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The influence of the coconut fiber treated as reinforcement in PHB (polyhydroxybutyrate) composites



Adriana da Silva Moura^{a,*}, Renan Demori^b, Rosineide Miranda Leão^c, Claudio Luis Crescente Frankenberg^d, Ruth Marlene Campomanes Santana^a

^a PPGE3M-LAPOL, Federal University of Rio Grande do Sul, UFRGS, RS, Brazil

^b Chemistry Institute, Federal University of Rio Grande do Sul, UFRGS, RS, Brazil

^c Faculty of Technology, University of Brasília, Brasília, Federal District, Brazil

^d Pontifical Catholic University of Rio Grande do Sul, PUCRS, RS, Brazil

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ABSTRACT

This study evaluated how the treatment of coconut fiber (CF) affected the fiber itself and the composites prepared with treated and *in nature* coconut fiber used as reinforcement in PHB (polyhydroxybutyrate) as a polymeric matrix. The coconut fiber *in nature* (CFi) underwent to a thermochemical treatment (CFt) with hot water (80 °C). The efficiency of treatment was evaluated by FT-IR analysis. The FT-IR and scanning electron microscope results showed partial removal of impurities such as waxes. The composites of (PHB/CFi or PHB/CFt) with weight rate of 90/10 and 80/20 were characterized by thermal and morphological properties. Thermogravimetric analysis showed that the presence of fiber in the PHB matrix improved thermal stability of the composite. The SEM analysis of the microstructure showed ta good interfacial adhesion between the PHB and coconut fiber especially when treated fiber was used.

1. Introduction

Advanced studies on polymer composites reinforced with vegetal fibers have been encouraged as a way to help the environment protection and to improve waste recovery feasibility [1].

In Brazil, natural fiber residues originating from monocultures planted to obtain food on a large scale are abundant and among these is the coconut (*Cocus nucifera*). The coconut palm reaches a height of up to 30 m and produces on average 130 fruits per year. The Brazilian Agricultural Research Corporation reports annual coconut production of approximately 1.3 billion fruits, and about 75% of the production is concentrated in the north and north-east regions, although the fruit is consumed all over the country [2,3]. The fibers of coconut are derived from the mesocarp, have the highest percentage of lignin about 25% of the total fruit volume [4]. Lignocellulosic materials are characterized by a high lignin content 30%, making these fibers harder than other natural fibers [5,6].

The green and mature coconut has a considerable fiber fraction. The shell, representing 80–85% of the gross weight (mesocarp), it is a waste that has not been fully tapped by the industry [7]. Therefore, using this residue is a plausible solution to decrease coconut residue in landfills [8]. Multiple processes using this waste to develop high added-value

materials have been investigated [9].

Natural fibers are used to reinforce polymer matrices and to produce numerous composite materials [10]. Although the strength of most natural fibers is lower than the glass fiber, natural ones have more potential use in composite materials [11]. The macromolecules that form the fibers are responsible for the physical properties of the lignocellulosic material [12]. In general, the natural fibers have an average of 40–60% of cellulose, 20–40% of hemicellulose and 10–25% of lignin [6,13].

Cellulose is hydrophilic, biodegradable and the most abundant natural polymer in the world. The lengthy linear chain and intramolecular bonds contribute to the properties related to rigidity due to its semi crystalline character [14,15]. Another component of the plant fiber is the hemicellulose, which is hydrophilic, with high degree of branched chains, amorphous nature and degree of polymerization ranging from less than 100 to the highest 200 monomers [16]. The lignocellulosic material is formed by low-density lignin with high abrasion, an important feature for replacing inorganic fillers [17].

The composition of cellulose, hemicellulose and lignin in the fibers is associated, among other factors, with the cultivation site and the absorption of nutrients. The coconut fiber has 56,8% of cellulose and 29,8% of lignin [6]. Furthermore, the use of lignocellulosic material can

* Corresponding author. E-mail addresses: adrimoura10@gmail.com, silva.moura@ufrgs.br (A. da Silva Moura).

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associate mechanical and thermal performances to the final material [18].

Another group of ecological material is the biodegradable plastic, which was developed to solve the problem of the conventional nonbiodegradable polymers in landfills [19]. The international market share of biodegradable plastics is minimal due to their limited use compared to synthetic plastics because they are less flexible and more expensive [20]. The polyhydroxybutyrate (PHB) is a particular polymer because is biodegradable under the appropriate conditions and it's obtained from renewable sources such as sugar cane. The mechanical properties of this thermoplastic are similar to polypropylene (PP), which may be substituted by biodegradable polymer [21].

The use of natural fibers to reinforce polymeric material depends on the interaction between both phases: natural fiber and matrix. Optimizing their adhesion is crucial for obtaining new material properties [22]. The adhesion between the fiber and matrix is enhanced by using a chemical product to change the physical and/or chemical structure of the fiber, thus allowing more interaction between the composite components [23]. This fiber-matrix interaction can be obtained by two types of chemical treatments to promote covalent, hydrogen, and acid-base bonds. There are several types of chemical treatments that can influence the properties of composites (fiber + polymer matrix), according to Thakur [24], treated fibers used in composite materials had improved mechanical properties.

This study aims to evaluate the thermal, mechanical and morphological properties and the necessity for coconut fiber treatment. However, this treatment aims at non-degradation of the fiber as well as not using solvents that can affect the environment.

2. Experimental

2.1. Materials

The coconut fibers, from the Agricultural Cooperative Formosa River of Responsibility Fruit Producers Ltd. (COOPERCOCOS), were provided by the Brazilian Institute of Environment and Renewable Natural Resources (IBAMA). The Federal University of Campina Grande (UFCG) provided the PHB manufactured by PHB Industrial. According to the manufacturer, PHB physical properties are: density 1.25 g/cm³ at 25 °C, average molar weight ranged from 273,000 to 563,000 g.mol⁻¹ and crystallinity content between 50% and 70%. The coconut fiber length used in this study presented size ranging from 500 to 1000 µm.

2.2. Coconut fibers treatment

The coconut fiber was dried in an oven at 105 $^{\circ}$ C for 24 h, to determine the moisture content by weight difference.

The thermochemical treatment alternative (hot water) was selected among the most used because it was the least aggressive to the fiber, solvent chemical free (such as alkaline solution) as well as minimized weight loss of lignin and cellulose. Whose objective is only the removal of superficial extractive (waxes). The methodology recommended by Leão [25] was followed in this study. The fibers were treated with hot water at 80 °C for two hours, and dried at 105 °C for 12 h.

2.3. Composite preparation

The PHB/CF composites were prepared with coconut fibers *in nature* (CFi) and thermo-chemically treated (CFt), as shown in Table 1. The samples were prepared in a Haake Rheomix mixing chamber at 60 rpm, 160 °C for 7 min by feeding the fiber first and then the polymeric matrix. Subsequently, the material was injected by using a Mini Injection Haake Thermo Scientific to prepare the specimens under 300 bar of injection pressure and 240 bar of hold pressure, with 5 s of injection

Table 1
Sample compositions.

Composite	PHB	CFi	CFt
PHB/CFi (90/10)	90	10	-
PHB/CFi (80/20)	80	20	-
PHB/CFt (90/10)	90	-	10
PHB/CFt (80/20)	80	-	20

CFi - coconut fiber (in nature), CFt - coconut fiber (treated).

time, temperature between 170 $^\circ C$ and 200 $^\circ C$ and 40 $^\circ C$ of mold temperature.

2.4. Characterization

Scanning electron microscopy (SEM), thermal analysis (thermogravimetry (TGA), Differential Scanning Calorimetry (DSC)) and Fourier-transform infrared spectroscopy (FT-IR) were used to characterize the fibers and the composites.

2.4.1. Thermal analysis

The TGA was performed in a thermogravimetric analyzer TGA model Q50, manufactured by TA Instruments, in N₂ atmosphere (flow 100 mL min^{-1}) with a heating ramp that heated from room temperature to 800 °C at a heating rate of 20 °C min⁻¹.

The DSC analysis was performed in a calorimeter model Q20, manufactured by TA Instruments, with heating from room temperature to 230 °C, at a heating rate of $10 °C min^{-1}$, in a N₂ atmosphere (flow 50 mL min⁻¹) The crystallinity content (Xc) in PHB and (PHB/CF) composite were determined by the Eq. (1),

$$Xc = \frac{\Delta H}{\Delta H^{\circ} f. w} \times 100 \tag{1}$$

Where, ΔH_f° 146 J g⁻¹ for 100% PHB crystalline material, ΔH_f is enthalpy of fusion for each sample; and, *w* is the PHB mass fraction of the composite (0,9 and 0,8) [26].

2.4.2. Scanning electron microscopy - SEM

The analysis was performed using a JEOL Scanning Electron Microscope (SEM) model JSM - 6060, 0.1 until 30 kV, with conventional observations of secondary electron image (SEI). The samples were submitted to gold plating in a Balzers Sputter Coater, Model SCD 050.

2.4.3. Fourier transform infrared spectrometry - FTIR

The Fourier Transform Infrared Spectrometry-FT-IR was performed by spectrum 1000 Perkin Elmer, the sample was prepared in KBr pellet.

3. Results and discussion

3.1. Influence of coconut fiber treatment

3.1.1. Physical properties

The thermochemical treatment resulted on 11% of average weight loss, which could be attributed to partial removal of extractives as waxes, low molecular weight compounds and soluble salts. This treatment removed part of the coconut fiber impurities, without removing internal fiber components or changing the fiber properties [25].

The hydrophilic characteristic of fibers is related to its chemical composition, specifically to the hydroxyl groups contained in cellulose and hemicellulose, and the geometric structure [22].

3.1.2. Fourier transform infrared spectrometry

The PHB FT-IR spectra showed a peak in the region at 3400 cm^{-1}



Fig. 1. FT-IR spectra of coconut fiber *in nature* and coconut fiber treated.

which is from hydroxyl group. The peak in the region of 2954 and 2850 cm^{-1} are from the C–H stretch and C–H aliphatic axial deformation, respectively [25]. On the other hand (Fig. 1), the coconut fiber spectra exhibit the typical characteristics of the lignin, cellulose and hemicellulose molecular structure in the region between 2954 and 2019 cm⁻¹ (C–H stretching vibration). A broad peak in the region at 3400 cm⁻¹ stretching vibration characteristic of the hydroxyl group. The peak 1538 cm⁻¹ was observed in the coconut fiber spectrum *in nature* corresponding to the C=C vibration of the aromatic ring and the presence of lignin and hemicellulose [31,12]. Also, in this region the absence of the same peak observed in the treated coconut fibers is observed. This confirms the partial removal of the extractives in the fibers due to the treatment as well as showing its efficiency [12] Fig. 1.

Fig. 2 shows the FT-IR spectra of the water before the fiber treatment and the effluent from the CF treatment. A peak was observed between 3000 and 3400 cm^{-1} in both spectra, corresponding to the hydroxyl group. This is the most pronounced peak in the effluent compared to water. This result shows the presence of hydroxyl groups



Fig. 2. FTIR spectra of pre-treatment water and effluent from the coconut fiber treatment.

Table 2

Compounds found in the effluent of the aqueous treatment of coconut fiber.

Compounds	Chemical	Melting temperature (°C)
Waxe	H ₃ C-(CH ₂)-O-CO-(CH ₂)-CH ₃	52 °C
Fatty acids (palmitic) stearic oil		68 °C
Monoglyceride Triglycerides	$H_{2}C-O-CO-R^{1}$ $H_{2}C-O-CO-R^{2}$ $H_{2}C-O-CO-R^{3}$	32-70 °C

(OH) in the effluent relative to water and also to the soluble compounds to hot water from the vegetable fiber, such as extractives and hemicellulose, among others. The peaks in the region between 2954 and 2850 cm^{-1} are due to CH stretching and axial deformation of the aliphatic CH [27,28].

The FT-IR results showed that the extractives contain various functional groups, according to their chemical structure, such as waxes, fatty acids, hydrocarbons, and soluble inorganic compounds. Greases consist of esters of carboxylic acids, such as glycerol, while the waxes are esters of fatty acids with alcohols [29]. Table 2 shows some of these components and their melting temperatures [30].

The peak in the region of 1473 cm^{-1} is also related to the C=C vibration and deformation of the hemicellulose and lignin [32]. The treated coconut fibers with peak in this region, confirm the partial removal of extractives from the fibers and, therefore, the treatment efficiency. In the bands observed at $1370-1013 \text{ cm}^{-1}$ was attributed to C-O and C-H groups of the aromatic ring from lignin [33]. On the other hand, the peak at $816-685 \text{ cm}^{-1}$ corresponding the symmetric C-H glycoside bonds of hemicellulose and cellulose [31]. The peak at 480 cm^{-1} is related to the vibration of the O-Si-O compound [34],



Fig. 3. SEM micrographs of coconut fibers *in nature* (a) and (b) and treated (c) and (d); the arrow is pointing to the partial removal of impurities before (b) and after (d) the treatment.

confirming the partial removal of extractives from the fibers due to treatment. This result is indicative that the vegetable fiber contains water-soluble silicon salts [6].

3.1.3. Scanning electron microscopy of the fibers

Fig. 3 shows SEM images of coconut fiber surface before and after treatment. The micrograph of the fiber *in nature* in Fig. 3(a) and (b) shows particles (impurities) and irregular surface, possibly indicating the presence of a cerumen layer covering the fiber.

Furthermore, the micrograph of the treated fiber Fig. 3(c) and (d) shows partial removal of impurities, cerumen, and extractives covering the pores, leaving a smoother surface and some pores (voids) on the fiber surface [35]. It is possible to verify that there are more pores in the treated fiber, which prove that the treatment used partially removed some impurities that obstructed these.



Fig. 4. TGA curves for coconut fibers in nature (CFi) and treated (CFt).

The fiber surface characteristic, such as roughness, pore size (empty), chemical composition, size and form directly influence in the interfacial adhesion between the fiber and polymer matrix, homogenization in the dispersion with the polymer matrix and, consequently, the affinity between the two materials [31]. All these parameters are important for the mechanical performance of the composite.

3.1.4. Thermogravimetric analysis

The Fig. 4 compares the TGA thermal decomposition curves of coconut fibers *in nature* and treated. Both samples showed a weight loss of 7–8% in the range between 60 and 120 °C, more pronounced for the non-treated fiber probably because of some soluble chemical component removed during the thermochemical treatment. Additionally, which may be due to the moisture removal from the fiber (confirming the percentage of water found experimentally), as well as some low molar weight extractives. It was observed that the treated fiber curve presented a greater loss of initial mass, relative to the presence of moisture and compounds of low molar mass present, when compared to the curve of the untreated fibers. This fact occurs due to the more amount of pores (vide Fig. 2(c)) in the treated fiber, thus allowing greater absorption of moisture.

Both curves show two decomposition stages corresponding to the decomposition of hemicellulose and cellulose, respectively, followed by the final decomposition of lignin at about 600 °C [32]. It is shown that the treated fiber has improved thermal stability compared the fiber *in nature*, since the decomposition temperature increased from 215 °C to 240 °C, an increase of 25 °C. This result can be attributed to the removal of low molecular weight compounds by the thermochemical treatment, which would degrade at a lower temperature [15]. However, the ash



Fig. 5. DTG Curves for in nature and treated coconut fiber.

content of both samples is quite high, indicating that coconut fibers contain high levels of silicates and other inorganic materials [33]. However, there is a difference of 9% relative to the ash content of the treated fiber, which is attributed to the removal of soluble inorganic salts during the thermal water treatment at 80 °C, as shown in Fig. 3 [34]. Confirming the FT-IR results (see Fig. 1).

Fig. 5 shows the DTG x temperature curves where is observed the presence of three peaks corresponding to kinetic maximal of fiber decomposition. The first peak at 80 °C indicates loss of water and extractives. The second peak at 273 °C for CFi and 284 °C for CFt corresponds to the temperature of maximum hemicellulose decomposition [31]. The third peak at 360 °C and 336 °C for CFi for FCt, respectively, corresponds to cellulose decomposition. These results show that the thermochemical treatment increased kinetic decomposition of cellulose and hemicellulose.

3.2. Influence of fiber treatment on the PHB/FC composites

3.2.1. TGA and DSC thermal analysis

The Fig. 6 show the TGA overlapping curves for the PHB matrix and PHB/CFi (90/10), PHB/CFi (80/20), PHB/CFt (90/10) and PHB/CFt (80/20) composites. It was observed that only the PHB matrix had a single decomposition stage starting at 256 °C. The composites had two decomposition stages, the first corresponding to the PHB matrix and the second to the coconut fiber. It should be noticed that the decrease in the beginning of composite decomposition, corresponds to the PHB matrix. Probably because the composite is obtained using two processes (Haake mixer and after injection molding) in which the mixture was exposed to thermomechanical oxidative conditions. In addition to these factors, the reinforcement in the matrix causes friction and abrasion due to the silica contained in the fiber [35].

The TGA curves show that the treated fiber composites exhibited higher thermal stability than the composite made with fiber *in nature* (temperature shift to the right). Regarding reinforcement, it is observed



Fig. 6. TGA curves for the PHB matrix and PHB/FC composites.

that composites with less CF (10% m/m) had greater thermal stability, probably due to the higher PHB content (increased thermal stability) and lower silica content from CF [36].

Table 3 summarizes the results of the TGA and DTG curves for the evaluated samples. It is observed that, in general, the composites with fiber *in nature* had higher ash content. This occurs because fibers have components that do not suffer thermal decomposition until the temperature of 400 $^{\circ}$ C [37]. The last stage of degradation starts after 305 $^{\circ}$ C and continues until 400 $^{\circ}$ C, indicating the degradation of the cellulose.

The thermal properties, such as melting temperature (Tm), enthalpy of fusion (ΔH_f) and degree of crystallinity (X_c) of PHB and composites were obtained by analyzing the DSC thermal curves, and the results are reported in Table 4. The X_c was calculated in relation to the PHB matrix.

In general, it was observed that the increase of filler content caused a decrease of the melting temperature (T_f) and enthalpy of fusion (ΔH_f), as well as the degree of crystallinity. The PHB/CFt (90/10 and 80/20) and PHB/CFi (90/10) composites had the highest melting temperatures compared to PHB. It is worth mentioning that the treated fiber composites have a higher degree of crystallinity compared to composites with untreated fibers, which could be related to the removal of extractives and low molecular weight compounds contained in the fiber, which hinder the formation of spherulites (crystalline phase).

The degree of crystallinity (Xc) was higher in pure PHB matrix compared to all composites analyzed. This reduction, probably due to the fact that the fibers, either *in nature* or treated, cause a disruption of the packing of polymer chains. The composites reinforced with 10% (m/m) fiber had a slightly higher degree of crystallinity compared to 20% (m/m), which allows concluding that Xc decreases as the coconut fiber content increases. This occurs due to the absence of transcrystallinity during recrystallization of the polymer [38]. Thus, the PHB degradation can change the crystallinity of this material, decreasing the crystalline fraction and, thus, increasing the amorphous fraction. These structural changes may cause the density to decrease while increasing stiffness and mechanical and thermal resistance [39]. Recent studies [40] have shown that PHB crystallinity decreases with processing and insertion of reinforcement in the matrix, a fact that was also observed in this study.

3.2.2. Tensile tests

The mechanical properties of composites are strongly dependent on the reinforcement and interfacial compatibility of the composite system. In this research, the observed fracture from mechanical strength showed brittle characteristics. The tensile modulus of these composites generally increased with increasing fibers loading [41]. According to Fig. 7, this suggests that a sufficient stress transfer across the polymer-fiber interface. The coconut fiber (CF) inserted in the matrix restricts the matrix stretching phase at the interface of each particle. Additionally, contributing to an overall increase in the elastic modulus by using up to 10% of fiber concentration for both, treated and non-treated ones [42]. However, the longitudinal structure of the fiber do not contributed to the increase of the composites ductility, compared to the pure polymer [43]. This result suggests the increase of the composite stiffness compared to the neat PHB. By comparing the results, the use of 10 or 20% of CF the better mechanical performance occurred by using treated CF. This result suggests that the removal of the low molecular mass molecules from CF after treatment improve adhesion and compatibility at the interface of fiber and polymeric matrix.

Nevertheless, mechanical performance of the composites showed with CF concentration of 10%, which mean that is relatively small as well as is the optimal concentration in order to improve mechanical properties of the PHB matrix.

3.2.3. Morphology analyses of the composites

Fig. 8(a) and (b) shows SEM micrographs of the specimen surface

Table 3

Temperature and	mass/weight	loss (%) of PHI	3 and PHB/CFi (90/10)	. PHB/CFi (80/20)	. PHB/CFt (90/10).	. PHB/CFt (80/20) composites.
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Samples			TGA			DTG	
	T5% _{m/m} (°C)	Humidity Mass (%)	Stage 1 Mass (%)	Stage 2 Mass (%)	Ashes at 400 °C (%)	Stage 1 Tp1 (°C)	Stage 2 Tp2 (°C)
PHB	275	0.83	99.17	0.11	-	290	_
PHB/CFi (90/10)	260	2.14	97.48	2.72	2.34	272	331
PHB/CFi (80/20)	259	1.30	97.95	3.37	2,62	267	332
PHB/CFt (90/10)	269	1.95	97.78	2.61	2.34	281	356
PHB/CFt (80/20)	266	1.44	97.88	2.36	1.68	277	346

Table 4

DSC thermal properties of PHB and PHB composites reinforced with varying proportions (% m/m) of coconut fiber.

Samples	Tonset (°C)	Tf (°C)	$\Delta Hf (J/g)$	Xc (%)
PHB processed	152.4	168.1	68.9	52.8
PHB/CFi (90/10)	152.1	177.9	47.8	34.4
PHB/CFi (80/20)	149.6	167.6	44.5	33.8
PHB/CFt (90/10)	146.1	180.5	56.6	40.8
PHB/CFt (80/20)	146.9	178.7	52.0	39.5

 $T_{onset\ -}$ melting temperature onset, Tm – melting temperature, ΔH_f – enthalpy of fusion, X_c – degree of crystallinity.

obtained after the rupture from mechanical properties. SEM was performed to evaluate whether the fiber treatment favored the adherence or the dispersion between the coconut fiber and the PHB matrix. The images showed good adhesion between the fibers in both samples *in nature* and treated to PHB matrix for the PHB/CFi (90/10) composites. This interaction can be related to the polarity of the matrix as well as fiber, due to the presence of functional groups in the fiber such as alcohols and esters that are originated from the components (cellulose, hemicellulose, and lignin) facilitating the interaction with the polar matrix [39]. At the same time, it was possible to observe that in Fig. 8(a) the sample without treatment fiber contains more pullouts than the sample of Fig. 8(b), reinforced with treated fiber.

A good interaction and distribution is observed between the matrix and fibers in both samples with reinforcement *in nature* and treated, where rupture of fibers can be seen close to the matrix, corroborating the study of Zhang and Thomas [44]. This behavior prevents the load from being transferred to the reinforcement over the area where it could be supported, thus obtaining weaker mechanical properties, if the fibers remain intact in the matrix [45]. However, Fig. 8(d), composite reinforced with the treated fiber, shows a better interaction between the fiber and the matrix, compared to Fig. 8(c), without treatment. This fact may explain the higher melt temperature of the PHB/CFt composite in DSC item 3.2.1, as well as the higher thermal stability compared to the composite PHB/CFi.

4. Conclusions

The heat treatment efficiency of the fiber was evaluated by the TGA, through amount of ashes, meaning that the treatment can also solubilize salts soluble in water. Additionally, the absence of C=C stretching peak by FT-IR analysis of the fiber corroborates with these results. The thermal treatment with hot water was responsible for the partial removal of low molar mass compounds, without altering the fiber structure. It proves that this methodology can be used to replace others chemical treatments that need solvents that affect the environment.

Regardless of the heat treatment influence, in general, the reinforcement of the polyhydroxybutyrate matrix was beneficial in both cases, with CF treatment and without treatment. All the composites maintained the thermal stability with increasing the melting temperature of the composites. The tensile strength test proved the increase of elastic modulus for all the composites, confirming the increase of the rigidity of the composites in relation to the PHB matrix.

The morphological analysis demonstrated good interfacial adhesion, thus proving the intrinsic affinity of the matrix with the reinforcement, without need of the use of additives that affect the environment. The results has showed, with slight variations, that for the reinforced composites with the treated fibers there was an increase in the degree of crystallinity and melt temperature when compared to the composites reinforced with the untreated fibers.

The treatment of the fiber had also provided a bigger thermal stability to the composites with dislocated degradation temperature by 3.5% to PHB/CF (90/10) and 2.7% to PHB/CF (80/20).

It was possible to evaluate through the SEM that the best interaction between fiber and matrix occurred for the composite PHB/CFt (90/10).



Tensile Strain (mm)

Fig. 7. Tensile Stress-Strain curve for composites PHB and PHB/CF.



Fig. 8. SEM Micrographs of the fractured surface of the composites PHB/CFi (90/10) (a), PHB/CFt (90/10) (b), PHB/CFi 80/20 (c) and PHB/CFt 80/20 (d).

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References

- V.S. Aigbodion, C.U. Atuanya, Improving the properties of epoxy/melon shell biocomposites: effect weight percentage and form of melon shell particles, Polym. Bull. 73 (2016) 3305, https://doi.org/10.1007/s00289-016-1657-8.
- [2] C.R. Martins, L.A.J. Júnior, Evolução da produção de coco no Brasil e o comércio internacional - Panorama 2010, EMBRAPA 164 (2011) 1–32.
- [3] M.G. Lomelí-Ramirez, R.R. Anda, et al., Comparative study of the characteristics of green and brown coconut fibers for the development of green composites. Coconut fibers, BioResources 13 (1) (2018) 1637–1660, https://doi.org/10.15376/biores. 13.1.1637-1660.
- [4] A.L.A. Mattos, M.F. Rosa, L.A. Crisóstomo, et al., Beneficiamento da casca de coco verde, EMBRAPA – Agroindústria Trop. 3830 (2012) 1–38.
- [5] F. Le Digabel, L. Avérous, Effects of lignin content on the properties of lignocellulose-based biocomposites, Carbohydr. Polym. 66 (2006) 537–545, https:// doi.org/10.1016/j.carbpol.2006.04.023.
- [6] P. Lertwattanaruk, A. Suntijitto, Properties of natural fiber cement materials containing coconut coir and oil palm fibers for residential building applications, Constr. Build. Mater. 94 (2015) 664–669.
- [7] E. Corradini, M.F. Rosa, B.P. Macedo, et al., Composição química, propriedades mecânicas e térmicas da fibra de frutos de cultivares de coco verde, Rev. Bras. Frutic 31 (3) (2009) 837–846.

- [8] M.F. Rosa, F.C. Bezerra, F.A.P. Abreu, et al., Processo agroindustrial: Obtenção de Pó da Casca de Coco Verde, Embrapa Agroindustrial. Comunicado Técnico 61 (2001) 6.
- [9] H.S. Yang, H.J. Kim, et al., Rice-husk flour filled polypropylene composites; mechanical and morphological study, Compos. Struct. 63 (2004) 305–312.
- [10] K. Pickering, M. Efendy, T. Le, A review of recent developments in natural fiber composites and their mechanical performance, Compos. Part A: Appl. Sci. Manuf. 83 (2016) 98–112.
- [11] M.F.M. Alkbir, S.M. Sapuan, A.A. Nuraini, et al., Fiber properties and crashworthiness parameters of natural fiber-reinforced composite structure: a literature review, Compos. Struct. 148 (2016) 59–73.
- [12] D. Fengel, G. Wegener, Wood: Chemistry, Ultrastructure, Reactions, 14° edn., Walter de Gruyter, Germany, 2003.
- [13] S. Chaitanya, A. Singh, I. Singh, Processing of lignocellulosic fiber-reinforced biodegradable composites, in: A. Lau, A. Ada Pui, Y. Hung (Eds.), Natural Fiber-Reinforced Biodegradable and Bioresorbable, Woodhead Publishing, 2017, pp. 163–181.
- [14] D. Klemn, B. Heublein, H.P. Fink, A. Bohn, Cellulose: fascinating biopolymer and sustainable raw material, Angew. Chem. Int. Ed. 44 (2005) 3358–3393.
- [15] A.I.S. Brigida, N.M. Clapson, P.G. Tripper, et al., Effect of chemical treatments on properties of green coconut fiber, Carbohydr. Polym. 79 (2010) 832–838.
- [16] M.A. Mosiewicki, M.I. Aranguren, A short review on novel biocomposites based on plant oil precursors, Eur. Polym. J. 49 (6) (2013) 1243–1256.
- [17] J. Elammaran, H. Sinin, E. Pushparaj, et al., Acoustic and thermal properties of polymer composites reinforced with lignocellulosic fibers, Appl. Mech. Mater. 624 (2014) 25–29.
- [18] L.E. Nielsen, R.F. Landel, Mechanical properties of polymers and composites, Mechanical Engineering, 2^a edn., Marcel Dekker, New York, 1994.
- [19] D.G. Garcia, J.M. Ferri, T. Boronat, et al., Processing and characterization of binary poly(hydroxybutyrate) (PHB) and poly(caprolactone) (PCL) blends with improved impact properties, Polym. Bull. 73 (2016) 3333.
- [20] A.K. Mohanty, M. Misra, L.T. Drzal, Natural Fibers, Biopolymers, and Biocomposites, CRC Taylor and & Francis, Boca Raton, FL, 2005.
- [21] M.R. Telles, L.M. Saran, S.H.U. Trevisolli, Produção, propriedades e aplicações de bioplástico obtido a partir da cana-de-açúcar, Ciência & Tecnologia FATEC-JB 2 (2011) 52–63.
- [22] E.M. Fernandes, J.F. Mano, R.L. Reis, Hybrid cork–polymer composites containing sisal fibre: morphology, effect of the fiber treatment on the mechanical properties and tensile failure prediction, Compos. Struct. 105 (2013) 153–162.

- [23] A. Hadjadj, O. Jbara, A. Tara, et al., Effects of cellulose fiber content on physical properties of polyurethane based composites composite, Structures 135 (2016) 217–223.
- [24] V.K. Thakur, Lignocellulosic Polymer Composites: Processing, Characterization, and Properties, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2014.
- [25] R.M. Leão, S.M. Luz, J.A. Araujo, K. Novack, Surface treatment of coconut fiber and its application in composite materials for reinforcement of polypropylene, J. Nat. Fibers 12 (6) (2015) 574–586.
- [26] M.L.C. Machado, N.C. Pereira, L.F. Miranda, et al., Study of mechanical and thermal properties of the polymer poly-3-hydroxybutyrate (PHB) and PHB/Wood flour composites, Polímeros: Ciência e Tecnologia 20 (1) (2010) 65–71.
- [27] S. Bloembergen, D.A. Holden, G.K. Hamer, et al., Studies of composition and crystallinity of bacterial poly (β-hydroxybutyrate-co-bhydroxyvalerate), Macromolecules 19 (1986) 2865–2871.
- [28] P.L. King, M.S. Ramsey, G.A. Swayze, Infrared spectroscopy in geochemistry, exploration geochemistry and remote sensing, J. Mineral. Assoc. Canada 33 (2004) 93–133.
- [29] M. Poletto, Effect of extractive content on the thermal stability of two Wood species from Brazil, Maderas. Ciencia y tecnología 18 (3) (2016) 435–442.
- [30] F. Gunstone, F. Padley, Lipid Technologies and Applications, Marcel Dekker, Inc., Publisher, 1997.
- [31] I.J. Morán, V.A. Alvarez, V.P. Cyras, et al., Extraction of cellulose and preparation of nanocellulose from sisal fibers, Celulose 15 (2008) 149–159.
- [32] F. Tomczak, T.H.D. Sydenstricker, K.G. Satyanarayana, Studies on lignocellulosic fibers of Brazil. Part II: morphology and properties of Brazilian coconut fibers, Composites: Part A 38 (2007) 1710–1721.
- [33] M.F. Rosa, E.S. Medeiros, J.A. Malmonge, K.S. Gregorski, et al., Cellulose nanowhiskers from coconut husk fiber: effect of preparation conditions on their thermal and morphological behavior, Carbohydr. Polym. 81 (2010) 83–92.

- [34] A.G.S. Prado, E.A. Faria, P.M. Padilha, Aplicação e modificação química da sílica gel obtida de areia, Quim. Nova 28 (3) (2005) 544–547.
- [35] S.S. Mir, M.N.S. Hasan, J.M. Hossain, M. Hasan, Chemical modification effect on the mechanical properties of coir fiber, Eng. J. 2 (2012) 16.
- [36] M.A. Paoli, M.S. Rabello, Aditivação de Termoplásticos, Arliber Editora SP, Brasil, 2013.
- [37] F. Chen, Z.C. Wang, C.J. Lin, Preparation and characterization of nano-sized hydroxyapatite particles and hydroxyapatite/chitosan nano-composite for use in biomedical materials, Mater. Lett. 57 (4) (2002) 858–861.
- [38] J.D.D. Melo, L.F.M. Carvalho, A.M. Medeiros, et al., A biodegradable composite material based on polyhydroxybutyrate (PHB) and carnauba fibers, Compos. Part B: Eng. 43 (7) (2012) 2827–2835.
- [39] J.S.V. Canevarolo, Técnicas de caracterização de polímeros, Artiber Editora Ltda, Brasil, 2007.
- [40] S.M. Suresh Kumar, D. Duraibabu, K. Subramanian, Studies on mechanical, thermal and dynamic mechanical properties of untreated (raw) and treated coconut sheath fiber reinforced epoxy composites, Mater. Des. 59 (2014) 63–69.
- [41] A. Anil, J.E. Tomlal, G. George, et al., Novel eco-friendly commingled polypropylene/banana fiber composite: studies on thermal and mechanical properties, Polym. Bull. 73 (2016) 2987–3005.
- [42] P. Cheang, K.A. Khor, Effect of particulate morphology on the tensile behaviour of polymer-hydroxyapatite composites, Mater. Sci. Eng. A 345 (2003) 47–54.
- [43] W. Callister, D. Rethwisch, Fundamentals of Materials Science and Engineering: an Integrated Approach, Wiley, Publisher, 2012.
- [44] M. Zhang, N.L. Thomas, Preparation and properties of polyhydroxybutyrate blended with different types of starch, J. Appl. Polym. Sci. 116 (2) (2010) 688–694.
- [45] A. Sudára, K. Rennera, J. Móczóa, T. Lummerstorferc, et al., Fracture resistance of hybrid PP/elastomer/wood composites, Compos. Struct. 141 (2016) 146–154.