Carbohydrate Polymers 86 (2011) 1712–1722

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Study of the properties of biocomposites. Part I. Cassava starch-green coir fibers from Brazil

María Guadalupe Lomelí Ramírez[a], Kestur G. Satyanarayana[b,*], Setsuo Iwakiri[c], Graciela Bolzon de Muniz[c], Valcineide Tanobe[c], Thais Sydenstricker Flores-Sahagun[d]

[a] Universidade Federal do Paraná, Centro de Ciências Florestais e da Madeira, Av. Pref. Lothário Meissner, 900, Curitiba, Paraná, Brazil
[b] UFPR, Curitiba, Brazil
[c] Prof. Dr. Universidade Federal do Paraná, Centro de Ciências Florestais e da Madeira, Av. Pref. Lothário Meissner, 900, Curitiba, Paraná, Brazil
[d] Prof. Universidade Federal do Paraná, Departamento de Engenharia Mecânica, Centro Politécnico da UFPR, Bairro Jardim das Américas, Curitiba, PR, Brazil

ARTICLE INFO

Article history:
Received 14 January 2011
Received in revised form 15 June 2011
Accepted 4 July 2011
Available online 12 July 2011

Keywords:
Biocomposites
Cassava starch
Green coconut fiber
Thermoplastic starch
Glycerol

ABSTRACT

Increasing environmental concerns in recent years focused greater attention on the development of biodegradable materials. This paper presents the preparation of cassava starch based composites incorporating fibers from Brazilian green coconuts. These composites were prepared with different amounts of coir fibers by thermal molding using glycerol as plasticizer for the starch. The matrix and composites were given thermal treatment. Both the untreated and treated matrices and their composites were characterized for their tensile properties, while water uptake, swelling on immersion in water and moisture absorption on exposure to humidity were evaluated for both untreated and treated matrix and its composites. The tensile properties of cassava starch improved with both the incorporation of fibers and thermal treatment. Fractographic studies through scanning electron microscopy were used to explain the observed strength properties. Water uptake, swelling and moisture absorption of TPS showed decrease with the incorporation of fibers, which is due to better interfacial bonding between the matrix and fibers as well as the hindrance to absorption caused by the fibers.

1. Introduction

Synthetic polymeric materials have been widely used in all areas of human activity. Because of this, plastics derived from petroleum represent about a fifth of urban trash by volume (Róz, da Carvalho, Morais, & Curvelo, 2001). The disposal of a high volume of plastics, which take a long time to decompose, poses a huge environmental problem (Lu, Xiao, & Xu, 2009; Vašková et al., 2008). With increased environmental awareness among society, there is growing recognition of the need to reduce the quantity of plastic materials discarded (Kuciel & Liber-Knec, 2009). Therefore, intense research has been carried out in the areas of engineering and biological sciences to develop polymeric materials that are easily disposable but not environmentally harmful, particularly for use in the packaging industry.

Starches are considered one of the most promising available natural polymer candidates for the development of biodegradable materials, because of their attractive combination of attributes such as low cost, abundant availability and thermoplastic behavior, besides the fact they are biodegradable, recyclable and renewable (Mali, Grossmann, García, Martino, & Zaritzky, 2008). However, starches have some drawbacks, such as poor melting processability, high water solubility, difficulty of processing and brittleness, causing the need for a plasticizer (Satyanarayana, Gregorio, & Fernado, 2009; Yu, Dean, & Li, 2006) to make them suitable for engineering applications.

However, under the action of high temperature and shear stress, starch can be processed into a thermoplastic starch (Mo, Zhong, Liang, & Yu, 2010) by breaking its structure (semi crystalline form), causing de-structuring of the starch chains, and leading to intermolecular rearrangement. This can be done by using plasticizers such as glycerin, water and other polyol compounds (Corradini, Texeira, Agnelli, & Mattoso, 2007; Gáspár, Benko, Dogossy, Reczey, & Czigany, 2005; Pradella, 2006). Besides, use of plasticizers would lead to change in properties of TPS, of course this change is a function of the amount of plasticizer used. For example, glass transition temperature (T_g) of cassava starch is reported as 131.9 °C and it decreases with increasing addition of glycerol. At 30% glycerol content, value of T_g is 62.2 °C (Bergo, Sobral, & Prison, 2009). Tensile properties are also reported to change accordingly.

Natural starch is normally made into thermoplastic by processing through the use of various industrial techniques, such as

* Corresponding author. Present address: Acharya Institute of Technology, Soldevanhalli, Bangalore, BMS College of Engineering, Bangalore and Poornaprajna Institute of Scientific Research, Bangalore (India). Tel.: +91 80 2666 0140; fax: +91 80 2661 4357.
E-mail addresses: glomeli12@hotmail.com (Ramírez M.G.L), kgs_satya@yahoo.co.in (K.G. Satyanarayana).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.07.002

injection, extrusion or use of a batch mixer connected to a torque rheometer (Corradini et al., 2007). TPS absorbs moisture when exposed to humidity and has inferior but useful mechanical properties compared to synthetic polymeric materials (Avérous & Le Digabel, 2006). One of the methods to overcome these negative attributes, as well as to improve the strength properties in general, has been to incorporate TPS by abundant and relatively inexpensive (Kuciel & Liber-Knec, 2009) lignocellulosic materials, such as hard and soft wood fibers or other plant fibers (jute, coconut, banana, cane bagasse, etc.). The resulting materials are termed "biocomposites" or "green" composites, which are considered to be totally biodegradable (Avérous & Boquillon, 2004; Fowler, Hughes, & Elias, 2006; Satyanarayana, 2007).

Other methods to improve the properties of starch-based materials drawing much attention are thermal or other treatments (Blanshard, 1987; Cereda et al., 2002; Gough & Pybus, 1971; Knutson, 1990; Zavareze & Dias, 2011). Thermal treatment consists of annealing starch to find the effect on gelatinization, as first demonstrated by Gough and Pybus (1971). They observed that annealing wheat starch, by heating it in water at 50 °C, occurs only when starch was heated to a temperature above its glass transition point, but not high enough to cause irreversible melting, or gelatinization (Knutson, 1990). Other studies (Blanshard, 1987; Cereda et al., 2002) have reported that annealing of starch below the gelatinization temperature leads to discrete molecular organization with the formation of a more organized structure with less free energy. This in turn affects the mechanical and other properties.

Considerable research on the development of starch-based composites reinforced with natural fibers has been reported in the past decade (Avérous & Boquillon, 2004; Avérous & Halley, 2009; Carvalho, Curvelo, & Agnelli, 2002; Curvelo, Carvalho, & Agnelli, 2001; Guimarães, Wypych, Saul, Ramos, & Satyanarayana, 2010; Kumar & Singh, 2008; Luna, Villada, & Velasco, 2009; Ma, Yu, & Kennedy, 2005; Mo et al., 2010; Rosas, 2008) with one of the main focuses of research being the improvement of the mechanical properties of these thermoplastic starch composites (Yu et al., 2006). For example, Ma et al. (2005) and Liu, Xie, Yu, Chen, and Li (2009) have pointed out problems such as non uniformity of the mass and poor flow properties can occur when TPS composites are processed through injection or extrusion, especially when a large amount of fiber is added. Another aspect studied in respect of TPS composites is the effect of moisture on properties particularly the mechanical properties, which also affects their life cycle. For example, TPS composites absorb moisture in humid environments and undergo dilatational expansion. Moisture can cause stress between fiber and polymer (matrix), resulting in reduced resistance to damage as well as structural changes. Many of the irreversible changes in the mechanical properties in these materials are known to be due to moisture absorption (Kuciel & Liber-Knec, 2009).

One aspect, which has not generally been considered in the case of lignocellulosic fiber incorporated composites including biodegradable ones, is their life cycle analysis (Satyanarayana et al., 2009). Normally biocomposites have been used in consumer products of short life cycles or those that can be discarded after rapid use. According to John and Thomas (2008), these materials can also be used for interior applications with a long lifetime.

In light of the above and considering that (i) Brazil has been in the forefront of the use of industrial wastes in recent years (Satyanarayana et al., 2009), (ii) the country has the highest production and yield per hectare of starch production in Latin America, particularly cassava (or manioc) starch and (iii) coconut is an important crop in northeastern Brazil, which produces fibers resulting from discarded green coconuts (Tomczak, Sydenstricker, and Satyanarayana, 2007), the objective of this work is development of cassava starch-green coir fibers of Brazil composite by compression molding technique to understand processing–property–structure correlations. This is expected to extend the use of this starch and green coconut fiber through diverse applications for their further value addition This paper presents the preliminary results of the preparation and characterization of biodegradable composites based on thermoplastic cassava starch (TPS) combined with different amounts (5–30 wt.%) of green coconut fibers. Direct thermo-plasticization was used to process the composites and glycerol was used as plasticizer. The effect of annealing of both the TPS matrix and its composites containing 5–30 wt.% coir fibers on the tensile properties and water absorption characteristics is also presented.

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 green coconut fibers were donated by COOBCOCO, a cooperative formed of street scavengers in Fortaleza, Ceará state, in northeastern Brazil. The glycerol used as plasticizer was of commercial grade and was donated by Labsynth, São Paulo, Brazil.

2.2. Methods

2.2.1. Preparation of composites

First the coconut fibers received were dried, milled and sieved to obtain fiber length of mostly 10 mm. Then the cassava starch was mixed thoroughly with 30 wt.% glycerol in a plastic bag until attaining a homogeneous mixture. This was followed by the mixing of coconut fibers with the mixture of starch and glycerol in an industrial mixer (Hobart) at high speed for 1 min, since the fibers became well dispersed in the starch during this time, while at longer mixing times the starch started adhering to the mixing vessel. The amounts of coconut fibers used to prepare the composites were 5, 10, 15, 20, 25 and 30%.[1]

These mixtures were transferred to plastic bags for storage until preparing the composite laminates. Then the composite mixture was poured into a stainless steel mold (170 mm × 170 mm × 3 mm) to obtain composite plates.

A hydraulic press (SOLAB) with a heating system and controlled cooling apparatus was used to obtain the laminates of both the matrix and composites. The processing conditions used were: temperature 160 °C with applied pressure of 410.4 kgf/cm^2 and pressurization time of 50 min.

2.2.2. Thermal treatment of the matrix and its composites

Laminates of both the TPS matrix and its composites containing different amounts (5–30 wt.%) of coir fibers after conditioning were thermally treated (annealed) in an air circulating oven at 60 °C for 12 h.

2.2.3. Morphological study of the composite

2.2.3.1. Optical microscopy. A Zeiss stereoscope microscope (Discovery VI2 model) equipped with a Zeiss AxioCam camera was used to observe the transparency obtained in the composites, porosity and the distribution of coconut fibers in the composites.

2.2.3.2. Scanning electron microscopy (SEM). A Philips XL-30 scanning electron microscope with operating voltage of 10–20 kV was used to obtain SEM micrographs taken from fractured tensile test samples of both the matrix and composites. For this purpose, all the

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

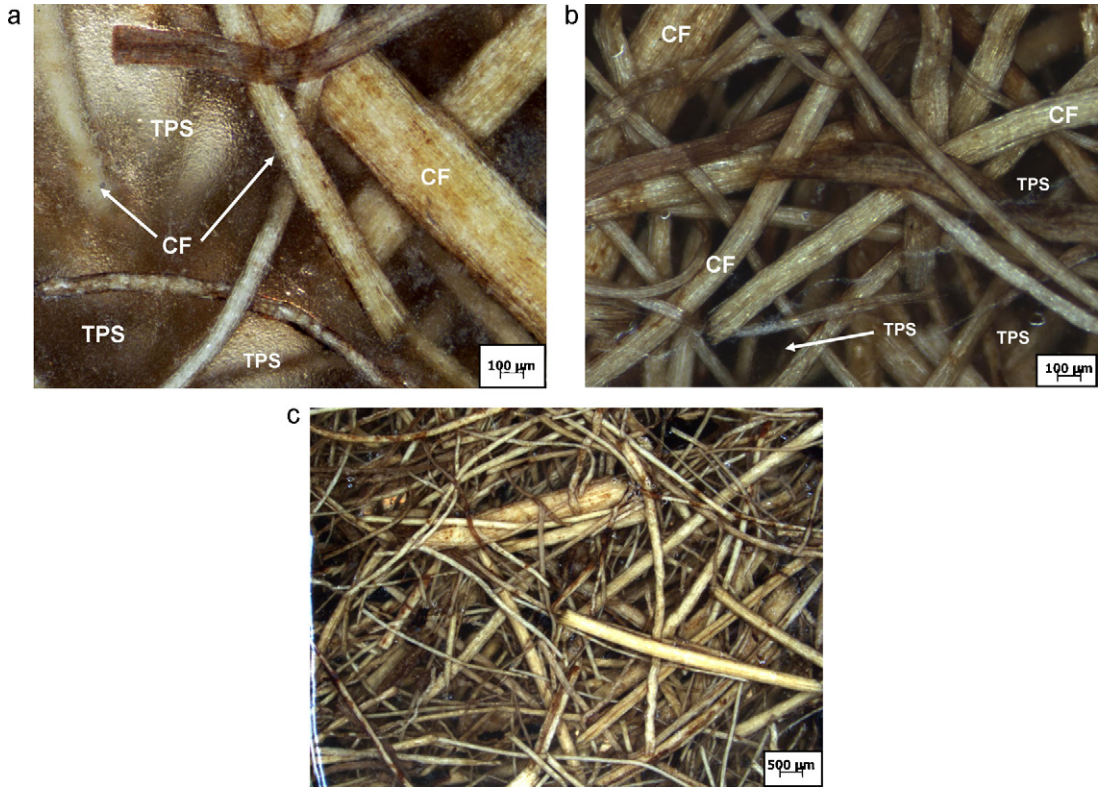

Fig. 1. Photographs of cassava starch composite (a) 5% and (b) 30% coconut fiber. (c) Panaromic view of the composite at higher magnification; TPS: thermoplastic starch; CF: coir fiber.

samples were coated with gold before observation by sputtering in a vacuum chamber.

2.2.4. Mechanical testing

Tensile samples of the matrix and the composites were cut from respective laminates (plaques) using a laser cutting machine (Gravograph model LS100). The samples obtained were tested in a universal testing machine (EMIC DL 20.000) following ASTM standard D 638M at room temperature and relative humidity of 75% at a testing speed of 5 mm/min. Six to seven specimens were tested for each sample and the average values of the tensile properties were recorded. All the specimens (TPS matrix and their coir composites, with or without thermal treatment) were tested after being conditioned for two weeks at 23 °C and RH of 75%.

2.2.5. Water absorption and swelling

Since it is well known that one of the problems of thermoplastic starch is its susceptibility to humidity and that prepared biocomposites are hydrophilic in nature, the water absorption and the swelling in thickness (both in %) were evaluated following the EN 317 standard [EN 317-1993-Particle boards and fiber boards-Determination of swelling thickness after immersion in water]. For this purpose, specimens measuring 30 × 30 × 3 mm cut from the laminates plaques were first dried in an air circulating oven at 60 °C and then immersed in water at room temperature (23 °C) for 2 and 24 h, respectively.

To determine the percentage of water absorption and swelling, the samples were weighed and their thickness was measured before and after immersion using a digital vernier (Model: Mitutoyo) having 0.01 accuracy.

The water absorption (WA) of the laminates was calculated using the following equation:

$$\text{WA}\ (\%) = \left[\left(\frac{\text{M1} - \text{Mo}}{\text{Mo}}\right)\right] \times 100 \quad (1)$$

where Mo and M1 are the masses of the sample before and after immersion in water.

The swelling thickness (ST) was calculated using the following equation:

$$\text{ST}\ (\%) = \left[\left(\frac{\text{Th1} - \text{Tho}}{\text{Tho}}\right)\right] \times 100, \quad (2)$$

where Tho and Th1 are the thickness of the samples (in mm) before and after immersion in water. The swelling observed in this study is termed "linear swelling" because the length of the samples was measured before and after water uptake. The linear swelling was calculated similarly, but instead of thickness the specimen length before and after immersion in water was used.

2.2.6. Conditioning to 75% relative humidity

Water sensitivity of composite to the environmental humidity may be one of the important selection parameters for some applications, since humidity affects the properties of starch-based composites (Müller, Laurindo, & Yamshita, 2009). Accordingly, isotherms of humidity sorption of the composites were obtained. For this purpose, first the samples were dried in an air circulating oven at 60 °C. Then these samples were conditioned by keeping them in a desiccator at 22–25 °C and relative humidity of 75 ± 2%, maintained using a saturated solution of sodium chloride (NaCl), prepared following the ASTM E 104 standard. The samples were taken out daily to check the water absorption as a function of time until the weight became constant.

The moisture content was calculated using the equation:

$$\text{Moisture content}\ (\%) = \left[\left(\frac{\text{M1} - \text{Mo}}{\text{Mo}}\right)\right] \times 100, \quad (3)$$

where Mo and M1 are the mass of the samples (in g) when they were taken from the oven and at time (T).

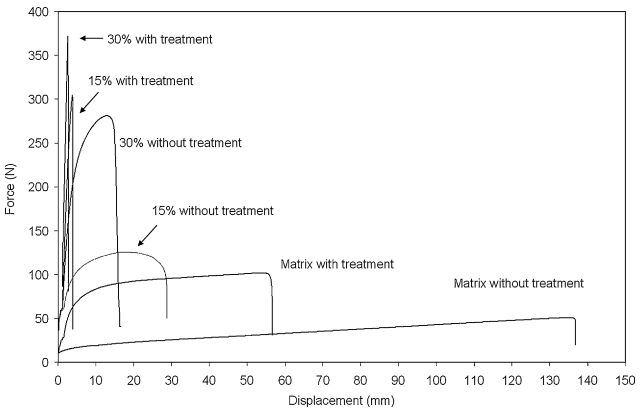

Fig. 2. Force–displacement curves of TPS matrix with and without treatment as well as those of their composites containing 15 and 30% coir fiber.

3. Results and discussions

3.1. Optical microscopy

Fig. 1(a and b) shows photographs of cassava starch–glycerol composites with 5 and 30% coir fibers as observed under a stereomicroscope. Random and uniform distribution of the coir fibers of different diameters can be seen in the transparent plasticized starch matrix without any air bubbles. Vallejos et al. (2010) have reported low dispersion of fibers during the preparation of thermo plasticized cassava starch composites, even with 10% sugarcane bagasse, processed in a rheometer (Haake) at 150 °C, 60 rpm for 6 min. Optimized thermo-plasticization of the composites was obtained without any of the cited problems occurring, even at a high fiber content of 30%.

3.2. Mechanical testing

Fig. 2 shows typical force–displacement curves obtained in the present study in tensile tests of TPS based materials, viz. TPS matrix with and without treatment (0% fiber), and two of their composites containing 15 and 30% coir fibers. Similar curves have been reported earlier for starch based composites with other natural fibers, including nano-bacterial cellulose containing thermo plasticized cassava starch (Alvarez, Ruseckaite, & Vazquez, 2003; Satyanarayana et al., 2009; Woehl et al., 2010). It can be seen that the curves for the TPS with and without the treatment as well as those with and without reinforcement show differences. The matrix (with or without treatment) shows typical curves of a ductile material with large deformations and low strength, both values being influenced by the thermal treatment, with the treated matrix showing higher breaking load and lower displacement compared to the untreated matrix. Similarly, TPS based composites without treatment show typical curves of ductile materials with some deformation, though less than that of both treated and untreated matrices with higher breaking loads. On the other hand, the composite subjected to the thermal treatment at 60 °C shows typical curves of a rigid, strong (higher breaking load, but lower displacement) but fragile material.

Fig. 3(a–d) shows the plots of tensile strength, Young's modulus, load and % elongation of coir fiber versus the fiber content respectively in the composites of TPS with and without treatment. It can be seen from these figures that for the treated matrix the tensile strength, Young's modulus and maximum load are higher (3.24 MPa, 59.81 MPa and 112.68 N, respectively) than for the untreated matrix (1.56 MPa, 14.56 MPa and 50.77 N, respectively). It is also interesting to see that the YM value obtained in this study is lower, while the tensile strength is slightly higher than the figures reported for its nanocomposites earlier for TPS cassava starch processed by the casting method (YM of the plasticized starch without reinforcement: 33.4 ± 4.3 MPa; tensile strength: 1.09 ± 0.39 MPa) (Woehl et al., 2010). The higher values of YM and TS of the treated TPS matrix suggest the effect of thermal treatment. Other studies (Blanshard, 1987; Cereda et al., 2002) have reported that annealing treatment (ANT) affects crystallinity, which in turn affects mechanical properties due to some level of discrete molecular organization. The higher strength properties of TPS cassava observed in this study compared to those observed earlier (Woehl et al., 2010) may be due to the processing method and conditions used.

Both the YM and TS increased with increasing fiber content up to 15% for both treated and untreated conditions. The YM showed continuous growth with increasing fiber content in both the treated and untreated matrix composites. Maximum values of ~373.5 MPa and ~176 MPa for treated composite and untreated composite, respectively, were obtained. Both these values are higher than those reported for nanocomposites of TPS (cassava) containing 2.5% untreated bacterial cellulose nanofibers processed by casting (140.6 ± 40.3 MPa) (Woehl et al., 2010).

On the other hand, the tensile strength of TPS composites with treatment increased from 3 MPa for 0% fiber content to 9 MPa for about 15% fiber content, after which it remained constant (~10–11 MPa). These values are higher than those reported for nanocomposites of TPS (cassava) containing 2.5% of both untreated and treated bacterial cellulose nanofibers and processed by casting (4.15 ± 0.66 MPa and 8.45 ± 2.35 MPa, respectively) (Woehl et al., 2010). Also, the strength values obtained in the present study for the composites with untreated matrix increased slowly with rising fiber content, reaching a maximum of 6 MPa for 30% fiber content.

These increases in YM and UTS may be due to the stronger bonding between the matrix and fiber, which leads to enhanced interfacial adhesion between them and therefore a greater transfer of stress from the matrix to the fibers during tensile testing (Herrera Franco & Valdez-González, 2005). This is justified from the scanning electron microscopic studies of the fractured tensile samples (see Section 3.3).

The % elongation decreased with increasing fiber content for both types of composites (treated and untreated). While the untreated matrix showed ~210% elongation, the thermally treated matrix showed ~112% elongation. The effect of treatment of the matrix/composite on the observed properties can be explained based on a discrete molecular organization taking place with the formation of a more organized structure with lower free energy (Blanshard, 1987; Cereda et al., 2002).

Furthermore, the differences in performance of the matrix and composites suggest that the thermal treatment used (60 °C for 12 h) in the present study is able to affect the function of the plasticizer, causing the starch chains to have better packing, resulting in better organization due to more intense interactions of macromolecules (amylase and amylopectin). This might have resulted in the positive effect on the mechanical properties, increasing the YM, UTS and load while reducing the % elongation compared with the composites without treatment.

The performance of polymers depends closely on the mobility of their macromolecules and the presence of plasticizers. For instance, enhanced mobility is generally due to reduction of the interaction of polymeric chains due to the presence of plasticizers (Billmeyer, 1971; Liu et al., 2009; Mali, Sakanaka, Yamashita, & Grossmann, 2005). As it is well known, a plasticizer is normally placed between polymeric chains to reduce the interactions between different chains, due to its physical presence between the chains, thus allowing polymers to exhibit higher elongations.

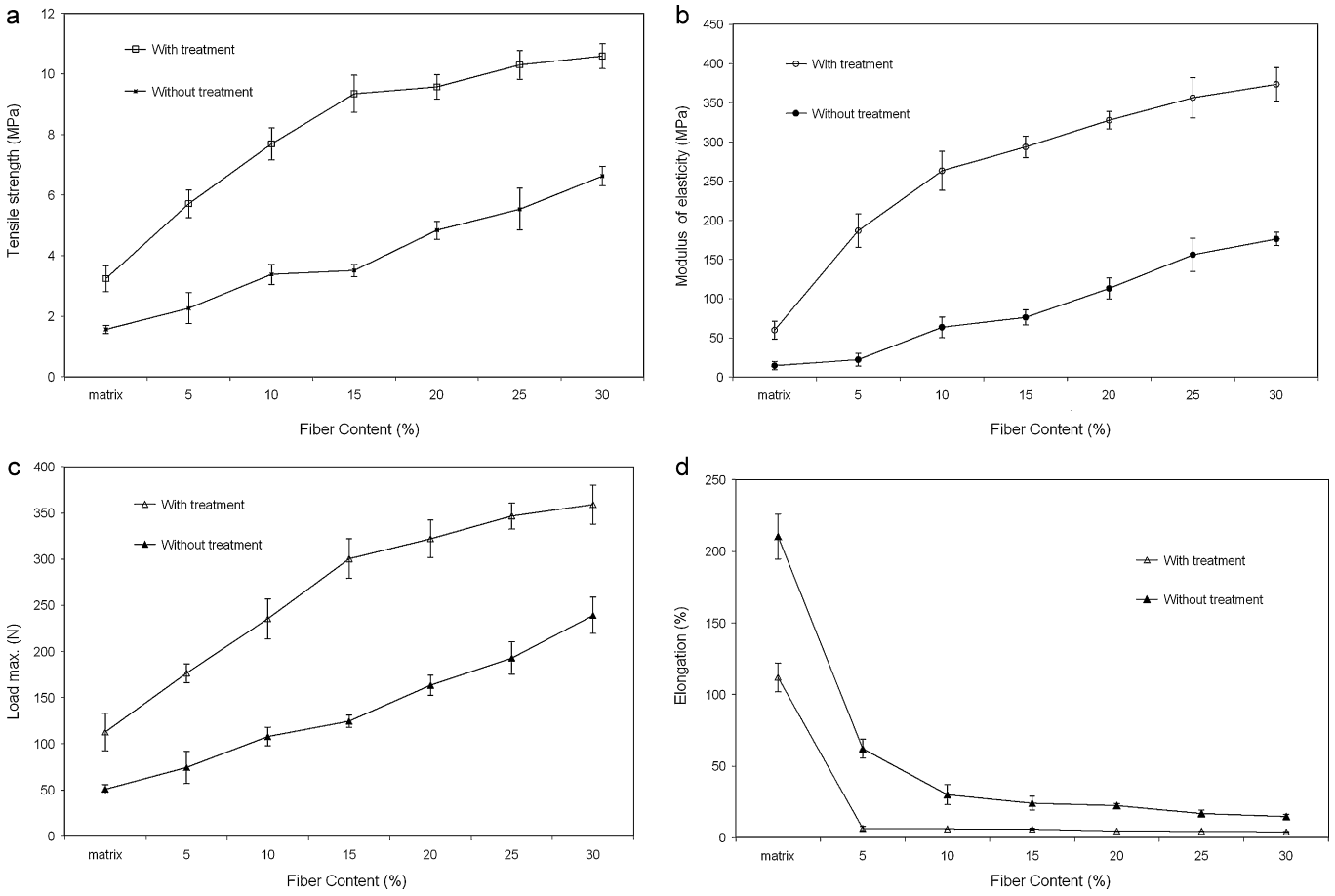

Fig. 3. (a) Plots of tensile strength of TPS matrix with and without treatment and their composites as a function of coir fiber content. (b) Plot of Young's modulus of TPS matrix (with and without treatment) and their composites as a function of coir fiber content. (c) Plot of load of TPS matrix (with and without treatment) and their composites as a function of coir fiber content. (d) Plots of % elongation versus coir fiber content in TPS matrix (with and without thermal treatment).

The tensile property results observed in the present study agree with those reported by other researchers for lignocellulosic fibers and/or cellulose nanofibers incorporated in thermoplastic starches (Curvelo et al., 2001; Gáspár et al., 2005; Guimarães et al., 2010; Ma et al., 2005; Müller et al., 2009; Torres, Arroyo, & Gomez, 2007; Woehl et al., 2010). These have been explained on the basis of chemical and structural compatibility between the matrix and reinforced plant fibers. In fact, when natural fibers are used as reinforcements in TPS, an obvious improvement in the mechanical properties and performance of the composite is expected. This is due to the chemical similarities between the fibers and starch, which provides good compatibility, particularly of the cellulose chains (Avérous & Boquillon, 2004; Ma et al., 2005; Mo et al., 2010; Müller et al., 2009).

It is well known that besides the geometry of the fiber, its morphology/architecture, orientation/arrangement and volume fractions have great influence on the mechanical properties of composites. Of these, the volume fraction is perhaps the most important factor, since most of the mechanical properties increase with increasing amounts of fiber, until a maximum amount, because at higher reinforcement loading, agglomeration and low dispersion of the fibers in the matrix can occur (Fowler et al., 2006).

Recognizing that the behavior of composite materials varies with various parameters, an attempt is made here to find a correlation between some of tensile properties and the maximum load. This is because maximum load may be one of the selection criteria for some applications and thus becomes a very important/interesting mechanical property. It may also be important to find the extent of correlation between various tensile properties indicating high significance (>0.9) through correlation coefficient suggesting the validity of the findings. In fact, such correlation may help in selecting maximum load as one of the criteria for some applications or vice versa. In the present study, it is observed that thermally treated thermo plastic starch (TPS) and its composites behaved in a very distinct way than that of the untreated TPS. The former (TPS matrix and composites) could bear higher loads and exhibited higher tensile strength values compared to the latter ones. They did not undergo any deformation even after the reaching the maximum load and thus they were stronger, but brittle. On the other hand, the untreated TPS and its composites showed high deformation after reaching the maximum load. This distinct behavior of treated TPS and its composites can be used for certain applications, because this treated material, though not offer resistance to load, may still undergo deformation, instead of presenting a catastrophic rupture.

Accordingly, it is interesting to find that a linear relation exists between tensile strength (TS) and maximum load (ML) as well as that with Young's modulus (YM) for both types of composites (treated and untreated), while an exponential tendency (S-curve) is observed between tensile strength (TS) and % elongation (E) for both types of composites.

The above mentioned correlations between tensile properties are shown below:

For untreated composites:

$$\text{TS untreated} = 0.373642 + 0.0263267 \times \text{ML} \quad (4)$$

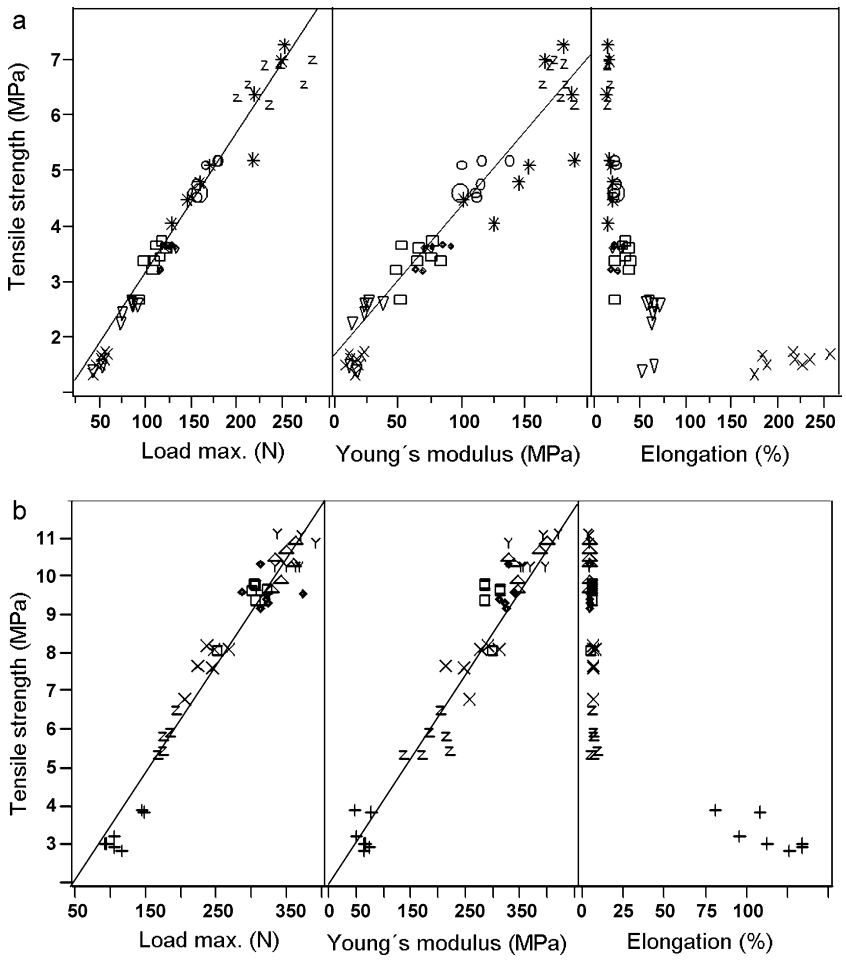

Fig. 4. (a) Linear and S-curve models for untreated composites. (b) Linear and S-curve models for thermally treated composites.

with a correlation coefficient of 0.9836.

For treated composites:

$$TS\ \ \text{treated} = 0.543639 + 0.0283516 \times ML \quad (5)$$

with a correlation coefficient of 0.9769.

For untreated composites:

$$TS\ \ \text{untreated} = 1.45977 + 0.0280689 \times YM \quad (6)$$

with a correlation coefficient of 0.9618.

For treated composites:

$$TS\ \ \text{treated} = 1.82754 + 0.0234878 \times YM \quad (7)$$

with a correlation coefficient of 0.9672.

For untreated composites:

$$TS\ \ \text{untreated} = \exp(0.45977 + 20.5902/E) \quad (8)$$

with a correlation coefficient 0.9092.

For treated composites:

$$TS\ \ \text{treated} = \exp(1.17648 + 4.95355/E) \quad (9)$$

with a correlation coefficient 0.9162.

These results show that the data are not scattered and there is a real dependency of these values, even when extrapolated to higher fiber content in the composites, as can be seen in Fig. 4(a and b). These can be explained as due to the significant contribution of the fibers in hindering elongation of the matrix. Further, the foregoing also suggests that TPS biocomposites with cassava starch can be tailored for any application requiring either low elongation using small amounts of fibers or higher modulus or strength using higher fiber contents.

The following section further explains the effect of incorporation of coir fibers and the effect of treatment of the matrix/composites.

3.3. Scanning electron microscopy (SEM)

Fig. 5 shows a series of SEM micrographs of the fractured surface of tensile tested specimens of cassava starch with and without treatment and their composites containing different amounts of coir fibers. Fig. 5a shows a fracture of a more resistant matrix material (treated), indicating a homogeneous and smooth surface, compared to that shown in Fig. 5b (untreated), which is a fragile fracture having a rough surface. This indicates that the effect of the thermal treatment of the matrix is to make the TPS material more brittle. Fig. 5(c and e) shows fractographs of composite specimens with treatment (annealing) containing 10 and 30% fibers, respectively. It can be observed that both of them show uniform and smooth fracture surfaces with a homogeneous matrix as well as good adhesion of the fiber to the thermoplastic starch matrix. Of course, a few holes caused by pulling out fibers during the tensile test are also evident. On the other hand, the fracture surfaces of untreated thermoplastic starch-based composites with 10 and 30% fibers, shown in Fig. 5(d and f) respectively, exhibit irregular fracture surfaces with cracks and pores in the matrix, produced by the mechanical stress during the tensile test. In addition, pull out of the coir fibers from the matrix after the test can be observed along with many holes. This suggests that the interface adhesion in

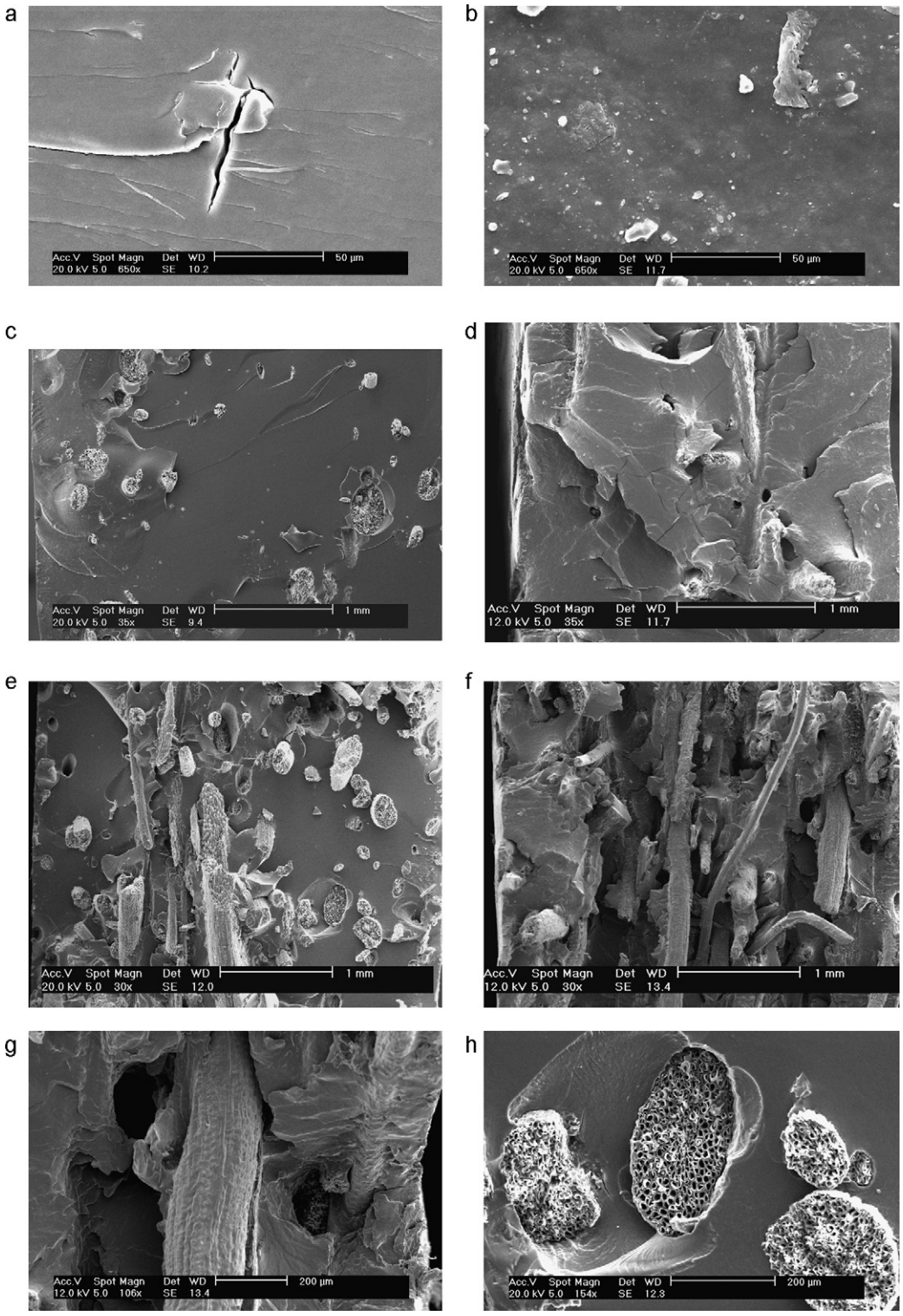

Fig. 5. SEM micrograph of fractured surface of TPS matrix and filled with different coconut fiber contents: (a) Matrix with treatment; (b) matrix without treatment. (c) *Composites with treatment*: 10% fiber; (e) 30 fiber%; (g) detail of fiber–matrix interface; (d) *Composites without treatment*: 10% fiber; (f) 30% fiber and (h) detail of fiber–matrix interface.

these composites may not have been as good as that of the treated composites.

The fiber–matrix interface in a composite is responsible for transmitting the tensile stress of the matrix to the fibers. This effective transfer of stress depends largely on fiber–matrix interface and the individual mechanical properties of fibers and polymers (Kuciel & Liber-Knec, 2009). Good adhesion between the fiber and the matrix leads to a resistant interface, consequently reinforcing the matrix (Fowler et al., 2006). Fig. 5(g) shows an interface with better fiber–matrix adhesion for the treated composite compared to that of the untreated composite, shown in Fig. 5(h). Therefore, besides the individual properties of each component of the composite, the interface between them should also be adjusted to obtain optimum properties. In both types of specimens, many fibers are

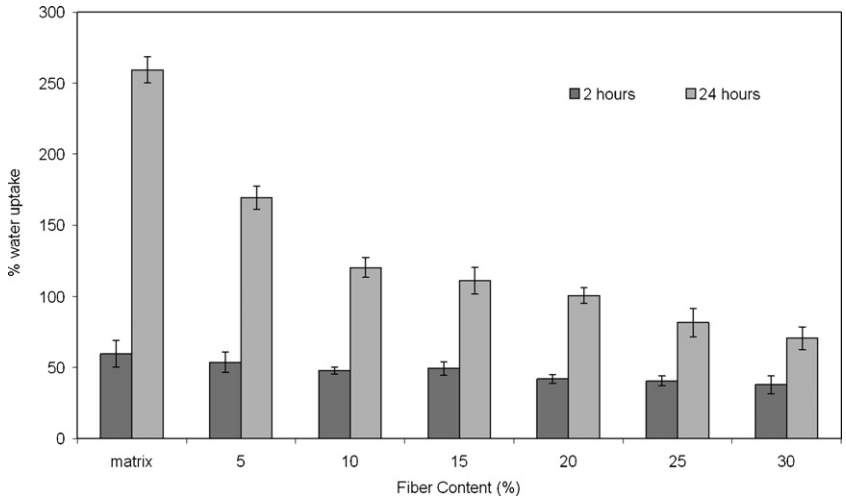

Fig. 6. Variation of water uptake by TPS composites as a function of amount of fiber content on immersion in water for 2 and 24 h.

seen attached to the starch matrix (Fig. 5e and f), which is one of the reasons for the increased resistance to fracture or higher tensile strength in these composites. Similar observations have been made on starch based composites by others (Avérous & Boquillon, 2004; Avérous and Halley, 2009; Avérous, Fringant, & Moro, 2001; Avérous, 2007; Satyanarayana et al., 2009; Teixiera, 2007).

3.4. Water absorption and swelling

The water absorption and swelling of thermoplastic starch-based composites is important in aqueous or humid environments because these properties determine their integrity and performance (Kuciel & Liber-Knec, 2009; Mathew & Dufresne, 2002). Thermoplastic starch composites are hydrophilic due to the chemical composition of starch (amylopectin and amylase), where hydroxyl groups and oxygen bonds with water are formed (Kuciel & Liber-Knec, 2009; Mathew & Dufresne, 2002). Also, the addition of a plasticizer increases the affinity to moisture (Mathew & Dufresne, 2002). Fig. 6 shows the comparison of % water uptake by the composites containing different amounts of coir fibers. It can be seen that after 2 h, the TPS matrix showed 59.83% water uptake, while the composite of TPS with 30% coir fiber showed only 37.99%. The effect of incorporating coir fibers into the starch matrix on water uptake is more evident after 24 h. One can see that after 2 h both, matrix and composites present almost the same water uptake, but after 24 h the matrix absorbed much more water than the composites, and as the fiber content increased, the water uptake decreased.

The percentage increase in water uptake between 2 and 24 h in all the composites indicates that increasing the fiber incorporation as well as its increasing amount in the composite reduces the water uptake of the matrix. Since no void was observed either visually or in SEM studies of the fractured composite samples, the above may be due to (a) probable reduction of void content in the composites (b) better interfacial bonding between the fibers, as observed in the scanning electron microscopic studies, (c) greater affinity of the matrix for water compared to that of the fibers and finally (d) the network formed by the higher fiber content, which hinders the diffusion of water through the matrix (Alvarez et al., 2003; Sreekumar, Saiter, & Thomas, 2009). In fact, there are reports (Rosa et al., 2009; Rout, Tripathy, Nayak, Misra, and Mohanty, 2001) that because of chemical composition of lignocellulosic fibers such as coir fibers with higher lignin content and also due to the presence of wax on its surface, absorption of water is prevented to some extent. The presence of fatty substances also reduces the water absorption. In the present study, the coir fibers used were not washed before using them so that these waxy materials were not removed.

The dimensional stability of a composite is an important property affecting the final performance, because the change in size of a specific product during service due to moisture absorption can be a serious disadvantage (Kuciel & Liber-Knec, 2009). As mentioned earlier, the change in the length of both the matrix and its composites was measured to determine the dimensional changes taking

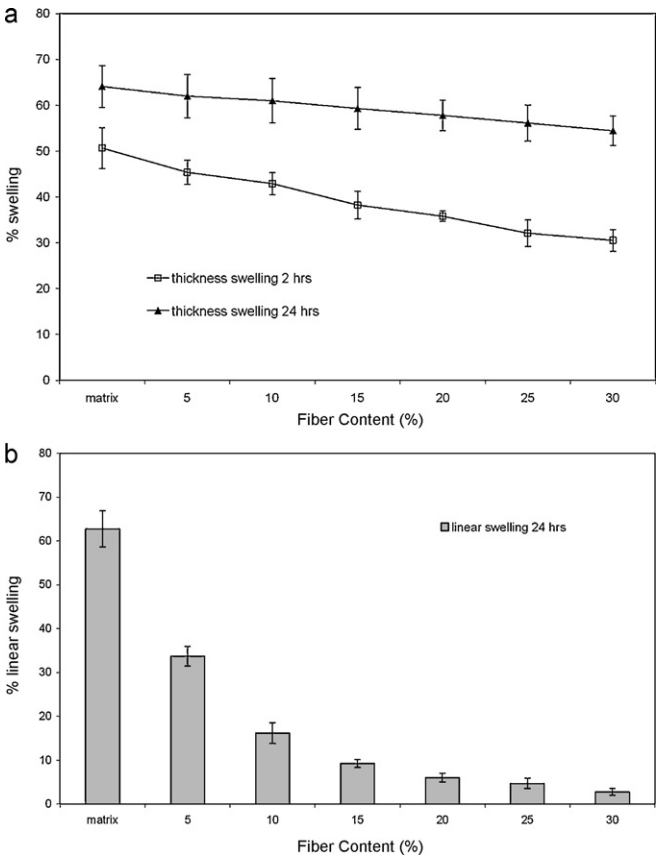

Fig. 7. (a) Variation in thickness of the TPS composites as a function of coir fiber content for immersion in water for 2 and 24 h. (b) Linear swelling of thermoplastic starch composite as a function of fiber content after being immersed in water for 24 h.

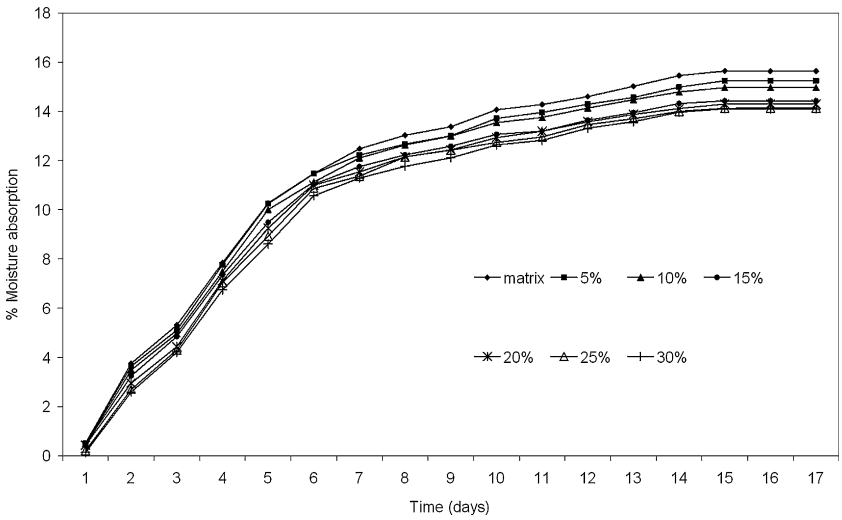

Fig. 8. Moisture adsorption versus time of TPS composites containing different amounts of coir fibers (conditioned at 75 ± 2% RH and temperature 23 ± 2 °C).

place in these materials after immersion in water for 2 and 24 h. For example, observed change in length measured for the samples after immersion was 3.8 mm, while the original sample (before immersion) had a length of 3 mm.

Fig. 7(a) shows the percentage increase in thickness of the thermoplastic cassava starch and its composites after immersion in water for 2 and 24 h. It can be seen that the thickness of these materials was affected by both the fiber content and the immersion time.

The matrix showed the highest swelling, while this decreased with increasing amounts of fiber in the composites. However, the difference in thickness for 2 and 24 h of immersion was higher with an increasing amount of fiber. Although starch and glycerol are more compatible with water than are lignocellulosic fibers (even though they are washed before using them, as in the present study), the matrix determines the water absorption in composites with low fiber contents, while the chemical nature of the plasticizer also affects the water uptake (Mathew & Dufresne, 2002). It should be noted that the matrix shows greater affinity with water than many lignocellulosic fibers due to the presence of wax on the surface, which prevents/reduces the absorption of water, as in the case of coir fibers (Rosa et al., 2009; Rout et al., 2001).

In the present study, a linear decrease in swelling of TPS-coir fiber composite was more evident, as shown in Fig. 7(b), suggesting the positive effect of coir fiber to overcome the changes in the linear dimensions of the composite. It can also be seen that with an increasing amount of fiber in the composite, the swelling decreased linearly.

The base matrix showed an increase of 62.7%, while this was only 2.78% for the composite with 30% coir fiber. The swelling of composite materials is caused by water uptake, which causes delamination of the fiber layers (Sreekumar et al., 2009). In the present study the water uptake was reduced by the incorporation of coir fibers into the TPS matrix. This explains the observed decrease in swelling in this study. It should also be mentioned that none of the composites disintegrated after swelling.

3.5. Conditioning to 75% relative humidity

A disadvantage of the starch-based materials is that their plastic properties are affected by moisture content (Avérous, Fauconnier, & Moro, 2000; Ma et al., 2005). Care should be taken, as TPS tends to absorb or desorb humidity from the environment. The absorption of moisture depends on storage conditions (temperature, time, relative humidity) (Avérous et al., 2001; Ma et al., 2005). While Fig. 8 shows the moisture sorption curves of the specimens in an atmosphere with RH of 75 ± 2% and temperature of 23 ± 2 °C. Table 1 lists the rate of absorption for the first stage as well as the values of equilibrium moisture of the untreated composite specimens in an atmosphere with RH of 75 ± 2% and temperature of 23 ± 2 °C. It can be seen from the table and Fig. 8 that the unfilled TPS matrix (0% fiber) absorbed more moisture than the filled TPS composites containing coir fibers, suggesting the effect of coir incorporation in the TPS.

Table 1
Moisture absorption and equilibrium moisture content of cassava matrix and cassava-coir fiber composite at different days of exposure.

	Moisture absorption (%)					Equilibrium moisture content
Material/days	1	2	3	4	5	15
Matrix	0.52	3.76	5.31	7.84	10.27	15.63
5%	0.51	3.64	5.11	7.77	10.25	15.24
10%	0.48	3.49	4.97	7.49	10.00	14.96
15%	0.47	3.25	4.85	7.34	9.48	14.42
20%	0.44	2.95	4.44	7.12	9.25	14.29
25%	0.21	2.69	4.30	7.04	8.93	14.13
30%	0.14	2.59	4.21	6.74	8.60	14.10

Also, from the figure it was observed that the rate of absorption was higher in the first six days and thereafter it increased at a slower rate (in view of this table shows up to 5 days only), tending to saturation, in agreement with the results reported by Gáspár et al. (2005). The equilibrium moisture for the TPS matrix was 15.6%, while the percentages for the TPS composites with 5–30% fibers showed slow decrease from 15.2% to 14.0%. These results can be understood as in the case of water uptake, i.e., when a better interfacial bond exists between the fiber and the TPS matrix, there is less chance of hydroxyl groups of the matrix coming into contact with water molecules (Sreekumar et al., 2009).

4. Concluding remarks

Increasing ecological concerns have given rise to renewed interest in the use of natural materials, considering their renewability and possibility of disposal at the end of their life cycle without damage to the environment (Avérous & Le Digabel, 2006; John & Thomas, 2008). The present study reveals the following:

1. It is possible to prepare composites free of fiber agglomeration using cassava starch with the incorporation of up to 30% coir fibers, using cassava starch matrix and green coconut fiber by thermo-plasticization using glycerol.
2. The strength properties (UTS and YM) of the TPS starch increase with a higher amount of coir fiber incorporation as well as with the thermal treatment.
3. The tensile strength (TS) and Young's modulus (YM) values of treated TPS matrix were higher (3.24 MPa, 59.81 MPa and 112.68 N, respectively) than those for the untreated matrix (1.56 MPa, 14.56 MPa and 50.77 N, respectively). Similarly, observed values were ~373.5 MPa and ~176 MPa for YM and 10–11 MPa and 3 MPa for TS for treated and untreated TPS composites containing 0–30% coir fibers respectively.
4. Water uptake, moisture absorption and linear swelling of TPS matrix decrease with increasing coir fiber content.
5. Water uptake of TPS matrix and its composite with 30% coir fiber after 2 h of immersion was about 60% and 38% respectively. The effect was more pronounced after 24 h immersion for all the composites.
6. Moisture absorption remained constant after about 10 days and 13 days respectively for the composites and the TPS matrix, with the equilibrium moisture for the TPS matrix being 15.6%, while it varied between 15.2 and 14% for the TPS composites with 5–30% fiber content.
7. Linear swelling of TPS matrix decreased with increasing amount of fiber content and immersion time.
8. The observed results of tensile properties, water uptake and moisture absorption are explained as due to better fiber–matrix interface (interfacial bond that exists between the fiber and the TPS matrix) obtained by good adhesion between the fiber and the matrix as evident from the fractographic studies conducted by SEM.

Acknowledgements

The authors would like to thank Pasquini Company of Brazil for supplying the cassava starch sample, Labsynth, São Paulo, Brazil for the donation of glycerol and COOBCOCO that donated the coconut fibers. The authors acknowledge the financial support of CAPES through the agreement PEC-PG and PROMEP-SEP (México). They also express sincere thanks to Mrs. Gloria Demetrio Sydenstricker and Mr. Guy Fulkerson for their reading the paper, suggestions and editing made in respect of English. One of the authors (KGS) also acknowledges the encouragement and support by the three Institutions with which he is presently associated with.

References

Alvarez, V. A., Ruseckaite, R. A., & Vazquez, A. (2003). Mechanical properties and water absorption behavior of composites made from a biodegradable matrix and alkaline treated sisal fibers. *Journal of Composite Materials*, *37*(17), 1575–1588.

Avérous, L. (2007). Cellulose-based biocomposites: Comparison of different multiphase systems. *Composite Interface*, *14*, 787–805.

Avérous, L., & Boquillon, N. (2004). Biocomposites based on plasticized starch: Thermal and mechanical behaviors. *Carbohydrate Polymers*, *56*(2), 111–122.

Avérous, L., & Le Digabel, F. (2006). Properties 553 of biocomposites based on lignocellulosic fillers. *Carbohydrate Polymers*, *66*, 480–493.

Avérous, L., & Halley, P. J. (2009). Biocomposites based on plasticized starch. *Biofuels, Bioproducts and Biorefining*, *3*(3), 329–343.

Avérous, L., Fringant, C., & Moro, L. (2001). Plasticized starch–cellulose interactions in polysaccharide composites. *Polymer*, *42*, 6565–6572.

Avérous, L., Fauconnier, N., & Moro, L. (2000). Blends of thermoplastic starch and polyester-amide: Processing and properties. *Journal of Applied Polymer Science*, *76*, 1117–1128.

Bergo, P. V. A. Sobral, P. J. A., & Prison, J. M. (2009). Physical properties of cassava starch films containing glycerol. www.geneconserve.pro.br/artigo067.pdf.

Billmeyer, F. W., Jr. (1971). *Textbook of polymer science* (2nd ed.). New York: John Wiley & Sons., p. 598

Blanshard, J. M. V. (1987). Starch granule structure and function: A physicochemical approach. In T. Galliard (Ed.), *Starch: Properties and potential*. New York: John Wiley.

Carvalho, A. J. F., Curvelo, A. A. S., & Agnelli, J. A. M. (2002). Wood pulp reinforced thermoplastic starch composites. *International Journal of Polymeric Materials*, *51*(7), 647–660.

Cereda, M. P., Franco, C. M., Daiuto, É. R., Demiate, I. M., Carvalho, L. J. C. B., Leonel, M., et al. (2002). *Propriedades gerais do amido. Série Culturas de Tubérculos Amiláceas Latinoamericanas, I*. São Paulo: Fundação Cargill., pp. 141–185.

Corradini, E., Texeira, E. M., Agnelli, J. A. M., & Mattoso, L. H. C. (2007). *Amido Termoplástico*. São Carlos, SP: Embrapa Instrumentação Agropecuária., p. 27.

Curvelo, A. A. S., Carvalho, A. J. F., & Agnelli, J. A. M. (2001). Thermoplastic starch574 cellulosic fibers composites. *Carbohydrate Polymers*, *45*, 183–188.

Fowler, P. A., Hughes, J. M., & Elias, R. M. (2006). Biocomposites: Technology, environmental credentials and market forces. *Journal of the Science of Food and Agriculture*, *86*, 1781–1789.

Gáspár, M., Benko, Z., Dogossy, G., Reczey, k., & Czigany, T. (2005). Reducing water absorption in compostable starch-based plastics. *Polymer Degradation and Stability*, *90*, 563–569.

Gough, B. M., & Pybus, J. N. (1971). Effect on the 583 gelatinization temperature of wheat starch granules of prolonged treatment with water at 50 °C. *Starch/Staerke*, *23*(6), 210–212.

Guimarães, J. L., Wypych, F., Saul, C. K., Ramos, L. P., & Satyanarayana, K. G. (2010). Studies of the processing and characterization of corn starch and its composites with banana and sugarcane fibers from Brazil. *Carbohydrate Polymers*, *80*, 130–138.

Herrera Franco, P. J., & Valdez-González, A. (2005). Fiber–matrix adhesion in natural fiber composites. In A. K. Mohanty, A. Misra, & L. T. Drzal (Eds.), *Natural fibers, biopolymers and biocomposites* (pp. 177–230). Boca Raton, FL, USA: CRC Press.

John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, *71*, 343–364.

Knutson, C. A. (1990). Annealing of maize starches at elevated temperatures. *Cereal Chemistry*, *67*(4), 376–384.

Kuciel, S., & Liber-Knec, A. (2009). Biocomposites on the base of thermoplastic starch filled by wood and kenaf fiber. *Journal of Biobased Materials and Bioenergy*, *3*, 1–6.

Kumar, A. P., & Singh, R. P. (2008). Biocomposites of cellulose reinforced starch: Improvement of properties by photo-induced cross linking. *Bioresource Technology*, *99*(18), 8803–8809.

Liu, H., Xie, F., Yu, L., Chen, L., & Li, L. (2009). Thermal processing of starch-based polymers. *Progress in Polymer Science*, *34*, 1348–1368.

Lu, D. R., Xiao, C. M., & Xu, S. J. (2009). Starch-based 613 completely biodegradable polymer materials. *eXPRESS Polymer Letters*, *3*(6), 366–375.

Luna, G., Villada, H., & Velasco, R. (2009). Thermoplastic cassava starch of reinforced with Fique's fiber: Preliminary studies (Almidón termoplástico de yuca reforzado con fibra de fique preliminares). *Dyna*, *76*(159), 145–151. ISSN 0012-7353.

Ma, X., Yu, J., & Kennedy, J. F. (2005). Studies on the properties of natural fibers-reinforced thermoplastic starch composites. *Carbohydrate Polymers*, *62*, 19–24.

Mali, S., Grossmann, M. V. E., García, M. A., Martino, M. N., & Zaritzky, N. E. (2008). Antiplasticizing effect of glycerol and sorbitol on the properties of cassava starch Films. *Brazilian Journal of Food Technology*, *11*(3), 194–200.

Mali, S., Sakanaka, L. S., Yamashita, F., & Grossmann, M. V. E. (2005). Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydrate Polymers*, *60*, 283–289.

Mathew, A. P., & Dufresne, A. (2002). Morphological investigations of nanocomposites from sorbitol elasticized starch and tunicin whiskers. *Biomacromolecules*, *3*, 609–617.

Mo, X. Z., Zhong, Y. X., Liang, C. H. Q., & Yu, S. J. (2010). Studies on the properties of banana fibers-reinforced thermoplastic cassava starch composites: Preliminary results. *Advanced Materials Research*, *87–88*, 439–444.

Müller, C. M. O., Laurindo, J. B., & Yamshita, F. (2009). Effect of cellulose fibers on the crystallinity and mechanical properties of starch-based films at different relative humidity values. *Carbohydrate Polymers*, *77*, 293–299.

Pradella, J. G. C. (2006). Biopolímeros e Intermediários Químicos. Subsídios para Elaboração da Política de Biotecnologia Industrial no Brasil. Relatório Técnico n° 84 396-205.Centro de Gestão e Estudos Estratégicos – MDIC. São Paulo, p. 119.

Rosas, K. A. (2008). Biocómpositos de almidón termoplástico con microfibras de celulosa. Tesis de maestría. Instituto Politécnico Nacional. Altamira, Tamaulipas, México, p. 90.

Rosa, M. F., Chiou, B., Medeiros, E. S., Wood, D. F., Williams, T. G., Mattoso, L. H. C., et al. (2009). Effect of fiber treatments on tensile and thermal properties of starch/ethylene vinyl alcohol copolymers/coir biocomposites. *Bioresource Technology*, *100*(21), 5196–5202.

Rout, J., Tripathy, S. S., Nayak, S. K., Misra, M., & Mohanty, A. K. (2001). Scanning electron microscopy study of chemically modified coir fibers. *Journal of Applied Polymer Science*, *79*, 1169–1177.

Róz, A. L., da Carvalho, A. J. F., Morais, L. C., & Curvelo, A. A. S. (2001). Comportamento térmico e de absorção de umidade de amidos plastificados com glicóis. In *Anais do 6° Congresso Brasileiro de Polímeros e do IX International Macromolecular Colloquium* Gramado, RS, (pp. 1445–1448).

Satyanarayana, K. G. (2007). Biodegradable composites based on lignocellulosic fibers. Keynote Lecture delivered at the International conference on Advanced Materials and Composites (ICAMC-2007), 24–27 October 2007, Thiruvananthapuram, Organized by National Institute for Interdisciplinary Science & Technology (NIIST), Thiruvananthapuram, Kerala-India, pp. 12–24 (in CD).

Satyanarayana, K. G., Gregorio, G. C. A., & Fernado, W. (2009). Biodegradable composites based on lignocellulosic fibers—An overview. *Progress in Polymer Science*, *34*, 982–1021.

Sreekumar, P. A., Saiter, J. M., & Thomas, S. (2009). Water absorption and ageing behavior of natural fiber composites. In S. Thomas, & L. A. Pothan (Eds.), *Natural fiber reinforced polymer composites: From macro to nanoscale* (pp. 446–472). USA: Published by Old City Publishing Inc (Chapter 17).

Teixiera, E. M. (2007). Utilização de amido de mandioca na preparação de novos materiais termoplásticos. In *Tese. Instituto de Química de São Carlos* Universidade de São Paulo, (p. 201).

Tomczak, F., Sydenstricker, T. H. D., & Satyanarayana, K. G. (2007). Studies on lignocellulosic fibers of Brazil. Part II. Structure and properties of Brazilian coconut fibers. *Composites. Part A, Applied Science and Manufacturing*, *38*, 1710–1721.

Torres, F. G., Arroyo, O. H., & Gomez, C. (2007). Processing and mechanical properties of natural fiber reinforced thermoplastic starch biocomposites. *Journal of Thermoplastic Composite Materials*, *20*, 207–223.

Vallejos, M. E., Curvelo, A. A. S., Teixeira, E. M., Mendes, F. M., Carvalho, A. J. F., Area, M. C., et al. (2010). Materiales compuestos producidos con almidones termoplásticos y fibras obtenidas del fraccionamiento etanol-agua de bagazo. In *Memorias del XXI Encontro Nacional da Tecnicelpa/VI Ciadicyp* 12–15 Outubro 2010 - Lisboa, Portugal, (p. 8).

Vašková, I., Alexy, P., Bugaj, P., Nahálková, A., Feranc, 675 J., & Mlynský, T. (2008). Biodegradable polymer packaging materials based on polycaprolactone, starch and polyhydroxybutyrate. *Acta Chimica Slovaca*, *1*(1), 301–308.

Woehl, M. A., Canestraro, C. D., Mikowski, A., Sierakowski, M. R., Ramos, L. P., & Wypych, F. (2010). Bionanocomposites of thermoplastic starch reinforced with bacterial cellulose nanofibres: Effect of enzymatic treatment on mechanical properties. *Carbohydrate Polymers*, *80*, 866–873.

Yu, L., Dean, K., & Li, L. (2006). Polymers blends and composites from renewable resources. *Progress in Polymer Science*, *31*, 576–602.

Zavareze, E. R., & Dias, A. R. (2011). Impact of heat-moisture treatment and annealing in starches: A review. *Carbohydrate Polymers*, *83*, 317–328.