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# Lemongrass Plant as Potential Sources of Reinforcement for Biocomposites: A Preliminary Experimental Comparison Between Leaf and Culm Fibers

Vincenzo Fiore<sup>1</sup> · Dionisio Badagliacco<sup>1</sup> · Carmelo Sanfilippo<sup>1</sup> · Roberto Pirrone<sup>1</sup> · Suchart Siengchin<sup>2</sup> · Sanjay Mavinkere Rangappa<sup>2</sup> · Luigi Botta<sup>1</sup>

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# Abstract

Nowadays, the world requires more sustainable and eco-friendly materials to replace or limit the usage of synthetic materials. Moreover, several researchers focused their attention on the use of agricultural sources as reinforcement for biocomposites since they are abundant, cost-effective and environmentally favorable sources. In such a context, purpose of the present paper is the evaluation of lemongrass plant (*Cymbopogon flexuosus*) as possible source of natural reinforcement for biocomposites. To this aim, natural fibers were obtained from the leaf and the stem of lemongrass and their main properties were compared for the first time. To this scope, mechanical and thermal characterizations, chemical investigation, Fourier-transform infrared spectroscopy, X-Ray diffraction and scanning electron microscope analysis were carried out. The experimental campaign showed that, despite having similar chemical composition (i.e., cellulose, hemicellulose and lignin contents equal to 44–45%, 28–29% and 17%, respectively), leaf fibers possess higher mechanical properties (i.e., + 55% and + 76% in the tensile strength and modulus, respectively) than stem ones. This result can be ascribed to different factors such as larger amount of absorbed water (i.e., +4%) and ash content (+2%) shown by stem fibers in addition to a more compact structure evidenced by leaf fibers which also present higher density (i.e., 1.139 g/cm<sup>3</sup> versus 1.019 g/cm<sup>3</sup>).

Keywords Lemongrass · Natural fibers · Tensile properties · Chemical composition · Thermal stability · Morphology

# Introduction

The use of natural fibers as reinforcement of biodegradable and/or bio-based polymers has currently gained a huge interest from both academia and industry. In addition to common fibers such as flax, jute, sisal and hemp, which are the subject of extensive investigations since the 1970s, several researchers worldwide suggested in the last decade the use of less common natural fibers, extracted from local plants/ trees, due to their low cost, high availability and quite good physical properties [1–4]. Nowadays, the high demand for natural fibers requires finding out new lignocellulosic reinforcements from agriculture cheap sources, having adequate properties.

In such a context, Khan et al. [5] have recently investigated a novel natural fiber extracted from the stem of Eleusine indica grass, founding that it shows high cellulose content (i.e., 61.3 wt%), low density (i.e., 1.143 g/cm<sup>3</sup>) as well as quite good tensile properties (i.e., tensile strength and Young's modulus equal to 22 MPa and 10.75 GPa, respectively). Based on these results, the authors stated that Eleusine indica grass can be considered a potential reinforcement for eco-friendly fiber-reinforced polymer materials. The same authors have shown that a further alternative source for natural reinforcement is represented by Cortaderia selloana grass, from which fibers were extracted through manual retting process [6]. The experimental campaign clearly evidenced that this grass fiber possesses promising properties such as high thermal stability (i.e., 320 °C).

Vincenzo Fiore vincenzo.fiore@unipa.it

<sup>&</sup>lt;sup>1</sup> Department of Engineering, University of Palermo, Viale delle Scienze, Edificio 6, 90128 Palermo, Italy

<sup>&</sup>lt;sup>2</sup> Natural Composites Research Group Lab, Department of Materials and Production Engineering, The Sirindhorn International Thai-German Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok (KMUTNB), 1518 Pracharat 1, Wongsawang Road, Bangsue, Bangkok 10800, Thailand

Another interesting investigation was focused on the characterization of fibers obtained from leaves of purple bauhinia trees, showing that these fibers have the potential to be used as reinforcement of polymer composites with good mechanical and thermal properties [2].

One of the latest paper on this topic was done by Lemita et al. [7], who evaluated the usability as polymer composites reinforcement of natural fibers extracted from the stem of the Strelitzia reginae plant. In particular, they evaluated the effect of mercerization treatment on the properties of fibers, by soaking them in a 2 wt.% NaOH solution for 1 and 4 h, respectively.

Other studies were focused on natural fibers extracted from Chrysanthemum morifolium stem [8], Aristida adscensionis [9], Cattail grass [10], Symphirema involucratum stem [11], Calotropis gigantea fruit bunch [12], Stipa obtusa and Jarava ichu leaves [13] and so on.

Among this wide range of chances, our attention has been focused on lemongrass plant (*Cymbopogon genus*), a clumped and tall perennial grass which belongs to the Poaceae family. This *genus* grows worldwide, mainly in tropical and subtropical area of the Indian subcontinent, South and North America, Africa, Australia and Europe. It comprises more than 55 species but Cymbopogon flexuosus and Cymbopogon citratus are the main ones. Indeed, the latter are nowadays widely cultivated all over the world in order to extract an essential oil having high citral content [14, 15]. The most popular method for the oil extraction from lemongrass plant is the steam distillation that releases a lignocellulosic biomass or residue. At the beginning of the last decade it was estimated that about 30000 tons per annum of lemongrass residue were globally generated by this industrial extraction process [16]. The annual world production of lemongrass oil was increased from around 1000 tons in 2006 [17] to 5000 tons in 2014 [18]. The typical flagrance of lemongrass is actually used in perfumery as well as in food preservation [19]. Furthermore, this plant is extensively utilized in pharmacological activities due to its antiseptic, antibacterial, antimicrobial, antifungal and anti-inflammatory properties, as well as in therapeutic applications and agriculture [20–22]. Further uses of lemongrass are as raw material for biogas and silica production [23, 24], for pulp and paper products [25] and for heavy metals biosorption [26]. A schematization of the main applications of lemongrass plant is shown in Fig. 1.



Fig. 1 Main uses of lemongrass plant

To the best of our knowledge, few papers were recently published concerning the use of lemongrass and, in particular, the Cymbopogon flexuosus species as natural reinforcement of composites [27-32]. Nevertheless, no research effort was dedicated to date for evaluating which part of lemongrass plant (Cymbopogon flexuosus) is more suitable to obtain natural reinforcement with promising features. To fill this gap, a preliminary investigation is carried out in the present paper to compare leaf and stem lemongrass fibers. In particular, the chemical composition of the compared fibers was investigated through standard methods. Moreover, the main properties of these fibers were evaluated by means of thermogravimetric analysis (TGA), scanning electron microscope (SEM), Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and helium pycnometer analysis. To compare their mechanical properties, fifty tensile tests were carried for both kind of fibers and the twoparameter Weibull statistical model was applied to interpret statistically the experimental results thus making reliable the mechanical data.

It is worth noting that before using lemongrass fibers as reinforcement of polymeric matrices, an opportune treatment must be carried out [33–37]. This approach is often required because, as widely known, the main drawback of natural fibers is their low compatibility with several hydrophobic polymeric matrices, due to the hydrophilic nature of lignocellulosic materials [38, 39]. This weak interfacial adhesion reduces the stress transfer capability between fibers and the surrounding matrix, thus worsening the mechanical response of the resulting composites.

# **Experimental Part**

## Materials

Lemongrass (*Cymbopogon flexuosus*) is commonly known as Cochin or Malabar grass, barbed wire grass, east Indian grass or citronella grass (Fig. 2). It belongs to the family of Poaceae grasses and is a genus of Asian, African, Australian, and tropical island plants in the grass family.

Lemongrass plants were collected from local agricultural land in the area of Bangkok (Thailand). After collecting the raw plants, the stem was separated from the leaves. Both parts were first washed with tap water to remove dirt and then dried in a hot air oven at 60 °C overnight. Afterward, fibers with a length between 100 and 150 mm were extracted from culms and leaves by mechanical separation.

### Single Fiber Tensile Tests

Fifty fibers extracted from stems and leaves of lemongrass were tested in tensile configuration with the aid of a



Fig. 2 Lemongrass plant

Universal Testing Machine (U.T.M.) model Z005 by Zwick-Roell, equipped with a load cell of 200 N. Following the ASTM standard [33], the strain rate was set equal to 2.5 mm/ min and gauge length to 30 mm. In particular, each single fiber was bonded onto a paper frame before clamping to the screw grips of the U.T.M. Before testing, the fiber diameter was measured at three different random locations along its length, by using an optical microscope model MS5 by Leica. It is widely known that natural fibers are characterized by a non-uniform cross section with irregular shape and high variable thickness. In spite of this, the apparent cross-section area of each fiber was measured by considering it as perfectly circular, as suggested by literature [40]. Furthermore, the mechanical properties of natural fibers are highly variable because they depend on several parameters such as geographical location, age of plant, growing condition, extraction process, defects presence and so on. Hence, a large scatter of values is expected. To overcome this issue thus making reliable the mechanical data, a statistical approach (i.e., two-parameter Weibull distribution) was used in this paper to interpret the experimental results, as suggested by the literature [41, 42].

## **Chemical Analysis**

Kushner and Hoffer method was employed to quantify the cellulose content of fibers [43]. The hemicellulose content was evaluated as per NFT 12-008 standard, while the lignin was measured using APPITA P11s-78. Ash content was determined by ASTM E 1755-61. The chemical structure of lemongrass fibers was evaluated by Fourier-transform infrared spectroscopy (FTIR) using a Cary 600 Series FTIR Spectrometer. This analysis was performed in transmission mode in a wavenumber range from 400 to 4000 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup>.

# **Thermal Analysis**

Thermogravimetric analysis (TGA) was performed to compare the thermal stability of natural fibers extracted from leaves and stems of lemongrass plant by using a thermal analysis machine TG/DTA model SDT Q 600 from TA instruments. Fiber specimens (80–150 mg) were placed in an alumina crucible and then heated from 30 to 1000 °C at a heating rate of 10 °C/min. Furthermore, the thermal analysis of fibers was performed under a nitrogen atmosphere in order to prevent combustion and, at the same time, allowing the components degradation to take place one by one.

## **X-ray Diffraction**

The crystallinity index and crystal size of both fibers were measured by using an X-ray diffractometer (XRD) model Empyrean Panalytical, Netherlands. The monochromatic radiation from CuK $\alpha$  has a wavelength  $\lambda$ =0.154 nm, and operates at 40 kV and 30 mA. The crystalline content (C<sub>r</sub>) was calculated in percentage according to the following equation:

$$C_{\rm r} = \left[\frac{I_{\rm Cr}}{\left(I_{\rm Cr} - I_{\rm am}\right)}\right] 100 \tag{1}$$

where  $I_{Cr}$  and  $I_{am}$  denotes the crystalline and amorphous intensities, respectively.

#### Density Measurement and Morphological Analysis

The volume of leaf and stem lemongrass fibers was measured by using a helium pycnometer by Thermo Electron Corporation model Pycnomatic ATC while an analytical precision balance model AX 224 by Sartorius was used to estimate the weight of both fibers. In more detail, average values density of ten measures were recorded for each kind of fiber and the measured standard deviations were lower than 0.01 g/cm<sup>3</sup>. The morphological analysis of leaf and stem lemongrass fibers was performed through Scanning Electron Microscopy (SEM) investigation by using a FEI Quanta 200 ESEM microscope operating at 20 kV. All the specimens were sputtered with a thin layer of gold to avoid electrostatic charging under the electron beam.

# **Results and Discussion**

## **Tensile Test**

Figure 3 shows the typical stress–strain curves of leaf and stem fibers obtained from the tensile characterization. As general consideration, it is possible to notice that both



Fig. 3 Typical stress-strain tensile curves of leaf and stem lemongrass fibers

fibers evidence a brittle nature. Like other natural fibers, the stress-train curves of lemongrass fibers are characterized by an initial phase in which the behavior can be assumed as a linear and elastic. Afterward, a nonlinear phase with decreasing slope (i.e., stiffness) can be observed at increasing the strain, indicating that a softening of the fiber structure happens under the increased tensile load. Finally, both fibers show a sudden load drop in correspondence to their complete failure.

In terms of comparison, it is worth noting that the mechanical behavior of lemongrass fibers greatly changes as function of the part of the plant from which they have been obtained. In particular, leaf fibers evidence higher stiffness and strength than stem fibers, as clearly shown in Fig. 3. On the other hand, stem fibers are able to reach highest strain at break values in comparison to fibers obtained from the leaf of lemongrass plant.

As widely known, the mechanical performances of natural fibers are greatly variable because they strongly depend on several factors such as climate, soil conditions, age of the plant, wheatear circumstances as well as the extraction process. Due to this issue, a large scatter in the tensile properties such as tensile strength and Young's modulus is expected for natural fibers. Hence, a statistical approach is needed to better evaluate the experimental results. In particular, a wide literature suggests the use of a two-parameter Weibull distribution to model the data obtained from single fiber tensile tests.

First of all, 50 fibers were tested for each kind (i.e., leaf and culm fibers) and the average values of the ultimate tensile strength and Young's modulus with the related standard deviations were shown in Fig. 4.

As already stated, leaf fibers show higher average values both of tensile strength (i.e., 89.4 MPa versus 56.5 MPa) and Young modulus (i.e., 10.8 GPa versus 6.4 GPa). On the other



Fig. 4 Average values and related standard deviations of tensile properties of lemongrass fibers

hand, stem fibers show larger elongation at break average values than leaf ones (i.e., 1.71% versus 1.60%).

Furthermore, it is possible to notice that fibers obtained from lemongrass stem show slightly larger dispersion of their tensile properties in comparison to leaf fibers. In more detail, the standard deviations of the ultimate tensile strength, Young's modulus and strain at break are about 28%, 26% and 24% of the related average values for leaf fibers, respectively. On the other hand, stem fibers present standard deviations approximately equal to 39%, 43% and 36% of the related average values of the ultimate tensile strength, Young's modulus and strain at break. These results are strictly correlated to the fiber morphology suggesting that leaf fibers are probably more homogeneous than stem ones.

Figure 5 shows the Weibull distributions for (a, d) tensile strength and (b, e) Young's modulus and (c, f) strain at break of leaf and stem fibers. By observing these graphs, it can be noticed that Weibull model provides a good fitting of the data, regardless of the mechanical property.

In particular, the shape parameter value indicates the variability of the data whereas the scale parameter defines the position of the Weibull curve [44]. As shown in Table 1, the shape parameter values obtained for all the tensile properties are in the typical range of natural fibers (i.e., between 1 and 6) while synthetic fibers usually have shape parameter in the range 2–20 [45]. Indeed, both fibers have a quite large scatter in their properties distribution, even though the shape parameters found for leaf fibers are always greater than stem fibers, regardless of the tensile property. This confirms that leaf fibers evidence lower dispersion in their mechanical properties, probably due to the better and more homogeneous morphology, in comparison to stem fibers.

By considering the scale parameter values obtained from the Weibull analysis, it can be highlighted that the tensile properties of both lemongrass fibers can be considered comparable to several natural fibers [46–48], thus evidencing that they can be used as reinforcement of biocomposites for semi-structural applications.

Furthermore, by comparing the scale parameter values (Table 1) it is confirmed that leaf fibers possess better



Fig. 5 Weibull probability plots for (a-c) leaf and (d,e) stem lemongrass fibers

	σ <sub>max</sub> [MPa]		E [GPa]		ε <sub>max</sub> [%]	
	Leaf	Stem	Leaf	Stem	Leaf	Stem
Scale parameter (A)	98.7	63.5	11.85	6.73	1.75	1.92
Shape parameter (B)	3.97	2.74	4.25	1.63	4.21	2.75
Median	89.1	51.4	11.32	5.69	1.52	1.60
IQR	29.2	27.9	4.67	4.77	0.46	0.62

mechanical properties than stem ones, in term of maximum resistance and stiffness. In particular, the tensile strength of leaf fibers is about 55% higher than stem fibers (i.e., 98.7 MPa versus 63.5 MPa). On the other hand, the Young's modulus is about 76% higher for leaf fibers (11.85 GPa versus 6.73 GPa). On the contrary, the strain at break of stem fibers is slightly higher than that of leaf fibers (i.e., 1.92% versus 1.75%). Hence, it is possible to state that the mechanical response of both lemongrass fibers is quite comparable to that of other less common natural fibers such as Chrysanthemum morifolium [8], Aristida adscensionis [9], Symphirema involucratum [11], piassava [49] Pennisetum purpureum [50], Grewia tilifolia [51], Sansevieria ehrenbergii [52] and so on.

These experimental results can be explained by considering several factors influencing the mechanical response of natural fibers such as their chemical composition, microfibril angle, crystallinity index, density and morphology. In particular, the cellulose content positively influences the tensile strength and the Young's modulus of natural fibers because the cellulose microfibrils are more compact and close packing for fibers with increased cellulose [53]. Low microfibril angles indicate that the helically wound cellulose microfibrils in the middle layer of the secondary wall are almost aligned to the main fiber axis, thus leading to improved tensile properties [54]. Crystallinity index is a measure of the amount of crystalline cellulose with respect to the global amount of amorphous constituents of natural fibers. This parameter usually increases with the cellulose content and it has direct proportionality with tensile strength and Young's modulus of natural fibers [55].

Furthermore, it is widely known that the fibers morphology has a great impact on the mechanical response of natural fiber reinforced composites [56]. Indeed, the presence of defects such as dislocations, kinks, microcompressions curls and crimps affects the morphology of natural fibers thus reducing their mechanical properties [57].

Overall, natural fibers with high cellulose content and small microfibril angles, having high crystallinity index, more compact and homogeneous morphology as well as low ash and water contents are the most suitable for the manufacturing of biocomposites with good mechanical performances [58, 59].

# **Chemical Analysis**

The amount of chemical constituents in natural fibers plays a significant role in influencing their properties such as thermal stability, moisture absorption tendency and overall mechanical response.

Natural fibers present a hierarchical structure, mainly consisting of cellulose, hemicellulose, lignin, pectin and other compounds. In particular, each fiber consists of helically wound microfibrils of cellulose, bounded together by an amorphous lignin matrix whereas the hemicellulose is considered as compatibilizer between cellulose and lignin. Cellulose is a linear homopolymer, consisting in strong and linear (i.e., with no branches) molecules of linked D-glucose units. It is widely known that this component is the main responsible for the structural stability of natural fibers. Hence, the amount of cellulose in a fiber affects its mechanical strength and stiffness, and thus the composite's mechanical strength and stiffness.

The chemical composition of the investigated fibers is reported in Table 2. It is interesting to notice that the cellulose content of leaf fibers is slightly higher in comparison to stem fibers (i.e., 45.5% versus 44.25%). Moreover, stem fibers contain a little bit more hemicellulose (i.e., 29.15% versus 28.15%) than leaf fibers. It is well known that hemicellulose is a polysaccharide having lower molecular weight than cellulose. Furthermore, it contains several different sugar units (i.e., glucose, glucuronic acid, mannose, arabinose and xylose) in addition to exhibit a high degree of chain branching. Overall, the resulted random, amorphous branched or nonlinear structures with low strength [60]. Lignin content is quite identical for leaf and stem fibers (i.e., ~17%). Lignin is an amorphous and cross-linked polymeric network whose structure is a complex composition of aromatic rings with various branches. It is less polar and possesses lower strength than cellulose [61].

These experimental results allow explaining just partially the noticeable difference between leaf and stem fibers in terms of mechanical properties. The only noteworthy difference can be observed in the ash content (i.e., about 2% lower in leaf fibers) that could one of the reasons why leaf fibers show higher mechanical properties than stem ones.

Another important microstructural feature that could influence the mechanical behaviour of natural fibers is their crystallinity index, which is strictly related to the cellulose content. Indeed, natural fibers with low amounts of cellulose usually exhibit low crystalline content and vice versa [55].

XRD analysis evidenced that both lemongrass fibers show very close crystallinity index values (i.e., 46.7% and 45.2% for leaf and stem fibers, respectively). Moreover, it was shown that leaf fibers contain as crystalline compound only cellulose I $\alpha$  whereas stem fibers contain both Cellulose I $\alpha$  and Potassium chloride. By also considering the same amount of cellulose in the compared fibers (see Table 2), this results means that leaf fibers are characterized by a higher fraction of crystalline cellulose than leaf ones, thus contributing to justify its higher tensile properties. In particular, the improved stiffness of the fibers is attributed to the crystalline cellulosic region of the fiber [62].

The results of FTIR analysis (Fig. 6) confirmed that leaf and stem fibers are quite similar in terms of chemical composition.

A large peak centered at  $3325 \text{ cm}^{-1}$  can be visible for both fibers. However, this peak, attributable to the O–H stretching vibration and hydrogen bond of the hydroxyl groups [63, 64] is noticeably greater in the spectrum of stem fibers. This means that stem fibers are able to absorb more water in comparison to leaf ones.

On the other hand, two narrow and similar peaks centered at 2916 cm<sup>-1</sup> and 2850 cm<sup>-1</sup>, characteristic of the C-H stretching vibration from CH and CH<sub>2</sub> in polysaccharides (i.e., cellulose and hemicellulose) [65], can be identified in both spectra. Moreover, the absorption peak at 1737 cm<sup>-1</sup> due to the C=O stretching vibration of linkage of carboxylic acid in lignin or ester group in hemicellulose [63, 66].

It is worth noting that the peak located at about  $1600 \text{ cm}^{-1}$  is larger for stem fibers, thus confirming the presence of a greater amount of water in the latter in comparison to leaf fibers [67]. Similar peaks at 1374 cm<sup>-1</sup>, 1317 cm<sup>-1</sup> and 1243 cm<sup>-1</sup> are observed in both spectra. In particular, these peaks are due to the bending vibration of C-H and C-O groups of the aromatic ring in polysaccharides [68] whereas the absorbance peak centered at 1243 cm<sup>-1</sup> can be ascribed to the C–O stretching vibration of the acetyl group in lignin [69]. The shoulder at 1157 cm<sup>-1</sup> is associated to C–O–C stretching vibration of the pyranose ring in polysaccharides [63].

Ta	bl	e 2	2	Chemical	composition	of	lemongrass	fibers
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	Leaf	Stem
α-Cellulose	$45.50 \pm 0.20$	$44.25 \pm 0.35$
Hemicellulose	$28.15 \pm 0.35$	$29.15 \pm 0.35$
Lignin	$17.05 \pm 0.35$	$17.35 \pm 0.35$
Ash	$5.15 \pm 0.05$	$7.05\pm0.05$

Finally, an intense peak associated to the C–O stretching modes of hydroxyl and ether groups in cellulose is visible at  $1031 \text{ cm}^{-1}$  in both the spectra [65].

#### **Thermal Analysis**

TG and DTG curves of lemongrass fibers are shown in Fig. 7. As seen in Fig. 7b DTG curves of both fibers are characterized by three main peaks, each related to one decomposition stage.

An initial step of degradation that takes place below 100 °C can be associated with the dehydration of loosely bound water and low molecular weight compound [70].

As suggested by several Authors [50, 71], the first main peak at about 100 °C is related to the evaporation of the absorbed water. By comparing the TG and DTG curves of leaf and stem fibers, it is possible to notice that a greater amount of water is absorbed in stem fibers than in leaf ones. Indeed, weight loss of 12.2% and 8.1% at 150 °C were found for stem and leaf fibers, respectively. This finding is in full agreement with the results of FTIR analysis.

A second main peak, mainly ascribed to the degradation of the hemicellulose [71], can be observed at around 250 °C for both fibers. As clearly shown in Fig. 7b, this peak is slightly larger for stem fibers, thus confirming that the latter contains more hemicellulose than leaf fibers.

The third main peak occurred at around 310 °C and can be ascribed to the thermal decomposition of  $\alpha$ -cellulose [72]. For this decomposition stage, leaf fibers present a somewhat larger peak due to their higher  $\alpha$ -cellulose content in comparison to stem fibers (see Table 2). Similar peaks were observed at 310 °C, 352 °C, 320 °C, 321 °C, 308.2 °C, 298.2 °C and 309.2 °C for other natural fibers such as okra [40] artichoke [44] arundo [60] bamboo, hemp, jute and kenaf [73], respectively.



Fig. 6 FTIR spectra of leaf and stem lemongrass fibers

Moreover, lignin is the most difficult component to decompose because its decomposition happens at a very low mass loss rate in the whole temperature range from room temperature to 900  $^{\circ}$ C [63].

#### **Density Measurement and Morphological Analysis**

The experimental density values measured through helium pycnometer are equal to  $1.019 \text{ g/cm}^3$  and  $1.139 \text{ g/cm}^3$  for stem and leaf, respectively. It is worth noting that these experimental values are comparable to other natural fibers like curaua (i.e.,  $1.1-1.2 \text{ g/cm}^3$ ), palm (i.e.,  $1.03 \text{ g/cm}^3$ ) and coconut (i.e.,  $1.15 \text{ g/cm}^3$ ) and smaller than cotton (i.e.,  $1.5-1.6 \text{ g/cm}^3$ ), flax (i.e.,  $1.51-1.54 \text{ g/cm}^3$ ), hemp (i.e.,  $1.48 \text{ g/cm}^3$ ), sisal (i.e.,  $1.45 \text{ g/cm}^3$ ) and banana fibers (i.e.,  $1.35 \text{ g/cm}^3$ ) [1, 61, 74].

Furthermore, it can be noticed that leaf fibers show 12% higher density than stem fibers, thus suggesting that the latter are characterized by a less compact structure. The higher density of leaf fibers is in accordance with the chemical analysis which evidenced a slightly higher amount of cellulose content in these last in comparison to stem fibers [75]. Furthermore, this difference in the density can be explained by observing the morphology of the compared fibers.

The SEM micrographs of the cross section of both the fibers at two different magnifications (i.e.  $1500 \times and 5000 \times$ ) are reported in Fig. 8. In both cases, it is possible to observe the typical morphology of lignocellulosic fibers characterized by the presence of vascular bundles and fiber-cells (i.e., elementary fibers) with polygonal shape bonded together by pectin and other non-cellulosic compounds to form a bundle [76]. Nevertheless, stem and leaf fibers show different structures, i.e. different sizes, shape and arrangement of their cells as well as nature of lumen. In particular, the cross section of stem fibers is characterized by two central lumens nearly spherical with very large diameter [60]. On the other hand, leaf fibers shows narrow and in some cases elongated

lumens [40]. Furthermore, the overall size of fiber-cells is smaller than that of stem fibers, as clearly visible in Fig. 8b and d. These morphologies are in well agreement with the experimental density values.

The more compact structure of leaf fibers in addition to their higher density contribute to explain their better mechanical properties in terms of tensile modulus and strength in comparison to stem fibers, as widely reported in literature [77, 78].

# Conclusions

In the present paper natural fibers obtained from the leaf and the stem of lemongrass (Cymbopogon flexuosus) were compared for the first time to assess which part of this plant is more suitable as potential source of reinforcement for biocomposites. To this aim, leaf and stem fibers were characterized for their density, chemical composition, crystallinity, morphology, tensile and thermal properties. The mechanical results showed that the tensile strength and modulus of leaf fibers are 55% and 76% higher than that of stem fibers, respectively. On the contrary, the strain at break of stem fibers is higher than leaf ones (i.e., +30%). The compared fibers show similar amounts of cellulose (i.e., 44-45%), hemicellulose (i.e., 28–29%) and lignin (i.e., 17%) even though both the ash content and the amount of absorbed water are greater for stem fibers in comparison to leaf ones. Moreover, it seems that leaf fibers contain higher crystalline cellulose. From a morphological point of view, a more compact structure was shown by leaf fibers which also evidence higher density than culm fibers (i.e., 1.139 g/cm<sup>3</sup> versus 1.019 g/cm<sup>3</sup>). All these findings allow us to explain the different mechanical behavior shown by the compared fibers. As a future perspective, leaf and stem lemongrass fiber reinforced biocomposites will be investigated by also evaluating the effect of some eco-friendly treatment on their performances.



Fig. 7 (a) TGA and (b) DTG curves for leaf and stem fibers



Fig. 8 SEM micrographs of cross section of (a,c) stem and (b,d) leaf fibers at low (1500x) and high (5000x) magnifications

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**Data Availability** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

# Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

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# References

- Sarasini F, Fiore V (2018) A systematic literature review on less common natural fibres and their biocomposites. J Clean Prod 195:240–267. https://doi.org/10.1016/j.jclepro.2018.05.197
- Rajeshkumar G, Devnani GL, Maran JP et al (2021) Characterization of novel natural cellulosic fibers from purple bauhinia for potential reinforcement in polymer composites. Cellulose 28:5373–5385. https://doi.org/10.1007/s10570-021-03919-2
- Asyraf MRM, Ishak MR, Syamsir A et al (2022) Mechanical properties of oil palm fibre-reinforced polymer composites: a review. J Mater Res Technol 17:33–65. https://doi.org/10.1016/j.jmrt.2021. 12.122
- Bahrain SHK, Rahim NNCA, Mahmud J et al (2022) Hyperelastic properties of bamboo cellulosic fibre-reinforced silicone rubber biocomposites via compression test. Int J Mol Sci 23:6338. https:// doi.org/10.3390/ijms23116338
- Khan A, Vijay R, Singaravelu DL et al (2021) Extraction and characterization of natural fiber from *Eleusine indica* grass as reinforcement of sustainable fiber reinforced polymer composites. J Nat Fibers 18:1742–1750. https://doi.org/10.1080/15440 478.2019.1697993
- Khan A, Vijay R, Singaravelu DL et al (2021) Characterization of natural fibers from *Cortaderia selloana* Grass (Pampas) as reinforcement material for the production of the composites. J Nat Fibers 18:1893–1901. https://doi.org/10.1080/15440478.2019. 1709110
- Lemita N, Deghboudj S, Rokbi M et al (2022) Characterization and analysis of novel natural cellulosic fiber extracted from *Strelitzia reginae* plant. J Compos Mater 56:99–114. https://doi.org/ 10.1177/00219983211049285
- Dalmis R, Kilic GB, Seki Y et al (2020) Characterization of a novel natural cellulosic fiber extracted from the stem of *Chrysanthemum morifolium*. Cellulose 27:8621–8634. https://doi.org/10. 1007/s10570-020-03385-2
- Manimaran P, Saravanan SP, Sanjay MR et al (2020) New lignocellulosic Aristida adscensionis fibers as novel reinforcement for composite materials: extraction, characterization and Weibull distribution analysis. J Polym Environ 28:803–811. https://doi. org/10.1007/s10924-019-01640-7
- Wu S, Zhang J, Li C et al (2021) Characterization of potential cellulose fiber from cattail fiber: a study on micro/nano structure and other properties. Int J Biol Macromol 193:27–37. https://doi. org/10.1016/j.ijbiomac.2021.10.088
- Raju JSN, Depoures MV, Kumaran P (2021) Comprehensive characterization of raw and alkali (NaOH) treated natural fibers from *Symphirema involucratum* stem. Int J Biol Macromol 186:886– 896. https://doi.org/10.1016/j.ijbiomac.2021.07.061
- Narayanasamy P, Balasundar P, Senthil S et al (2020) Characterization of a novel natural cellulosic fiber from *Calotropis* gigantea fruit bunch for ecofriendly polymer composites. Int J

Biol Macromol 150:793-801. https://doi.org/10.1016/j.ijbiomac. 2020.02.134

- Mori S, Charca S, Flores E, Savastano H (2021) Physical and thermal properties of novel native andean natural fibers. J Nat Fibers 18:475–491. https://doi.org/10.1080/15440478.2019.1629150
- Haque ANMA, Remadevi R, Naebe M (2018) Lemongrass (Cymbopogon): a review on its structure, properties, applications and recent developments. Cellulose 25:5455–5477. https://doi.org/10.1007/s10570-018-1965-2
- Robbins SRJ (1983) Selected markets for the essential oils of lemongrass, citronella and eucalyptus. In: Essential oils marketing, pp 54–68
- Kaur H, Dutt D, Tyagi CH (2011) Optimization of soda pulping process of lignocellulosic residues of lemon and sofia grasses produced after steam distillation. BioResources 6:103–120. https:// doi.org/10.15376/biores.6.1.103-120
- Skaria BP, Joy PP, Mathew S, Mathew G (2006) Lemongrass. In: Peter KV (ed) Handbook of herbs and spices. Woodhead Publishing Limited, Sawston, pp 400–418
- Hamzah MH, Che Man H, Abidin ZZ, Jamaludin H (2014) Comparison of citronella oil extraction methods from *Cymbopogon nardus* grass by ohmic-heated hydro-distillation, hydrodistillation, and steam distillation. BioResources 9:256–272
- Tran TH, Tran TKN, Ngo TCQ et al (2021) Color and composition of beauty products formulated with lemongrass essential oil: cosmetics formulation with lemongrass essential oil. Open Chem 19:820–829. https://doi.org/10.1515/chem-2021-0066
- Kamaruddin ZH, Jumaidin R, Selamat MZ, Ilyas RA (2021) Characteristics and properties of lemongrass (*Cymbopogan cit-ratus*): a comprehensive review. J Nat Fibers. https://doi.org/10. 1080/15440478.2021.1958439
- Mukarram M, Choudhary S, Khan MA et al (2022) Lemongrass essential oil components with antimicrobial and anticancer activities. Antioxidants 11:20. https://doi.org/10.3390/antio x11010020
- 22. Lima LR, Andrade FK, Alves DR et al (2021) Anti-acetylcholinesterase and toxicity against *Artemia salina* of chitosan microparticles loaded with essential oils of *Cymbopogon flexuosus*, *Pelargonium* x ssp and *Copaifera officinalis*. Int J Biol Macromol 167:1361–1370. https://doi.org/10.1016/j.ijbiomac.2020.11.090
- Alfa IM, Dahunsi SO, Iorhemen OT et al (2014) Comparative evaluation of biogas production from Poultry droppings, Cow dung and Lemon grass. Bioresour Technol 157:270–277. https:// doi.org/10.1016/j.biortech.2014.01.108
- Nur Firdaus MY, Osman H, Metselaar HSC, Rozyanty AR (2015) A simple method for the production of pure crystalline silica from lemon grass. BioResources 11:1270–1279. https://doi.org/10. 15376/biores.11.1.1270-1279
- Sharma N, Godiyal RD, Bhawana et al (2022) Insight into papermaking characteristics of D0EPD1-bleached soda, soda-AQ and kraft pulps of citronella grass (*Cymbopogon winterianus* Jowitt). Biomass Convers Biorefinery 12:427–440. https://doi.org/10. 1007/s13399-020-00730-0
- Babarinde A, Ogundipe K, Sangosanya KT, AkintolaHassan BDAOE (2016) Comparative study on the biosorption of Pb(II), Cd(II) and Zn(II) using Lemon grass (*Cymbopogon citratus*): kinetics, isotherms and thermodynamics. Chem Int 2:89–102. https://doi.org/10.5281/ZENODO.1470603
- Jing H, He H, Liu H et al (2021) Study on properties of polylactic acid/lemongrass fiber biocomposites prepared by fused deposition modeling. Polym Compos 42:973–986. https://doi.org/10.1002/pc. 25879
- Raja S, Rajesh R, Indran S et al (2021) Characterization of industrial discarded novel *Cymbopogon flexuosus* stem fiber: a potential replacement for synthetic fiber. J Ind Text. https://doi.org/10.1177/ 15280837211007507

- Soma Sundaram Pillai R, Rajamoni R, Suyambulingam I et al (2021) Synthesis and characterization of cost-effective industrial discarded natural ceramic particulates from *Cymbopogon flexuosus* plant shoot for potential polymer/metal matrix reinforcement. Polym Bull. https://doi.org/10.1007/s00289-021-03913-5
- Bekele LD, Zhang W, Liu Y et al (2017) Preparation and characterization of lemongrass fiber (*Cymbopogon* species) for reinforcing application in thermoplastic composites. BioResources 12:5664–5681. https://doi.org/10.15376/biores.12.3.5664-5681
- Sundaram RS, Rajamoni R, Suyambulingam I, Isaac R (2021) Comprehensive characterization of industrially discarded *Cymbopogon flexuosus* stem fiber reinforced unsaturated polyester composites: effect of fiber length and weight fraction. J Nat Fibers. https://doi.org/10.1080/15440478.2021.1944435
- 32. Kamaruddin ZH, Jumaidin R, Ilyas RA et al (2022) Biocomposite of Cassava starch-*Cymbopogan citratus* fibre: mechanical, thermal and biodegradation properties. Polymers 14:514. https://doi.org/ 10.3390/polym14030514
- Fiore V, Badagliacco D, Sanfilippo C et al (2021) An innovative treatment based on sodium citrate for improving the mechanical performances of flax fiber reinforced composites. Polymers 13:1–19. https://doi.org/10.3390/polym13040559
- Fiore V, Sanfilippo C, Calabrese L (2019) Influence of sodium bicarbonate treatment on the aging resistance of natural fiber reinforced polymer composites under marine environment. Polym Test 80:106100. https://doi.org/10.1016/j.polymertesting.2019.106100
- dos Santos JC, Siqueira RL, Vieira LMG et al (2018) Effects of sodium carbonate on the performance of epoxy and polyester coirreinforced composites. Polym Test 67:533–544. https://doi.org/10. 1016/j.polymertesting.2018.03.043
- 36. dos Santos JC, de Oliveira LÁ, Gomes Vieira LM et al (2019) Eco-friendly sodium bicarbonate treatment and its effect on epoxy and polyester coir fibre composites. Constr Build Mater 211:427– 436. https://doi.org/10.1016/j.conbuildmat.2019.03.284
- Asyraf MRM, Syamsir A, Supian ABM et al (2022) Sugar palm fibre-reinforced polymer composites: influence of chemical treatments on its mechanical properties. Materials 15:3852. https://doi. org/10.3390/ma15113852
- Haris NIN, Hassan MZ, Ilyas RA et al (2022) Dynamic mechanical properties of natural fiber reinforced hybrid polymer composites: a review. J Mater Res Technol 19:167–182. https://doi.org/ 10.1016/j.jmrt.2022.04.155
- 39. Asyraf MRM, Ishak MR, Norrrahim MNF et al (2022) Potential of flax fiber reinforced biopolymer composites for cross-arm application in transmission tower: a review. Fibers Polym 23:853–877. https://doi.org/10.1007/s12221-022-4383-x
- De Rosa IM, Kenny JM, Puglia D et al (2010) Morphological, thermal and mechanical characterization of okra (*Abelmoschus esculentus*) fibres as potential reinforcement in polymer composites. Compos Sci Technol 70:116–122. https://doi.org/10.1016/j. compscitech.2009.09.013
- Andersons J, Sparniņš E, Joffe R, Wallström L (2005) Strength distribution of elementary flax fibres. Compos Sci Technol 65:693–702. https://doi.org/10.1016/j.compscitech.2004.10.001
- Peponi L, Biagiotti J, Torre L et al (2008) Statistical analysis of the mechanical properties of natural fibers and their composite materials. I. Natural fibers. Polym Compos 29:313–320. https:// doi.org/10.1002/pc.20408
- Kushner R, Hoffer A (1933) Cellulose and cellulose derivate. Fresenius' J Anal Chem 92:145–154
- Fiore V, Valenza A, Di Bella G (2011) Artichoke (*Cynara cardunculus* L.) fibres as potential reinforcement of composite structures. Compos Sci Technol 71:1138–1144. https://doi.org/10.1016/j. compscitech.2011.04.003

- Wang F, Shao J (2014) Modified Weibull distribution for analyzing the tensile strength of bamboo fibers. Polymers 6:3005–3018. https://doi.org/10.3390/polym6123005
- Trujillo E, Moesen M, Osorio L et al (2014) Bamboo fibres for reinforcement in composite materials: strength Weibull analysis. Compos Part A Appl Sci Manuf 61:115–125. https://doi.org/10. 1016/j.compositesa.2014.02.003
- Sayeed MMA, Paharia A (2019) Optimisation of the surface treatment of jute fibres for natural fibre reinforced polymer composites using Weibull analysis. J Text Inst 110:1588–1595. https://doi.org/ 10.1080/00405000.2019.1610998
- Ravandi M, Hajizadeh P (2022) Application of approximate Bayesian computation for estimation of modified weibull distribution parameters for natural fiber strength with high uncertainty. J Mater Sci 57:2731–2743. https://doi.org/10.1007/ s10853-021-06850-w
- d'Almeida JRM, Aquino RCMP, Monteiro SN (2006) Tensile mechanical properties, morphological aspects and chemical characterization of piassava (*Attalea funifera*) fibers. Compos Part A Appl Sci Manuf 37:1473–1479. https://doi.org/10.1016/j.compo sitesa.2005.03.035
- Ridzuan MJM, Abdul Majid MS, Afendi M et al (2016) Characterisation of natural cellulosic fibre from *Pennisetum purpureum* stem as potential reinforcement of polymer composites. Mater Des 89:839–847. https://doi.org/10.1016/j.matdes.2015.10.052
- Jayaramudu J, Guduri BR, Varada Rajulu A (2010) Characterization of new natural cellulosic fabric *Grewia tilifolia*. Carbohydr Polym 79:847–851. https://doi.org/10.1016/j.carbpol.2009.10.046
- 52. Sathishkumar TP, Navaneethakrishnan P, Shankar S, Rajasekar R (2013) Characterization of new cellulose sansevieria ehrenbergii fibers for polymer composites. Compos Interfaces 20:575–593. https://doi.org/10.1080/15685543.2013.816652
- Sathishkumar TP, Navaneethakrishnan P, Shankar S et al (2013) Characterization of natural fiber and composites—a review. J Reinf Plast Compos 32:1457–1476
- Senthamaraikannan P, Kathiresan M (2018) Characterization of raw and alkali treated new natural cellulosic fiber from *Coccinia* grandis L. Carbohydr Polym 186:332–343. https://doi.org/10. 1016/j.carbpol.2018.01.072
- Moriana R, Vilaplana F, Karlsson S, Ribes A (2014) Correlation of chemical, structural and thermal properties of natural fibres for their sustainable exploitation. Carbohydr Polym 112:422–431. https://doi.org/10.1016/j.carbpol.2014.06.009
- Hughes M (2012) Defects in natural fibres: their origin, characteristics and implications for natural fibre-reinforced composites. J Mater Sci 47:599–609. https://doi.org/10.1007/ s10853-011-6025-3
- 57. Baley C (2002) Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase. Compos Part A Appl Sci Manuf 33:939–948. https://doi.org/10.1016/S1359-835X(02) 00040-4
- Ververis C, Georghiou K, Christodoulakis N et al (2004) Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production. Ind Crops Prod 19:245–254. https://doi.org/10.1016/j.indcrop.2003.10.006
- 59. Badagliacco D, Sanfilippo C, Megna B et al (2021) Mechanical and thermal properties of insulating sustainable mortars with *Ampelodesmos mauritanicus* and *Pennisetum setaceum* plants as aggregates. Appl Sci 11:5910. https://doi.org/10.3390/app11 135910
- Fiore V, Scalici T, Valenza A (2014) Characterization of a new natural fiber from *Arundo donax* L. as potential reinforcement of polymer composites. Carbohydr Polym 106:77–83. https://doi.org/ 10.1016/j.carbpol.2014.02.016

- Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. Prog Polym Sci 24:221–274. https://doi.org/ 10.1016/S0079-6700(98)00018-5
- Kalia S, Kaith BS, Kaur I (2009) Pretreatments of natural fibers and their application as reinforcing material in polymer composites-a review. Polym Eng Sci 49:1253–1272. https://doi.org/10. 1002/pen.21328
- Yang H, Yan R, Chen H et al (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86:1781–1788. https:// doi.org/10.1016/j.fuel.2006.12.013
- Seki Y, Sarikanat M, Sever K, Durmuşkahya C (2013) Extraction and properties of *Ferula communis* (chakshir) fibers as novel reinforcement for composites materials. Compos Part B Eng 44:517–523. https://doi.org/10.1016/j.compositesb.2012.03.013
- Paiva MC, Ammar I, Campos AR et al (2007) Alfa fibres: mechanical, morphological and interfacial characterization. Compos Sci Technol 67:1132–1138. https://doi.org/10.1016/j.compscitech. 2006.05.019
- Alawar A, Hamed AM, Al-Kaabi K (2009) Characterization of treated date palm tree fiber as composite reinforcement. Compos Part B Eng 40:601–606. https://doi.org/10.1016/j.compositesb. 2009.04.018
- Olsson AM, Salmén L (2004) The association of water to cellulose and hemicellulose in paper examined by FTIR spectroscopy. Carbohydr Res 339:813–818. https://doi.org/10.1016/j.carres.2004. 01.005
- LeTroedec M, Sedan D, Peyratout C et al (2008) Influence of various chemical treatments on the composition and structure of hemp fibres. Compos Part A Appl Sci Manuf 39:514–522. https:// doi.org/10.1016/j.compositesa.2007.12.001
- Liu W, Mohanty AK, Drzal LT et al (2004) Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites. J Mater Sci 39:1051–1054. https://doi.org/10.1023/B:JMSC. 0000012942.83614.75
- Jumaidin R, Sapuan SM, Jawaid M et al (2017) Thermal, mechanical, and physical properties of seaweed/sugar palm fibre reinforced thermoplastic sugar palm Starch/Agar hybrid composites.

Int J Biol Macromol 97:606–615. https://doi.org/10.1016/j.ijbio mac.2017.01.079

- Saravanakumar SS, Kumaravel A, Nagarajan T et al (2013) Characterization of a novel natural cellulosic fiber from *Prosopis juliflora* bark. Carbohydr Polym 92:1928–1933. https://doi.org/10. 1016/j.carbpol.2012.11.064
- Albano C, González J, Ichazo M, Kaiser D (1999) Thermal stability of blends of polyolefins and sisal fiber. Polym Degrad Stab 66:179–190. https://doi.org/10.1016/S0141-3910(99)00064-6
- Yao F, Wu Q, Lei Y et al (2008) Thermal decomposition kinetics of natural fibers: activation energy with dynamic thermogravimetric analysis. Polym Degrad Stab 93:90–98. https://doi.org/10. 1016/j.polymdegradstab.2007.10.012
- Aquino EMF, Sarmento LPS, Oliveira W, Silva RV (2007) Moisture effect on degradation of jute/glass hybrid composites. J Reinf Plast Compos 26:219–233. https://doi.org/10.1177/0731684407 070030
- Mwaikambo LY, Ansell MP (2001) The determination of porosity and cellulose content of plant fibers by density methods. J Mater Sci Lett 20:2095–2096. https://doi.org/10.1023/A:1013703809 964
- 76. Razali N, Salit MS, Jawaid M et al (2015) A study on chemical composition, physical, tensile, morphological, and thermal properties of roselle fibre: effect of fibre maturity. BioResources 10:1803–1823. https://doi.org/10.15376/biores.10.1.1803-1824
- 77. Rohen LA, Neves ACC, de P. Mantovani D et al (2017) Hemp fiber density using the pycnometry technique. In: Minerals, metals and materials series. Springer, Berlin, pp 423–428
- Adeniyi AG, Onifade DV, Ighalo JO, Adeoye AS (2019) A review of coir fiber reinforced polymer composites. Compos Part B Eng 176:107305. https://doi.org/10.1016/j.compositesb.2019.107305

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