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Studies of the processing and characterization of corn starch and its composites with banana and sugarcane fibers from Brazil

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ABSTRACT

This paper presents results on the characterization of corn starch by X-ray powder diffraction and thermal analysis, as well as processing and characterization of starch–banana/sugarcane bagasse fiber composites. X-ray diffraction studies revealed that the starch sample belongs to the A-type, common in cereals. Thermal analysis showed good thermal stability for making composites, while fractographic studies of 70 wt.% starch and 30% glycerol matrix revealed cracks between smooth and rough surface and dimples in rough regions, suggesting the sample was ductile. The composites of this matrix with banana and bagasse fibers prepared by compression molding showed more homogeneous composites with crude glycerin and structural changes in both the fiber composites, while their morphology was dictated by the properties of the fibers rather than by those of the matrix. Improvements in tensile properties were observed in these composites over those of the matrix, which are explained based on fractographic observations.

1. Introduction

It is well known that starch is present in all seeds (wheat, corn, etc.), tubers (potatoes), roots (cassava), and to a lesser proportion in plant leaves. Starch is a mixture of polysaccharides (amylose and amylopectin in different proportions) that are easily assimilated, making it of great importance in the food industry. However, other attractive characteristics of this material, such as natural availability, biodegradability, low cost, and ease of subjecting it to chemical changes, has led to various other applications. According to the Institute for Scientific Information (ISI – Web of Knowledge) database, in a search by the authors in September 2009 with the keyword combination “starch and plasticizer” and searching in “topic”, about 337 papers had been published, while “starch and thermoplastic” returned about 502 papers.

One of the areas investigated in the papers found is the development of biodegradable composites. Several studies reported on the development of such composites, including blends of starch with polyethylene of low and high density (LDPE, HDPE), starch and poly(vinyl alcohol) (PVA), and poly(3-hydroxybutyrate co-3-hydroxyvalerate) (PHBV) with lignocellulosic fibers such as pineapple leaf, sisal, jute and ramie fibers, in all of which the fiber content can reach 70 wt.% (Avella, Martuscelli, & Raimo, 2000; Averous & Boquillon, 2004; Cao, Shibata, & Fukumoto, 2006; Carvalho, Curvelo, & Agnelli, 2001; Chen et al., 2006; Choi et al., 2004; Cunha, Liu, Feng, Yi, & Bernardo, 2001; Curvelo, Carvalho, & Agnelli, 2001; Dufresne & Vignon, 1998; Fang & Fowler, 2003; Godbole, Gote, Latkar, & Chakrabarti, 2003; Huang, Kuo, & Yang, 2006; Leão, Rowell, & Tavares, 1998; Lim, Chang, & Chung, 2001; Luo and Netravali,1999; Mattoso, Leão, & Frollini, 2002, 2004; Misra, Tripathy, Misra, Mohanty, & Nayak, 2002; Mohanty, Misra, & Hinrichsen, 2000; Müller, Laurindo, & Yamashita, 2009; Nishino, Matsuda, & Hirao, 2004; Ochi, 2006; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Satyanarayana, Wypych, Ramos, Amico, & Sydenstricker, 2005; Shamai, Bianco-Peled, & Shimoni, 2003; Shogren, 1998, chap. 2; Stepto, 2006; Teixeira, 2007; Torres, Arroyo, & Gomez, 2007; Tserki, Matzinos, & Panayiotou, 2006; Wool et al., 2002; Zobel, 1988). These publications also reported that the properties of some of these composites are comparable and competitive even to E-glass–epoxy composites and hence appropriate for various structural applications. However, one of the major problems to be solved in using starches is their high solubility in water (Carvalho et al., 2001; Curvelo et al., 2001), consequently their composites will be highly hydrophilic. Also, when plasticized using known plasticizers such as glycerol, very high % elongation at break (30–100%) has been observed, with low tensile strength (Averous & Boquillon, 2004; Müller et al., 2009; Woehl, 2009) at 40–75% relative humidity (RH). Another equally important factor to consider is the effect of humidity on its properties, particularly

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strength. An initial linear behavior was observed (Müller et al., 2009) in the stress–strain curves of composites of cassava starch plasticized with 30% of glycerol containing different amounts of cellulose fibers for 58% and 75% RH, with % elongation at break values for the matrix (starch + 30% plasticizer) as high as 83 ± 17 and 101 ± 15 at these two RH levels, respectively. These values decreased drastically with the introduction of short wood fibers.

Brazil produces large amounts of corn starch, whose use could be expanded to other non-food applications. However, in order to use these brittle starches in composites, they have to be made flexible by using a suitable plasticizer. Glycerol and other polyols are some of the used chemical. Glycerol can be obtained through chemical and fermentation methods in pure form, but can also be obtained as a co-product in the production of biodiesel, when transesterification reactions of vegetable oils and animal fats are used. In many cases this glycerin needs to be purified (hence called "crude glycerin"). Refining this crude glycerin is rather costly and limited by the installed refining capacity in countries like Brazil. This is aggravated by the steep rise in demand for biodiesel. According to National agency of Petroleum, Natural gas and Biofuels (ANP) of Brazil, the production of biodiesel jumped from about 402 million liters in 2007 to 1.16 billion liters in 2008 and till July 2009, it is about 654 million liters. (http://www.anp.gov.br/), while in European countries it doubled between 2002 and 2004 (Frondel & Peters, 2007). So, there is a growing need to develop alternative applications for crude glycerin so as to avoid its going to waste. One of these alternatives is the use of crude glycerin as a starch plasticizer, since glycerol provides stability and compatibility with hydrophilic packaging chains in starches (Cervera et al., 2004).

Because of the availability of starch, as mentioned above, along with the ample output of crude glycerin and abundant availability of lignocellulosic fibers in Brazil (Satyanarayana, Guimarães, & Wypych, 2007), our research team has begun systematic studies on their utilization for composite making (Guimarães, Satyanarayana, Wypych, & Ramos, 2006a; Guimarães, Satyanarayana, Wypych, Ramos, & Cursino, 2006b; Guimarães et al., submitted for publication; Mali, Karam, Ramos, & Grossmann, 2004; Pinto, Arizaga, Wypych, Ramos, & Satyanarayana, 2009; Wilhelm, Sierakowski, Souza, & Wypych, 2003a, 2003b).

In light of the global concern for recycling of wastes such as crude glycerin and proper use of natural resources such as corn starch and lignocellulosic fibers that is driving the search for alternative processes and development of novel materials, this paper presents preliminary results of the preparation and characterization of starch composites containing both commercial and crude glycerin as plasticizer and banana and sugarcane bagasse fibers as reinforcements.

2. Experimental

2.1. Materials

2.1.1. Fibers

Two types of fibers were used, namely banana fibers, obtained from the banana pseudo stem and sugarcane bagasse fibers, obtained from a nearby mill (Jussara, PR, Brazil). Extraction of the banana fibers and preparation of both banana and bagasse fibers were carried out as explained elsewhere (Guimarães, Frollini, Silva, Wypych, & Satyanarayana, 2009a). In short, the banana fibers were extracted from the pseudo stem, shredded and air-dried for about a week, followed by oven drying at 65 °C until constant mass. The dried fibers were milled for 1–3 h in a vibratory ball mill to get fibers of 3–5 mm in length. No such preparation was required for the sugarcane bagasse, since the fibers only have to be cut randomly to improve their homogeneity, using a suitable cutter. Both fibers were maintained in a hot air oven before the composite preparation was started.

2.1.2. Matrix materials

The starch used, designated Amidex-3001 (with about 28% amylose), was supplied by Corn Products Brazil (Balsa Nova, PR, Brazil). It contained about 11% moisture. As this starch sample was not thermoplastic, glycerin was used as a plasticizer to maintain the integrity of the composites and avoid the formation of pores and cracks (Dufresne & Vignon, 1998; Shogren, 1998; Curvelo et al., 2001). Glycerol was also used to improve the processability and mechanical properties of the composites, in addition to reducing their glass transition temperature (Fang & Fowler, 2003; Rodriguez-Gonzalez et al., 2003; Chen et al., 2006; Huang et al., 2006; Stepto, 2006; Tserki et al., 2006). Two types of glycerin were used. The first was commercial "Synth PA", which is henceforth referred to as "glycerol", and the second was glycerin derived from ethanolysis of soybean oil using sodium hydroxide as the reaction catalyst precursor (Domingos, Wilhelm, & Ramos, 2008; Kuchek, Wilhelm, Domingos, & Ramos, 2007), from here on called "crude glycerin" or simply "glycerin". This crude glycerin consisted of a mixture of glycerol (81.7%), water (4.4%), traces of methanol and ethanol (0.01% and 0.03%, respectively), soaps and the alkaline catalyst (Assmann, 2009). The purpose of using the glycerin was to find possibility of substitution of commercial glycerol.

2.2. Fabrication of composites

First, laminates of the matrix were prepared at different starch–glycerol ratios using two types of mixers, a ball mill and a mechanical mixer with a steel vat and blades. After mixing, the blend was subjected to thermal molding with load from 3 to 7 ton in steel molds of size 120 × 120 × 25 mm and temperatures between 110 and 170 °C to obtain laminates. These composites were processed by the method (patented) described previously (Guimarães et al., 2006b). In short, both fibers prepared as explained above were mixed homogeneously with the starch in a Fritzch ball mill. Later, a vibratory mill was used with mixing time of 1–3 h before the mixture was subjected to pressure and thermal treatment. Hydraulic press (LABSOL), one with manual control and the other with automatic control (hereafter also called 'controlled condition' or 'controlled method') for both temperature and pressure, and the steel molds mentioned above were used to prepare composite plates. Two thermocouples, one in each plate of the mold, were used to measure the temperature, which was maintained within ±3 °C of the specified molding temperature.

To understand the effect of the types of glycerol, processing methods (manual/automatic controls), types of fibers and the fiber content on the tensile property and morphology of their composites, the following laminates/composites were prepared using the above molds, with loads between 4–9 ton and temperature range of 150–190 °C: (i) starch and glycerol (B-0); (ii) composites with different amounts (20, 25 and 35 wt.%) of banana fiber with starch + glycerol (B-4, B-3 and B-1, respectively); (iii) composites with 25 and 30 wt.% banana fiber with glycerin (BN1 and B-6); and (iv) 25 wt.% of bagasse with two types of glycerol (B11, CN2 and CN22). Composites prepared by automatic control are designated as BN1, CN2 and CN22. Compositions of all the laminates processed are listed in Table 1.

Two composites, one with lower fiber content (10 wt.%) based on a fiber:glycerol:starch ratio of 10:30:60, hereafter called "A", and another with higher fiber content (60 wt.%) based on a 60:30:10 ratio, called "B", were also prepared to shed preliminary light on the effect of incorporating lower and higher fiber contents on the composites' properties.

Table 1
Details of composite constituents.

Samples	Starch Amidex-3001 (%)	Plasticizer (%)	Type of reinforcing fiber (%)
B-0	70	30 Glycerol	Nil
B-4	50	30 Glycerol	20 Banana
B-3	45	30 Glycerol	25 Banana
B-1	35	30 Glycerol	35 Banana
CN2	45	30 Glycerol	25 Bagasse
BN1	45	30 Glycerin	25 Banana
B-6	40	30 Glycerin	30 Banana
CN22	45	30 Glycerin	25 Bagasse
B-11	45	30 Glycerin	25 Bagasse

2.3. Characterization of raw materials and composites

A Shimadzu model XRD 7000 X-ray diffractometer, adjusted to a scanning speed of 1°/min with copper radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 Å, was used to determine the crystallinity of starch and its composites with banana fibers. X-ray powder diffraction studies of composites "A" and "B" were also carried out under the same conditions. Thermal analysis (TGA/DTA) was performed on the starch samples using a Metler-Toledo TGASDTA – 851E. Mass losses in the starch samples were determined by heating them to 1000 °C under oxygen atmosphere with a flow rate of 15 mL/min, according to the ASTM E1131 method.

To understand the tensile behavior of starch based composites with both the fibers, two types of glycerol (pure and crude glycerin) as well as of processing methods, a tensile test trial was performed using an Instron testing machine (Model Emic DL2000) using an extensometer with 5 kN load cell. From the obtained stress–strain curves, we evaluated Young's modulus (YM), ultimate tensile strength (UTS), yield stress (YS) and % elongation for both the matrix and its composites.

After preparation, all the samples (matrix laminates and the composites) were equilibrated by keeping them in desiccators (RH ~ 40–50%) before subjecting them to any testing.

3. Results

3.1. X-ray diffraction studies

Fig. 1a shows the X-ray powder diffraction pattern of the starch sample Amidex-3001. The main diffractions peaks, centered at 15.2, 17.2, 19.9, 23.3 and 26.5° of 2θ (interplanar distances "d" of 5.82, 5.15, 4.46, 3.82 and 3.36 Å, respectively), are characteristic of an A-type starch, and the crystalline structure is typical of cereals (Shamai et al., 2003; Zobel, 1988). Starches have two main components, namely amylose and amylopectin. Their ratio dictates the pattern of crystallization during composite making. Hence, the two peaks mentioned at 19.9° and at 23.3° of 2θ (d = 4.46 and 3.82 Å) may have been related to the occurrence of these starch components (Shamai et al., 2003), which in the case of Amidex-3001 corresponds to about 70% amylose and 30% amylopectin, according to the information from the starch manufacturer.

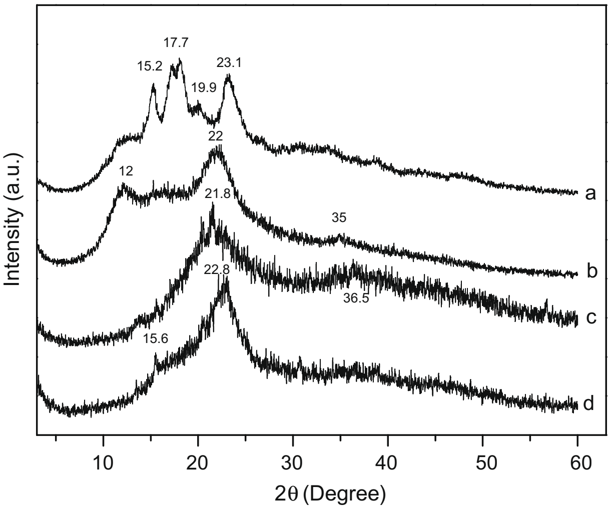


Fig. 1. X-ray diffraction patterns of (a) starch 3001, (b) banana fiber and their composites (c) A and (d) B.

Fig. 1(b–d) shows the X-ray diffraction patterns of banana fibers and their composite with 10 and 60 wt.% fiber content. Banana fibers are partially crystalline, as seen by the three diffraction peaks at 10, 25 and 35° in 2θ (d = 8.84, 3.56 and 2.56 Å), corresponding to the cellulose I structure. On the other hand, the composites show much lower crystallinity (20–21%) compared to that of banana fibers (39%), as expected with the plastification of starch. The composite with 10% fiber content shows a diffraction peak at $2\theta = 22°$, which evidently comes from the crystalline region of the banana fiber. This diffraction peak has a wide shoulder from 15° to 22°, values which incidentally are in the same region of the starch diffraction peak. In contrast, in the composite with 60% fiber, the diffraction peak at $2\theta = 22°$ belongs to the fiber, with no contribution coming from the starch.

In the case of composite "A" (Fig. 1c), the diffraction peak disappears between 2θ values of 5° and 20°, which can be associated with the condensation of starch, its cross linking with glycerol and the consequent destruction of the starch's crystalline region. The third diffraction peak, located between 20° and 30° of 2θ, can be attributed to the contribution of the native structure of cellulose (cellulose I) (Nishino et al., 2004). On the other hand, in the case of composite "B" (Fig. 1d), a narrower diffraction peak centered at 22.85° of 2θ and a shoulder (small peak) at 35° of 2θ were observed, indicating the presence of loose fiber. However, the peak at 12.5° of 2θ was missing, suggesting that changes had occurred in the fiber structure of both composites. Furthermore, there was not much variation between the crystallinity indices (20–21%) of both composites.

3.2. Moisture content

While preparing the laminates of both the starch matrix and their composites, some bubbles were observed in the central region of the plates, probably due to the evaporation of the water present in the middle. Hence, moisture content in all the raw materials was determined following standard methods. These values (%) were 10.8, 4.4, 5 and 7 for starch, crude glycerin, banana fiber and sugarcane bagasse fibers, respectively. The moisture content of the commercial glycerol was almost zero. The value observed for starch is in agreement with that reported earlier (Curvelo et al., 2001).

3.3. Thermal characterization

Fig. 2 shows the TGA/DTA curves obtained for Amidex-3001, showing a mass loss of 10.8% up to 200 °C due to the presence of hydrated/adsorbed water, which is associated with a broad endothermic peak centered at 140 °C. The mass loss of 86.1% between 315 and 495 °C due to the burning of organic matter is also associated with two endothermic peaks at 339 and 487 °C. The remaining 3.1% is due to the presence of inorganic material in the starch, probably silicates.

TGA/DTA studies of both types of fibers used here have been carried out and reported elsewhere (Guimarães et al., 2009a)

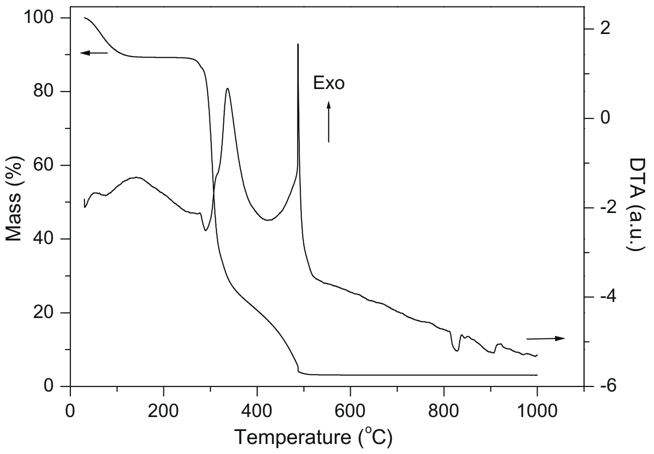


Fig. 2. Thermal analysis (TGA/DTA) curves obtained for starch (Amidex-3001).

3.4. Mechanical Properties

Table 2 shows values of tensile properties of the following (i) starch with commercial glycerol as well the composites of starch plasticized with commercial glycerol with different amounts of banana fibers; (ii) starch plasticized with crude glycerin and 30 wt.% banana fibers as well as 25% of bagasse fibers, all processed by manual method; (iii) starch + crude glycerin with 25% banana fibers and (iv) starch plasticized with both commercial glycerol and crude glycerin with 25% bagasse fibers, both of these(iii and iv) processed under controlled conditions. An analysis of these reveals the following:

Plasticized starch shows low tensile strength, but high % elongation at break in agreement with some of the earlier reported values (Averous & Boquillon, 2004; Müller et al., 2009; Woehl, 2009). Even though the boiling point of glycerol is 209 °C, according to Torres et al. (2007) starch–glycerol matrices exhibit higher strength properties when glycerol is completely decomposed compared to what happens when it acts exclusively as a plasticizer. Hence, tensile strength of such matrices may not be very high (~3.5 MPa), as observed in the present study, where the value was comparable with those reported earlier (Ochi, 2006). The fractographic studies suggested possible high elongation value. Fig. 3(a and b) shows the fractographs of 70 wt.% starch 3001-A with 30% glycerol. The surface shows a continuous phase, as earlier observed with pea starch (Ma, Chang, Yang, & Yu, 2009) and cassava starch (Müller et al., 2009; Woehl, 2009).

The matrix fracture surface (Fig. 3a) was nonporous, transparent, rather smooth above the cracked region, but slowly becoming rough beyond the cracks (crack shown by straight arrow and rough region by dotted arrow). Higher magnifications (Fig. 3b) also reveal dimples (broken arrow) at the crack in addition to the enhancement of the cracked region, suggesting that the starch/glycerol sample is ductile and not properly homogenized. A similar structure was observed earlier with cassava starch (Teixeira, 2007). These large starch granules are unstructured, probably due to the presence of glycerol in higher amounts than necessary concentrations, whose plasticizing effect reduces the viscosity of the mixture. Also, the probable breaking of starch granules by water and glycerol as the temperature rises leads to the disruption of both inter- and intra-molecular hydrogen bonds, which also increases plasticity in the starch (Ma et al., 2009). This explains the observed high percentage of elongation for the starch–glycerol matrix.

Incorporation of lignocellulosic fibers into the plasticized starch improved the Young's modulus and yield strength, but without changing the tensile strength and decreasing the percentage of elongation at break over that of the matrix (starch + glycerol). This is in agreement with earlier reports on starch–glycerol composites containing different reinforcements including lignocellulosic fibers (Averous & Boquillon, 2004; Carvalho et al., 2001; Curvelo et al., 2001; Gáspar, Benkó, Dogossy, Réczey, & Czigány, 2005; Ma, Yu, & Kennedy, 2005; Müller et al., 2009; Woehl, 2009). This is attributed by these researchers to the compatibility (both chemical and structural) between the reinforcements (cellulose chains) and the starch–glycerol matrix. Improvement in Young's modulus in such systems is also attributed (Kunanopparat, Menut, Morel, & Guilbert, 2008) to deplastification of starch caused by the partition of glycerol between the constituents of the composites (matrix and fibers).

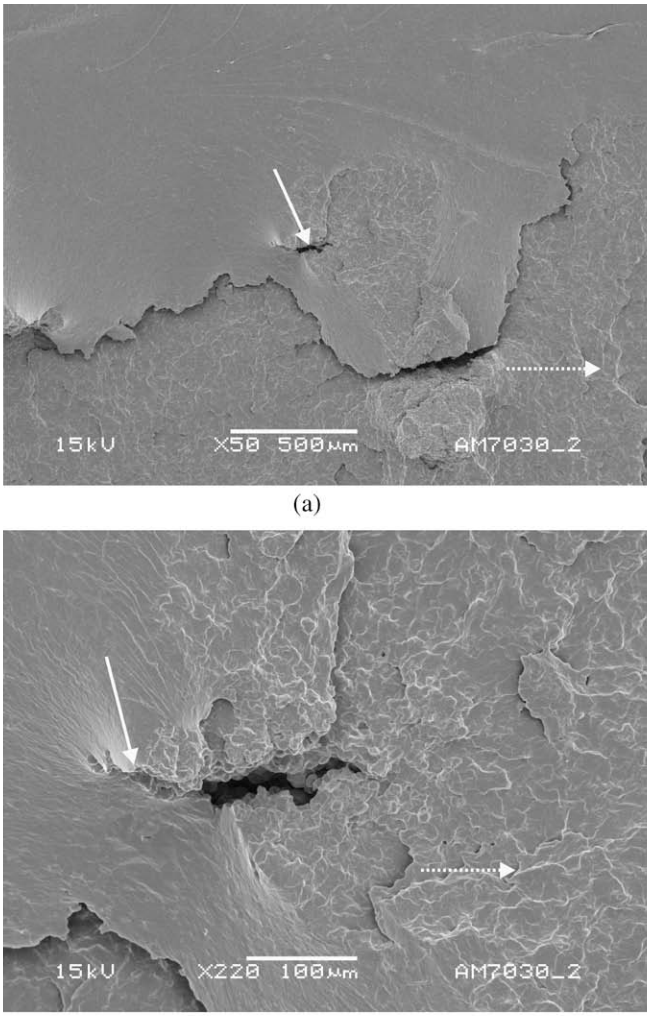
3.4.1. Effect of the amount of fiber incorporated in the starch–glycerol composites

The Young's modulus increased by 186%, 294% and 201% over the matrix for banana fiber contents of 20%, 25% and 35%, respectively, in the starch + glycerol matrix, while the ultimate tensile strength (UTS) remained relatively constant. The yield strength (YS) increased by about 129%, 141% and 133% for 20, 25 and 35 wt.% fiber contents, while the% elongation decreased about fivefold for 20 wt.%, sixfold for 25 wt.% and sevenfold for 35 wt.% fiber content. The increase of YS with increasing fiber content is understandable from the rule of mixtures. In view of this, a decrease in percentage of elongation with increasing fiber content is also expected, as reported for other composite systems, as mentioned above. Variation of YM with increasing fiber content indicates that 25 wt.% may be the maximum amount of fibers to give stiffness to the matrix, so that higher fiber content does not improve it any further. This was found to be true in the case of both types of glycerol for this fiber. However, the constancy of UTS with increasing fiber content, similar to that observed with corn starch–chitin composite (Andrade, Souza, Barbosa, & Silva, 2000), is not understood so far, although a decrease in UTS could be due to poor interfacial

Table 2
Tensile properties of starch–glycerol and their composites with banana and bagasse fibers.

Sample	Sample composition	Tensile properties			
		YM (MPa	UTS (MPa)	YS (MPa)	Elongation (%)
B-0	70 S: 30 G	24.68 ± 4.16	4.00 ± 0.38	1.06 ± 0.05	75.57 ± 2.12
B-4	50 S:30 G: 20 BAF	70.81 ± 9.03	4.07 ± 0.19	2.43 ± 0.11	14.96 ± 0.80
B-3	45 S: 30 G: 25 BAF	97.12 ± 8.93	4.05 ± 0.18	2.56 ± 0.19	12.23 ± 0.17
B-1	35 S: 30 G: 35 BAF	74.35 ± 3.08	3.56 ± 1.34	2.48 ± 0.77	10.63 ± 0.86
CN2	45 S: 30 G: 25 BGF	162.50 ± 19.12	4.15 ± 0.20	–	10.30 ± 1.31
BN1	45 S: 30 G: 25 BAF	484.04 ± 150.86	4.34 ± 2.30	–	1.20 ± 0.22
B-6	40 S: 30 CG: 30 BAF	80.88 ± 8.81	1.73 ± 0.16	0.97 ± 0.01	4.50 ± 0.25
B-11	45 S: 30 CG: 25 BGF	199.48 ± 18.68	2.92 ± 0.21	2.90 ± 0.21	5.09 ± 0.15
CN22	45 S: 30 CG: 25 BGF	468.28 ± 59.23	3.85 ± 0.35	–	2.75 ± 0.46

S, starch; G, glycerol; CG, crude glycerin; BAF, banana fiber; BGF, bagasse fiber.



(a)

(b)

Fig. 3. SEM images of 70% starch sample (Amidex-3001)–30% glycerol after tensile test: (a) crack surface with a remarkable smoothness and increasing roughness near voids; (b) higher magnification of the cracked region marked in "a"; (c and d) enhanced details of "b"[For details see the text].

bonding, as reported for polypropylene composites containing steam-exploded wood fibers (Mat Taib, Mohd Ishak, Rozman, & Glasser, 2007, chap. 20). On the other hand, the YM should have increased with increased fiber content, but the lower stiffness of banana fibers may have compromised the YM enhancement beyond fiber incorporation levels of 25 wt.%. Nevertheless, the % elongation decreases with fiber addition, because in addition to the reasons mentioned earlier, the matrix is more ductile than the fibers themselves.

The above results are similar to those reported for plasticized corn starch–chitin systems (Andrade et al., 2000) and wheat starch with leaf wood cellulose fibers (Averous & Boquillon, 2004; Le Digabel, Boquillon, Dole, Monties, & Averous, 2004). The former, prepared by extrusion, exhibited increased YS and 36–55% elongation with increasing chitin content (0.1–1%), without any significant increase in tensile strength. However, in the latter case, both the strength properties and the water content of the composite decreased in relation to that of the starch matrix, which was much better than the composite of the same fibers with a poly (ethylene) matrix. On the other hand, UTS remained virtually constant between B-0 and B-3, while YS was higher for B-3 than for B-0. However, all the above observations suggest comparatively good compatibility between the fibers and the matrix, indicating the reinforcing effect of these fibers.

3.4.2. Effect of processing conditions and type of glycerol with the same fibers

To analyze the possible replacement of commercial glycerol with crude glycerin, we studied the tensile properties of starch plasticized with crude glycerin and reinforced individually with 25 and 30 wt.% banana and 25 wt.% bagasse fibers to determine whether these properties are dictated by the type of reinforcing fiber used for composite making. In the case of banana fiber composites, with slightly different amounts of fiber in the starch–glycerol (25 wt.%) and starch–crude glycerin (30 wt.%) matrices, the YM value was higher and% elongation was lower for the two composites (B-4 and B-6 respectively) compared to those of the pure matrix (B-0). YM and UTS values for 25 wt.% banana fiber composite with crude glycerin (BN1) were higher compared to those with all composites with commercial glycerol indicating the effect processing method. However, with controlled conditions, even 25% banana fiber composite with crude glycerin (BN1) showed higher values of YM and UTS over both the 25% fiber with commercial glycerol (B-3) and 30% fiber with crude glycerin (B-6). Similarly, with controlled conditions, for the same amount of bagasse fiber content (25%) starch + glycerin composites (CN22) showed about 188% increase in YM over the starch + glycerol composite (CN2), while strain at break showed reverse trend with about 274% higher for starch + glycerol. UTS value almost remained constant in these cases.

Further, under the same conditions of automatic processing, composites with the same amount of fiber content (25%), YM and UTS values for both types of fiber composites of starch + crude glycerin (BN1and CN22) did not show much difference, while the values of percentage of strain at break were higher for bagasse composite (CN22) over that of banana fiber composite (BN1). Higher value of standard deviation with banana fiber composite may be due to behavior of banana fiber compared to compact nature of bagasse fiber leading to non-homogeneous distribution of fibers. On the other hand, YM and UTS values for these composites (BN1 and CN22) with equal amount of fiber content (25%) were higher than those of similar composite of bagasse processed with manual control (B-11), which in turn was higher than those of composites containing even higher amount of banana fiber (B-6) under the same processing method (manual). Another interesting observation was that values of UTS and YS were almost similar for all the composites processed under controlled method.

All the above results indicate that (i) comparatively good adhesion between the fibers and the matrix is provided by both types of glycerol whereby the fibers reinforce the matrix, enhancing its strength properties; (ii) crude glycerin gives better adhesion between the fibers and the starch and (iii) controlled processing conditions improve the adhesion irrespective of the type of glycerol used thus increasing the tensile properties suggesting the positive effect of controlled processing conditions on the tensile properties of corn starch composites.

Further analysis of Table 2 shows that under manual processing method, the starch–bagasse composite (B-11) exhibits higher tensile properties than those of starch–banana composites (B-6), even when the former have lower fiber content (25 wt.%) than the latter (30 wt.%). The improvements of YM, UTS, YS and% elongation values in starch–crude glycerine–25% bagasse fiber composites were about 59%, 41% 67% and 11%, respectively. Even when compared with the same amount of banana fiber (25 wt.%) but with the same amount of glycerol (30 wt.%), the YM and YS values were higher for bagasse fiber composite with crude glycerin.

The improvements observed in YM and YS for both banana and bagasse fiber composites may be due to the formation of large fiber clumps and voids in the test specimens, which lowered the tensile strength, as reported elsewhere (Torres et al., 2007). These improvements could also be partly due to the quality of adhesion between the fibers and the matrix and to the greater compactness of the bagasse fiber composite while compressing (Cao et al., 2006). This can be understood with the help of fractographic studies carried out on these composites. For comparison, fractographic studies of composites containing equal amounts of these fibers were carried out to understand the quality of adhesion of these fibers with the same matrix.

Tensile fractographs of starch–banana and starch–bagasse fiber composites are shown in Figs. 4(a–e) and 5(a–e), respectively. Both composites contained crude glycerin as plasticizer.

Fig. 4a shows rough fracture surface with a large amount of cracks and fibers lying parallel to the fracture surface (straight arrows); Fig. 4b is the same as Fig. 4a, showing a pulled out fiber (dotted arrow) and fiber fracture, pull-outs and some voids. Fig. 4c shows clean fibers (without coating of matrix - straight arrow) that are lying parallel to the fracture surface, some pull-outs (dotted arrows), voids (dash and dot arrow) and ruptured fibers perpendicular to the crack (dashed arrow), while at higher magnification there is a ruptured fiber lying perpendicular to the fracture surface (Fig. 4d). Also, fiber rupture occurred probably before the matrix failure was completed, as indicated at different magnifications in Fig. 4c and d. Fig. 4e shows more fibers lying parallel to the fracture surface (straight arrows), residues of a split parallel fiber (dotted arrow) and pull-out fiber/fiber breakage (dash and dot arrow). All these impair the strengthening effect in the composite.

Generally, fibers would break at the fracture surface itself without any broken fibers protruding from that surface or any resin sticking to the fibers, when good bonding existed between the fiber and the matrix. On the other hand, weaker bonding is exemplified

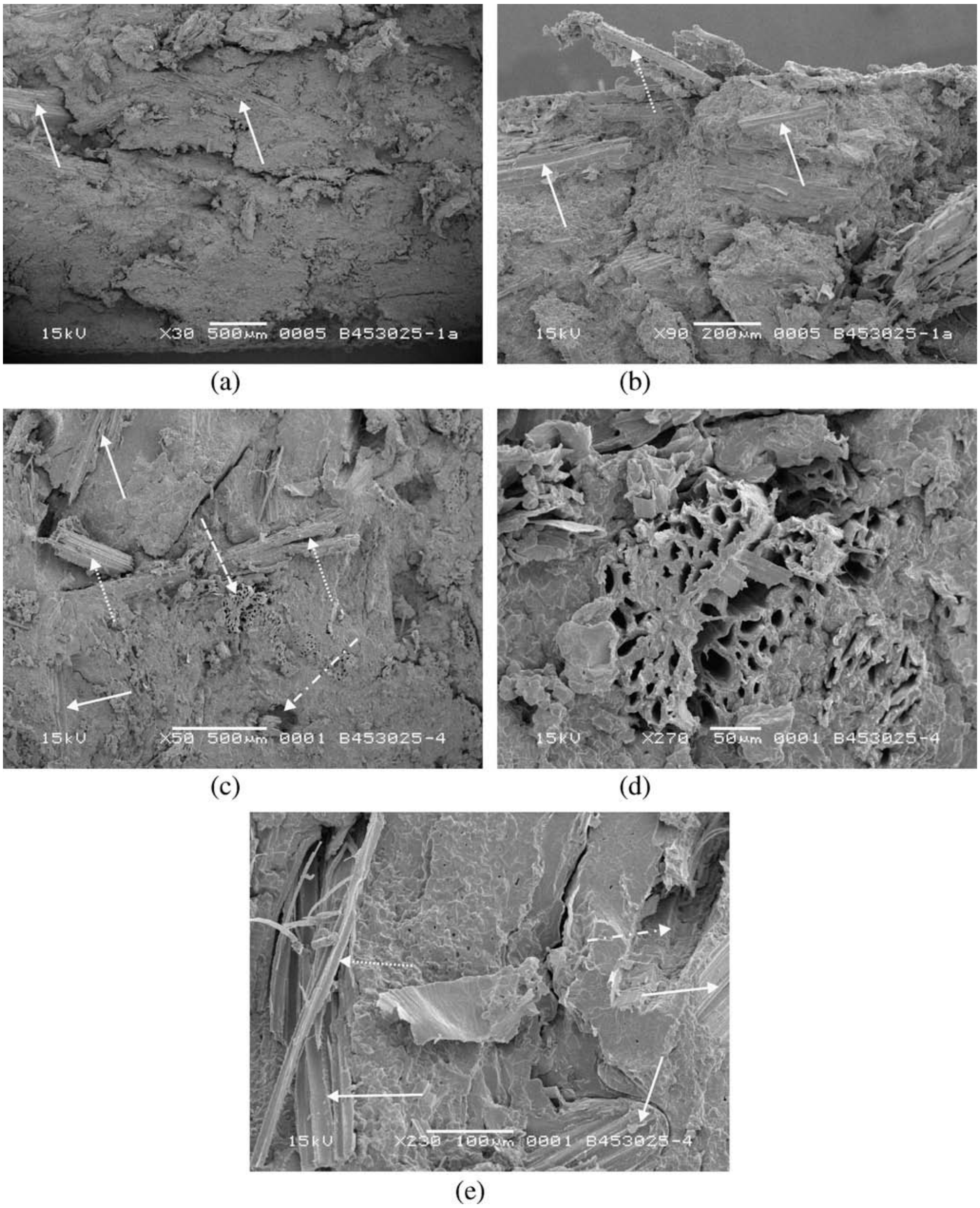


Fig. 4. SEM tensile fractographs of fractographs of 45% Starch (Amidex-3001)–30% crude glycerin–25% banana fiber composite. (a) rough fracture surface with lot of cracks and fibers lying parallel to the crack surface; (b) same a, pulled out fiber and fiber fracture, pull-outs and some voids; (c) fibers lying parallel to the crack surface, some pull-outs, ruptured fibers perpendicular to the crack and clean fiber surface without coating by the matrix; (d) ruptured perpendicular fiber at higher magnification; (e) more fibers lying parallel to the crack region, residues of a split parallel fiber and pull-out fiber/fiber breakage. [For details see the text].

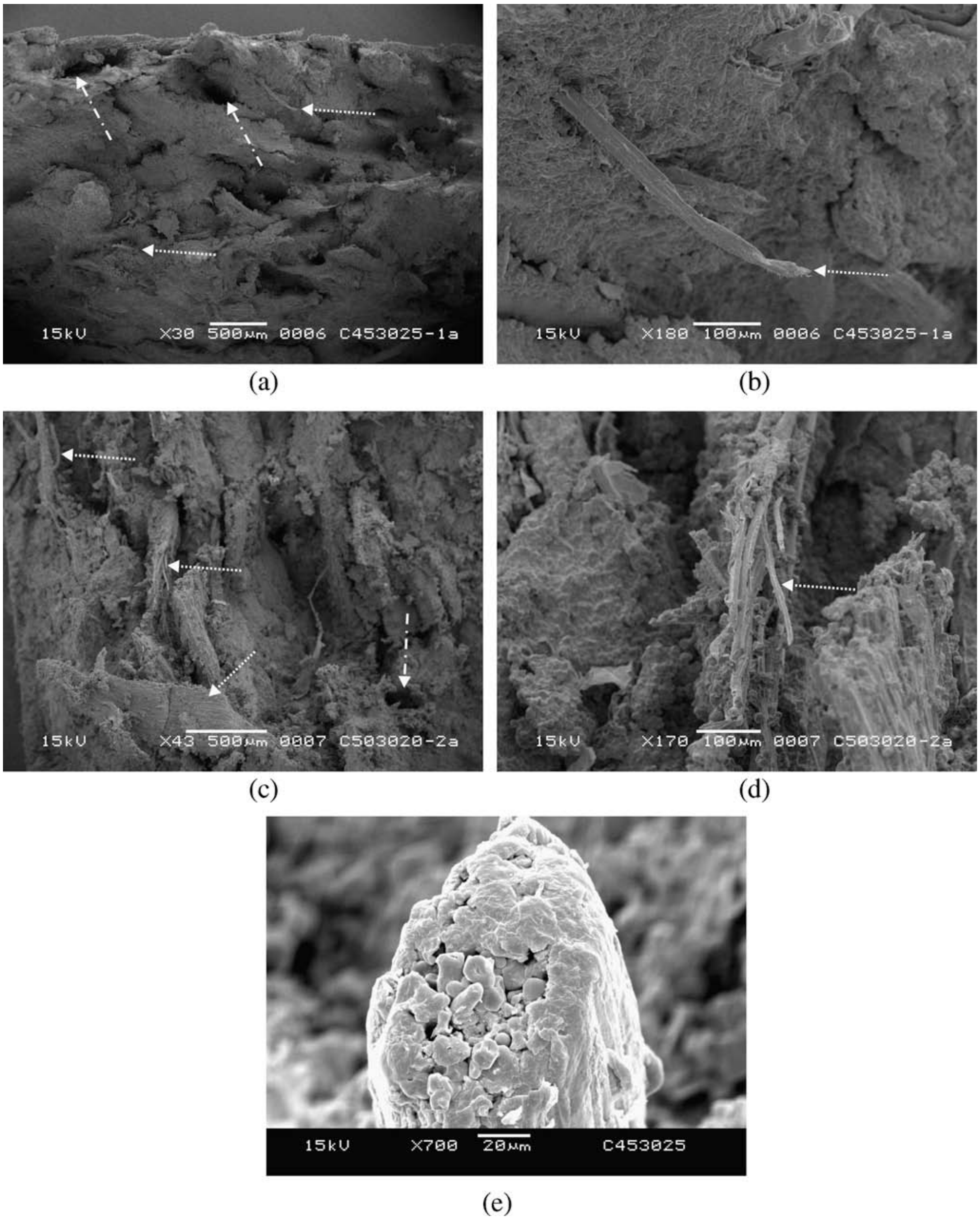


Fig. 5. SEM tensile fractographs of 45%Starch (Amidex-3001)–30% crude glycerin–25% bagasse fiber Composite. (a) highly rough fracture surface with lot of small size fibers pull-outs and micro cavities; (b) Same as a, pulled out fibers and fiber fracture; (c) many fiber residues some pull-outs; (d) splitting of fiber and small globular clusters attached to the fiber surface; (e) coating of matrix on the bagasse fiber surface in the composite. [For details see the text].

by the longer pull-out fibers, as in Fig. 4c (Luo & Netravali, 1999; Tserki et al., 2006), with concomitant sliding of the fiber into the matrix and friction between them.

Fig. 5a shows higher rough fracture surface with a lot of small fiber pull-outs (dotted arrows) and pull-out holes appearing as cavities (dash and dot arrows), while Fig. 5b is the same as Fig. 5a, showing pulled out fiber with the fiber fracture. Many fiber residues (dotted arrows) and some pull-out holes (dash and dot arrows) can be seen in Fig. 5c, while Fig. 5d shows a split fiber (dotted arrow) and small globular clusters attached to the fiber surface. Fig. 5e shows good coating of the matrix on the bagasse fiber surface in the composite, contrary to a free fiber surface observed in banana fiber composites (Fig. 4e).

As reported elsewhere (Choi et al., 2004), the addition of fiber changed the surface character, with the bagasse fiber composite showing a rougher surface (Fig. 5a) than that of the banana fiber composites (Fig. 4a). Furthermore, the roughness of its surface was higher than that of the matrix, as seen in Fig. 4a. The presence of voids in the composites prepared with glycerol can be attributed to the formation of gas bubbles during evaporation of water (Torres et al., 2007).

Also, the bagasse fiber composite displayed a larger number of fibers and their pull-outs (Fig. 5b and c) compared to the banana fiber composite (Fig. 4b, 4c). On the other hand, more fibers seemed to be lying parallel to the surface in the latter (Fig. 4c) compared to the perpendicular alignment of the fibers in the former (Fig. 5c and d). It is known that lignocellulosic fibers break not only in the transverse direction to their axis, similar to synthetic fibers, but also by axial splitting of microfibrils (elementary fibers), and hence the fiber fractures observed in the present study agree with earlier reports for other natural fibers with starch matrices (Alvarez, Bernal, & Vazquez, 2005; Bernal & Lauke, 2007, chap. 11; Rohmany, Karger-Kocsis, & Czigány, 2003). This may be the reason for the observed tendency of increased tensile properties (YM, YS and

UTS) in the bagasse fiber composite. Also, pull-out fibers sticking to the matrix in different directions was evident as observed earlier with starch–sisal fibers (Misra et al., 2002).

Furthermore, the bagasse fibers were split and fractured (Fig. 5b, d), which is common in composites fabricated at molding pressures of 6 MPa (Sousa, Monteiro, & d'Almeida, 2004). They were well coated by the starch (Fig. 5e), as observed earlier in the case of starch–cellulose acetate and wood flour composites, indicating good bonding between the fiber and the matrix (Torres et al., 2007). In such cases, the lower strength properties (lower UTS compared to matrix with commercial glycerol) are attributable to the shorter fiber aspect ratio. It is important to comment here that only after establishing effective strong bonding between the reinforcement and the matrix can the effect of reinforcement really be maximized (Wypych & Satyanarayana, 2005).

Besides this, the YM and YS values of starch–crude glycerin–25 wt.% bagasse composite were higher than those of the starch–glycerol matrix, except for the elongation.

The above discussions suggest the possibility of substituting commercial glycerol with crude glycerin by taking some appropriate steps, as given below:

(i) The moisture content must be controlled in the composites before testing; (ii) air bubbles must be reduced in the composite laminates by selecting appropriate processing conditions; (iii) proper mixing of the components must ensure that glycerol is in contact with all of the plasticizable component and that fibers are really well dispersed; (iv) and all the starch granules must be disrupted by heating the sample at the right temperature and proper heating time. Use of crude glycerin (recovered glycerol) indicated some early success, with the resulting dark brown composite laminates showing good homogeneity and good processability at higher fiber contents with the absence of either bubbles or small fissures in the test specimens.

4. Concluding remarks

X-ray diffraction (XRD) studies revealed that the starch sample (Amidex-3001) chosen for this study was of the A-type, typical of crystalline structure cereals. Thermal analysis studies of Amidex-3001 showed good thermal stability for composite making, while fractographic studies of starch composites containing 70 wt.% Amidex-3001 and 30% commercial glycerol revealed matrix cracks between smooth and rough surfaces and dimples in rough regions, suggesting that the composite sample was ductile and not properly homogenized.

Starch/banana and starch/bagasse fiber composites can be prepared by compression molding in two different processing methods using both commercial glycerol and crude glycerin as plasticizers. XRD studies revealed structural changes in both fiber composites, but without much variation in their crystallinity index (20–21%).

The morphology of these composites was dictated by the properties of the fibers rather than by the properties of the matrix. Compared to banana fiber composites, fractographs of bagasse fiber composites showed a large number of fiber pull-outs and fibers lying perpendicular to the fracture surface, and these seemed to explain the tendencies observed in their tensile properties. Good bonding between the bagasse fibers and the matrix was shown by the starch coating on these fibers, compared with the free surface of banana fibers.

Tensile testing of these composites indicated marginal improvements in strength properties over those of the matrix. In the case of composites, tensile properties showed dependence on the processing methods with automatic control of temperature and applied pressure improving the properties for the same amount of fiber content irrespective of type of glycerol used. Crude glycerin produced more homogeneous composites, which may lead to better properties than those produced with commercial glycerol. Thus, a direct destination is offered to the main co-product of the biodiesel industry, without any requirement for its chemical treatment and upgrading.

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