printing tests. Following an empirical approach and a defined protocol, an experimental matrix was developed. Then, samples were prepared following the methodology from Huerta-Cardoso et al. [21]. The experimental protocol was kept evolving throughout the study. This paper reports the obtained experimental protocol. The results of this study lead to the validation of the cold milling efficiency for agave bagasse fibres and PLA. This study proposes a new chemical-free elaboration method of polymeric mixtures for 3D printing, intended for industrialists and researchers to create a new polymer-based composite or improve the existing material results.

Materials and Methods

Fibre Treatment

The agave bagasse fibres (ABF) for this study were used “as received” and chemically untreated. Before using them, they were separated manually in order to have finer fibres without impurities. Subsequently, to facilitate better milling, the finer fibres were chopped to produce fibre lengths of approximately 10 mm as shown in Supplementary Information (S1.1). The fibres were then sieved to remove any impurities. The pure PLA pellets used were Ingeo™ Biopolymer 4043D, from NaturalWorks. To remove humidity inside the pellets and prepare them for the milling process, a Binder ED 23 classic line 20L heating oven was used. The pellets were spread on a sheet of aluminium foil to be dried in the oven for 1 h at 50 °C without ventilation. The strong translucent appearance of the pellets afterwards implied that the humidity had been removed.

Milling Process

Mechanical alloying method consists of rotating balls inside a pot of the same material; these balls possess sufficient energy to weld and fracture the particles of the mixture repeatedly as shown schematically in the Supplementary Information (S1.2). Prior to milling, 6 samples of 3 different mixtures were prepared separately at 10%, 20% and 40% of chopped fibres and dried PLA balanced. The quantities of materials (g) used to produce each mixture are summarized in the Supplementary Information (S1.3). Following the planned materials mixtures, samples were milled following the experimental matrix in Supplementary Information (S1.4). After mixing, the samples were poured into steel or ceramic ball mill pots. Samples were milled at 200 RPM during 4 h, per 1 h cycle. The ball mill used was a Pulverizette 5 planetary ball mill from Fritsch. The time of exposure to air after drying until the pellets are crushed was kept to minimum. At the end of each cycle, the fibres accumulated at the pot-lid joint were pushed down to keep the fibres in touch with the balls during the milling. The parameters investigated to understand the effect of the milling process, were ball number and the ball material. The other criteria relative to the ball

mill were kept constant to simplify the process. Following these criteria, a Chromium Steel ball with a density of 7.8 was used (Comp C) as well as a Zircon Oxide ball (97% ZrO_2) with a density of 5.7 (Comp D). The abrasive properties defined by the manufacturer for these balls were respectively classified as good and very good by the Pulverisette 5 user's manual. The material ball properties are listed in the Supplementary Information (S1.5). Given the experimental results, the number of fibres unmilled was too high for the smallest ceramic balls; that is the reason why these balls were removed from the study (Comp E). The "Pulverizette 5" ball mill user's manual specifies that the mixture should occupy $\frac{2}{3}$ of the volume of the jar. Following this method, $\frac{2}{3}$ of the bowl volume was occupied by the grinding material and the grinding balls while $\frac{1}{3}$ of the bowl volume was free as space to develop the ball inertia during the milling. This process is schematically described in the Supplementary Information (S1.6) (a) and experimentally represented in (S1.6) (b). It is observed in (S1.6) (a) $\frac{2}{3}$ of volume occupation and $\frac{1}{3}$ in picture (S1.6) (b). Once completing full milling cycle, the mixture was removed from the jar to separate the unmilled fibres from the pellet with embedded powder. The finality of this method is to keep the mixture where the adhesion fibres/pellet is a success. A mass measuring was made for each sample to quantify the mixture loss that did not penetrate the pellets. The visual aspect in the Supplementary Information (S1.6) (b) shows the mixture proceeded with steel ball after 2 h of grinding. The unground fibres of each sample were compared to assess the effect of the material milling balls. Thus, the objective of having pulverized fibres was achieved for both mixtures. It was observed that less ground fibres and less aggressive pellets were removed for mixture milled with ceramic milling balls. The milling steps described previously were executed in a logical order, the steps and the methods kept evolving to improve the results. Figure 1 is the proposed milling method final version.

Extrusion into a Filament

The filament extrusion phase was carried out by pre-heating the Noztek pro extruder for 1 h before extruding a given mixture, to avoid the PLA glass transition during extrusion. The PLA glass transition is close to the extrusion temperature defined in the protocol to extrude the filament, which is 150 °C, thus, keep heating the nozzle before using is necessary to be sure that the nozzle has reached the 180 °C. When the temperature was completely settled after 1 h, the cooling system as well as the extruder screw was turned on. A test with the pure PLA and constant settings were realized to check the filament quality. The starting temperature for the tests was set at 180 °C regarding the Ingeo technical documentation supplied. This temperature was adapted according to the different mixtures tested to obtain a correct viscosity. A constant rotational speed for the winder was used during extrusion which is an automatic system to wind the filament directly on a spool. This system applies no extra tensile on the filament produced and controls the filament diameter by compressing the filament between two wheels to keep the right diameter. The extrusion temperature for all tests was kept in the range of 175–185 °C. The winder speed was set from 24 to 36 tr/s. The extrusion steps described previously were executed in a logical order as well as the milling process, the steps and the methods were kept evolving to improve the results. Figure 2 is the final version.

Thanks to a rotational speed and a temperature properly controlled, a final spool for the proof of concept was extruded. The filament spool shown in the Supplementary Information (S1.7) was obtained by following the protocol. Other spools were produced following the concentrations on the experimental matrix (S1.4) from 10% ceramic and steel grinding to 20% ceramic and steel grinding.

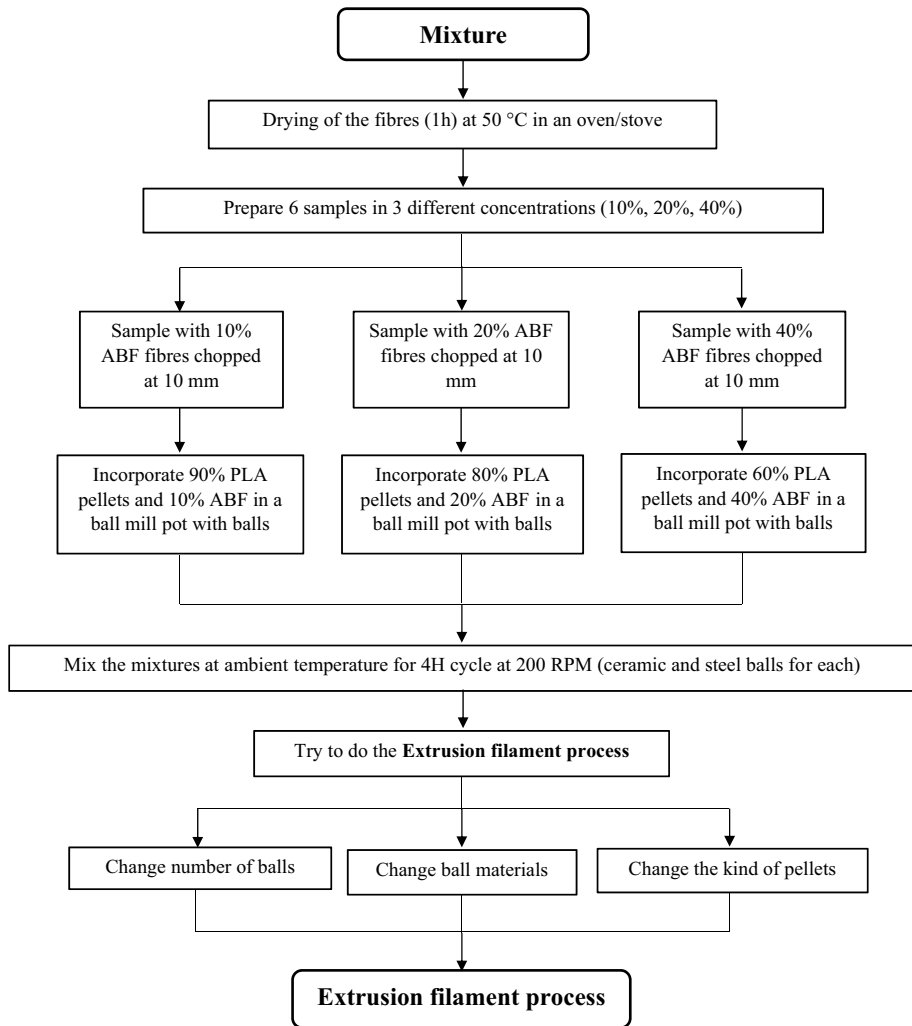


Fig. 1 Mixture milling in pellets final protocol

Results and Discussion

Effect of the Milling Process

The samples A-1, A-2, C-5 and C-6 have been discarded because they did not provide more visual information, but they appear in the results. Samples B-3 and B-4 were metallographically prepared and observed with a digital microscope VHX-6000e. Further examinations were carried out using standard analytical techniques such as an optical and ESEM microscopy. All samples were processed in the ball mill according to the protocols from Fig. 1 and Fig. 2 and the experimental matrix (S1.4). The damage mechanism of the pellets can be seen at first sight in sample cross-sections showed in the Supplementary Information (S2.1). The white areas appear to be cracks in picture (a), which break the pellets. These

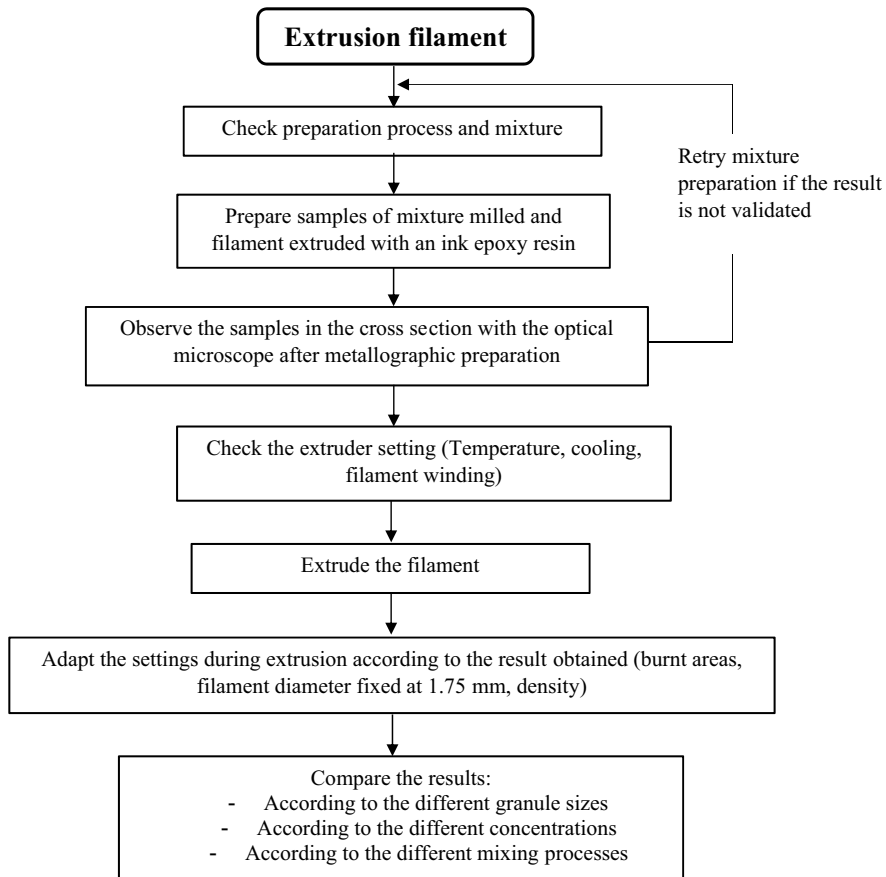


Fig. 2 Extrusion into a filament final protocol

cracks show the aggressiveness of the steel balls on the PLA. The result on the picture (b) where the PLA pellets do not seem to be damaged can be compared with the picture (a), no cracks are displayed on the picture (b). Furthermore, the pellets shape with the steel balls seems to be more irregular than with the ceramic balls probably because the force exerted by the steel balls on the pellets surface is greater than the allowable yield strength of the PLA. Agave bagasse particles are observed in number on the surfaces of the PLA pellets in S2.1 picture (a) and (b). It seems that the pellets in picture (b) contain a bigger quantity of ABF particles. It could suppose that the ball setting was better for the fibre's penetration. Accumulations of fibres can be seen in places, but it is not possible to assess their adhesion and penetration with the PLA or the size of these particles. It is supposed that the adhesion between the fibres and the PLA matrix is a way to evaluate the efficiency of mechanical grinding. To quantify the size of the particles, the method of Feret's diameter was used during the measurement with the digital microscope VHX-6000. Feret's diameter is a measurement method used in particle sizing to accurately determine the size of imperfect, non-spherical or randomly shaped particles. It seems that the size of the pellets has not changed much as shown by Feret's diameters summarized in the Supplementary Information (S2.2). The pictures in S2.1 confirmed this hypothesis as well. Indeed, Feret's diameters for the samples B-3 and B-4 are almost similar to the pure PLA values, around

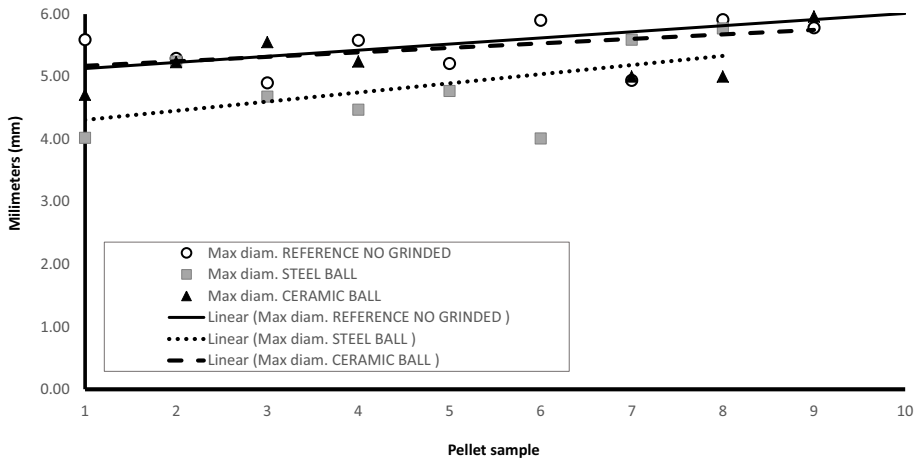


Fig. 3 Maximum Feret's diameter measurement on samples B-3 and B-4 and pure PLA at $\times 150$ magnification with the digital microscope VHX 6000

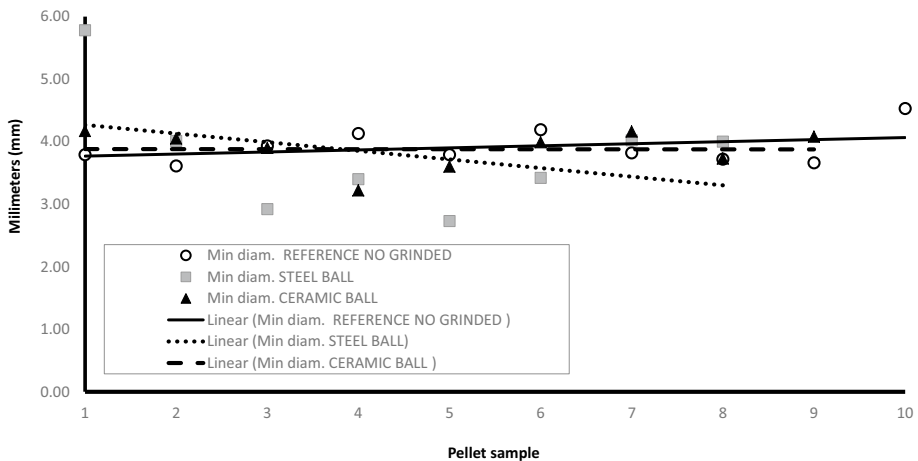


Fig. 4 Minimum Feret's diameter measurement on samples B-3 and B-4 and pure PLA at $\times 150$ magnification with the digital microscope VHX 6000

4.36 mm and 4.22 mm for the pure PLA, 3.96 mm and 4.23 mm for the sample B-3, and 4.46 mm and 4.13 mm for the sample B-4. Thus, Feret's diameters of the PLA pellets are close to the ground pellet samples B-3 and B-4 so the milling does not appear to have had much effect on pellet size. Another indicator of the milling ball materials effects, i.e. steel vs. ceramic, is depicted as distributions in Fig. 3 and Fig. 4 from 10 samples.

It appears that in Fig. 3, steel grinding causes the most damage to the pellets after ceramic grinding. This is also the case in Fig. 4, where steel grinding is the most aggressive procedure, producing small pellet sizes. Another observation made is that ceramic grinding does not deteriorate the pellets if we compare the trend curve of the unground reference PLA pellet with those of ceramic grinding in Fig. 3. This observation confirms the assumption made in S2.1 (a) and (b) where the pellets by ceramic grinding were visibly not cracked in contrast

to steel grinding. It is believed that this effect is due to the lower density of ceramic balls that may result in a grind that releases less energy. Clear non-processed PLA pellets size is 4.36 mm and 4.22 mm, which is approximately 0.1 mm more than the B-3 and B-4 samples values. Moreover, the pellets surface states for B-3 and B-4 samples in Fig. 4 were significantly affected by the milling balls density during the grinding in comparison with clear PLA pellets that are consistently circular and smooth. This shows that the milling ball material and density has an important role on the grinding process. This pellet study in the effect of the milling process section aimed to identify the effect of the ball mill on the pellets and understand what this implies for the adhesion and cohesion of the fibres and ultimately, the quality of the resulted mixture. Therefore, next section aims to know whether the cracks or the surface condition obtained by milling help the ABF to adhere to the main PLA matrix.

Effect of the Milling Process in ABF/PLA Particle Cohesion/Adhesion

Previous studies on fabricating material pieces from natural waste-fibres in PLA, have demonstrated that this mixture can be processed without decreasing the clear PLA mechanical properties via extrusion up to concentrations of 40% [21, 22] and via 3D printing up to 20% [2]. This background set the parameters to systematically explore 3D printing using the agave bagasse. In this study, the agave bagasse particles after extrusion presented imperfections inside the produced filaments; these impurities are thought to potentially cause a quality issue when the filament is used to print. The Supplementary Information (S2.3) shows a cross-section comparison of the lab-scale produced filaments (a) sample B-3 vs. (b) sample B-4. Both shows a longitudinal distribution of agave bagasse visible as brown dots. However, brown dots are less present in sample B-3, filament created from steel milling material (a) whereas, the filaments in B-4, ceramic milling materials, (b) seems to contain more agave bagasse particles. The distribution of these dots is homogeneous but there are sometimes irregularities. These results do not allow to say whether this is a piece of fibre or burnt spots during extrusion. This is attributed to insufficient grinding of the fibres when using ceramic milling materials, corroborating the effectiveness of the steel milling materials observed in S2.3 (a), or perhaps too high temperature is involved during the extrusion process. Therefore, further studies need to be carried out to determine whether these irregularities are pieces of fibres or burn spots during the extrusion process and their effect in the 3D printed pieces microstructure and performance.

Generally, a ball mill is used for grinding mixtures composed of powders. In this study, the mixture is composed of powder with solid elements (the pellets) with the purpose of promoting adhesion between agave bagasse particles and PLA pellets. Once the milling was completed, all the powder particles not fully adhered to the pellets were considered a loss for the time being. This is because is not recommended to extrude with a mixture composed of powder without adhesion with pellets. A summary of the unmilled fibres per sample is presented in the Supplementary Information (S2.2). Significant losses were obtained, which are in the order from 9 to 42%, it is supposed that the concentrations at the end are much lower. Even with the mass of the fibres unmilled, estimate the agave bagasse concentration in the PLA pellets after sieving was not possible because the unmilled mixture is also composed of PLA powder which result in pellet damaged. By using the optical analysis, it has been possible to evaluate the real concentration inside the filament because it is a manner to evaluate the efficiency and the durability of the mechanical alloying process for a polymer application [27]. The real concentration of each sample before using the optical microscope was unknown due to the loss after sieving. Therefore, the Keyence VHX software (microscope measurement

software) was used to define the quantity of agave particles. This software detects automatically brown spots that have been identified during the ESEM analysis to be agave fibres. The method used by the software is to differentiate dark spots from lighter ones or vice versa. Once the software has detected the right area, it colours the shape in red. Figure 5 shows how the software recognizes the brown shapes which are the pellets and how the software detects the agave bagasse particles in the filament following the same methods.

The Feret diameter results for the pellet are summarized in S2.2. The method (a) in Fig. 5 was used to recognize the pellet shape. The agave bagasse content for the sample is in S2.2 as well. The method (b) in Fig. 5 was used to detect the content and the grain size. To observe the agave bagasse particle distribution, two filament orientations were tested. As observed in Fig. 5 picture (b), the samples prepared in the length direction were useful to know the grain size but inaccurate to measure the agave bagasse volumetric content. The other method consisted of cutting the filament in the cross-section. This orientation has been useful to know the grain size as well and especially the agave content. The fact is that it is easy to calculate the cross-section diameter of the filament, so the entire filament area. And comparing to the length direction method, the entire filament area was not precisely determined unlike the cross-section expressed as:

$$\text{Entire filament area (In the cross section)} = \pi \frac{\text{Filament diameter}^2}{4}$$

Knowing that the average is 1.75 mm for the filament diameter, the entire cross-section is 2.4 mm².

Then, the area ratio/real concentration is expressed as:

$$\text{Agave content \%} = \frac{\text{Fibres area filament (mm}^2\text{)}}{\text{Entire filament area (mm}^2\text{)}} \times 100$$

These data have allowed the calculation of the porosity content of the material expressed as:

$$V_p = 1 - V_f - V_m$$

This value is between 0 and 100% and defines the number of voids/pores inside the samples and gives information on the sample's flow. The results are displayed in Table 1.

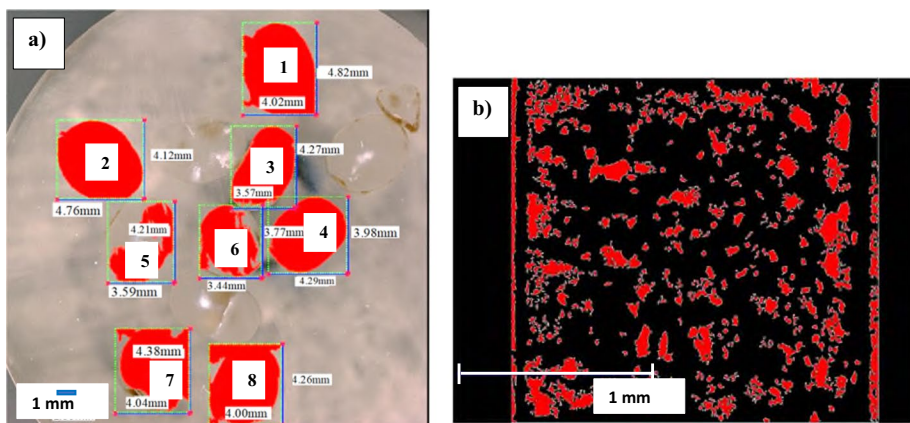


Fig. 5 Sample cross-sections on **a** Feret's diameter principle applied on the pellets and **b** agave bagasse particle distribution applied on a filament

All the data in Table 1 was calculated by using the values per sample summarized in the Supplementary Information S2.4.

All samples were metallographically prepared and examined with a digital microscope VHX-6000. Samples mounted with ink-resin were the ones that gave the most realistic results for the real concentration, which are 8% and 13% for samples 3 and 4 instead of 20%, according to Table 1. Of course, the concentration without loss would be a desirable 20% bagasse adhesion to PLA, increase surface hydrophilicity without posing a risk on processability and mechanical properties of clear PLA. Surface hydrophilicity may promote biodegradability of the material at the end-of-life stage [2, 21]. The results are well defined for a future progression by considering the new process losses. The theoretical porosity content is typically range from less than 0.5% for solid granite to more than 50% for peat and clay. According to Table 1, we obtained respectively 8.8% and 11.49% by supposing a homogenous section. This means that the filament flow will be a little bit disturbed if the filament is melted. The porosity content calculation (V_p) was determined by using the PLA content (V_m) and fibre content (V_f).

Nevertheless, the samples C-5 and C-6 with the higher concentration did not present any fibres on the surface, as well as for the samples 1 and 2. A conclusive outcome was expected but the results did not provide any information which suppose neither the sample was not representative nor the concentration was too high. As show in Table 1 as well, the average length agave bagasse fibres were 604.41–639.9 μm inside the filament extruded with 20% agave content. A different result was observed by changing the agave content at 10%, the average length of agave fibres was now 312.53–226.59 μm . Reducing the size of the pellet or changing their shape would improve the final concentration. This hypothesis could not be verified during this study. The authors recommend investigating this hypothesis as immediate next step to forward the understanding of mechanical recycling for agricultural wastes for the additive manufacturing sector. The penetration of fibres into the pellets is not possible as shown in Supplementary Information S2.1 photographs. Therefore, the assumption of reducing the size of the pellets will decrease the losses and improve the concentration. The grain size measurements were made according to the JIS-G0551, ISO-643 and ASTM-E1382 standards. The principle of the measurement is to identify the agave bagasse particles as known geometric shapes such as circles, lines and diagonals. This gives us the orientation of the particles/fibres and the predominant shapes (Supplementary Information S2.5). Average line segment length is given by the particle length value divided by the number of captured grains. In Fig. 6 and Fig. 7, most of the shapes are circles that are supposedly an efficient milling process where the fibres are totally milled in powder. The fibres not totally milled are still there with the line shapes detected who suppose fibres. The hypothesis of changing the ball material between steel and ceramic makes a difference. Indeed, Fig. 7, the number of grains is more important for the milling with steel balls than the milling with ceramic balls, it shows that the steel balls are more efficient in terms of penetration for a polymer application. The random and multidirectional orientation of the agave fibres inside the filament was graphically confirmed in the cross-sections showed in the Supplementary Information S2.6. This fact is confirmed with the grain size (Fig. 6 and Fig. 7) as well where a variety of different shapes exist. A hypothesis was submitted which is the circle shapes are potentially fibres oriented perpendicular to the surface observed by the microscope; thus, it might be not powder but fibres. This hypothesis brings interesting information. It is anticipated that the mechanical performance of the filament may be influenced by these distributions. Researchers must remain vigilant when assessing mechanical properties.

The ball mass is a determining factor in the fibre's penetration, kinetic energy for a ball depends directly on its mass and the rotational speed of the planetary ball mill [28]:

Table 1 Extrusion characterization

Sample no	Test no	Vert. Feret diameter (mm)	Hor. Feret diameter (mm)	Grain size (µm)	Number of grain	Fibres area/ filament (mm ²)	Area ratio/real concentration	Real mass con- centration (g)	Theoreti- cal porosity content	Hours 4 h
A	1	0.11	0.06	312.53	-	-	-	-	-	●
	2	0.08	0.06	226.59	-	-	-	-	-	●
B	3	0.10	0.07	604.41	20.70	0.32	13.10%	9.82	8.80%	●
	4	0.09	0.09	639.90	19.00	0.20	8.21%	6.16	11.49%	●
C	5	-	-	-	-	-	-	-	-	●
	6	-	-	-	-	-	-	-	-	●

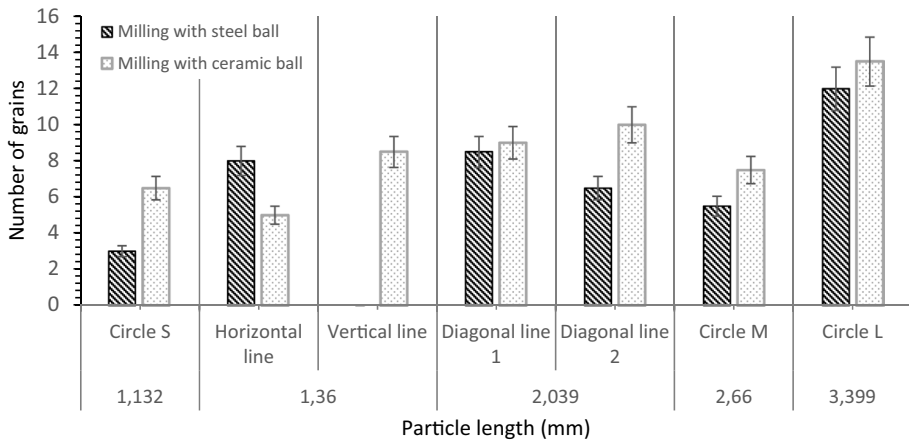


Fig. 6 Agave fibre grain size — 10% ABF

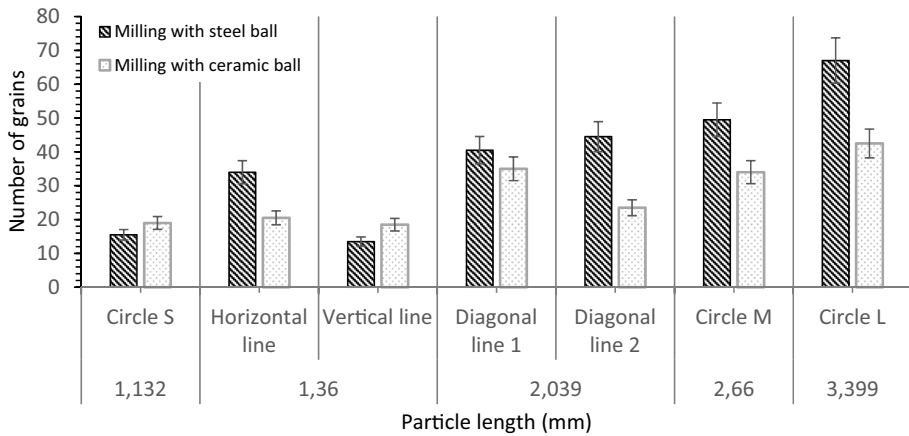


Fig. 7 Agave fibre grain size — 20% ABF

$$Vc^2 = (R\Omega)^2 + (r - r_b)^2 \omega^2 \left(1 + \frac{2\omega}{\Omega}\right) \quad (1)$$

$$\gamma_c^2 = (R\Omega)^2 + [(r - r_b)\omega]^2 \quad (2)$$

$$E_k = \frac{1}{2} m Vc^2 \quad (3)$$

$$E_t = \frac{N_b E_k t}{W_p} \quad (4)$$

Equation 1 is the ball mill velocity (m/s); Eq. 2 is the acceleration of the ball (m/s²); Eq. 3 is the kinetic energy of the ball (J); Eq. 4 is the total kinetic energy in a pot (J/g).

These ball velocity and acceleration for a planetary ball mill have been determined by Abdellaoui and Gaffet [29]. The same equations have been used by Gheisari et al. [30] to quantify the kinetic energy inside a ball mill. The total energy considering the milling time and the number of ball have been expressed by Dastanpoor and Enayati [31]. Following Eqs. 1, 2, 3 and 4, the kinetic energy inside a pot has been determined according to the different rotational speeds for our planetary ball mill. These calculations results are summarized in Table 2.

Further ESEM examinations provided information about the chemical composition in each sample. PLA with the chemical formula $C_3H_4O_2$ is the main component of this mixture. The agave bagasse fibres are composed of 15.9% lignin and 64.8% α -cellulose in the majority [22], which are organic elements.

The most interesting part is that calcium and silicon elements were detected as elements which works together to form a lot of accumulation on the pellet boundaries, visible in Fig. 8 pictures (a) and (c). The accumulations of powder on the boundaries supposed a cohesion between the calcium, the silicon and the PLA. Silicon is not present in the 10% sample and in the pure PLA pellet pictures (a) and (b) displayed in the Supplementary Information S2.7, which means that the silicon is present when there are several agave particles. Indeed, silicon is part of the Agave composition thus we can exclude the hypothesis of an experimental perturbation. This hypothesis has been confirmed by Mondragón et al. [32].

As well as calcium is present when there are agave bagasse accumulations as in the picture (c). The most interesting part of this ESEM analysis is in picture (a) and (c) where the silicon and the oxygen are present exactly on the same location around the pellet's boundaries. It suggests traces of silicon dioxide SiO_2 specific to plant fibres, so the agave particles are identified on the boundaries as first element. Furthermore, it seems that the silicon is deposited on the PLA boundaries first as shown in Fig. 8 in picture (c) with the silicon. This observation is confirmed as well with the picture (a). Then, the calcium is adhered to the silicon as shown in the picture (a) and picture (c).

Therefore, the accumulation of agave bagasse is formed by layers of the silicon and the calcium contained inside the fibres and the silicon participates in the adhesion of calcium. After the extrusion, the filament contained visible particles in the pictures (b) and (d) where there are the same elements than in the agave particles accumulations. In this way, agave particles in the filament were identified. In this case, the Carbon element in the filaments (c) and (d) is not the predominate component so it is supposed that the extrusion

Table 2 Grinding energy for a planetary ball mill with a polymer mixture

	Rotational speed Disk RPM (Ω)/ pot RPM (ω)	Ball velocity (m/s)	Acceleration of the ball (m/s^2)	Kinetic energy of the ball (J)	Total energy in the pot (J/g)
Steel	50/107.5	0.1399	0.1610	0.0011	0.64
	100/215	0.2798	2.5761	0.0045	2.57
	150/322.5	0.4198	13.0417	0.0100	5.79
	200/430	0.5597	41.2182	0.0179	10.29
Ceramic	50/107.5	0.1427	0.1610	0.0007	0.28
	100/215	0.2854	2.5761	0.0029	1.13
	150/322.5	0.4281	13.0417	0.0066	2.54
	200/430	0.5708	41.2182	0.0118	4.52

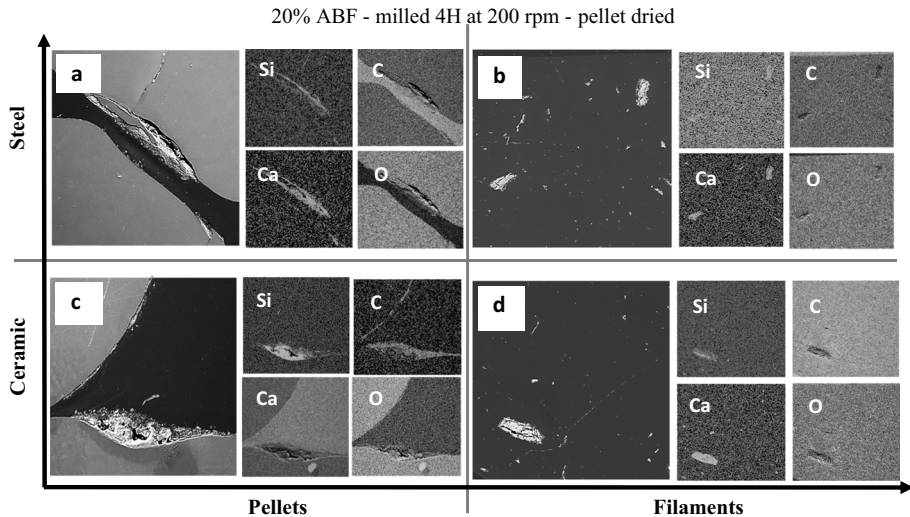


Fig. 8 Back scattered images and EDX- mapping for sample B-3 (steel milling balls) and B-4 (ceramic milling balls) pellets (a) and (c) and filaments (b) and (d)

temperature did not burn a lot of the agave fibre. Furthermore, the melting points of silicon and calcium are respectively 1400 °C and 840 °C so these chemical elements cannot burn during the extrusion process.

Screening Environmental Impact of the Ball Mill Process

Electricity consumption for the ball mill process used in this study was expressed as 12.7 kW/h as a maximum in the energy consumption list showed in the Supplementary Information S2.8. It shows the high level of energy-consuming of the mechanical alloying process by using a ball mill. Another energy consumption was conducted by Rajaonarivony et al. [28]. This milling solution is efficient to create a mixture with agave bagasse and PLA but energy consumption should be considered for a large application scale. For example, other model with less energy consuming processes in the grinding part might contribute more to the overall sustainability of the process. The ball mill energy consumption calculated for this study is approximately 12.7 kW/h for a completed grinding of 4 h. We can compare the consumption of the ball mill to a washing machine which consumes on average 1 kW/h. The ball mill process consumes three times more than a washing machine. Nevertheless, a complete cycle, optimized with the maximum number of samples that can be crushed in one cycle, the process produces up to 300 g of mixture, which is the equivalent of one full spool of commercial 3D filament (usually sold in 250-g spools), by also considering the loss we can have during the manufacturing process.

Return on Investment and Energy Consumption of the Extrusion's Equipment by Considering the Advantages of FDM 3D Printing

Extruding commercial grade filament requires a professional extruder and associated winder. The cost of purchasing this equipment can be amortized over a few years if the

number of parts printed by FDM 3D printing is properly optimized in the 3D slicer to print multiple parts in one as showed by Faludy et al. [33]. Using desktop FDM 3D printing rather than professional methods such as professional FDM 3D printing or plastic injection makes the process financially viable when it is compared to the electron-beam melted (EBM) printing process, which uses the following cost formulation:

$$C_{Build} = (C_{indirect} \times T_{Build}) + (m \times Price_{Rawmaterial}) + (E_{Build} \times Price_{Energy})$$

Detailed formulation in the cost analysis is developed by Baumer et al. [34]. The particularity of FDM 3D printing is that it allows, for example, to reduce the mass of the parts by topological optimization without deteriorating the mechanical advantages of the filament. As a result, the mass term “ m ” is predicted to be lower. The energy consumed “ E_{Build} ” of a desktop 3D printing has been estimated as 9 MJ (the maximum value in any desktop 3D printing). Relative to the EBM technology calculated by Baumer et al. [34], which is 200 MJ, it is 22 times less. This suggests that FDM 3D printing energy consumption is not significant compared to the ball mill one. Following the energy consumption principle, the NoztekPro extrusion device used in this study, is not significantly energy consuming. From the manufacturer information, the global system runs at 260 W when it is combined with the motor and the heater. This is equivalent to lighting two and a half 100w light bulbs.

In this study, the agave bagasse initial separation has been performed manually at laboratory scale. This is because the agave bagasse “as-received” not only contain bundles of fibres but a size variety of coarse clumps with different masses. To foresee a scale up of the proposed process, an automated system should be integrated to the overall process, for example, a commercial biomass shaker. It is known that sieve sizes should be selected to minimize the energy consumption while maximizing, in this case, the ball milling process stage and the resulted particle sizes [35]. This study has determined that the particle sizes obtained from the ball mill plays a determinant role in the fibre-pellet adhesion process. Future research should be conducted to understand and apply the ideal correlation between the sieve size and the agave bagasse particle sizes to maximize energy consumption when separating the bagasse automatically.

Prototyping

Tequila-shot glasses prototypes were printed for proof-of-concept and to assess the perspective of this bio-composite material based on reusing agave bagasse fibres. Processing temperature, flow and infill speed are critical parameters to obtain high quality 3D printing pieces. For pure PLA, processing temperature and infill speed for pure PLA filament are 215 °C and 90 mm/s, respectively [36]. Subject to the 3D printing technology used, the printing flow can be modified with the software to 45–50 mm/s and conserve the product quality. In this study, a FMD (Fig. 9a) depicts a specimen printed with a processing temperature of 215 °C and 40 mm/s infill speed. A thorough visual appreciation in Fig. 9a provided the confidence to move forward as the most common surface distortions and defects on 3D printed pieces were not observe, for example, under-filling (dry printing), over-filling or the presence of cracks without adequate adhesion [37]. Printing infill speed was modified to produce the proof-of-concept prototypes. Clear PLA control prototype was printed to mimic a commercial tequila-shot glass dimensions and beverage capacity. Based on this PLA control-prototype printing parameters, a new filament (PLA + 20%

ABF milled 4 h at 200 rpm) prototype was printed. As shown in Fig. 9b, the resulted prototypes demonstrated that printing quality of pure PLA filament is similar to the new material prototype.

The mixture quality obtained following the mechanical alloying enabled to create a printing quality comparable to a commercial quality filament. This proof-of-concept is at its infant stage, but the beginning is very promising. Improvements to the process can be made. Future investigations will rely on studying the effect of concentrations/ratios of agave bagasse fibres (e.g. 40, 60% ABF) with PLA mixtures for producing filament, and evaluating the FDM produced prototypes [38].

In the proposed method waste is repurposed (agave bagasse) and environmental impact such as raw-material use is reduced (PLA). Our method has designed-out chemical substances; i.e. mechanical alloying process does not require the fibres to be chemically pre-treated to enhance adhesion properties, in line with the circular economy guidelines [39].

Conclusions

The hypothesis of using mechanical alloying process for a polymer application to create a bio-composite material has been carried out with success.

The use of steel ball in the milling process showed to be more efficient for this bagasse-polymer application. Currently, the unmilled fibre in the ball mill varies within the amount of 7–12%. It is desirable that these amounts are further reduced. Reducing the losses during the milling process will increase the fibre content of the pellets, therefore, improving the overall efficiency of the new process. Several solutions have been identified to enable future studies to address this issue, one of which is to reduce the size of the PLA pellets. Considering that agave penetration after milling is often absent, increasing the surface to volume ratio will improve the fibre content. In addition, an aggressive grinding process with high density pellets will create cracks that will accommodate more fibres inside. Following a satisfactory increased fibre content, chemical and mechanical characterization must be carried out in line with the ASTM material standards to the new filaments and 3D printed pieces.

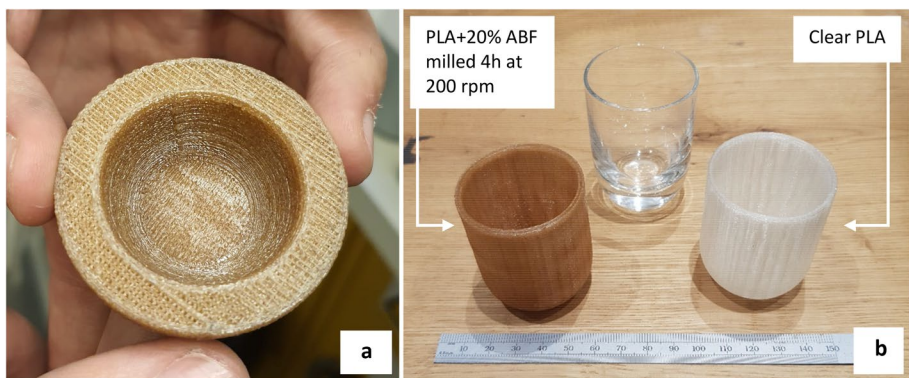


Fig. 9 Tequila-shot glass prototyping; infill quality at the left (a) and material obtained comparison to the PLA standard measurement of tequila glass at the right (b)

This new principle could be useful in the additive manufacturing industry as it offers other perspective to create a filament only by using a mechanical energy without chemical processes during its manufacturing. Therefore, further positive socio-economic and environmental impact is anticipated. The energy consumption of this new process was considered in this study at laboratory scale. Full LCA analysis is recommended when upscaling the process. The protocols developed in this study allow upcycling for the tequila distillery bagasse waste and have the potential to be applied to other agricultural waste crops. Furthermore, the protocols will contribute to the circular economy transition within the additive manufacturing sector.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43615-022-00241-2>.

Acknowledgements The authors would like to thank T Roberts, J Hurley, T Pryor and C Kimpton for providing their expertise and assistance during the experimentation of this work. The authors also thank Tequila Los Abuelos S.A. de C.V. “Destileria La Fortaleza” for providing first-hand agave tequilana bagasse and a valuable insight within the Tequila industry.

Author Contribution M Salignon: investigation, data curation, visualization, methodology, writing—original draft.

T Rose: methodology, review and editing.

S Gray: conceptualization, supervision, methodology, review and editing.

A Encinas-Oropesa: conceptualization, supervision, methodology, visualization, writing—original draft, review and editing.

Data Availability The datasets generated during and/or analysed during the current study are available in the Cranfield University repository.

Declarations

Ethics Approval and Consent to Participate Not applicable.

Consent for Publication Not applicable.

Conflict of Interest The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. Cali M, Pascolettib G, Gaetac M, Milazzod G, Ambue R (2020) New filaments with natural fillers for FDM 3D printing and their applications in biomedical field 30th International Conference on Flexible Automation and Intelligent Manufacturing (FAIM2020) 15–18 June, Athens, Greece. *Procedia Manuf* 51: 698–703
2. Scaffaro R, Maio A, Gulino EF, Alaimo G, Morreale M (2021) Green composites based on PLA and agricultural or marine waste prepared by FDM. *Polymers* 13:1361. <https://doi.org/10.3390/polym13091361>
3. Rajeev R, Deepak K, Manoj K, Subhash CM (2022) A critical review on classification of materials used in 3D printing process. Volume 61. Part 1:43–49. <https://doi.org/10.1016/j.matpr.2022.03.308>

4. Sousa S, Costa A, Silva A, Simões R (2019) Poly(lactic acid)/cellulose films produced from composite spheres prepared by emulsion-solvent evaporation method. *Polymers* 11:1. <https://doi.org/10.3390/polym11010066>
5. Lee CH, Padzil FNB, Lee SH, Ainun ZMA, Abdullah LC (2021) Potential for natural fiber reinforcement in PLA polymer filaments for fused deposition modeling (FDM) additive manufacturing: a review. *Polymers* 13:9. <https://doi.org/10.3390/polym13091407>
6. Alison L, Menasce S, Bouville F, Tervoot E, Mattich I, Ofner A, Studart AR (2019) 3D printing of sacrificial templates into hierarchical porous materials. *Sci Rep* 9(1):1–9. <https://doi.org/10.1038/s41598-018-36789-z>
7. Sai Saran O, Prudhvidhar Reddy A, Chaturya L, Pavan Kumar M (2022) 3D printing of composite materials: A short review. *Materials Today: Proceedings* 64:615–619. <https://doi.org/10.1016/j.matpr.2022.05.144>
8. Duque-Acevedo M, Belmonte-Ureña LJ, Cortés-García FJ, Camacho-Ferre F (2020) Agricultural waste: review of the evolution, approaches and perspectives on alternative uses. *Global Ecology and Conservation* 22:e00902. <https://doi.org/10.1016/j.gecco.2020.e00902>
9. Adebayo MA, Areo FI (2021) Removal of phenol and 4-nitrophenol from wastewater using a composite prepared from clay and Cocos nucifera shell: Kinetic, equilibrium and thermodynamic studies. *Resources, Environment and Sustainability* 3:100020. <https://doi.org/10.1016/j.resenv.2021.100020>
10. Singh S, Mangla J, Singh S (2021) Evaluation of aspergillus fumigatus NTCC1222 as a source of enzymes for detergent industry. *Resources, Environment and Sustainability* 5:100030. <https://doi.org/10.1016/j.resenv.2021.100030>
11. Consejo Regulador del Tequila (CRT) Consumo de Agave para Tequila y Tequila 100% de Agave. URL (2016) <http://www.crt.org.mx/EstadisticasCRTweb/>. Accessed Aug 2020
12. Chávez-Guerrero L, Hinojosa M (2010) Bagasse from the mezcal industry as an alternative renewable energy produced in arid lands. *Fuel* 89(12):4049–4052. <https://doi.org/10.1016/j.fuel.2010.07.026>
13. RangelHeredia IK, Garza-Tovar L, Sánchez-Cervantes EM, Torres-González LC (2021) Activated carbon from agave wastes for supercapacitors via potentiostatic floating test. *J Mater Sci Mater Electron* 32(16):21432–21440. <https://doi.org/10.1007/s10854-021-06649-0>
14. Caballero M, Chinas-Castillo F, Montes-Bernabé JL, Alavéz-Ramírez R, Silva ME (2018) Effect on compressive and flexural strength of agave fiber reinforced adobes. *J Natural Fibers* 15:575–585
15. Moreno-Anguiano O, Cloutier A, Rutiaaga-Quinones JG, Wehenkel C, Rosales-Serna R, Rebollo P, Carrillo-Parra A (2022) Use of Agave durangensis bagasse fibers in the production of wood-based medium density fiberboard (MDF). *Forests* 13(2):271. <https://doi.org/10.3390/f13020271>
16. Álvarez-Chávez J, Villamiel M, Santos-Zea L, Ramírez-Jiménez AK (2021) Agave by-products: an overview of their nutraceutical value, current applications, and processing methods. *Polysaccharides* 2(3):720–743. <https://doi.org/10.3390/polysaccharides2030044>
17. Kumar A, Ram C (2021) Agave biomass: a potential resource for production of value-added products. *Environ Sustain* 4(2):245–259. <https://doi.org/10.1007/s42398-021-00172-y>
18. Jaiswal D, Devnani G (2022) Bagasse fibers, their composites and applications. *Plant Fibers, their Composites, and Applications* 111–130. <https://doi.org/10.1016/B978-0-12-824528-6.00005-9>
19. García-Méndez R F, Cortés-Martínez C I, Almendárez-Camarillo A (2020) Thermochemical and tensile mechanical properties of fibers mechanically extracted from leaves of agave angustifolia Haw. *J Natural Fibers* 1–15. <https://doi.org/10.1080/15440478.2020.1840480>
20. Langhorst AE, Burkholder J, Long J, Thomas R, Kiziltas A, Mielewski D (2018) Blue-agave fiber-reinforced polypropylene composites for automotive applications. *BioRes* 13:820–835. <https://doi.org/10.15376/biores.13.1.820-835>
21. Huerta-Cardoso O, Durazo-Cardenas I, Longhurst P, Simms NJ, Encinas-Oropesa A (2020) Fabrication of agave tequilana bagasse/PLA composite and preliminary mechanical properties assessment. *Ind. Crops Prod* 152:112523. <https://doi.org/10.1016/j.indcrop.2020.112523>
22. Huerta-Cardoso O, Durazo-Cardenas I, Marchante-Rodriguez V, Longhurst P, Coulon F, Encinas-Oropesa A (2020) “Up-cycling of agave tequilana bagasse-fibres: A study on the effect of fibre-surface treatments on interfacial bonding and mechanical properties. *Results Mater* 8:100158. <https://doi.org/10.1016/j.rinma.2020.100158>
23. Rowell RM (1998) Property enhanced natural fiber composite materials based on chemical modification. In: Prasad PN, Mark JE, Kandil SH, Kafafi ZH (eds) *Science and technology of polymers and advanced materials*. Springer, Boston, MA. https://doi.org/10.1007/978-1-4899-0112-5_63
24. George J, Sreekala MS, Thomas S (2001) A review on interface modification and characterization of natural fiber reinforced plastic composites. *Polym Eng Sci* 41:1471–1485. <https://doi.org/10.1002/pen.10846>

25. Bledzki AK, Reihmane S, Gassan J (1996) Properties and modification methods for vegetable fibers for natural fiber composites. *J Appl Polym Sci* 59:1329–1336
26. Maurice DR, Courtney TH (1990) The physics of mechanical alloying: A first report. *Metall Trans A* 21(1):289–303. <https://doi.org/10.1007/BF02782409>
27. Mohanty AK, Wu F, Mincheva R et al (2022) Sustainable polymers. *Nat Rev Methods Primers* 2:46. <https://doi.org/10.1038/s43586-022-00124-8>
28. Rajaonarivony KR, Mayer-Laigle C, Piriou B, Rouau X (2021) Comparative comminution efficiencies of rotary, stirred and vibrating ball-mills for the production of ultrafine biomass powders". *Energy* 227:120508. <https://doi.org/10.1016/j.energy.2021.120508>
29. Abdellaoui M, Gaffet E (1994) A mathematical and experimental dynamical phase diagram for ball-milled Ni10Zr7. *J Alloys Compd* 209(1–2):351–361. [https://doi.org/10.1016/0925-8388\(94\)91124-X](https://doi.org/10.1016/0925-8388(94)91124-X)
30. Gheisari K, Javadpour S, Oh JT, Ghaffari M (2009) The effect of milling speed on the structural properties of mechanically alloyed Fe-45%Ni powders. *J Alloys Compd* 472(1–2):416–420. <https://doi.org/10.1016/j.jallcom.2008.04.074>
31. Dastanpoor E, Enayati MH (2015) Effect of milling intensity on mechanical alloying of Cu-Zr-Al system. *Indian J Eng Mater Sci* 22(5):521–526
32. Mondragón M, Elizalde L E, Rejón V (2021) Silicon in Agave Angustifolia Haw Leaves, Proceedings of the 7th World Congress on Mechanical, Chemical, and Material Engineering (MCM'21) Paper No. ICCPE 112. <https://doi.org/10.11159/iccpe21.112>
33. Faludi J, Hu Z, Alrashed S, Braunholz C, Kaul S, Kassaye L (2015) Does Material Choice Drive Sustainability of 3D Printing? *Int J Mech Mechatron Eng* 9:2. <https://doi.org/10.5281/zenodo.1098116>
34. Baumers M, Dickens P, Tuck C, Hague R (2016) The cost of additive manufacturing: Machine productivity, economies of scale and technology-push. *Technol Forecast Soc Change* 102:193–201. <https://doi.org/10.1016/j.techfore.2015.02.015>
35. Zhang M, Song X, Deines T W, Pei Z J, Wang D (2012) Biofuel manufacturing from woody biomass: Effects of sieve size used in biomass size reduction. *J Biomed Biotechnol* 2012. <https://doi.org/10.1155/2012/581039>
36. Chamil A, Pimpisut S, Anura F (2020) Optimization of fused deposition modeling parameters for improved PLA and ABS 3D printed structures. *Int J Light Mater Manuf* 3(3):284–297. <https://doi.org/10.1016/j.ijlmm.2020.03.003>
37. Fastowicz J, Grudziński M, Teclaw M, Okarma K (2019) Objective 3D printed surface quality assessment based on entropy of depth maps. *Entropy* 21(1):97. <https://doi.org/10.3390/e21010097>
38. Mazzanti V, Malagutti L, Mollica F (2019) FDM 3D Printing of Polymers Containing Natural Fillers: A Review of their Mechanical Properties. *Polymers* 11:1094. <https://doi.org/10.3390/polym11071094>
39. Kiser B (2016) Circular economy: Getting the circulation going. *Nature* 531:443–446. <https://doi.org/10.1038/531443a>



DSPACE

<https://dspace.org/>

A new preparation method for 3D bio-composite filament manufacturing: a study on the effects of ball milling on the cohesion/adhesion of an agave tequilana bagasse /PLA pellet mixture

Salignon, Mathias; Gray, Simon; Rose, Timothy; Encinas-Oropesa, Adriana

2023-09-01

Springer

<https://doi.org/10.1007/s43615-022-00241-2>

Salignon M, Gray S, Rose T, Encinas-Oropesa A. (2022) A new preparation method for 3D bio-composite filament manufacturing: a study on the effects of ball milling on the cohesion/adhesion of an agave tequilana bagasse/PLA pellet mixture. Circular Economy and Sustainability, Volume 3, September 2023, pp. 1441-1459