Preparation and characterization of biodegradable composites based on brazilian cassava starch, corn starch and green coconut fibers

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ABSTRACT
Increasing search for new materials with high premium on eco-friendliness, new trend is emerging in materials development such as composites, which are well established for a wide variety of applications. With growing interest and importance of renewable bioresources has led to more stress on the use of locally available materials. This paper presents preliminary results on the preparation and characterization of composites based on Brazilian coconut fibers and starches of cassava and corn. The raw materials were characterized for their morphology, chemical composition, and thermal properties and X-ray diffraction studies. Coir fibers were also tested for their tensile properties showing increasing strength and Young’s modulus with decreasing diameter, while the % elongation remaining constant. Lignin content of coir was found to be 35%. Structure and properties of composites containing 0, 5 10, 15% fibers in both the matrices and prepared by compression molding would be compared. For the 2 types of starch, there was an increase in the tensile strength by the increasing proportion of fiber. The effect of moisture in the composite stress affects the strength and percentage elongation. The water absorption was higher in the composites made from cassava starch.

Keywords: Cassava starch, corn starch, coconut fiber, glycerol.

1 INTRODUCTION
It is well known that plastic materials are very versatile materials with wide range of applications and hence their production and consumption have been increasing. However, most of these are synthetic materials and hence inert to attack by microorganisms and therefore pose environmental problem in their disposal [1]. In view of this, investigations have been directed to find eco-friendly materials, which are recyclable or biodegradable. Such materials are made of natural materials, while biodegradable composites will have biodegradable matrix and reinforcements as their constituents. A number of polymeric materials (natural resins or synthetic resins), which are biodegradable, is available. One such natural resin is starch, which is normally made into thermoplastic by processing using several industrial techniques as injection, extrusion or the use of a batch mixer [2] connected to a torque rheometer. Unfortunately this type of material has the problem of absorption of humidity and it exhibits inferior mechanical properties compared to the synthetic plastic materials [3]. This has been overcome by incorporating lignocellulosic fibers such as coir fibers into the natural resin matrices, since these provide big advantage over the synthetic fibers such as light weight, low cost, non-abrasiveness, etc.

In recent years Brazil has been in the forefront for the use of industrial residuals. One such material available here is the fiber resulting from discards of the green coconut, which is a very important option in the northeast of Brazil. On the other hand, Brazil is the principal Latin American country that presents the highest production and yield per hectare in the production of cassava starch.

Recognizing the above facts, this study presents the preliminary results on preparation and characterization of biodegradable composites based on thermo plastic starch (TPS) of cassava starch and different amounts of coconut fibers obtained from green coconuts by direct thermo-plastification using plasticizer such as glycerol.
2 MATERIALS AND METHODS

Native cassava starch used (Manihot esculenta), was donated by the J. A. Pasquini & Cia. Lda. (Brazil) and corn starch (Zea mays) by Corn Products Brazil (Amidex 3001). The coconut fiber from green coconuts (Cocos nucifera) was donated by the COOBCOCO Company in the Northeast of Brazil. Commercial glycerin was used as plasticizer. Chemical composition of fiber was determined by Tappi and NBR standards. Thermal analysis (TGA) of both the fiber and the starch were determined using NETZSCH thermogravimetric balance, (model TG – 209).

The fibers of green coconut were dried, milled and sorted to obtain fiber sof 10 mm size. Different amounts of coconut fibers (0, 5 10 and 15 wt. %) and 30% of glycerin were used to prepare the composites using mold of size 17 cm\(^2\) and thickness of 3 mm, compression molded using a hydraulic press with hot pressing facility (Solab) applying 8 tons of pressure. From the laminates thus obtained, tensile specimens were made with specimen size as peer ASTM standard D 638M-93 [4]. While the coir fibers were tensile tested using INSTRON 4467 universal testing machine, their starch composites were tested using EMIC DL-2000 universal testing machine. The composites were tested at two different humidity (6-7% and with 3-4%).

Crystallinity of both the fiber and the starch was determined by X-ray diffraction using Shimadzu machine model: XRD 7000, adjusted with a scanning speed of 1°/min with copper radiation at 40kV and 20 A.

Morphology of the fibers and starch was examined using Olympus (CX410) optical microscope and PHILIPS XL-30 scanning electron microscope. A stereomicroscope Zeiss make, model: Discovery V12 was used to observe the distribution of fibers in the thermoplastic starch matrix.

Since it is well known that one of the problems of thermoplastic starch is its susceptibility to humidity, water absorption of both the composites and the matrices were determined after immersing them for 2 and 24 hours following [5] EN 317 standard.

3 RESULTS AND DISCUSSION

Table 1 shows chemical analysis of coir fibers used. It can be seen that lignin content obtained in this study are lower than those reported for similar fibers elsewhere [6]. This is understandable as due to variation of chemical composition of fibers depends on various factors such as locality, age, etc. [7]. Since fiber used in the present case is from green coconuts, it might have been less lignified.

![Figure 1](image1.png)

Figure 1 shows the cross section of the coconut fiber. It is observed that the coconut fiber is multicellular with a central part called lacuna. The porous surface of the fiber is useful for a better interlocking between the fiber and the matrix [6, 8].

The density of coir fiber was found to be 1200 kg.m\(^{-3}\). Table 2 shows the results of tensile testing of fibers. It can be seen that coir fibers of 0.25 mm diameter exhibited higher tensile strength and Young’s modulus as expected (smaller diameter of fiber, higher is the strength) comparable to the values reported earlier fro similar fibers [2].

The shape and size of starch grains vary according to botanical origin and degree of maturity of the plant. Figure 2 (a&b) shows the morphologies of corn and cassava starch granules. It can be seen that corn starch granules show polyhedra or polygon shape (Fig. 2a), while those of cassava are globular (Fig. 2b), similar to those observed earlier by Cereda [10]. Also, cassava starch has about 18 amylose% and 82% amilopectin, while those of corn starch are 28 and 72% respectively. These differences are understandable as due to starch of cereals are more rigid, while those of tubers are more viscous and transparent [11].
Figure 1: SEM of cross-sections of coconut fiber.

Table 2: Results of the tensile test of green coir fiber.

| Fiber | Diameter (mm) | Load max. (N) | Stress max. (MPa) | Elongation at Break (%) | MOE (Young) (MPa) |
|-------|---------------|---------------|-------------------|-------------------------|-------------------|
| Raw   | 0.39          | 13.58         | 113.98            | 43.50                   | 1166.86           |
| Fine  | 0.25          | 7.31          | 158.54            | 41.28                   | 1959.47           |

Figure 2: SEM of corn (a) and cassava starch (b) granules.

Figure 3 shows TG/DTA curves of the coir fiber. Three main degradation points can be seen, first one at 160 °C corresponding to the mass loss due to loss of moisture and highly volatile materials, the second at 360 °C due to decomposition of hemicelluloses and the final at 480 °C to the decomposition of the lignin [12]. On the other hand, in the case of cassava starch (Fig. 4a), the first mass loss occurred between 30 and 180 °C, with an endothermic peak at 100 oC due to the 13.73% of dehydration followed by second thermal decomposition occurring at an endothermic peak at 320 oC and another at 520 °C, which corresponded to a mass loss of 71.45% and 14.03% respectively.

In the case of the corn starch (Fig. 4b), though the endothermic peaks occurred at the same temperatures, the mass losses were 11.71%, 70.89% and 15.29% respectively.
Figure 3: Thermal analysis (TG) curve obtained for green coir fibers.

Figure 4: Thermal analysis (TG/DTG) curves obtained for cassava (a) and corn (b) starch.

Figure 5(a) shows XRD patterns of corn starch (Amidex 3001) sample used. Main diffraction peaks were at 20 values of 15.19, 17.23, 18.06, 19.9 and 23.04 which coincide with earlier reported by Guimarães et al. [13], who used the same type of starch. The main diffraction angles indicate the starch belongs to starch Type A, characteristic of the cereals [9]. In the case of the cassava starch (Fig. 5b), five main peaks are seen at different diffraction angles (20) of 15.19, 17, 23, 18.13, 20.10 and 23.10. These, according to Kawabata [14] and Schlemmer [15] correspond to a type A-b structure (also denominated as CA (C in the vicinity of the one A) having crystallinity of 90% of the A type and 10% of type B. Similar results were also reported by Biliaderis [16] and Lacerda [17]. The restructuring of starch grains during the plastificacion (glycerine, temperature and pressure) in the thermo forming process during compression caused changes in the crystallographic profile similar to that observed for the corn starch composite and that of cassava starch with 0% and 15% of coconut fiber.

Figure 6 (a&c) shows photographs of both corn starch-glycerol composite with 5 and 15% coir fibers while Figure 6 (b&d) show those of cassava starch-glycerol with 5 and 15% coir fibers as observed under stereomicroscope. Random and uniform distribution of the coir fibers of different diameters in the transparent matrices of plasticized starches can be seen.

Figure 7 shows the results of the water absorption of cassava and corn starch matrices and their composites with 5-15% coir fibers after immersion for 2 and 24hrs. It can be seen that cassava starch composites showed higher percentage of water absorption compared to that of corn starch composites. This may be due to higher rigid nature of corn starch compared to viscous nature of cassava starch as mentioned earlier. It can also be seen that similar tendency continues with both the composites but, increasing fiber content decreases the water absorption in these composites.
Figure 5: X-ray diffraction patterns of (a) corn starch and their composites, and (b) cassava starch and their composites (0%, 15% coir fiber).

Figure 6: Stereomicroscope photographs corn starch composite with (a) 5% and (c) 15% coir; cassava starch composite with (b) 5% and (d) 15% coir fibers.

The prepared composites showed a density of approximately 1300 kg.m⁻³. Table 3 lists the results of the tensile tests of composites containing different amounts of green coir fibers at two different humidities. It can be seen that maximum load for break and tensile strength improved with the incorporation of coir fiber, which increased with increasing amount of fibers, while % elongation decreases significantly in both the composites at 6-7% humidity.
Figure 7: Water absorption of composites of corn and cassava starch immersed in water for 2 to 24 hours.

Table 3: Results of the tensile test of composites cassava starch and corn starch reinforcing with different amounts of coconut fibers.

| Material       | Amount fibers % | Load Max. (N) | Tensile Max. (MPa) | Elongation % |
|----------------|-----------------|---------------|--------------------|--------------|
|                | Humidity 6-7%   |               |                    |              |
| Corn starch    | 0               | 34.44         | 0.89               | 145.57       |
|                | 5               | 63.73         | 1.94               | 49.92        |
|                | 10              | 105.53        | 2.88               | 22.11        |
|                | 15              | 118.41        | 3.31               | 16.65        |
| Cassava starch | 0               | 50.77         | 1.56               | 210.33       |
|                | 5               | 74.44         | 2.26               | 62.16        |
|                | 10              | 107.83        | 3.38               | 30.05        |
|                | 15              | 124.52        | 3.51               | 24.01        |
|                | Humidity 3-4%   |               |                    |              |
| Corn starch    | 0               | 234.38        | 7.56               | 38.46        |
|                | 5               | 248.70        | 7.81               | 8.39         |
|                | 10              | 255.37        | 8.08               | 7.79         |
|                | 15              | 266.91        | 8.13               | 6.82         |
| Cassava starch | 0               | 112.68        | 3.24               | 111.92       |
|                | 5               | 176.55        | 5.71               | 6.43         |
|                | 10              | 235.37        | 7.68               | 6.16         |
|                | 15              | 300.40        | 9.34               | 5.93         |

On the other hand, these values were low at two different humidities. It can be seen that maximum load for break and tensile strength improved with the incorporation of coir fiber, which increased with increasing amount of fibers, while % elongation decreases significantly in both the composites at 6-7% humidity.

On the other hand, these values increased marginally for corn starch composites at 3-4% humidity, probably due to the rigidity of the matrix, while it was higher in the case of cassava starch composites at the same humidity. These results are in agreement with those reported elsewhere [3, 18].

4 CONCLUSIONS

Coir fibers from Brazilian green coconuts showed density of 1200 kg.m\(^{-3}\), lignin content of 35.46% and higher tensile strength and Young’s modulus for fibers of 0.25 mm diameter.
Corn starch granules were of polyhedra or polygon shape with 28% amylose and 72% amilopectin, while those of cassava were globular with about 18% amylose and 82% amilopectin.

Composites of both corn starch and cassava starches reinforced with coir fibers could be prepared by thermo molding using glycerol as plasticizer, which resulted in random, but uniform distribution of fibers in transparent matrices. Both the maximum load for break and tensile strength improved with the incorporation of coir fibers into both the starches, which increased with increasing fiber content, while % elongation decreased significantly in both the composites at 6-7% humidity. Though these values increased marginally with corn starch composites at 3-4% humidity, they were higher in the case of cassava starch composites at the same humidity.

Also, cassava starch composites showed higher percentage of water absorption compared to that of corn starch composites. Similar tendency of decreasing water absorption with increasing fiber content was observed for both the composites.

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