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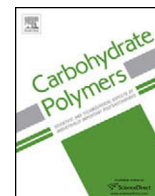


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Bio-composites of cassava starch-green coconut fiber: Part II—Structure and properties



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ABSTRACT

Development of any new material requires its complete characterization to find potential applications. In that direction, preparation of bio-composites of cassava starch containing up to 30 wt.% green coconut fibers from Brazil by thermal molding process was reported earlier. Their characterization regarding physical and tensile properties of both untreated and treated matrices and their composites were also reported. Structural studies through FTIR and XRD and thermal stability of the above mentioned composites are presented in this paper. FT-IR studies revealed decomposition of components in the matrix; the starch was neither chemically affected nor modified by either glycerol or the amount of fiber. XRD studies indicated increasing crystallinity of the composites with increasing amount of fiber content. Thermal studies through TGA/DTA showed improvement of thermal stability with increasing amount of fiber incorporation, while DMTA showed increasing storage modulus, higher glass transition temperature and lower damping with increasing fiber content. Improved interfacial bonding between the matrix and fibers could be the cause for the above results.

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1. Introduction

A number of bio-polymers based on renewable resources such as starch, cellulose, soya, polylactic acid, polyhydroxy alkanates, among others, have been investigated as alternate materials to conventional synthetic polymers. This is because some of these materials are less environmental friendly [Ma, Yu, & Kennedy, 2005]. Of these, starch is the most promising material for the production of biodegradable plastics and their composites, because it is natural, abundant, sustainable and biodegradable in addition to being capable of exhibiting thermoplastic in behavior under the action of high temperature and shear stress [Mo, Zhong, Liang,

& Yu, 2010]. Materials produced using such material are characterized by their high solubility in water, high hygroscopy, poor melting point, faster aging due to retrogradation (a process in which the amylase and amylopectin chains realign themselves making the liquid starch turn to gel) and lower mechanical properties in comparison with the materials based on synthetic polymers. Besides these aspects, starch is one of the most difficult materials to process, because of its brittleness. Therefore, it requires addition of some plasticizers to make it suitable for engineering applications [Satyanarayana, Carbajal, & Wypych, 2009]. In fact, a number of studies on various aspects such as chemical composition, changes in chemical structure, thermal properties and X-ray diffraction studies (for crystallinity) of different types of starches (both natural from different botanical sources and modified starches) and in some cases their bio-composites even with the incorporation of nanofibrils have been carried out [Damer, Engelsen, Blennow, Møller, & Motawia, 2010; Gómez, Torres, Nakamatsu, & Arroyo, 2006; Kaewtatip & Thongmee, 2012; Ma, Chang, Yu, & Stumborg, 2009; Prachayawarakorn, Sangnitdej, & Boonpasith, 2010; Sarifuddin, Ismail & Ahmad, 2012; Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005; Teixeira et al., 2009].

In addition to improving the processability of starch (continuous phase named matrix), its mechanical properties can be enhanced by

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the incorporation of plant-based fibers (kenaf, jute, sisal, coconut fiber, sugarcane fiber, bagasse, etc., or cellulose fibers of wood from eucalyptus or coniferous *Pinus*) to obtain composites called “bio-composites” or “green composites” [Avérous & Halley, 2009; Mohanty, Misra, & Drzal, 2002]. Such composites are completely biodegradable and compostable and therefore considered “environmentally friendly” since, at the end of their useful life, they can be discarded without causing any damage to the environment [Dobircan et al., 2009]. The use of natural fibers to reinforce brittle polymers is not only a good alternate application for these agro-products (which would otherwise go to waste), but also clear advantages because of their renewability, abundant availability, biodegradability and relative low cost [Kuciel & Liber-Knec, 2009].

These new materials, which include bio-composites of cassava starch and green coconut fibers, would fulfill the sustainable development perspectives and current ecological design of safe environment [Avérous & Digabel, 2006; John & Thomas, 2008; Lomelí et al., 2011]. Such bio-composites have been used in products that can be discarded after use, as well as in products having longer lifetimes preferably for interior applications [John & Thomas, 2008].

Besides the great advantages of using bio-composites as described above, our interest in this material is also due to the following facts: (i) Brazil has the highest production and yield per hectare of starch production in Latin America, particularly cassava or tapioca (‘mandioca’ in Portuguese) starch; (ii) coconut is an important crop in northeastern Brazil, which produces abundant fibers resulting from discarded green coconuts [Tomczak, Sydenstricker, & Satyanarayana, 2007]; and (iii) in recent years, Brazil has been in the forefront of the use of industrial wastes for value addition [Satyanarayana et al., 2009]. The present authors have previously carried out studies to understand processing–property–structure correlations of bio-composites of cassava starch reinforced with 5–30 wt.% of fibers from green coconuts (hereafter called ‘coir fibers’) using glycerol as plasticizer. The first part of this study reported [Lomelí et al., 2011] the preparation of the above composites by compression (thermo) molding process and their characterization regarding tensile properties, and water sorption characteristics both before and after thermal treatments of the matrix and its composites. It was possible to prepare composites free of fiber agglomeration with the incorporation of up to 30% coir fibers. It was observed that both tensile strength (TS) and Young’s modulus (YM) of the thermoplastic starch (TPS) increased with the incorporation of coir fibers; those of composites increased with increasing amount of fibers as well as with the thermal treatment. It was observed that treated TPS matrix showed 207%, 410.8% and 221.9% enhancement in tensile strength, Young’s modulus and maximum load respectively, over the corresponding values of untreated TPS matrix. Similarly, in the case of composites containing 30% w/w of fibers, the enhancement of Young’s modulus and tensile strength are 212.2% and 366.7% respectively, for the treated TPS composites over the untreated TPS composites. These results were explained as due to better fiber–matrix interface obtained by good adhesion between the fiber and the matrix as observed in their fractographs. On the other hand, water uptake, swelling and moisture absorption of TPS decreased with the incorporation of fibers, attributed to better interfacial bonding between the matrix and fibers as well as the hindrance to absorption caused by the fibers.

In the present paper, structural [through Fourier transform infra red spectroscopy (FTIR) and X-ray diffraction (XRD) techniques] and thermal studies [through differential thermal analysis/differential thermo-gravimetry (DTA/DTG) and thermo-mechanical analysis (DMTA)] of the thermoplastic cassava starch (TPS) and its composites containing 5–30 wt.% of coir fibers are reported. It is hoped that these results along with those reported in

Part I [Lomelí et al., 2011] will contribute to the understanding of the relationship between composition of composite materials and properties of these materials. This information could be used to propose practical applications for this bio-composite, which would have the additional benefits of enhanced use of coir fibers and generating employment along with economic advantages for all the coconut growing countries of the world.

2. Experimental

2.1. Materials

The native cassava starch (*Manihot esculenta*) used in this study was donated by J. A. Pasquini and Cía Ltda., Nova Esperança, Paraná, Brazil. The coir fibers were donated by COOBCOCO, a street scavengers cooperative in Fortaleza, Ceará state, in north eastern Brazil. Commercial grade glycerol used as plasticizer was donated by Lab-synth, São Paulo, Brazil.

2.2. Methods

2.2.1. Preparation of composites

The method has been described previously [Lomelí et al., 2011]. Briefly, the coir fibers were first dried followed by milling and sieving to obtain fibers with an average length of about 10 mm. Then, the cassava starch was mixed thoroughly with 30 wt.% of glycerol in a plastic bag until a homogeneous mixture was obtained. Into this, 5–30 wt.%² previously prepared coconut fibers in steps of 5 wt.% were mixed using an industrial mixer (Hobart) at high speed to obtain a good dispersion of the fibers in the starch. These mixtures were then transferred to plastic bags for storage until the preparation of the composite laminates. This material was then poured into a stainless steel mold (170 mm × 170 mm × 3 mm), which was placed in a hydraulic press (Solab make) with a heating system and controlled cooling apparatus to obtain the laminates. Laminates of matrix (cassava starch + glycerol) were also prepared for comparison. Laminates of both the TPS matrix and their composites were prepared with the processing conditions of 160 °C and 410.4 kgf cm^{−2} applied pressure for about 50 min.

2.2.2. FTIR analysis

The native starch was chemically characterized by FTIR spectroscopy in a Bio-Rad Excalibur instrument. The starch spectrum was obtained using the potassium bromide disk technique.

In the case of bio-composites samples, the FTIR analyses were performed in a Vertex Excalibur spectrophotometer by means of the ATR (attenuated total reflectance) technique. All IR spectra were the average of 64 scans with a resolution of 4 cm^{−1} within a frequency of 4000–700 cm^{−1}.

2.2.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) studies were carried out using a Shimadzu diffractometer (Model XRD 7000), with monochromatic Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), at operating conditions of 40 keV and 20 mA to determine the crystallinity of the materials.

All samples were dried at 60 °C during 8 h, and the composites specimens used had dimensions of 40 mm × 20 mm × 0.3 mm, while the starch sample was in powder form. The analysis was carried out in the 2θ angle range of 2.5–60° with a scanning speed of 1°/min. The relative crystallinity of starch and composites was calculated according to Eq. (1) proposed by Frost, Kaminski, Kirwan, Lascaris, and Shanks (2009), based on the deconvolution calculus

² Throughout this paper, the composition of composites is in wt.% unless otherwise mentioned.

of amorphous and crystalline areas calculated with the aid of the ORIGIN 5.0 program:

$$RC = \frac{AC}{AC + AA} \quad (1)$$

where RC is the relative crystallinity, AC is the crystalline area and AA is the amorphous area in the XRD pattern obtained.

On the other hand, the crystallinity index or the degree of crystallinity is defined as a percentage of the crystalline regions in relation to the total material. This is an important parameter to consider, because it influences the chemical, physical and technological properties of starch [Lopez-Rubio, Flanagan, Gilbert, & Gidley, 2008]. Crystallinity of the starch was initially calculated through a method similar to that followed by Lopez-Rubio et al. (2008) to calculate the cellulose crystallinity. These methods are based on the existence of two phases in the material with crystalline domains considered to be relatively perfect (crystallites) interpolated inside less organized or amorphous regions.

2.2.4. Thermo-gravimetric analysis (TGA)

The thermal stability of starch and its composites was investigated through thermo-gravimetric analysis (TGA) according to the ASTM E 1131 standards. TGA was carried out in a Netzsch (Model TG-209) instrument and the samples were heated from 20 °C to 550 °C in nitrogen atmosphere (15 mL/min), with a heating rate of 20 °C/min, for the pyrolysis of the organic material. Then, the experiment was continued with oxygen atmosphere (15 mL/min) with the same heating rate, until 800 °C, to promote the burning of any remaining organic material during the pyrolysis.

2.2.5. Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical thermal analyses (DMTA) for the cassava starch composites in all compositions were carried out according to ASTM D 5026. The measurements were made in a Netzsch model 242 m dynamic-mechanical analyzer using tensile mode in the following conditions: frequency of 5–20 Hz; temperature range of –100 to 150 °C; heating rate of 3 °C/min and nitrogen flow of 50 mL/min.

3. Results and discussion

3.1. FTIR spectroscopy

Fig. 1 shows the spectra of native starch, the TPS matrix and its composites containing 5–30% of coir fibers. In general, all the spectra of TPS composites showed the same pattern of bands. This suggests that the starch is neither chemically affected nor modified by the influence of glycerol or the amount of fiber during the plasticizing process. Moreover, the association between them may be exclusively attributed to molecular interactions.

On the other hand, changes in the bandwidth and frequency of OH band are observed in the native starch spectrum compared with those of matrix and composites in the region of 3381–3303 cm^{−1}. This change might have occurred as a consequence of the plasticizing process. This suggests that the intra and intermolecular hydrogen bond network between the starch molecules are affected by the presence of glycerol [Ma et al., 2009; Shi et al., 2007].

Furthermore, in the case of native starch, this band is broader than those of the TPS matrix and its composite samples due to the structure of the polysaccharide (as already described) and also to the possible association of water with this poly-hydroxylated system.

In all the spectra obtained, a band around 2925 cm^{−1} related to C–H vibrations of aliphatic groups from hydrocarbon backbone of starch, glycerol–starch (matrix) and TPS composites is observed. The effect of increasing fiber content in the composites is reflected

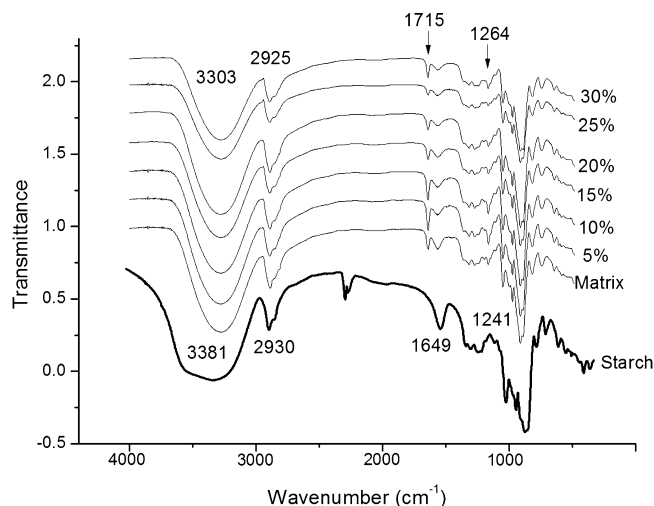


Fig. 1. FTIR spectra of starch, TPS matrix and the bio-composites with different amounts of fibers of green coconut.

inversely to the shape of this band (less defined band). According to Tongdeesoontorn, Mauer, Wongruong, Sriburi, and Rachtanapun (2011), the band located at 1658 cm^{−1} corresponds to adsorbed water in the samples. As can be observed in the spectra (Fig. 1), native starch shows the most intense signal in this frequency, which is reflected by the breadth and intensity of the OH band at 3381 cm^{−1}. On the other hand, this band decreases in the TPS matrix sample as well as in its bio-composites. Besides this, in these thermoplastic samples, the intensity of the band changes gradually (decreasing) in proportion to the increase in the amount of fibers added. This result suggests that the starch is mainly responsible for this water band and therefore, the coir fibers do not have any observable contribution because of their low moisture content (less than 5%).

In comparison with native starch, the spectra of the TPS matrix and its composites show a new band at 1720 cm^{−1}, which may be attributed to stretching vibrations of carbonyl groups (C=O) in the samples. On other hand, the addition of the different amounts of coir fibers to the matrix does not seem to have any influence on the intensity of this carbonyl band in the composites (Fig. 1). Thus, the compounds of the matrix sample are mainly responsible for the band at 1720 cm^{−1} due to the possible presence of carboxylic acid, ketones or aldehydes compounds produced by thermal decomposition of the native starch when TPS matrix and its bio-composite samples were prepared at 160 °C for 50 min. This carbohydrate decomposition catalyzed by temperature (>100 °C) is a well-known mechanism called 'caramelization' [Fagerson, 1969; Maga, 1989, chap. 4; Yordanov & Stoilova-Ivanova, 1996]. It was also expected to occur due to the conditions of the molding process.

However, the intensity of this C=O band suggests that decomposition of the starch is not complete. In fact, most of the native polysaccharide remains chemically unmodified under this thermal process, which means that properties of neither the matrix nor the TPS composites are significantly affected by the compression molding process. This may be due to decomposition taking place only on the surface of the bio-composite laminate, where both temperature and compression (load) are applied.

Finally, all the samples show similar pattern of bands between 1400 and 900 cm^{−1} where C–O vibrations of alcohol or ether groups from glycerol and carbohydrate starch in the matrix are involved. On the other hand, in the case of composites, this C–O pattern is also extended because of the higher amounts (70–95%) of matrix present in them.

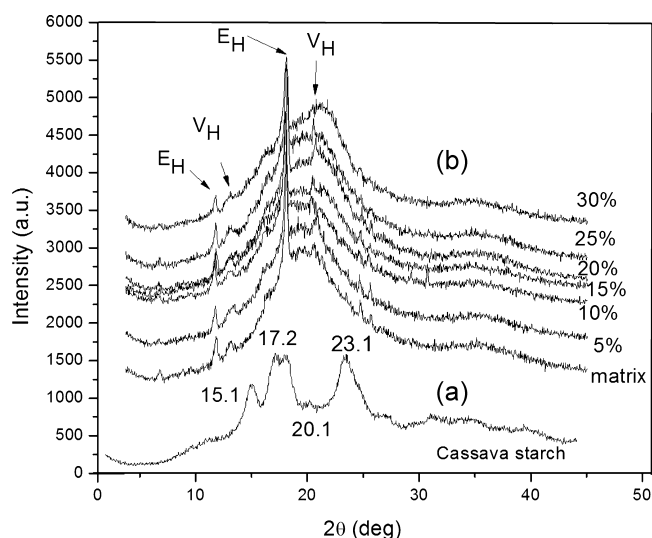


Fig. 2. (a): X-ray diffractograms of (a) cassava starch and (b) TPS matrix and its composites with fibers of green coconuts.

3.2. X-ray diffraction (XRD)

Fig. 2(a) is an X-ray diffraction curve of cassava starch. It can be seen that the diffractogram of the matrix showed main diffraction peaks at different positions (angles) of 2θ (15.2° , 17.2° , 18.1° , 20.1° and 23.1°). These values are similar to those observed by Teixeira, Róz, Carvalho, and Curvelo (2005) (15° , 17° , 18° , 22 – 23° and 26.9°) and Yuan, Zhang, Dai, and Yu (2007) (15.2° (strong), 17.4° (strong), 20° (weak), 23.3° (strong) and 26.2° (weak)) for cassava starch. According to Kawabata, Sawayama, Nagashima, Rosario, and Nakamura (1984), the observed pattern corresponds to a crystallinity pattern of the A-B type, also known as C_a (C in the proximity of A) presenting about 90% of type-A crystallinity and 10% of type-B crystallinity. Similar results have been reported by Zobel (1988) and Perez, Baldwin, and Gallant (2009, chap. 5).

The relative crystallinity of cassava starch obtained in this study is 27.3%, similar to the value (27.8%) reported by Srichuwong et al. (2005) for type C starch (cassava). Nuwamanya, Baguma, Emmambux, and Rubaihayo (2010) reported a range of values (28.8–37.4%) for the relative crystallinity in many varieties of cassava starch.

Fig. 2(b) shows the diffractograms of TPS matrix and its composites. It can also be observed that the direct plasticization process in the press, under the combined action of temperature, pressure and plasticizer, caused granular disruption, leading to a change in the characteristic profile of the native starch from type-C to type V_H . It was reported earlier that the crystallinity of the V_H type can be transformed into V_A type in dehydration conditions and vice versa [Dai, Chang, Geng, Yu, & Ma, 2009]. According to these authors, thermoplastic starch samples exposed to air for 90 days with relative humidity of 50% underwent transformation of crystallinity from V_A to V_H due to hydration. Therefore, it is important to report the conditioning aspect of starch based samples, since this parameter influences the crystallinity of the materials, which in turn affects various physical chemical and technological properties. Furthermore, there is also a correlation between crystallinity and mechanical strength of polymers in that the increase of crystallinity may be related to the enhancement of tensile strength of the bio-composites. In fact, the materials studied here showed increased tensile properties of plasticized starch, except for deformation not only with the incorporation of fibers, but also with their increasing content and with thermal treatment of the fibers [Lomeli et al., 2011]. Both these contribute to the enhancement of

Table 1

Relative crystallinity of plasticized cassava starch and its composites with fibers of green coconuts.

Cassava ATP (%)	Relative crystallinity
Matrix	0.39
5	0.42
10	0.44
15	0.46
20	0.46
25	0.55
30	0.62

crystallinity of the materials. Additionally, an increase in the value of the storage modulus with increasing amount of coconut fibers content in the composites under study was observed [see Section 3.4]. These observations of the effect of fiber loading on the properties of bio-composites are in agreement with those reported recently in TPS matrix of Sago incorporated kenaf core fibers and other fibers [Oniszczyk & Janssen, 2009; Sarifuddin et al., 2012].

Furthermore, it is also reported that processing temperature, residence time and cooling speed affect the final crystallographic pattern of starch based materials [van Soest, Hulleman, de Wit, & Vliegenthart, 1996]. Accordingly, time and temperature used during the processing step in the present study may be considered to have contributed to the formation of other types of crystallinity (E_H and V_H structures), which are the crystallographic patterns predominant in the thermoplastic cassava starch. While E_H type of crystallinity is not considered stable and in general, the structure converts into the V_H type on an aging process [Van Soest & Knooren, 1997]. It is interesting to note the sharp peaks in the diffractograms of the matrix and its composites (Fig. 2(b)). This is understandable since it is well known that higher the number of crystals in one plane of the structure, the more intense and narrow will be the X-ray diffraction peaks.

Table 1 presents the relative crystallinity of TPS based composites. It can be observed that the proportional increase of coir fibers in the matrix caused enhancement of the relative crystallinity. Fibers, synthetic or natural, are orientated materials and therefore, their crystallinity is higher than the crystallinity of starch.

Therefore, an enhancement of relative crystallinity in the TPS based composites is expected with increasing amount of coconut fibers [Amash & Zugenmaier, 2000; Ma et al., 2005]. Besides this, it has been reported that when amylase in potato and high amylase in corn starch films are oriented, physical properties of such starches change [Shogrent, 2007]. In the present case, all TPS materials were not oriented, even though reinforcing fiber content in the TPS matrix increased, leading to improved crystallinity index of these composites.

3.3. Thermogravimetric analysis (TGA)

Fig. 3(a) shows TGA curves of coir fiber and cassava starch, with and without plasticizer glycerol (matrix) and their bio-composites, while Fig. 3(b) shows DTG curves of these materials. It can be seen from Fig. 3(a) that the TGA curves of TPS matrix and its composites are very similar and are superposed on one another, but show some differences with those of the fiber and the starch (shown in the inset). Further, it can be also seen that the matrix of cassava starch and its composites exhibit a small and gradual mass loss in the range of 25–200°C, which is associated with the losses of water and perhaps, glycerol (boiling point of glycerol is 198°C). It should be noted that both the composites and matrix were dried at 60°C before the TGA analysis and hence most of the moisture was already removed, resulting in smaller mass loss of matrix and composites. Further dehydration, in the range of 25–200°C, was small, which is also confirmed in the DTG curve [Fig. 3(b)], where

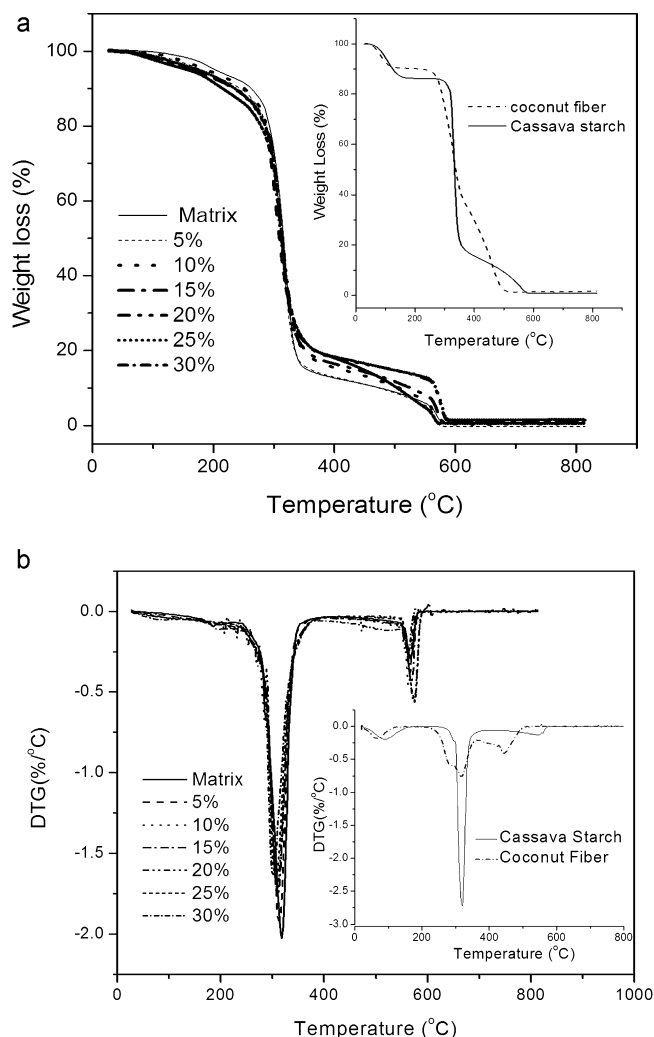


Fig. 3. Thermogram – (a) TGA curves and (b) DTG curves of fiber of green coconut, cassava starch, TPS matrix and its composites with fibers of green coconuts.

no inflexion point (peak) is seen in this temperature range. This result is in agreement with the observation of Gómez et al. (2006), who also reported the absence of mass loss due to moisture and attributed this behavior to the processing conditions. However, the mass losses by dehydration of the native starch and coir fibers were higher in the range 25–200 °C. Fig. 3(a) shows that the degradation of cassava starch begins after 300 °C, while thermal degradation of the coconut fiber begins with the degradation of hemicelluloses (200–260 °C), cellulose (240–350 °C) and lignin (280–500 °C).

It has been reported that fiber addition to a starch matrix improves its thermal stability when there is good adhesion between the fiber and the matrix, which reduces the mass loss in the sample [Ma et al., 2005; Phattaraporn, Waranyou, Fazilah, & Thawien, 2010; Prachayawarakorn et al., 2010]. Also, improvement in the thermal stability of the bio-composites of TPS has been reported when natural fibers are aggregated [Phattaraporn et al., 2010; Ruseckaite & Jimenez, 2003].

It can be observed from the DTG curves of the matrix and bio-composites shown in Fig. 3(b) that there are two endothermic processes. The first occurs in the range of 300–320 °C, corresponding to the degradation of the fraction of thermoplastic starch and cellulose, while the second, in the range of 560–580 °C corresponds to the degradation of lignocellulosic material. These peaks are similar to those reported by Rudnik (2007), for bio-composites reinforced with flax. In fact, the second peak has been attributed to

the degradation and formation of pitch, which is the main component of the residual mass [Davallencourt, Saiter, & Capitaine, 1996; Dobircu et al., 2009]. Also, Fig. 3(b) shows the DTG of coconut fiber and the starch (shown in the inset). The DTG curve exhibits an endothermic peak around 289 °C, related to the degradation of hemicelluloses, and a well-defined peak around 316 °C due to thermal degradation of cellulose. Another peak can be seen around 443 °C and can be related to lignin degradation. It is well known that it is difficult sometimes to separate each event clearly, because of the complexity of the reactions that occurs during the degradation process. The degradation peak of starch can be seen in the DTG at approximately 320 °C.

In general, dehydration and de-polymerization processes are the main mechanisms associated with degradation of polysaccharides [Rudnik, 2007]. There is inflection in the curves due to the loss of water. According to Avérous and his coworkers [Avérous & Halley, 2009], the degradation temperature of composites is between the temperatures of their components, namely, the reinforcing fibers and the matrix.

Table 2 lists the values for mass loss, degradation temperature and onset of the degradation process for the TPS of cassava starch. Comparing the parameter values obtained for the matrix with those of the composites, it can be said that the presence of coir fibers in the thermoplastic cassava starch matrix does not significantly influence the onset value. However, the mass loss decreases with increasing fiber content, which is explained later. This suggests chemical interaction between thermoplastic starch matrix and coir fiber due to the chemical compatibility. Also, the mass loss is related to the presence of inorganic materials, as can be observed in TGA curve of the fiber (inset in Fig. 3(a)), which is a consequence of the amount of fibers or increasing fiber content in the composites.

Teixeira et al. (2009) reported the value of initial decomposition for cassava thermoplastic starch reinforced by cellulose nano-fibers at 280 °C, which they attributed to the de-polymerization of starch and cellulose. On the other hand, Avérous and his coworkers have attributed the differences in mass loss at the onset temperature as due to variations in the equilibrium moisture and the crystallinity of the reinforcement [see ref. in Avérous & Halley, 2009]. The addition of crystalline cellulose or lignocellulosic fiber to the starch matrix reduces both the polar character and the moisture content due to many interposed interactions of the fibers, which occupies the original place of water in the matrix. Therefore, mass loss decreases with the increase of fiber content.

3.4. Dynamic mechanical thermal analysis (DMTA)

Fig. 4(a) and (b) present plots of damping modulus ($\tan \delta$) and storage modulus (E') as functions of temperature for cassava starch, TPS matrix and its composites with different amounts of coir fibers, respectively. Two peaks can be seen in the figure indicating that the materials present two relaxation phases. The first relaxation (β) below ambient temperature corresponds to a phase poor in starch and rich in glycerol, while the second relaxation process corresponds to the glass transition temperature of the phase rich in cassava starch (relaxation α), which undergoes a displacement or shift at higher temperatures in proportion to the increase in the amount of coconut fiber in the composite [Belhassen et al., 2009; Famá, Gerschenson, & Goyanes, 2009]. This behavior was also reported for composites of thermoplastic starch reinforced by Spanish grass (*Stipa tenacissima*) [Belhassen et al., 2009].

The storage modulus increases when coconut fibers are added, so good interaction between fibers and matrix promotes better anchorage of the fibers in the matrix of the thermoplastic starch and results in a higher thermal transition temperature. In fact, a shift in the glass transition temperature (T_g) to higher values has been reported, which may be associated to the restriction or

Table 2

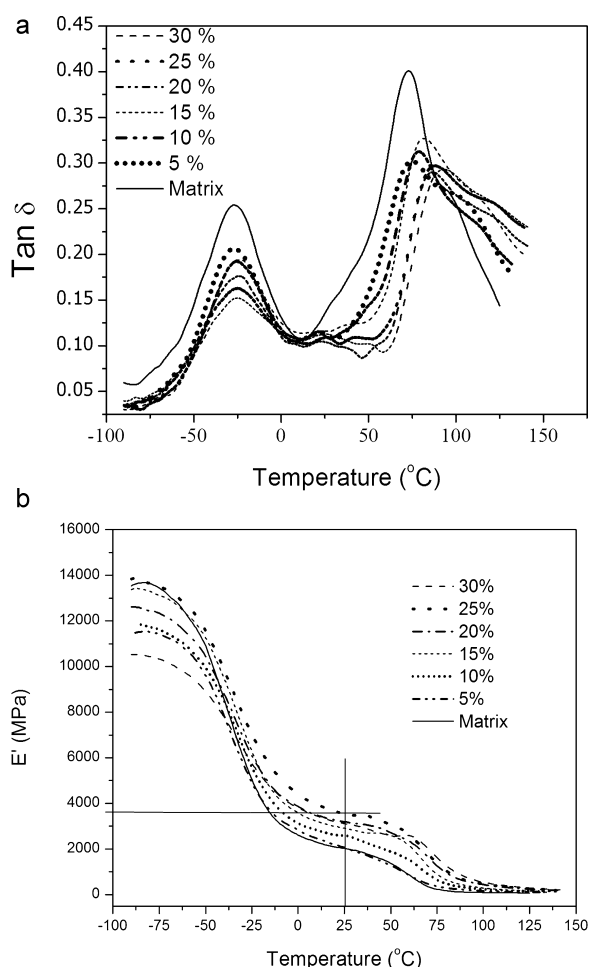
Thermo-gravimetry analysis data of TPS (cassava starch) matrix and its composites with fibers of green coconuts.

ATP type (%)	Degradation temperature (°C) First peak DTG	Onset temperature (°C)	Weight loss (%)	Degradation temperature (°C) Second peak DTG	Weight loss (%)
Matrix	319.4	295.9	89.0	568.1	10.3
5	314.9	293.7	88.9	562.9	11.3
10	312.2	293.1	86.7	565.3	12.8
15	311.9	292.4	85.6	571.0	13.2
20	310.6	291.8	83.8	575.5	14.8
25	309.1	290.2	83.3	576.8	15.2
30	305.9	288.8	82.2	564.3	16.2

Table 3

DMTA results of TPS (cassava starch) matrix and its composites with fibers of green coconuts.

TPS-cassava starch + Coir fibers (%)	Temperature (°C) β relaxation	Intensity	Temperature (°C) α relaxation	Intensity	E' (MPa) ^a
0	-27	~0.15	73	~0.29	2027
5	-27	~0.10	75	~0.20	2066
10	-25	~0.09	79	~0.20	2587
15	-24	~0.08	82	~0.20	2908
20	-24	~0.08	86	~0.20	3198
25	-25	~0.06	89	~0.20	3534
30	-25	~0.05	94	~0.20	3215

^a At 25 °C.**Fig. 4.** Dynamic mechanical thermal analysis results – plots of (a) damping modulus ($\tan \delta$) and (b) storage modulus (E') as functions of temperature for cassava starch, TPS matrix and its composites with fibers of green coconuts.

reduction of mobility of the polymer chains caused by the strong molecular interactions between fiber and matrix [Avérous & Halley, 2009; Belhassen et al., 2009]. Another important observation is the reduced intensity of this transition with fiber incorporation in

the matrix. A reduction in the peak heights of $\tan \delta$ with the fiber addition to polymer matrix has been observed, which has been attributed to the restricted mobility of polymer molecules [Famá et al., 2009; Taib, Ramarad, Ishak, & Todo, 2009].

From Fig. 4(a), it can be seen that the damping ($\tan \delta$) of the β relaxation also show small variation (2 °C) toward smaller values when the fiber content in the bio-composites increases. This indicates the start of the mobility region of groups and segments of short chains [Shi et al., 2007].

It can be seen from Fig. 4(b) that the storage modulus (E') of the composites, gradually decreases with increasing temperature. In the region between 10 °C and 70 °C, a decrease in the height of the peak can be clearly observed. This can be attributed to the flexibility or segmental mobility of the TPS matrix [Taib et al., 2009].

Further, from Fig. 4(b) it can be noted that around 25 °C, the values of E' (storage modulus) increase when the fiber content increases up to 25% and then decreases at 30% fiber content. This suggests that the reinforcing fibers increase the rigidity of the starch-based composites when there is a good interaction with the matrix. When the quantity of fibers increase to 30%, the matrix phase of the thermoplastic starch is reduced and therefore, it is not possible to obtain a homogeneous distribution of fibers in the composite. In fact, when the fiber content goes beyond 30% in the plasticized starch matrix, a process referred to as “anti-plasticizing effect” can take place [Oniszcuk & Janssen, 2009].

Table 3 shows the values of different parameters in the DMTA analysis for all the composites of cassava starch-coir fibers prepared in this study. According to Martins, Napolitano, Visconte, Nunes, and Furtado (2002), α relaxation or maximum $\tan \delta$ value is related to the glass transition temperature (T_g). This represents a temperature where chain mobility is restricted due to molecular cohesion (rotation of lateral groups around primary links).

A shift of T_g to higher temperatures may be attributed to mobility restriction of segments of polymer molecules in the proximity of fibers, where many molecular interactions occurs [Taib et al., 2009]. Moreover, the increase of $\tan \delta$ indicates the composite is becoming more viscous as the temperature increases [Liu, Zhong, Chang, Li, and Wu, 2010]. The shift of glass transition temperature (T_g) to higher temperatures has been reported when lignocellulosic fibers are incorporated into the polymer matrix, suggesting molecular interaction between fibers and matrix. In other words, better interfacial adhesion is established [Avérous & Halley, 2009; Belhassen et al., 2009; Phattaraporn et al., 2010]. The transition temperature

(α relaxation) has also been reported in the literature, which can vary to a great extent, since it depends on the chemical composition of the polymer used as matrix, presence of plasticizer, fiber addition, test conditions, etc. [Liu et al., 2010; Moriana, Vilaplana, Karlsson, and Ribes-Greus, 2011; Phattaraporn et al., 2010]. For instance, some of the reported values of T_g by these researchers are as follows: 148 °C for rice starch films reinforced with palm press fibers [Phattaraporn et al., 2010]; 99 °C for plasticized pea starch composites reinforced with bamboo cellulosic crystals [Liu et al., 2010] and 80 °C for thermoplastic starch copolymers (Mater-Bi KE03B1) and bio-fibers (cotton, hemp and kenaf) [Moriana et al., 2011].

4. Conclusions

The present investigation was carried out with the objectives of studying the structural and thermal properties (thermal stability) of bio-composites of glycerol plasticized cassava starch containing fibers of green coconuts through FTIR, XRD, DTA/DTG and DMTA techniques. This added the understanding of processing–property–structure correlations and revealed the following:

- The thermal molding process for preparing the bio-composites caused slight decomposition of the starch in the TPS matrix and TPS composites as revealed by the presence of carbonyl compounds shown by a small signal at 1715 cm^{-1} in their FTIR spectra. However, most of the starch remained chemically unmodified keeping the properties of the prepared composites unaffected during the plasticizing process.
- Increasing additions of coir fibers from 0% to 30 wt.% to the TPS matrix resulted in (i) increased relative crystallinity from 39% to 62%, (ii) enhanced thermal stability, shown by decreasing degradation temperature, and (iii) increasing storage modulus (from 2027 MPa to 3215 MPa), higher glass transition temperature and lower damping as revealed by as revealed by XRD studies, TGA/DTG studies and DMTA studies respectively.
- Chemical compatibility in the TPS composites promoted by a better interfacial bonding interaction between the matrix and fibers can be attributed to the above mentioned results.

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