

# Analysis of Polymeric Composites of Phormium Tenax

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**Abstract:** *Phormium tenax* is a vegetal fiber with a mechanical strength of  $711 \pm 61.1$  MPa, which is higher than the range of sisal (468-640MPa) and similar to the well-known curauá fiber (913 MPa). In this study, *Phormium tenax* composites coated with maleated polypropylene in a polypropylene matrix were prepared with 20%, 30%, and 35wt% of fibers, with and without aluminum sheets made from beverage cans. Some samples were made by extrusion and compression molding process, and others only through compression molding. In addition, density tests indicated lightness in composites of *Phormium tenax*. Samples were submitted to thermal analyzes, X-ray diffraction, Fourier Transform with Infrared Region, and scanning electron microscopy. Their fibers content of cellulose, hemicellulose, lignin, ashes, and total extractives are respectively 44.27%, 13.20%, 15.02%, 23.4%, and 4.11%. Some based-PP composites reinforced with *Phormium tenax* showed improvement in the flexural strength, such as based-PP reinforced with long and continuous fibers, with a flexural strength of 64.94 MPa, and 52,30 MPa, respectively. It was concluded that tensile strength in PP-based composites reinforced with *Phormium tenax* could be enhanced with some adjustments in the material processing.

**Keywords:** vegetal fibers; chemical characterization; composites properties; *Phormium tenax*.

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## 1. Introduction

Incorporating lignocellulosic fibers into polymeric materials used in numerous fields, such as construction transportation, is increasing [1]. Plant fibers can improve the properties of polymer blends and their lightness and, depending on their chemical composition, increase strength and thermal stability. Moreover, they are abundant, low-priced, renewable, less abrasive, and biodegradable [2,3]. Natural fibers are preferable to synthetic ones due to increased climate awareness, scarcity of petroleum resources, and material availability and sustainability. Additionally, they are potential reinforcement materials in the composites industry and, since they are less expensive than the polymer matrix, reduce products' cost [4].

*Phormium tenax* is a plant belonging to the family *Hemerocallidaceae*. It is native to New Zealand and adjacent islands. It grows spontaneously from floodplains to hillsides and from sea level to 1,200 m altitude [5], adapting to equatorial, oceanic, subtropical, and tropical climates [6]. Furthermore, some of its varieties are variegated, meaning they present long stripes of colors different from the leaves' predominant one [7]. The estimated holocellulose amount in *Phormium tenax* is approximately 57.5%, which is similar to that of sources traditionally used in the pulp and paper industry, such as *Pinus sylvestris* (~68%) [26] and *Eucalyptus grandis* (59.8%) [8]. A recent study on *Phormium tenax* as a polymer composite

reinforcement was carried out by Palanisamy *et al.* [9], who used its fiber to reinforce natural rubber composites. Li *et al.* [10] explored the recent advances in natural fiber-reinforced polymer composites in a literature review analyzing studies focused on using this fiber. In addition, experiments using nanocelluloses from *Phormium tenax* were performed to examine the fiber behavior in the production of cellulose nanocrystals and nanofibers - however, with no use of chemical treatments [11].

Considering the worldwide increased demand for natural resources - which is related to concerns regarding scarcity of materials and environmental conservation [12] - this study proposes using *Phormium tenax* fibers to prepare polymer composites since they are a low cost and renewable resource. Materials produced with *Phormium tenax* have a good appearance and possible antioxidant activities due to the plant's large hydrophilic portion, which defends the organism against insect attacks [13]. This antioxidant property that prevents mold can be applied in ornaments, rigid packaging, small containers, and furniture such as chairs and tables used in cafeterias and bakeries. By applying techniques such as changing the composites processing and using compatibilization, alkaline treatment, or surface modification, it is possible to improve the mechanical properties for semi-structural applications [14]. In addition, composites containing polypropylene (PP) and aluminum sheets made from beverage cans stimulate the packaging reuse and PP recycling, adding value to the materials recycled or disposed into the environment. As for *Phormium tenax* fiber-reinforced composites, they can contribute to recyclers' income generation. In light of this context, this study aims to chemically characterize *Phormium tenax* fibers, correlating its results with the mechanical properties of *Phormium tenax* composites. The combination of metal sheets (FML, fiber-metal laminates) and a polymeric matrix is investigated for applications in civil construction structures due to its synergistic effect on several properties, such as corrosion resistance, thermal conductivity, density, and stiffness, justifying studies on the development of new materials using aluminum sheets [15,16].

## 2. Materials and Methods

This section addresses the materials and procedures of chemical characterization, composite manufacturing, mechanical characterization, density analysis, XRD analysis, morphological characterization, FTIR analysis, and thermal characterization.

### 2.1. Chemical characterization.

Leaf samples of *Phormium tenax* were collected in the town of Quatro Barras (Paraná State), located in southern Brazil, a subtropical climate region. Manual collection occurred in October 2018, during spring, a period of frequent rainfall. The leaves were dried naturally in sunlight for two months. Although natural drying is slower than the artificial one, this method was considered more appropriate since the study used a limited amount of leaves (meaning it was not very short-term research) and considered costs with energy and equipment, as well as with greenhouses or environments thermally controlled at temperatures between 70 °C and 100 °C [17]. In addition to the fiber extraction technique, climate and soil conditions, that is, the cultivation area, interfere in the diversification of fiber properties, especially regarding chemical composition [18].

The samples were prepared according to the TAPPI T257 sp-14 method [19]. Moisture content was determined according to the TAPPI T264 method [20]; ash content according to

the TAPPI T211 om-16 [21]; total extractives according to the TAPPI T204 cm-17 [22], and Klason lignin (insoluble lignin) according to the TAPPI T222 om-15 [23]. Soluble lignin was determined using the method proposed by Goldschimid [24], meaning the filtered content was measured by ultraviolet spectroscopy (UV1800, Shimadzu, UV Probe Photometric software, Probe version 2.33). Total lignin was determined by the sum of the soluble and insoluble lignin amounts. The remaining filtered material was classified as holocellulose (cellulose + hemicellulose). All procedures were performed in triplicate. Cellulose and hemicellulose contents were determined by the NREL/TP 510 method [25] using a Shimadzu chromatograph (model LC10AD) equipped with a Rezex column, as well as the Labsolution software (Shimadzu).

## 2.2. Composites manufacturing.

Table 1 shows the nine composite samples prepared for this study, which were named from C1 to C9. Samples C1, C2, C3, C4, C5, and C6 were produced by extrusion and compression molding, whereas samples C7, C8, and C9 solely by compression molding. Maleated polypropylene (MAPP) was produced by reactive extrusion of PP using 1% (w/w) maleic anhydride and 0.5% (w/w) dicumyl peroxide [26]. All compositions are presented in Table 1.

**Table 1.** Composition in wt% for nine samples of PP-based composites reinforced with *Phormium tenax* fibers.

| Composites | PP composition (wt%) | <i>Phormium tenax</i> fiber composition (wt%) | MAPP composition (wt%) | Aluminum sheet composition (wt%) |
|------------|----------------------|-----------------------------------------------|------------------------|----------------------------------|
| C1         | 70                   | 20                                            | 10                     | 0                                |
| C2         | 64                   | 20                                            | 10                     | 6                                |
| C3         | 60                   | 30                                            | 10                     | 0                                |
| C4         | 54                   | 30                                            | 10                     | 6                                |
| C5         | 55                   | 35                                            | 10                     | 0                                |
| C6         | 49                   | 35                                            | 10                     | 6                                |
| C7         | 70                   | 20                                            | 10                     | 0                                |
| C8         | 70                   | 20                                            | 10                     | 0                                |
| C9         | 70                   | 20                                            | 10                     | 0                                |

C1 to C6 samples were produced using short *Phormium tenax* fibers approximately 5 mm long. Short fibers of *Phormium tenax*, MAPP, and PP were dried at 60 °C in an oven for 48 hours. Extrusion was carried out in two stages: first, the fibers were coated with MAPP and 40% of the PP needed for each specimen production. Since the purpose of the compatibilizer agent is to improve fibers' wettability and produce a strong interaction between their surface and PP molecules [27] - in addition to reducing the process's high material loss -, the MAPP coating was conducted to approximate the fibers to the compatibilizer, avoiding to blend them amidst the PP matrix. In the second, composites were reprocessed to complete each composition's remaining proportion of PP and homogenize the material. Santos, Flores-Sahagun, and Satyanarayana [26] used the methodology both with one and two steps of extrusion for the same extruder and observed that the samples produced in two steps were more resistant than those produced in only one. A single-screw extruder (model EMT-25, Teck Trill) with 30 W/D (width to diameter ratio), three heating zones, and one head was used to manufacture the samples. The material was processed at 172 °C in all three zones and 174 °C in the head, using a maximum electrical current of 6.4 A and spindle speed between 15 rpm and 20 rpm. The heated material produced by the extruder was cooled in water at room

temperature and granulated under a rotation of 200 rpm. All materials were weighed to produce 1 kg of composite.

After extrusion, composite specimens for tensile, impact, or flexural tests were produced by compression molding using a Solab press (model SL099). The molding was conducted at 180 °C in three continuous and consecutive steps, with a pressure ranging from 1 to 4 tonnes-force. Then, the specimens were submitted to surface treatment. In some samples, an aluminum sheet with the specimen dimensions and thickness of a few tenths of a millimeter was placed in the middle of each mold cavity and covered by two composite films, one on each side. Subsequently, the mold was closed. The aluminum sheets were obtained by stretching beverage cans with no varnish or painting, which were removed by chemical and mechanical treatments. The aluminum sheets were used in some samples to evaluate possible improvements in the quality of the composites regarding structural applications since it is a resistant material of low density and capable of strengthening sandwich beams.

Samples C7, C8, and C9 composite were produced only by compression and using, respectively, 5 mm short fibers, 50 mm long fibers, and continuous fibers according to the size of each specimen. Nine samples were produced and tested for nine varieties of composite materials and pure PP. The average useful dimensions were 68.5 x 13 x 3 mm for all tensile test specimens, 80 x 13 x 3 mm for flexural test specimens, and 63.5 x 12.5 x 3 mm for IZOD impact test specimens.

### 2.3. Mechanical characterization.

For the tensile test and the composites samples, nine fiber samples of 80 mm length were used *in natura*, that is, with no chemical or physical treatment. According to ASTM D638-14 [28], the tensile tests were carried out using an Instron tester (model 5567) with a 5 kN load cell and at a test speed of 5 mm/min. Data were generated by Bluehill 2 software. The flexural tests were carried out according to ASTM D790-10 [29] and using flexion at three points in an EMIC device (model DL-2000) with a 20 kN load cell and a test speed of 15 mm/min. The distance between supports was maintained at 80 mm for all specimens, and data were generated by the Tesc software. The IZOD impact tests were performed according to ASTM D 256-10 [30] on an EMIC impact pendulum equipped with a 5.4 J hammer. Samples remained un-notched due to their brittle behavior and low toughness. Five thickness measurements were performed using a digital caliper with 0.01 mm resolution in order to calculate the cross-sectional area of each sample. All tests were carried out at room temperature.

### 2.4. Density analysis.

The experimental density was obtained using the ASTM D2395-14 method [31] and compared with the theoretical density, in which volume was calculated according to the dimensions of each specimen. The volume of the samples was obtained by measuring the displaced water volume in a graduated cylinder with 0.5 ml markings using a caliper with 0.05 mm resolution.

### 2.5. Morphological characterization.

Fifteen composite samples were selected for a scanning electron microscopy (SEM) analysis at 200x magnification in a TESCAN microscope (model VEGA3). All images were obtained through secondary electrons using voltage acceleration between 10 kV and 20 kV and

after gold metallization. Thermogravimetric analysis (TGA) of the fibers was carried out in a 50 ml.min<sup>-1</sup> synthetic air atmosphere under constant heating of 10 °C.min<sup>-1</sup>.

## 2.6. XRD analysis.

X-ray diffraction (XRD) was performed in triplicate samples of PP, MAPP, fiber, and composites with 20%, 30%, and 35% (w/w) fiber. All materials were powdered by a household blender (Oster). In total, eighteen analyses were performed. The XRD tests were performed at 40 kV and 20 mA over an angular range of 5° to 60° and with a constant scan rate of 1° per minute. For the XRD tests, an XRD-7000 diffractometer equipped with a CuK<sub>α</sub> radiation source ( $\lambda=1.54$  Å) was used in a temperature-controlled room at 25 °C. Data were analyzed via PCXRD Software.

## 2.7. FTIR analysis.

Samples of *Phormium tenax* fibers were analyzed by Fourier Transform Infrared spectroscopy (FTIR) in the region of 4,000 - 374 cm<sup>-1</sup>, which performed approximately 30 scans per spectrum with a resolution of 1.4 cm<sup>-1</sup>. An Alpha P-ATR Infrared Spectrophotometer and the Simple Single Channel Software were used.

## 2.8. Thermal characterization.

Finally, *Phormium tenax* fiber samples were analyzed by Differential Scanning Calorimetry (DSC) using a Perkin Elmer DSC 8500 equipment and the Pyris Series Thermal Analysis Software (version 11.1). For this purpose, only powdered samples weighing between 4.2 mg and 4.5 mg were used (the analysis was performed on a digital scale model AD6). The experiment was conducted in a single temperature run from -30 °C to 180 °C and with a constant speed of 10 °C/min. The equipment used a nitrogen atmosphere of approximately -120 °C, and the samples were encapsulated in a 50 µl aluminum crucible. The experiment was performed in triplicate.

# 3. Results and Discussion

This section is divided into chemical characterization, mechanical characterization, density analysis, XRD analysis, FTIR analysis, morphological and thermal characterization. Morphological characterization is described throughout the mechanical characterization, density characterization, and FTIR analysis.

## 3.1. Chemical characterization.

The cellulose and hemicellulose *Phormium tenax* contents were 44.27% and 13.20%, respectively (holocellulose was 57.97%). The cellulose content is similar to the 46% found by Giorgio *et al.* [11] and below the 60% found by Fortunati *et al.* [32]. For comparison purposes with the *Phormium tenax* chemical composition, Table 2 presents the composition of both *Phormium tenax* and other plant fibers. The mean values and their respective standard deviations are also presented.

**Table 2.** Chemical composition of vegetable fibers.

| Sample | Total extractives (%) | Lignin (%) | Moisture (%) | Cellulose (%) | Hemicellulose |
|--------|-----------------------|------------|--------------|---------------|---------------|
| Cotton | 7.3                   | 0.0        | 10           | 82.7          | 5.7           |

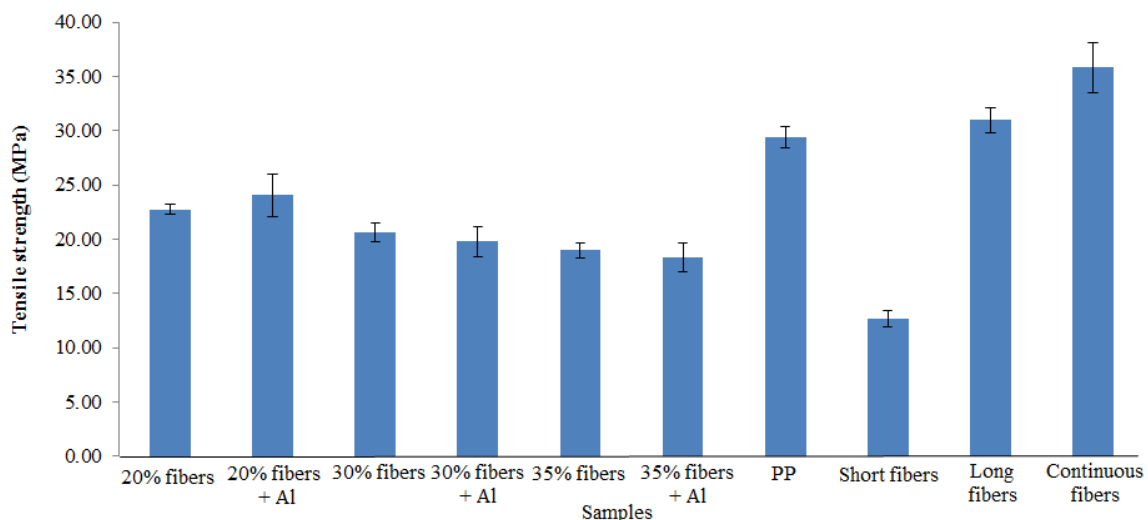
| Sample                | Total extractives (%) | Lignin (%) | Moisture (%) | Cellulose (%) | Hemicellulose |
|-----------------------|-----------------------|------------|--------------|---------------|---------------|
| Jute                  | 1.8                   | 11.8       | 10           | 64.4          | 12.0          |
| Linen                 | 7.2                   | 2.0        | 10           | 64.1          | 16.7          |
| <i>Phormium tenax</i> | 23.4                  | 15.0       | 11           | 44.3          | 13.2          |
| Ramie                 | 7.7                   | 0.6        | 10           | 68.6          | 13.1          |
| Sisal                 | 2.3                   | 9.9        | 10           | 65.8          | 12.0          |

*Phormium tenax* moisture content was approximately 11%, revealing an influence of the material climatic and storage conditions. Ash content was similar to the average rates found by Accioly [33], who analyzed 100 grass species and found values ranging between 4.01% and 8% in 79 of them. The high amount of *Phormium tenax* total extractives is due to its shrub foliage, which is susceptible to insect, fungi, and other pathogens' attacks. The plant's hydrophilic portion, used for self-defense, presents high *in vitro* activity. The *Phormium tenax* macro constituents (cellulose, hemicellulose, and lignin) correspond to approximately 72.5% of its composition. It comprises the cellulose fraction, which is responsible for the structural and support functions of the plant. This is because lignin and hemicellulose are impurities lying in intra-fibrillar regions - lignin causes the fiber's stiffness and hydrophobicity.

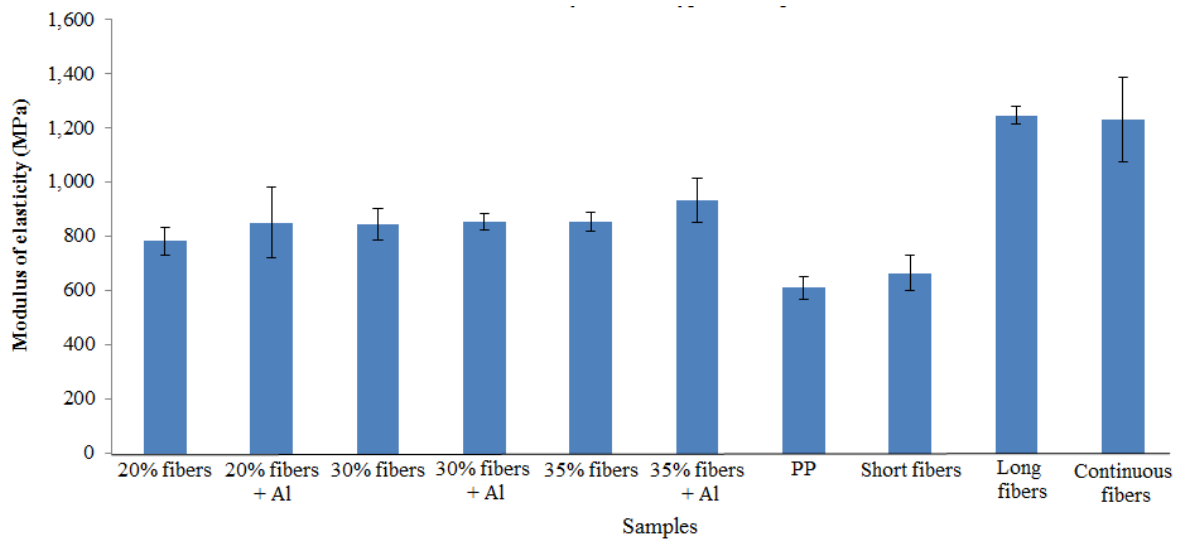
In contrast, the hydrogen bonds that connect hemicellulose to fibrils' cross-sections also cause stiffness [34]. The high amount of total extractives provides the plant its antioxidant properties, a better appearance, and a pleasant smell. Considering the standard deviation, the cellulose content found in this study can reach 45.2%, similar to that found by Giorgio *et al.* [11] and within the range from 45.10% to 72% indicated by Rosa, Santulli, and Sarasini [35].

### 3.2. Mechanical characterization.

Figures 1, 2, 4, and 5 present the mean values of the five best results among the nine samples of each variety of composite material and pure PP. The tensile strength presented by the tensile tests for *in natura Phormium tenax* fibers was  $711.9 \pm 61.1$  MPa, and its modulus of elasticity was  $36.3 \pm 8.7$  GPa. Figures 1 and 2 show the values for materials subjected to tensile tests. The initial length of each specimen was 80 mm, and elongation was approximately  $5.11 \pm 3.18\%$ . The Figures show the mean value of five samples for each variety.

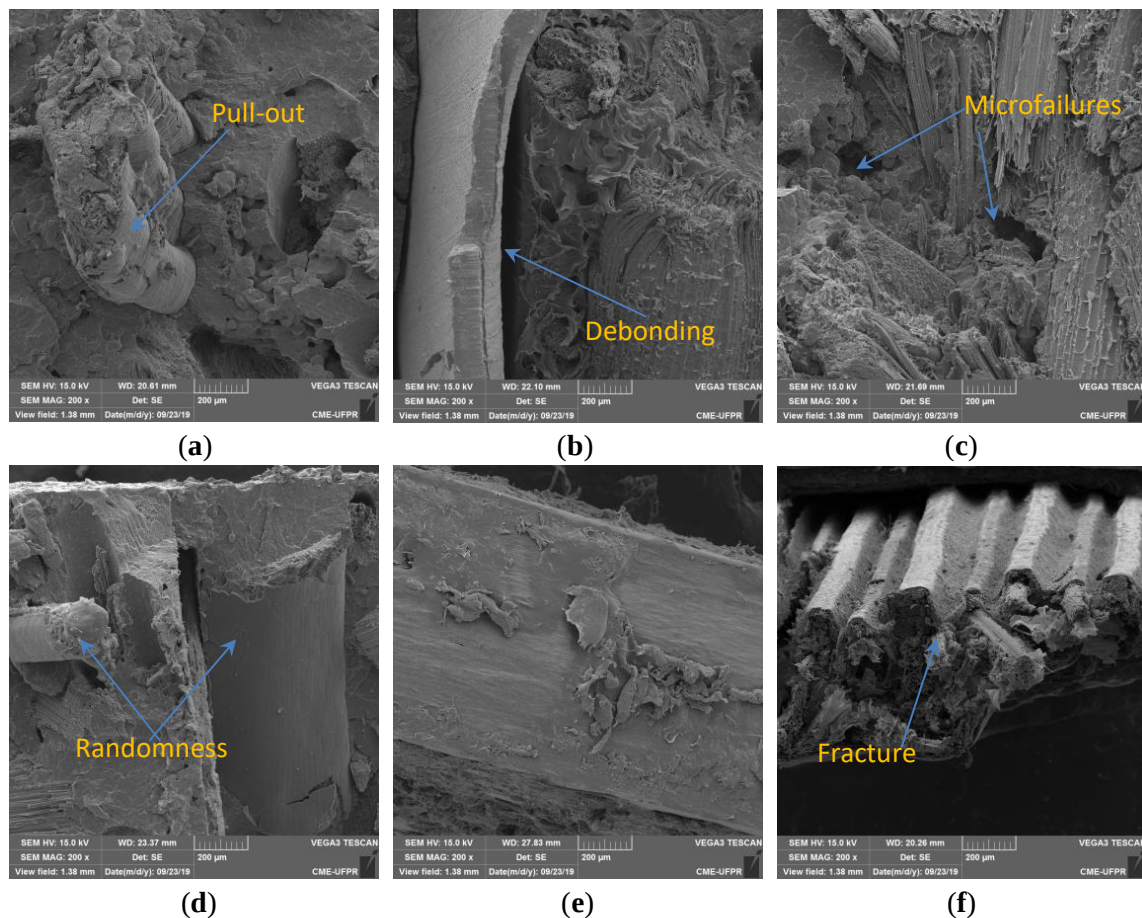


**Figure 1.** Comparison between the tensile strength in MPa of different types of composite materials and pure PP.\*



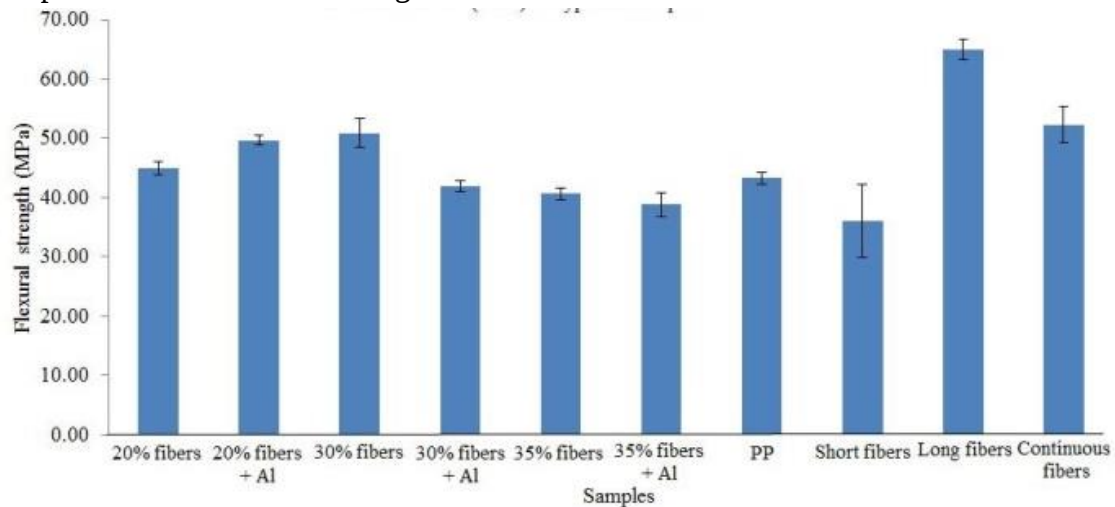
**Figure 2.** Comparison between the modulus of elasticity in MPa of different types of composite materials and pure PP.

The tensile strength of *Phormium tenax* fibers was in the range of  $711.9 \pm 61.1$  MPa, which is higher than the sisal range (468-640 MPa) and similar to the well-known curaua fiber (913 MPa) [36]. Figure 1 shows the results obtained from different *Phormium tenax* composites and the value of pure PP. According to Figure 1, the *Phormium tenax* highest potential reinforcement was not obtained.

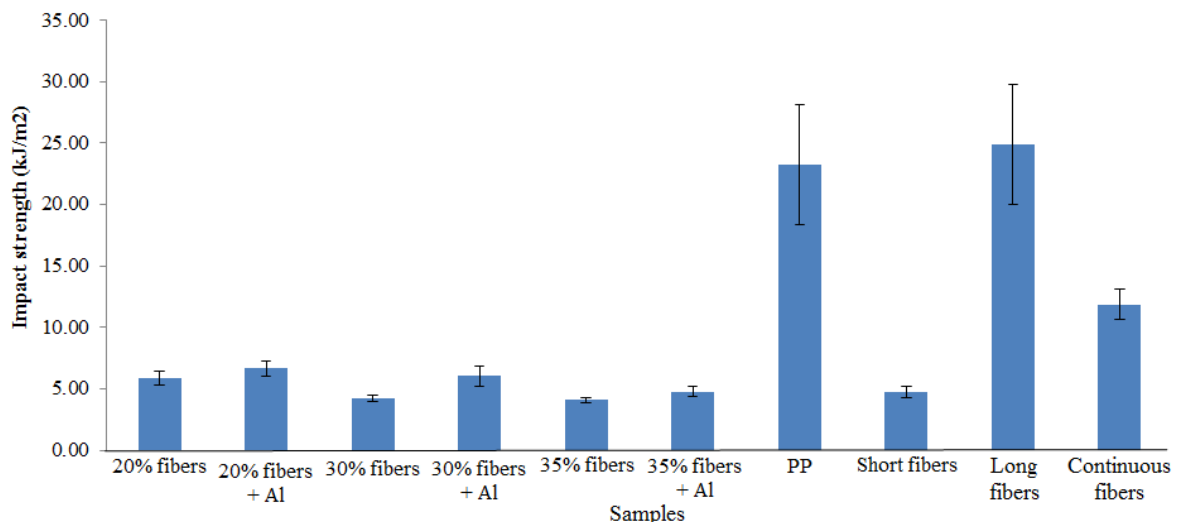


**Figure 3.** Scanning electron microscopy of the fracture of the samples submitted to tensile tests at 200X magnification for composites: (a) 20% w / W of fibers; (b) 20% w / W of fibers and Al; (c) 35% w / W of fibers; (d) 35% w / W of fibers and Al; (e) Pure PP; (f) *Phormium tenax* fibers.

These results may be related to the insufficient physical interaction regarding the fiber-matrix adhesion. If a slightly higher concentration of dicumyl peroxide and maleic anhydride were used to prepare the MAPP, it would present a better dispersion and the fibers a better wettability during the coating step [26]. However, if 0.5% (w/w) dicumyl peroxide were added to the MAPP, the reactive extrusion process would become harder due to its high fluidity index, which would be 149.85 g/10min compared to the 27.08 g/10min of the MAPP used in this study [37]. Another problem regarding short fiber-reinforced composites is the high number of edges due to the concentrated mechanical strength, which creates a brittleness region in the material that reduces with increasing fiber length [38]. Overall, parameters such as composite manufacturing methods, matrix types, dimension, direction, and length affect mechanical properties [39]. For Várdai *et al.* [39], the most frequent processes in fiber-reinforced composites are the matrix's debonding, pullout, fiber fracture, and shear yielding. Some of the listed phenomena are shown in Figure 3.



**Figure 4.** Comparison between the flexural strength in MPa between different types of composite materials and pure PP.



**Figure 5.** Comparison between the IZOD impact strength in MPa of different types of composite materials and pure PP.

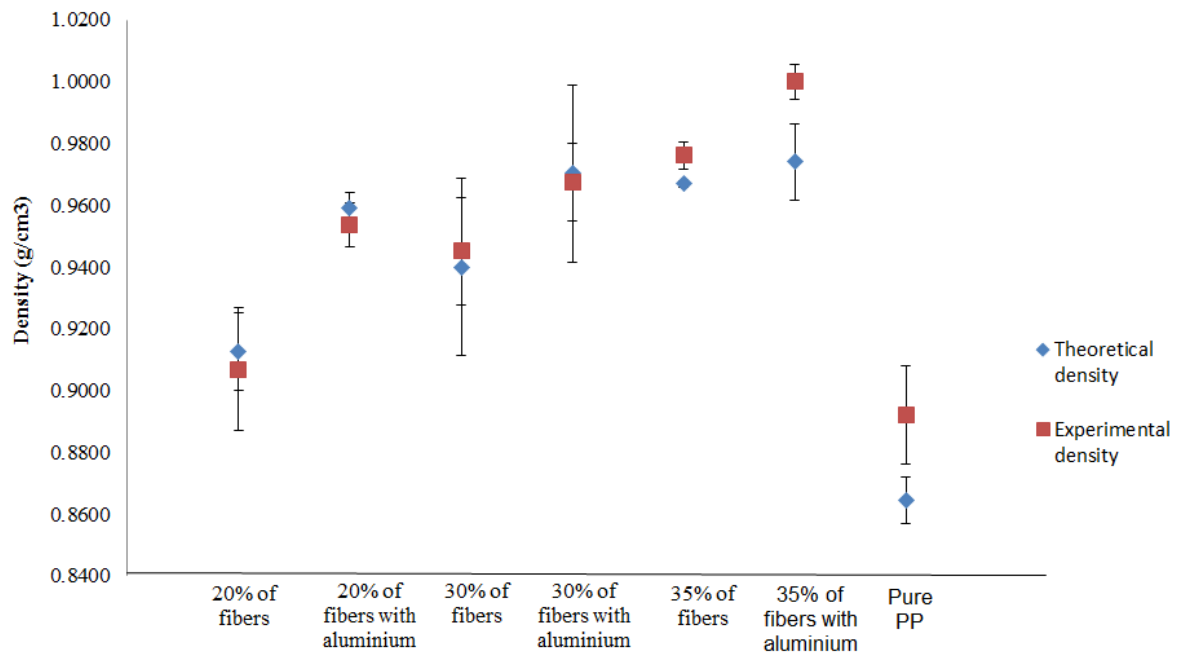
When compared with the other materials presented in Figure 2, *Phormium tenax* fibers showed a higher modulus of elasticity, while the pure PP showed the lowest one, as expected. The composites presented intermediate modulus of elasticity values, with a small increase by the addition of fibers mass fraction, as well as by incorporation of aluminum sheets.

Figures 4 and 5 show, respectively, the values for materials analyzed in the flexural test and the IZOD impact test. *In natura*, fibers were not submitted to the flexural and impact tests, meaning they are not included in the mentioned figures. Regarding the prepared composites, flexural strength values ranged between 38 MPa and 65 MPa. The mean values result from five samples for each specimen.

The improvements in flexural strength were not significant, which can be justified by an inefficient distribution of the fibers, the presence of microcavities and fissures at the interface between fiber and matrix, and poor adherence of the aluminum sheet to the polymeric matrix [35]. Long fiber-reinforced composites presented the highest flexural strength, followed by the continuous fiber-reinforced ones, which is explained by the better distribution of the long fibers throughout the matrix. Figure 5 shows, as expected, the higher impact strength of PP, which is a very ductile material at room temperature. Its impact strength is much higher than that of composites, which are brittle materials even when reinforced with aluminum sheets. As can be observed in Figure 5, the ductility of PP was not hindered in long fiber-reinforced composites. *Phormium tenax* long fiber-reinforced composites similar results when compared to pure PP.

### 3.3. Density analysis.

Figure 6 shows a comparison between experimental and theoretical density values and their respective standard deviations. Four samples of each variety were tested. On average, the aluminum sheet represented 6% (w/w) of each composite.



**Figure 6.** Comparison between the theoretical and experimental densities of the composite samples and pure PP samples produced in the laboratory.

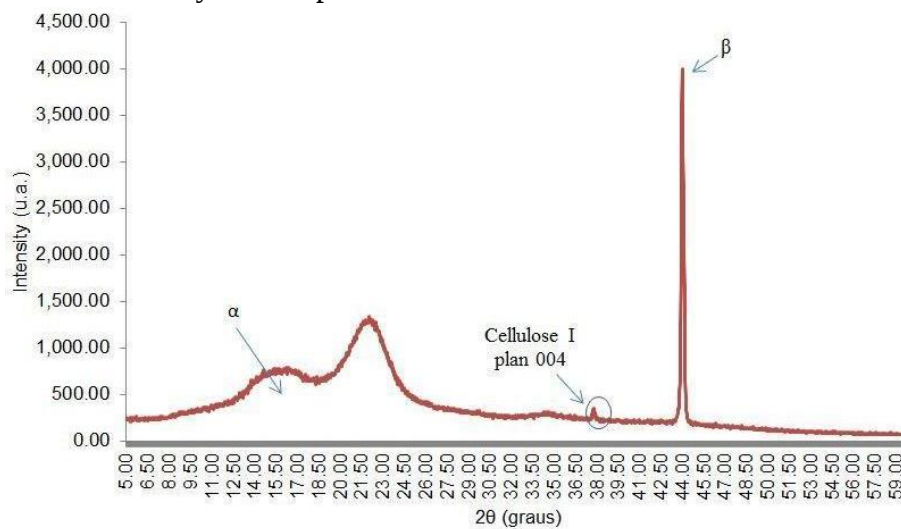
According to Figure 6, the fiber density is higher than that of PP, which explains the increase in the composite material density with the increasing fiber mass fraction. Using equation (1), the experimental value of fiber density was  $1.06 \pm 0.08 \text{ g.cm}^{-1}$ , which is below that estimated by Mann *et al.* [41] ( $1.3 \text{ g cm}^{-3}$ ). This can be explained by insufficient material compaction during the specimens' manufacture, formation of defects and pores, presence of lumens in the cut fibers that remained with no materials, or presence of air bubbles (Figure 3).

$$\frac{1}{\rho_C} = \frac{W_{PP}}{\rho_{PP}} + \frac{W_{MAPP}}{\rho_{MAPP}} + \frac{W_f}{\rho_f} + \frac{W_{Al}}{\rho_{Al}} \quad (1)$$

In equation (1),  $\rho$  is the density,  $w$  is the mass fraction, and the sub-indices  $C$ ,  $f$ , and  $Al$  are composite fibers and aluminum, respectively.

### 3.4. XRD analysis.

Figure 7, which was created in the Excel software (Microsoft), shows the XRD analysis of *Phormium tenax* fiber with four peaks. This figure provides information on *Phormium tenax* crystallinity. The diffractogram measures the intensity of x-rays scattered in the sample using arbitrary units as a function of the  $2\theta$  angle measured in degrees. The results obtained are the mean values for each analyzed sample.



**Figure 7.** XRD graphical analysis of *Phormium tenax*.

According to Figure 7, the first peak appears near  $16.26^\circ$  and presents an intensity of 793.33 a.u. It is immediately followed by the second peak, which is near  $22.06^\circ$  and presents an intensity of 1,337.33 a.u. These first two peaks are similar to those found by Jedyn [37] for Pinus sawdust fibers, whose peaks appear between  $14^\circ$  and  $23^\circ$ . Bledzki and Gassan [42] demonstrated the monoclinic spenodic crystal structure for cellulose fiber formation. The third peak appears near  $37^\circ$  and, according to Giorgio *et al.* [11], it may be the cellulose phase I (plane 004). The last peak, which is near  $45^\circ$ , suggests the formation of a new phase that was not found by Jedyn [37] nor Giorgio *et al.* [11]. According to Table 3, crystallinity index values for PP and MAPP are similar, ranging between 62% and 65%. However, the crystallinity of *Phormium tenax* fibers was 36.7%, which is similar to sawdust [37].

**Table 3.** The crystallinity index of samples obtained by XRD.

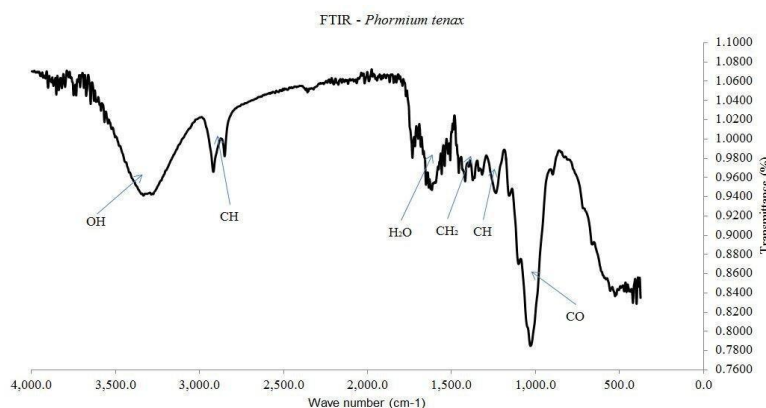
| Samples                             | Crystallinity index (%) | Standard deviation (%) |
|-------------------------------------|-------------------------|------------------------|
| Composites with 20% w / W of fibers | 59.00                   | 2.00                   |
| Composites with 30% w / w fibers    | 52.33                   | 6.66                   |
| Composites with 35% w / W of fibers | 49.67                   | 4.16                   |
| <i>Phormium tenax</i>               | 36.67                   | 1.15                   |
| Pure polypropylene                  | 62.33                   | 4.04                   |
| Maleated polypropylene              | 62.00                   | 3.61                   |

The crystallinity differences between PP and MAPP are minor and can be explained by the interference of dicumyl peroxide, which, by forming free radicals on PP's tertiary carbons, causes chain scission, reducing the molecular weight of the material and, consequently,

increasing crystallinity. There are two contradictory effects regarding the MAPP crystallinity index values: while shearing of PP chains tends to increase the crystallinity index, the addition of maleic anhydride succinic groups tends to reduce the PP crystallinity by forming MAPP, which presents succinic groups [26, 37]. The crystallinity index values of the composite samples ranged between the ones presented by the *Phormium tenax* fibers and PP. Composites with higher fiber volume fraction presented lower crystallinity, which was expected since fiber addition tends to increase the number of imperfections in the crystalline structure, producing more scarce and smaller crystals due to the high crystallization rate[43]. Thus, despite the higher crystallization rate, many imperfections in the crystal structure are produced, which can, in turn, reduce the crystallization rate of the samples.

### 3.5. FTIR analysis.

Figure 8 shows the functional groups of *Phormium tenax* obtained by FTIR analysis. All functional groups are highlighted. Functional groups such as OH, H<sub>2</sub>O, and CO are important to understand the composites' mechanical strength due to their affinity for water and potential to create pores in the composites.



**Figure 8.** Functional groups of *Phormium tenax* fiber obtained by FTIR.

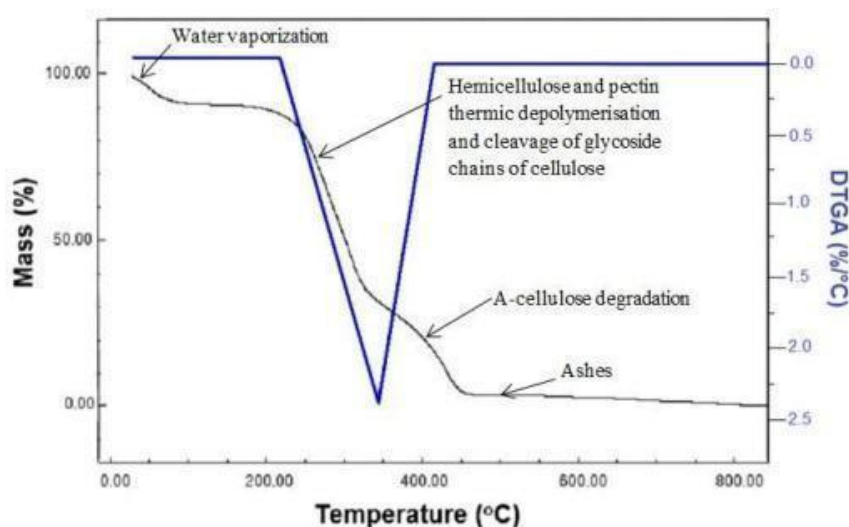
Furthermore, Figure 8 also shows some functional groups of *Phormium tenax*, such as hydroxyl, which is present between the 3,000 and 3,500 cm<sup>-1</sup> bands [11]. Since hydroxyl groups are the main promoter of water-fiber connection, it explains why *Phormium tenax* is a hydrophilic fiber [38]. Spaces occupied by water can empty when it evaporates due to the increasing temperature, creating microcavities (or micro-failures as shown in Figure 3) in the composite (Figure 3). The presence of hydrophilic groups also impairs mechanical strength as it interferes with the efficiency of the charge-transfer mechanism by reducing the surface area of the fibers' filled particles [44]. *Phormium tenax* showed stretching of the CH group in the band between 3,000 and 2,700. Water appears in the range from 1,820 to 1,630 [45, 46]. In the bands 1.334 and 1.318, there was a stretching of the CH<sub>2</sub> group and, in the bands 1.370 and 1.206, a stretching of the CH group. The CO functional group is present in the range of 1,110 to 987 [11].

### 3.6. Thermal characterization.

This subsection is divided into thermogravimetric analysis (TGA) and differential exploratory calorimetry (DSC). TGA analysis was carried out only in *Phormium tenax* fibers and DSC in PP composites with 20%, 30%, and 35% (w/w) fiber, PP, and MAPP.

### 3.6.1. TGA analysis.

Figure 9 shows the TGA of *Phormium tenax*. The TGA curve presents three degradation ranges, which are indicated in Figure 9: between 38 °C and 130 °C, between 200 °C and 325 °C, and from 325 °C to 450 °C.

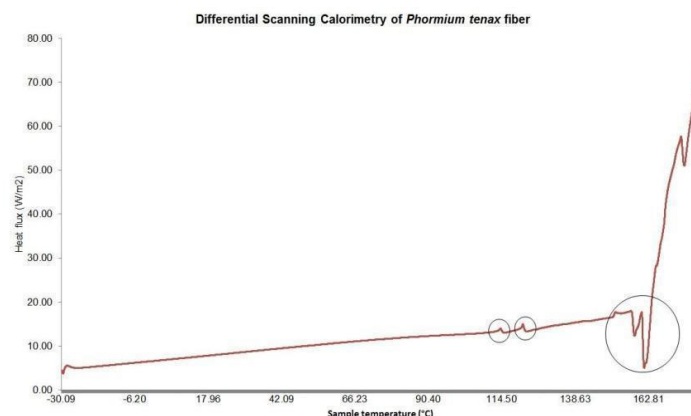


**Figure 9.** TGA curve of *Phormium tenax*.

Figure 9 shows that the degradation temperature of *Phormium tenax* occurs near 200 °C, which is within the range of nanocellulose degradation. This range occurs approximately between 200 °C and 300 °C, requiring control of the manufacturing process up to the 200 °C range in order to avoid degradation [47]. The processing temperature reached 90% of this value, which can reduce the fiber's mechanical strength since this stability difference can limit the fibers' efficiency in the polymer matrix and, consequently, in composites [48]. In addition, Figure 9 explains what occurs in each degradation range [35]. The maximum degradation occurs at 450 °C (onset) since an inflection point appears in the degradation curve during the thermal depolymerization of hemicellulose and pectin.

### 3.6.1. DSC analysis.

The interest in the fiber DSC analysis is due to the loss of mass and release of compounds with increasing temperature. In Figure 10, two endothermic events were observed near 115 °C and 122 °C.



**Figure 10.** DSC Analysis of the means of *Phormium tenax* samples tested.

Another endothermic event was registered near 150 °C, followed by two exothermic events, one near 157 °C and the other near 161 °C, when a large endothermic process starts, probably due to the release of a considerable amount of extracts present in the fiber.

In Figure 10, the first two endothermic events may be associated with the volatilization of fiber's substances, while the exothermic events occurring immediately before the large endothermic peak may correspond to the decomposition of residual material related to fiber impurities, as discussed by Bernal *et al.* [49]. According to Rosa, Santulli, and Sarasini [35], *Phormium tenax* has impurities on its surface, which presents a soft protective layer that holds the fibers together. The expressive endothermic event starting at 161 °C may correspond to the volatility of a large number of fiber's total extractives, which indicates that they can be released during the extrusion step when temperatures reach up to 174 °C. Consequently, these extractives involve the whole polymer matrix, endowing the composites with specific characteristics, such as dark brown coloration and the plant's distinctive pleasant odor.

#### 4. Conclusions

The *Phormium tenax* chemical composition analysis indicates it is a resistant fiber whose macro constituents represent approximately 72.5% of the holocellulose, 44.27% of which is cellulose. This was confirmed by the mechanical tensile tests ( $711.9 \pm 61.1$  MPa), which demonstrated the high strength of *Phormium tenax*. Although the results show no significant improvements in tensile strength due to low fiber-matrix adhesion, the tests evaluating flexural strength, which is considered an important property for composites' structural applications, showed interesting results in some samples. Thus, composites reinforced by long and continuous fibers of *Phormium tenax* are promising alternatives for future studies related to improvements in structural applications. Adjustments in processing, such as using a higher grafting level of the succinic group in the MAPP or using a chemical treatment (NaOH) on the fiber, may contribute to better results.

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#### Conflicts of Interest

The authors declare no conflict of interest.

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