

Fabrication and characterization of a filament for 3D printing from polylactic acid with *Cryptostegia grandiflora* fiber

Research Article

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Received 29 February 2024; Accepted 03 April 2024

Abstract: Additive manufacturing (AM), i.e., 3D printing, has seen significant growth in recent years in all industries due to its potential advantages, requiring the polymers that are adapted as for melt flow index (MFI) to this use to have adequate tensile strength as well. Hence, in this work, a novel ligno-cellulosic fiber from *Cryptostegia grandiflora* (CG) and polylactic acid (PLA) were blended to obtain a filament for AM using a twin screw extruder. To determine the filament's suitability for the 3D printing process, MFI and thermal degradation were examined. In order to identify the distribution and the effect of CG fiber (CGF) filler on the matrix, the filaments were examined using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). CGF powder distribution was observed in the microstructure of the CGF/PLA composite filament. Due to the high compatibility between PLA and CGF, their blending slightly increased the degradation temperature, though did not lead to any crystallinity loss, and the CGF/PLA filament showed 12.5% better tensile characteristics than the pure PLA filament. Based on their performance, the CGF may represent a suitable and compatible filler to improve the properties of the PLA filament for 3D printing applications.

Keywords: Hybrid 3D filament • Biomass waste • Natural fibers • Thermal characterization • X-ray diffraction • FTIR characterization • Tensile properties

1. Introduction

Since 1984, 3D printing, also referred to as additive manufacturing (AM), has been used for commercial purposes related to rapid prototyping, which has grown tremendously to reach consumer applications in the household [1]. Also, 3D printing technology has become a new industrial growth area in fields, such as medical research, aerospace, defence, precision goods, and jewelry manufacturing, due to its benefits of reducing manufacturing waste, simplifying assembly, and mass customization. The principal materials used for 3D printing filament production are high impact polystyrene (HIPS) [2], thermoplastic elastomer (PCTPE) [3], transparent polycarbonate (PC) [4], acrylonitrile butadiene styrene (ABS) [5], nylon (polyamide, PA) [6], and polylactic acid (PLA) has attracted

particular interest being a bio-based material and, at least in principle, has been adapted to be coupled with other biomass materials [7]. By 2026, the filament market is expected to grow to \$6.6 billion [8].

PLA, an important alternative polymer to replace petrochemical polymers, is mainly produced from agricultural products such as sugarcane and corn starch, which means it to be affected under appropriate conditions by hydrolytic degradation [9]. Presently, PLA is among the primary feedstock materials for desktop 3D printers because of its advantageous mechanical properties and environmentally friendly synthesis processes from renewable resources [10].

Considering the limits of PLA, including its limited resistance to shear, hardness, toughness, and not exceptional stiffness [11], filling it with particles that are able to offer some enhancement of these properties is a possible strategy to be pursued and that had some success in recent years.

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In practice, the fillers for addition can be either ceramic or lignocellulosic, in both cases giving preference, in terms of circular economy, to secondary raw materials obtainable from waste/by products of an economic system. As regards the former, in a recent study, a composite PLA filament was fabricated by blending 10–30 wt% of hydroxyapatite (HA) powder with PLA by using a screw extruder for the fused deposition mode (FDM) process [12]. Due to the concern about the possible reduction of thermal degradation temperature, attempts to fill PLA filaments with carbon from agro-waste (coconut husk) have also been proposed [13]. Both ligneous (nutshell powder) (up to 2.5 wt%) and ceramic waste (eggshell powder) (up to 5 wt%) were used in the study of Lohar et al. [14], and the improvement in terms of tensile strength was found to be very significant for the former filler, while not for the latter.

In general terms, therefore, it appears that the addition of lignocellulosic materials to PLA 3D filaments would be beneficial. A number of examples do exist actually. In particular, various biomass-based wastes have been added to filaments for FDM, including hemp fibers (from 15 to 25%), hemp leaves (from 10 to 15%), tomato scraps (from 15 to 25%), carob flour (from 10 to 20%), and orange pruning waste (from 10 to 20%) [15]. Tomato and pruning waste offered substantial improvements toward pure PLA. Another possibility is the use of lignin and hemicellulose as filament fillers, following extraction from biomass waste, in a biorefinery concept: it is noteworthy that this involves further use of some chemicals, though ultimately proving to be effective [16]. More simply and immediately, though possibly with concerns over the results, PLA 3D filaments can be filled with different natural fibers, such as hemp, phormium, flax, coir, and bamboo; the amount of added fillers not to impair FDM functioning normally does not have to exceed 25 wt% [17].

In this research, a 3D printing composite filament was fabricated by blending the *Cryptostegia grandiflora* fiber (CGF) with PLA. The CGF was already investigated for potential introduction in polymer composites, as a fiber with cellulose content close to 80% and significant crystallinity, resulting in an average tensile strength as high as 791 MPa [18]. In this work, its introduction into the PLA filament has been attempted, and the relevant properties were investigated, such as tensile strength measurement, thermal analysis (TA), chemical investigation by Fourier transform infrared (FTIR) spectroscopy, crystallinity evaluation by X-ray diffraction (XRD), and surface morphology evaluation by microscopy. According to the results mentioned above regarding introducing agricultural waste, it is not deemed necessary to introduce

more than a minimal amount of CGFs, which would be sufficient to prove the suitability of the process.

2. Materials and methods

2.1 Materials

In this experiment, the novel natural fiber was extracted from the CG plant, identified in the Virudhunagar district, Tamil Nadu. The common local name of the CG plant is rubber vine. The CG plant has been discovered in many countries, where it is commonly eradicated as it is an invasive plant. The CG fiber extraction was reported in the study of Udhayakumar et al. [18]. Also, PLA pellets with a density of 1.2 g/cm³ and a molecular weight of 6.7×10^4 were used in the study, and they were obtained from Banka Biolo Ltd., Hyderabad-500076, Telangana, India.

2.2 Methods

2.2.1 Powder making process

The CGF was cut into pieces with a length of 10 (± 0.5) mm. In a beaker, 30 g of cut CGF pieces was immersed in a 10% potassium hydroxide (KOH) solution for approximately 4 h. KOH was selected for its lower alkalinity with respect to sodium hydroxide (NaOH), which is deemed to be more effective on a fiber like CGF, as proven previously with a similar shrub fiber, namely *Butea parviflora* [19]. The CGF was then washed in a water bath at 90°C for an hour and allowed to cool at ambient temperature (25°C). Following that, the processed fiber was heated in a hot air oven at 60°C temperature for a duration of 2 h to ensure sufficient drying, after which the powder was produced by grinding in a ceramic mortar and dried in a hot air oven. Particles of dimensions exceeding 80 μ m were filtered out and used for further testing, namely XRD and FTIR spectroscopy.

2.2.2 Composite filament production

The PLA pellets and CGF powder were first manually blended. A twin-screw extruder (Brabender, Duisburg, Germany) with a 32 mm screw diameter and a 16:1 L/D ratio was then used to ensure mixing for production. The temperatures in the rear, middle, and front of the extruder were adjusted at 130, 165, and 200°C, respectively. The haul-off speed was finetuned to control the filament strand diameter. Through this procedure, a 10 wt% CGF +

PLA filament with a diameter of $1.75 (\pm 0.05)$ mm was produced. The CGF powder–PLA composite filament making procedure is shown in Figure 1.

2.2.3 MFI

A melt flow measuring apparatus, model 3883, manufactured by Elmech Pneumatic Industries Ltd., New Delhi, India, was used to analyze the MFI of extruded filaments in accordance with the ASTM D1238-10 standard. Approximately 20 g of chopped PLA–CGF filament was tested at 200°C after 60 min of preheating.

2.2.4 TA

Thermogravimetric analysis (TGA) was carried out as per the ASTM E1131-20 standard using a STA8000 thermal balance from PerkinElmer (Waltham, MA, USA). The filament samples were allowed to heat in a nitrogen environment at a continuous rate of 5°C/min up to a 400°C temperature limit. The weight loss of the filaments with temperature increase was measured.

2.2.5 XRD analysis

In order to determine the phase shift of a crystalline substance, XRD analysis was performed using an X'Pert Pro diffractometer (Malvern Panalytical, Malvern, UK) that emits CuK α radiation with a wavelength of $\lambda = 1.5406$ nm. X-ray tube operation parameters used were 40 kV and

30 mA. The XRD spectra were recorded in the 2θ angle range between 10° and 80°.

2.2.6 FTIR spectroscopy analysis

FTIR spectroscopy (Shimadzu, Kyoto, Japan, model IR Tracer 100), which recorded infrared absorption spectra, was used to explore the chemical functional groups in the composite filament. This system reproduces the spectrum with a resolution of 1 cm^{-1} at a temperature of 30°C and a relative humidity of 65%.

2.2.7 Morphology analysis

A Leica (Wetzlar, Germany) MC 120 HD 2.5 Megapixel microscope and a CARL ZEISS (Jena, Germany) SIGMA scanning electron microscope were used to examine the morphology of the blended PLA–CGF filament. Particular attention was paid to examining the distribution of CGF powder in the PLA matrix.

2.2.8 Tensile tests

Tensile testing of the blended PLA–CGF filament was performed using a TINIUS OLSEN (Philadelphia, USA), model: H50KL universal testing machine with a load capacity of 100 N at room temperature of 24°C and a relative humidity of 65%, subject to the ASTM D 3822-07 standard. A 150 mm long filament was used for tensile testing. A gauge length of 50 mm was used to determine the maximum tensile



Figure 1. Production process of the filament.

stress and strain. In order to ensure the accuracy of the data, tests on the filament sample were replicated 5 times, and average values were reported.

3. Results and discussion

After being ground, particles with a maximum dimension of 80 μm and short fibers, spanning up to a few mm length, were selected for further analysis, as reported above; the CGF filler was further filtered using a 10 μm polyethylene filter to keep the powder within specific dimensions to be possibly used as the reinforcement for composite filament fabrication.

Following that, to verify the suitability of the CGF with this dimension, using the MFI value as the parameter, the flow ability of the polymer in the molten state was measured at 200°C. In practice, when introducing 10 wt% of fiber loading, compared to pure PLA, the MFI of the composite filament is decreased by 14%, from 6.1 (± 0.1) g/10 min to 5.2 (± 0.1) g/10 min. This appears suitable for FDM printing, considering that most commercial PLA filaments' MFI range from 8.3 to 4.3 g/10 min [20].

To assist in the comparison with other natural fillers added to 3D printing filaments, some data are reported in Table 1. From these data, MFI values are very scattered and not very significant, though it can be recognised that the specific case examined yielded a sufficient value of MFI to allow 3D printing.

The morphological examination of the filament structure, as studied by optical microscopy, whose image is displayed in Figure 2, suggests sufficient adhesion of the

Filler	Amount (wt%)	Treatment	MFI (g/10 min)	Ref.
<i>Cryptostegia grandiflora</i>	10	10 vol% KOH	5.2 (200°C)	Here
Sugar palm fiber	2.5	6 vol% NaOH 2 vol% silane	17.6 (190°C)	[21]
Hemp hurds	10	No treatment	2.16 (190°C)	[22]
Almond shell powder	10	5 wt% NaOH	11.92 (160°C)	[23]
Walnut shell powder	10	5 wt% NaOH	11.7 (160°C)	[23]

Table 1. MFI data for PLA filaments added with lignocellulosic fillers.

CG particles, most of which are between 5 and 10 μm , to the PLA matrix. Despite this, the fracture may have occurred also partly by decohesion of the CG fibril from the matrix, as observable, or by differential deformation of the two, considering the bulging CG fibril. However, some of them produce evident damage, and the distribution of the particles might not always be considered uniform, though the diameter of the filament did not vary by more than $\pm 3\%$, preserving the level of tolerance offered by pure PLA. This is promising, since in other cases more evident scattering is observed, due to the introduction of harder particles, such as corn cob fragments, in it [24]. The tensile properties, reported in Table 2, suggest an increase of strength and stiffness exceeding the proportion of the

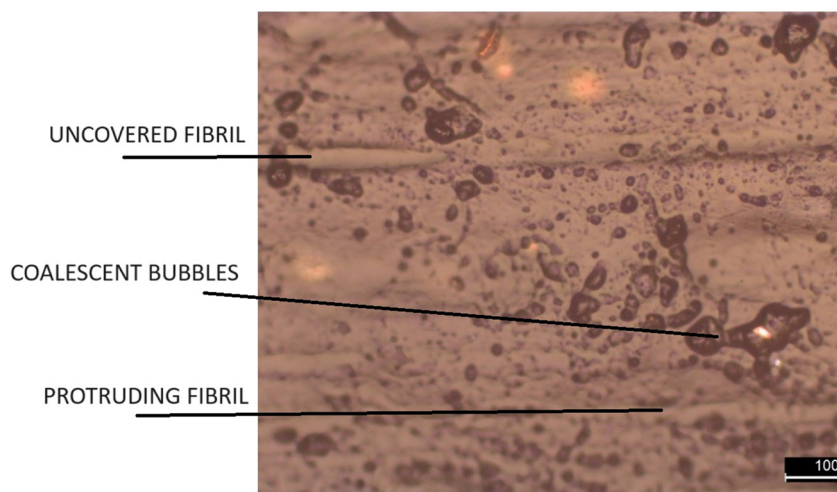


Figure 2. Optical microscopy image of a section of PLA/10% CGF filament.

Filament	Diameter (mm)	Tensile strength (MPa)	Ultimate strain (%)	Young's modulus (GPa)
PLA	1.75 ± 0.05	43.6 ± 2.8	4 ± 0.5	2.3 ± 0.2
90% PLA + 10% CGF	1.75 ± 0.05	49.1 ± 3.3	3.2 ± 0.7	2.7 ± 0.4

Table 2. Tensile performance of the unfilled and filled filaments.

added filler, whilst on the other hand the strain to failure is greatly influenced.

As far as FTIR spectroscopy is concerned (Figure 3), the distinct bands of pure PLA are observed at 768, 864, 1,033, 1,182, and 1,458 cm^{-1} . In particular, the transmittance peak at 768 cm^{-1} is produced by the deformation of the CO and CH groups in polysaccharides connected to aromatic rings [25]. The additional absorption peak at 1,182 cm^{-1} is associated with the CO bond [26]. The C–H group's bending vibrations and the C–C group's stretching vibrations are responsible for the peaks observed at 864 and 1,458 cm^{-1} , respectively. The pyranose chain vibrations of the C–H group are attributed to the absorption band seen at 1,033 cm^{-1} [27].

In contrast, the characteristic peaks of the CGF spectra, mostly related to fiber cellulose, are found at 716, 898, 1,165, 1,431, and 1,633 cm^{-1} . More specifically, bending of the CH group of the anhydride ring is indicated by the peak at 716 cm^{-1} [25]. The degradation of C–O–C groups attributed to amorphous cellulose is indicated by the peak observed at 898 cm^{-1} [28]. The absorption peak at 1,165 cm^{-1} is ascribed to the asymmetric C–O–C bridge stretching [29], whilst the peak at 1,431 cm^{-1} is the result

of hydroxide in-plane deformation [30]. The peak at 1,633 cm^{-1} is attributed to water interaction and therefore to hydroxide vibration [31]. A specific peak is reported only for CGF at 3,196 cm^{-1} , due to the OH group vibration of carboxylic acid [32].

As far as the spectra of PLA/10% CGF filament are concerned, most of the peaks are repeated from either PLA or CGF. A specific peak that offers indications on the interaction of the two components is at 1,747 cm^{-1} : this has been attributed to the stretching vibration of the C=O group, most likely due to acetyl and carbonyl groups in hemicelluloses, the signal being normally concealed in the bulk of the fiber [33]. However, in general terms, the large similarity between the spectra of pure PLA and 10 wt % CGF composite indicates that the addition of CGF did not substantially modify the chemical composition of the pure PLA during blending and extrusion. As the consequence of substantially unaltered properties, it is largely expected that the mechanical properties would not decline by filler addition.

TGA curves of pure PLA and PLA + 10 wt% CGF composite filaments are shown in Figure 4. The moisture present in the sample evaporates and mechanically looser particles are gradually dissolved, which leads to a minor weight loss observed in both samples between 95 and approximately 250°C. Following this, the deterioration of the two filaments takes place, starting slightly earlier for pure PLA filament, as it is also revealed by the graphic measurement of the degradation peak, according to the method used, e.g., in the study of Johny et al. [34]. The situation appears different in the residue measured at 600°C, which as for PLA appears in alignment with the literature, suggesting a minimal char residue at that

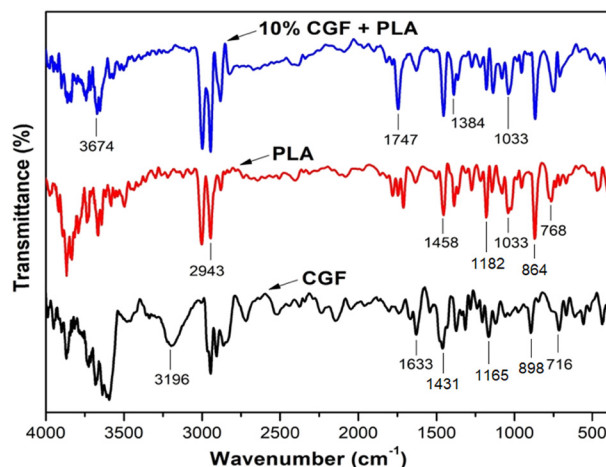


Figure 3. FTIR spectra for pure PLA, and CGF powder, and their 90/10 composite.

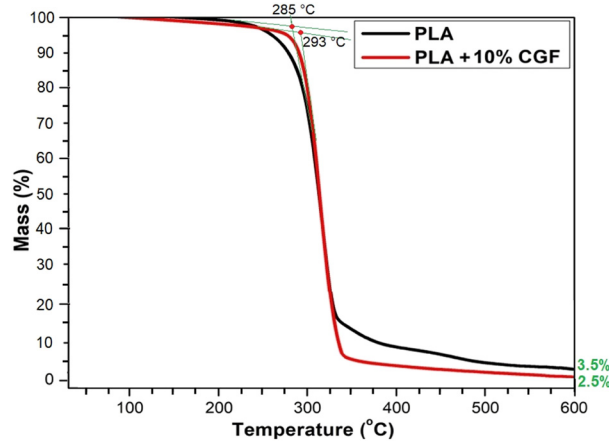


Figure 4. TGA curves for pure PLA and its 90/10 composite with CGF.

temperature [35], and even slightly lower in the case of presence of CGF, which is low in lignin (2.5%), therefore basically degrades only as the effect of the collapse of the crystalline cellulose structure [36]. The conclusion that can be obtained from TGA is that the filler slightly shifts up the degradation of the filament, which can be considered positive.

XRD patterns of pure PLA, pure CGF, and 10 wt% CGF/PLA composite filament are shown in Figure 5. The PLA polymer has a fully amorphous structure, according to the broad peak at 16.4° [37] and a smaller peak at 29.2° , observed also in the study of Revati et al. [38], yet not discussed there. The XRD pattern of cellulose I in CGF shows peaks at 2θ values of around 14.72° , 16.64° , 22.58° , and 34.24° related to their respective reflection planes (101), (110), (200), and (004) [39]. The XRD pattern of CGF allowed measuring the crystallinity index (CI) from Segal's law [40], according to the formula based on the

corresponding crystallinity peak height I_{002} and amorphous local minimum I_{am} , namely $100 \times (I_{002} - I_{am})/I_{002}$, which yields a value of CI equal to 79.7%. Also, the smaller peaks suggest that CGF have relatively large crystallite size, so that (101) and (110) are not superposed. Calculation was done according to the Scherrer's formula of the crystallite size D_{002} according to the diffraction peak broadening in the XRD curves, in practice, using equation (1):

$$D_{002} = k\lambda/(\beta_{002} \times \cos \theta), \quad (1)$$

where k is a constant, normally considered equal to unity, λ is the X ray wavelength used in XRD (in nm), and β_{002} is the true peak broadening at full-width half maximum (FWHM) in radians. The value obtained for the crystallite size was 41.6 nm.

Although no specific calculations were performed, the notable appearance of the (110) peak in the 90% PLA/10%

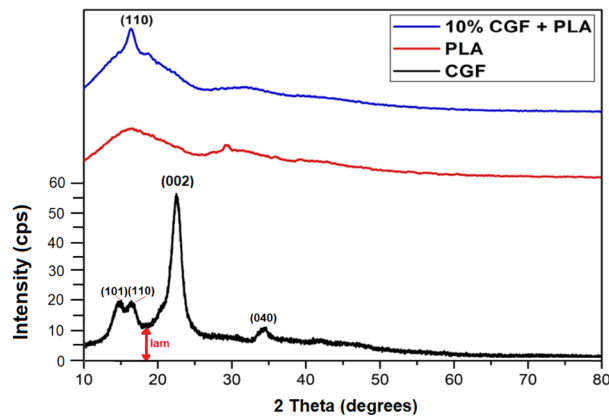


Figure 5. XRD spectra of CGF, PLA, and its composite.

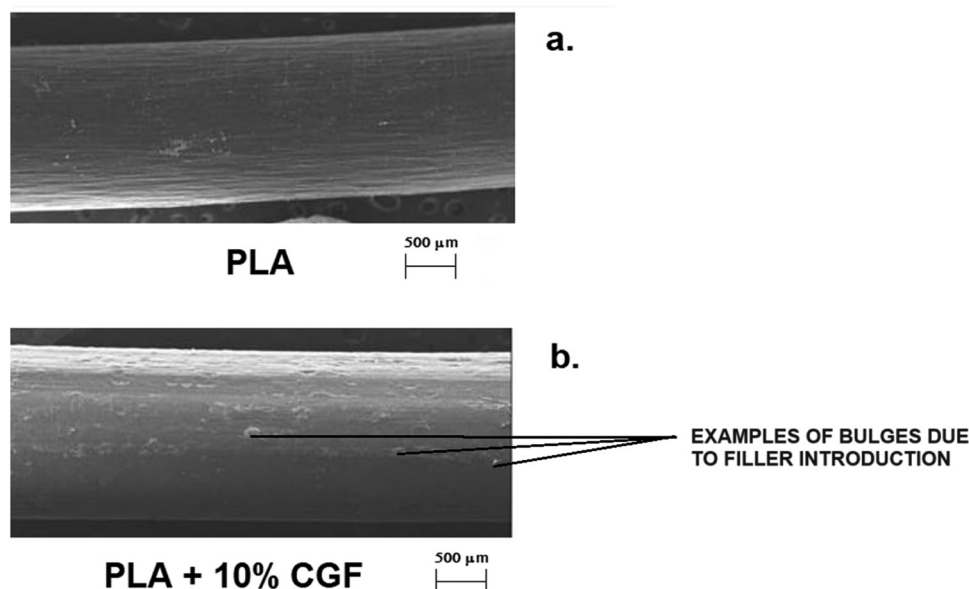


Figure 6. 50× SEM images representing the (a) neat PLA filament and (b) 90% PLA + 10% CGF filament.

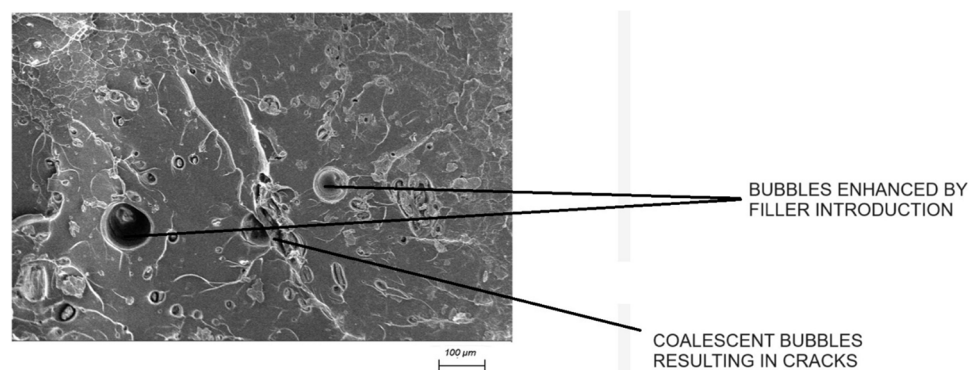


Figure 7. Image (300×) of the composite filament section with CGF particles.

CGF filament XRD spectrum suggests that the crystallinity of the filament is enhanced by the introduction of CGF powder, even in small amounts. This is also well recognized with other plant fibers introduced in limited quantity into PLA composites, such as it is the case for *Borassus flabellifer* [41]. It is expected that this high value of crystallinity for the filament would enhance its performance; however, the possibility to introduce a higher amount of filler depends on whether it increases its brittleness or not, by representing an inclusion in the polymer structure.

Morphological investigation using SEM micrographs suggests that with respect to the bare PLA filament section shown in Figure 6(a) the composite filament is slightly rougher and less uniform, with obvious presence of

some small bulges, obtained by the introduction of the filler, as reported in Figure 6(b). The composite filament section in Figure 7 with a larger magnification (300×) shows, on one hand, the visible formation of an effective interface between the matrix and the CGF, yet on the other hand slight disruptions (e.g., crack formations around CGF coalescing clusters) are also apparent.

4. Conclusions

Adding agro-waste to 3D filaments produced from PLA appears to be an option, which is particularly of interest, whenever local biomass residue is available, as is the case

for rubber vine, CGF. In this case, the addition of a limited amount of CGF powder to the PLA filament proved to be a success, in the sense that the crystallinity and tensile strength of the matrix were increased while maintaining a sufficiently viable MFI and not affecting thermal degradation. Thinking of an increase in the amount of filler introduced, which shows sufficient interfacial contact with the matrix, further verifications will be needed about the roughness of the filament. This will rule out the presence of differential stresses, which might lead to possible enhanced cracking, especially in view of clustering of the CGF particles. In the absence of roughness studies, microscopical investigations indicate the presence of some cracking as a result of filler presence, especially enhanced in the presence of air inclusions during polymer molding.

Acknowledgement

The authors acknowledge the funding from Researchers Supporting Project number (RSP2024R355), King Saud University, Riyadh, Saudi Arabia.

Author contributions

A. Udhayakumar, K. Mayandi, N. Rajini, and M. Murali – Developed the experimental work on novel fiber extraction and characterization studies. Faruq Mohammad, Hamad A. Al-Lohedan, and Kumar Krishnan – Optimized the process parameters for 3D printing. Carlo Santuli – Analysed the novel fiber characterization studies.

Conflict of interest statement

Authors state no conflict of interest.

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