

Biodegradable Composites Based on Starch/EVOH/Glycerol Blends and Coconut Fibers

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Received 5 May 2008; accepted 7 July 2008

DOI 10.1002/app.29062

Published online 10 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Unripe coconut fibers were used as fillers in a biodegradable polymer matrix of starch/ethylene vinyl alcohol (EVOH)/glycerol. The effects of fiber content on the mechanical, thermal, and structural properties were evaluated. The addition of coconut fiber into starch/EVOH/glycerol blends reduced the ductile behavior of the matrix by making the composites more brittle. At low fiber content, blends were more flexible, with higher tensile strength than at higher fiber levels. The temperature at the maximum degradation rate slightly shifted to lower values as fiber content increased. Comparing blends with and without fibers, there was no drastic change in melt temperature of the matrix with increase of fiber content, indicating that fibers did not lead to significant

changes in crystalline structure. The micrographs of the tensile fractured specimens showed a large number of holes resulting from fiber pull-out from the matrix, indicating poor adhesion between fiber and matrix. Although starch alone degraded readily, starch/EVOH/glycerol blends exhibited much slower degradation in compost. Composites produced 24.4–28.8% less CO₂ compared with starch in a closed-circuit respirometer. Addition of increasing amount of fiber in starch/EVOH/glycerol composite had no impact on its biodegradation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 612–618, 2009

Key words: coir fiber; starch; biocomposites; EVOH

INTRODUCTION

The use of biodegradable materials from renewable resources has gained more attention in recent years. Starch is one of the most abundant natural polymers and is relatively inexpensive; however, the use of pure starch in composites results in brittle materials. This can be improved by destructure, a process in which the granular structure of starch is destroyed by the combined use of shear, temperature, and time, usually in the presence of a plasticizer, to provide a homogeneous material. The properties of this destructure starch can be improved by blending with other polymers, plasticizers, and fibers.^{1–4}

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may be suitable.

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Contract grant sponsors: EMBRAPA, Labex/program, CNPq, FINEP, CAPES, ARS/USDA.

Journal of Applied Polymer Science, Vol. 111, 612–618 (2009)
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Ethylene vinyl alcohol (EVOH), a synthetic biodegradable copolymer, has high crystallinity and good mechanical properties and is usually used for packaging because of its excellent gas barrier properties.⁵ EVOH is a good candidate for replacing synthetic polymer in blends, because the hydroxyl groups promote compatibility with starch, and the ethylene groups can provide water resistance and good mechanical properties in starch-based formulations.^{1,6}

Extruded starch-EVOH-glycerol blends provide an interesting polymer system with a wide range of potential mechanical properties. However, its high cost is a major barrier for its widespread acceptance as a substitute for traditional nonbiodegradable polymers.^{3,5,7}

The incorporation of lignocellulosic material as a filler into polymer composites has received increased attention particularly for price driven and high volume applications. The advantages of natural fiber composites are their low density, low cost, renewable characteristics, and complete biodegradability.

Because coconut fiber is much less expensive than EVOH, it is desirable to maximize the fiber content in starch/EVOH/glycerol composites as long as an acceptable level of performance is maintained. In

this study, unripe coconut fiber (coir)* is used as a filler in a biodegradable polymer matrix of starch/EVOH/glycerol. The lignocellulosic fiber is extracted from coconut husk. Coir has been traditionally used as yarn, rope and floor coverings, or mats.⁸ However, in many countries, this natural fiber is considered an undesirable waste, with serious problems when disposed of in landfills. Recently, coir is finding new applications as an eco-friendly substitute for many traditional materials. Technologies have been developed for manufacturing coir composites as substitutes for wood and synthetics.⁹⁻¹¹

The objective of this investigation was to evaluate the influence of the addition of coir to the properties of starch/EVOH/glycerol composites. The tensile, thermal, biodegradation, and X-ray diffraction properties were characterized. Also, the fiber/matrix interface was characterized by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Midsol 50 native wheat starch (12% moisture) was supplied by Midwest Grains. (Atchinson, KS). Poly (ethylene-co-vinyl alcohol) copolymer (EVOH) was provided by EVAL Company of America (Pasadena, TX) under the trade name EVAL-E105. This particular sample is a random copolymer with roughly 35% ethylene copolymer. Glycerol was obtained from Sigma-Aldrich Corporation (St. Louis, MO). Unripe coconut fiber, from the northeast region of Brazil, was provided by Embrapa Agroindústria Tropical (Brazil, CE). The coconut fiber had high lignin (38%) and low cellulose (32%) contents.

Blend extrusion

Blends of thermoplastic starch (50 wt %), EVOH (30 wt %), water (10 wt %), and glycerol (10 wt %), as plasticizer, were melt-extruded with different amounts of unripe coconut fiber. Fiber was added in varying proportions, i.e., 5, 10, and 15% of the total weight of the polymer (starch + EVOH). The fiber was chopped in a knife mill and sieved using a 40-mesh sieve. Before extrusion, starch, EVOH, and coconut fiber were premixed by hand and sealed for 24 h. Subsequently, glycerol and water were blended. The mixture was introduced into a co-rotating twin-screw extruder (Leistritz Micro 18). The ex-

truder had six heating zones with the first five cooled by water. The temperatures for each zone were set at 85, 95, 105, 115, 110, and 105°C from feed to die. The screws had a diameter of 18 mm, and the barrel had a length to diameter ratio of 30 : 1. A K-Tron Soder T-20 loss-in-weight feeder was used to control the solids (starch, EVOH, and fiber) feed rate. A Bran + Luebbe N-P31 metering pump was used to control the liquid (deionized water and glycerol) feed rate.

Following extrusion, the blended material was ground to pellets and injected in an injection molding machine (BOY Machines Inc., Model 15S, screw diameter = 22 mm, injection time = 7 s, cooling time = 20 s, dimensions mold: 73.5 mm × 49 mm × 1.5 mm) at 149–151°C.

Tensile properties

Tensile strength (TS), tensile modulus (E), and elongation at break (ϵ) were determined according to ASTM D3039, under ambient conditions, using an Instron 5500R Universal Testing Machine (Instron, Canton, MA). Prior to testing, samples were left to equilibrate at 50% relative humidity in a sealed chamber containing a saturated solution of calcium nitrate. The testing conditions used were as follows: cross head speed of 5 mm/min and load cell of 0.1 kN. Dumbbell samples (1.5-mm thick) were tested with a gauge length of 20 mm. The reported values are the average of at least 12 measurements.

Thermal properties

Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere. The samples were heated from room temperature to 800°C at a heating rate of 10°C/min and a nitrogen gas flow rate of 60 mL/min. The derivative of TGA curves was obtained using TA analysis software.

Differential scanning calorimetry (DSC) measurements were carried out under nitrogen atmosphere. Each sample (3 mg) was accurately weighed and encapsulated in aluminum pans, and then heated from 25 to 250°C at a scan rate of 20°C/min. The measurements were obtained by using the Thermal Analysis Instruments Universal Analysis 2950 program, V 5.4A.

Scanning electron microscopy

Coconut fiber samples were mounted onto aluminum specimen stubs using double-sided adhesive carbon tabs (Ted Pella, Redding, CA). Fractured composite materials, recovered from the Instron testing, were mounted onto specimen stubs with carbon

*Coconut fiber represents an additional agroindustrial nonfood feedstock (agroindustrial and food industry waste) that should be considered as feedstock for the formulation of eocompatible composite materials.

TABLE I
Mechanical Properties Obtained by Tensile Tests with
Different Coconut Fiber Contents

Composite	TS (MPa)	ϵ (%)	E (MPa)
0% fiber	10.2 ± 0.5^a	67 ± 27^a	99 ± 11^a
5% fiber	9.4 ± 0.4^b	50 ± 13^b	114 ± 8^b
10% fiber	8.7 ± 0.5^c	38 ± 9^c	124 ± 11^c
15% fiber	8.9 ± 0.6^{dc}	28 ± 10^d	147 ± 20^d

TS, tensile strength; ϵ , elongation at break; E , tensile modulus.

Identical letters in the same column do not represent a significant difference to a level of 5% in the Student's t -test.

tabs with the fractured surface facing up. All specimens were coated with Gold-Palladium alloy for 45 s in a Denton Desk II sputter coating unit (Denton Vacuum, Moorestown, NJ). Specimens were analyzed under Hitachi S4700 field emission SEM (Hitachi HTA, Japan) at 2 kV.

Biodegradability tests

Samples were milled to fine consistency (average particle size 25 μm) using a hammer mill under liquid nitrogen environment. About 0.2 g of each sample was mixed with 20 g of compost under appropriate conditions in a 250-mL reaction chamber. Sample chambers were connected to an automated and fully computerized closed-circuit Micro-Oxymax Respirometer System (Columbus Instruments, Columbus, OH) equipped with an expansion interface and a condenser. This system allows monitoring the concentration of gas contained within an enclosed head space (reaction chamber) into which the material being monitored gives off CO_2 as a breakdown product. Periodic sensing of the gas concentration, along with an equally accurate measurement of the volume of the head space, allows calculations of incremental and accumulated values for the production of CO_2 resulting from the material biodegradation. Experiments were carried out at room temperature ($24^\circ\text{C} \pm 0.2^\circ\text{C}$) over a period of 1600 h. The respirometer was programmed to measure CO_2 evolution (mg) from each sample every 6 h as an indicator of biodegradation. Each sample was run in triplicate and averaged. Samples were accompanied by at least duplicate blanks (compost alone) to measure the background CO_2 .

X-ray diffraction

X-ray powder diffraction analyses were performed with a Philips 1820 diffractometer operated at 45 kV, 40 mA with graphite-filtered $\text{Cu-K}\alpha$ radiation. Data were acquired in a 2θ scale from 5° to 35° .

RESULTS

Mechanical properties

Table I shows the mechanical properties of the composites at different coconut fiber loadings.

As shown in Table I, the ϵ of the starch/EVOH/glycerol blends decreased and E increased considerably by $\sim 50\%$ with the incorporation of fibers. Therefore, the ductile behavior of the composites was reduced as a consequence of the rigid nature of the fibers. High elastic modulus composites are usually required in several important applications such as in structural materials.

At low fiber content, the blends were more flexible, with higher TS than at higher contents. The decreased flexibility was expected because the stiffness of coconut fiber is higher than starch and EVOH. Thus, an optimum balance of the mechanical properties (TS, ϵ , E) would occur at low fiber

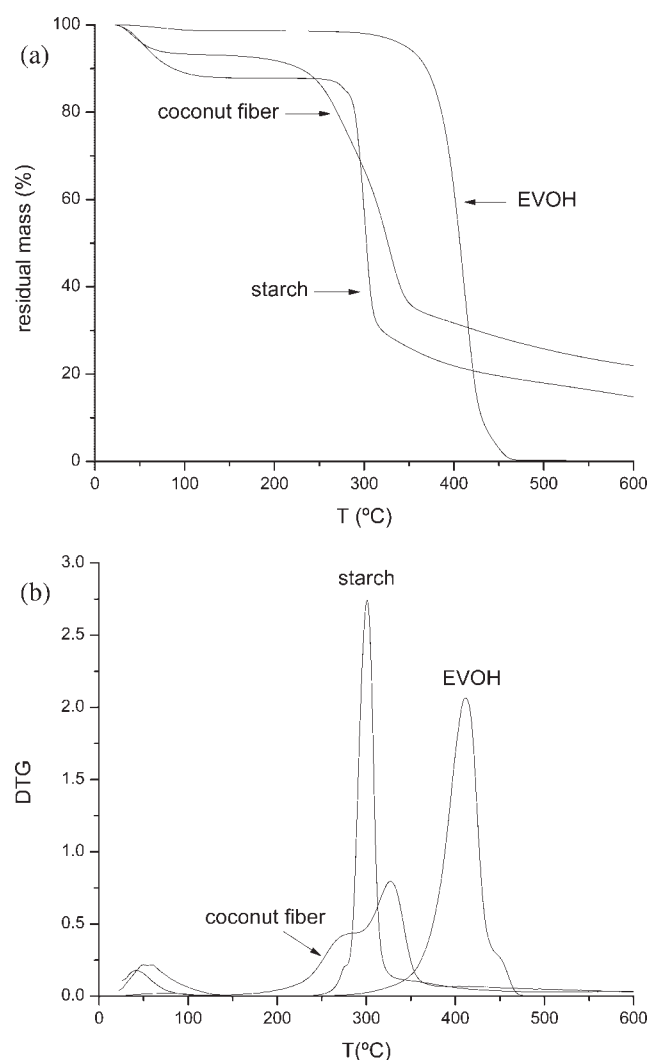


Figure 1 TGA (a) and DTGA (b) curves obtained for coconut fiber, starch, and EVOH.

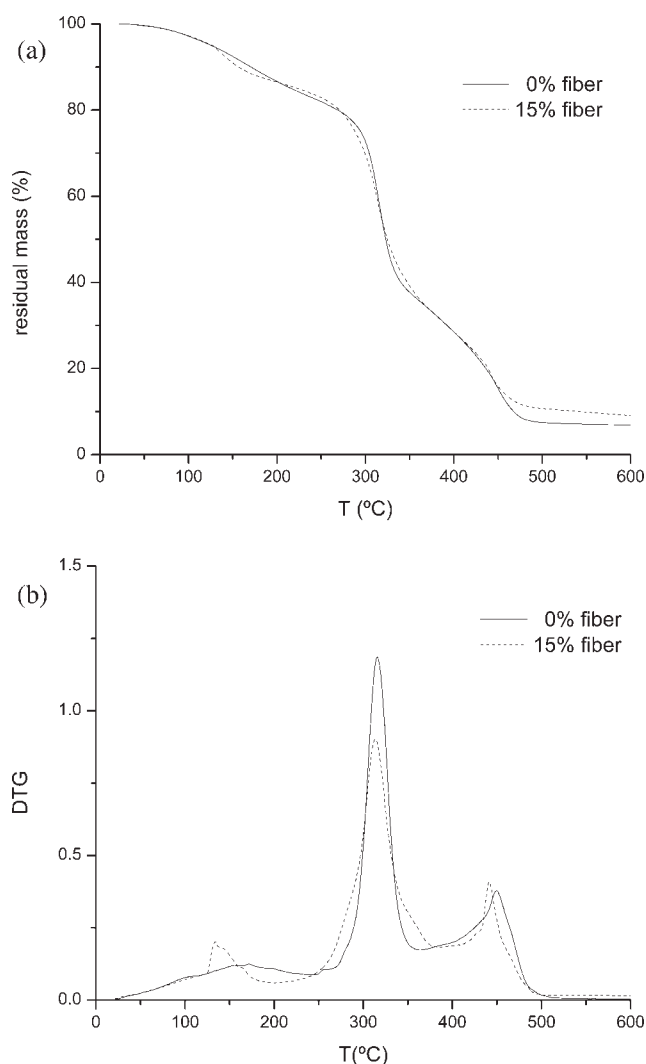


Figure 2 TGA (a) and DTGA (b) curves obtained for starch/EVOH/glycerol composites with 0 and 15% of coconut fibers, as indicated.

contents for certain applications. The decrease in flexibility with increasing fiber has also been observed for other randomly oriented natural fiber reinforced composites.¹² The decrease in TS at the highest fiber loading is associated with a greater possibility of fiber–fiber contact, resulting in an inefficient stress transfer between fibers.¹² Generally, the expected reinforcing effect, among other factors, depends on the interfacial adhesion between matrix and filler, which allows an efficient stress transfer from the matrix to the fibers.

Fiber agglomeration can take place at high fiber loadings, which leads to decrease in stress transfer between the matrix and fiber. Moreover, at higher fiber loading, the possibility of microvoid formation is also higher.¹³

Other studies have also indicated that the incorporation of filler into thermoplastic matrices might not necessarily increase the TS of the composite.^{14–16}

In general, the capacity to support stress transfer from the matrix is poor for fibers with irregular size and shape, such as coconut fibers. Coconut fiber also has low cellulose and high lignin contents and a high microfibrillar angle, which may also account for low stress transfer.¹⁷ However, the adhesion between fiber and matrix can be improved by surface modification of the fibers.⁹

Thermal properties

Thermogravimetric analysis

The results of thermogravimetric analyses of starch, EVOH, and coconut fiber are shown in Figure 1.

The loss of weight at temperatures between 25 and 130°C is attributed to the evaporation of water. The initial degradation of fiber occurs at about 190°C. Coconut fiber presents two decomposition steps: the first between 190 and 290°C corresponding to hemicellulose degradation, and the second step occurs between 290 and 360°C and corresponds to the thermal degradation of cellulose. Lignin degrades between 280 and 500°C.^{18,19} Starch has one decomposition peak with a maximum degradation rate occurring at 301°C. Guinesi et al.²⁰ studied the thermal behavior at several heating rates for starches from corn, rice, potato, and cassava and reported the second step between 274 and 374°C. The second step degradation can be related to the depolymerization and degradation of the starches in a nonoxidative process.²¹ EVOH has the best thermal stability with initial decomposition temperature at about 360°C and one peak at 414°C.

Figure 2 shows TGA and DTGA curves obtained for different biocomposites (0 and 15% fiber).

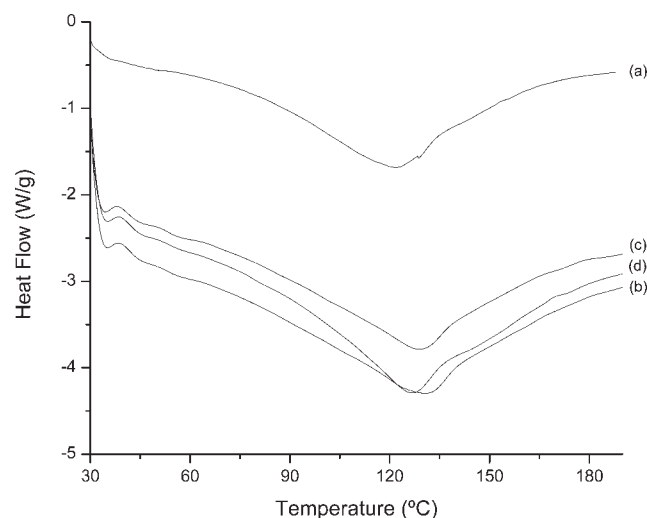


Figure 3 DSC curves for starch/EVOH/glycerol composites with: (a) 0%, (b) 5%, (c) 10%, and (d) 15% coconut fibers.

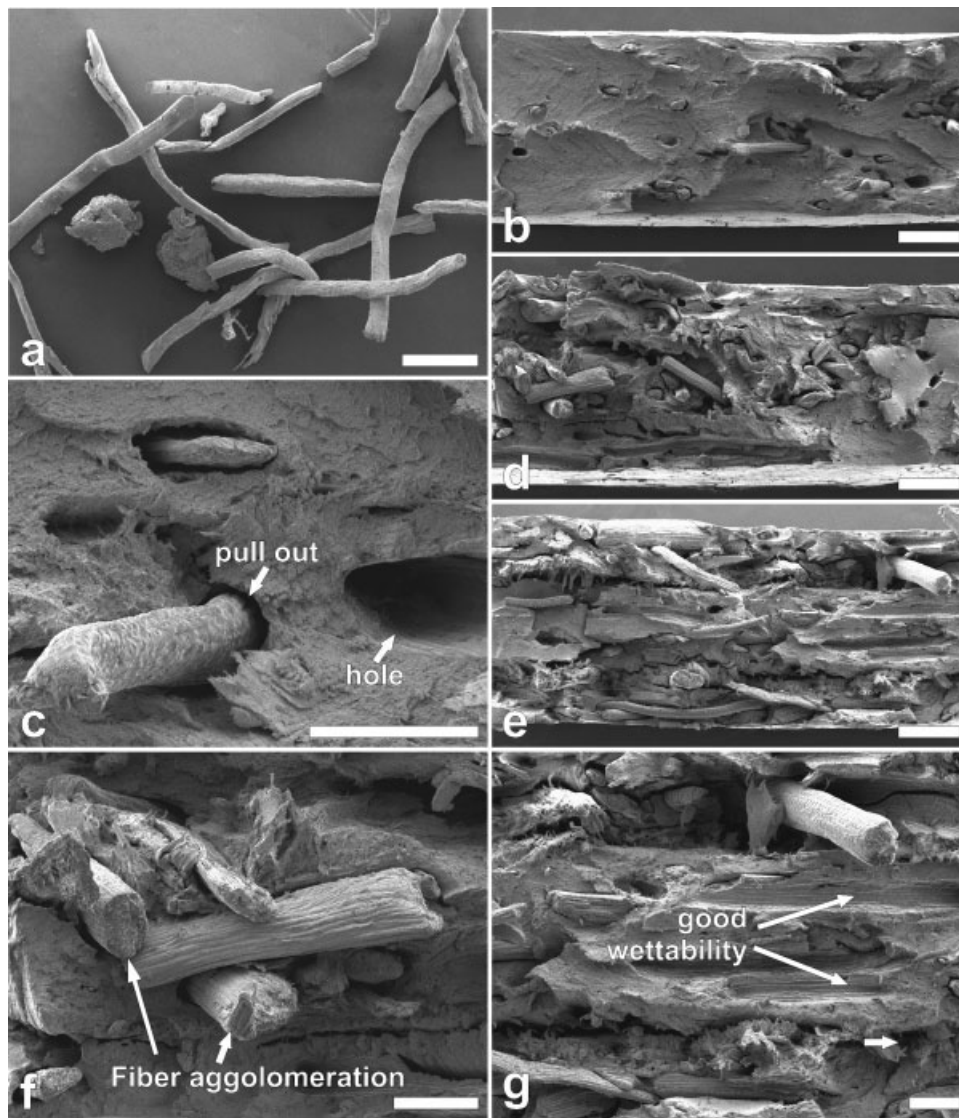


Figure 4 Scanning electron micrographs of (a) coconut fibers and (b–g) fracture surfaces of starch/EVOH/glycerol composites of varying fiber content. (a) Coconut fibers, (b, c) starch/EVOH/glycerol and 5% coconut fiber, (d, f) starch/EVOH/glycerol and 10% coconut fiber, (e, g) starch/EVOH/glycerol and 15% coconut fiber. Scale bars: a, b, d, e = 500 μm ; c, f, g = 200 μm .

Starch/EVOH/glycerol/coconut fiber composites show three different peaks: one at around 150°C, another one at 316–319°C, and the last one at around 445°C. The first, second, and third peaks can be assigned to the decomposition of coconut fiber, starch, and EVOH, respectively. Starch/EVOH/glycerol composites with or without fibers had similar mass loss curves.

The temperature at the maximum degradation rate was shifted slightly to lower values as the fiber content increased because of the decrease in EVOH, which is much more thermally stable than coconut fibers. In addition, the presence of cellulosic fiber decreased the thermal stability of the composite material, compared with that of the raw matrix,

because of the lower degradation temperature of coconut fibers. This is consistent with the work of Albano et al.²² in polyolefin/sisal composites.

Differential scanning calorimetry

Differential scanning calorimetry measurements were performed to characterize the thermal behavior of composites in the presence of coconut fiber. The DSC curves (Fig. 3) show clear transition points; however, there is no drastic change in peak temperature with increasing fiber content. Thus, fiber does not lead to a significant change in the crystalline structure of the matrix (corroborating X-ray diffraction analyses as will be seen later in this work), i.e.,

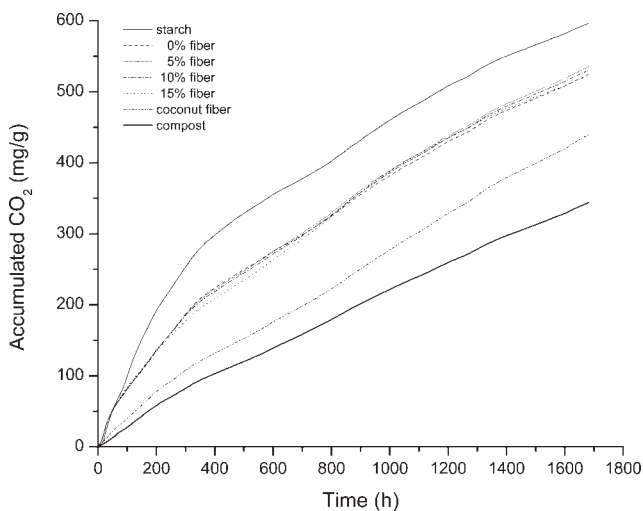


Figure 5 CO₂ released (cumulative) in closed-circuit respirometry of starch/EVOH/glycerol composites with different contents of coconut fiber in compost. Control was compost samples without any additive.

melting temperature is not very dependent on the fiber content of the composites within the temperature range in this study. However, the baseline of the composite curves, when compared with the pure matrix curve, the blend with 0% fiber, shifted toward lower values, which can be related to the increase in the specific heat capacity (C_p) of the composite because of addition of fiber with a different heat capacity [$C_p(25^\circ\text{C}) = 1.34 \text{ J g}^{-1} \text{ deg}^{-1}$].²³ These authors also pointed out that the weight loss associated with water can be observed over a large range, depending on the degree of hydrogen-bonding interaction. The water loss may be evident in a DSC experiment as changes in the baseline.

Scanning electron microscopic studies

Figure 4(a) shows a SEM micrograph of coconut fibers. Fibers appear to vary in shape and size which can explain their poor capability to support stress transfer from the matrix. Figure 4(b–g) shows SEM micrographs of fractured surfaces of starch/EVOH/glycerol composites with different fiber contents.

These micrographs clearly indicate that, despite having an apparently good wettability, the interfacial adhesion between the fibers and the matrix is relatively poor, which results in a less efficient stress transfer between the matrix and the fiber. This can be readily seen from the large number of holes resulting from the fiber pull-out from the matrix.

In spite of the good wettability, there is no evidence or traces of the matrix resin adhering to the fibers. This is an indication that there was not good adhesion between fiber and matrix and the failure process was dominated by the matrix/fiber interface.

The interfacial shear strength between the natural fibers and the thermoplastic matrix might be improved by chemical modification of the fiber surface. Because lignin contains both polar hydroxyl groups and nonpolar hydrocarbon and benzene rings, it is believed that a pretreatment may increase the surface roughness, thereby resulting in better mechanical interlocking. Pretreatments such as mercerization and bleaching may also increase the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites.²⁴

Biodegradability tests

Initially, all samples degraded rapidly in compost. However, after 200 h, samples consisting of starch alone, starch/EVOH/glycerol with or without fiber, and fiber alone all exhibited distinctly different rates and extents of degradation. As expected, starch alone degraded most rapidly followed by starch/EVOH/glycerol composites with or without fiber. As shown in Figure 5, composites subjected to biodegradation produced 24.4–28.8% less CO₂ when compared with starch in the test system. Fiber alone degraded much more slowly than the other samples, which can be attributed to the very high lignin content (38%) present in the fibers. Interestingly, the presence

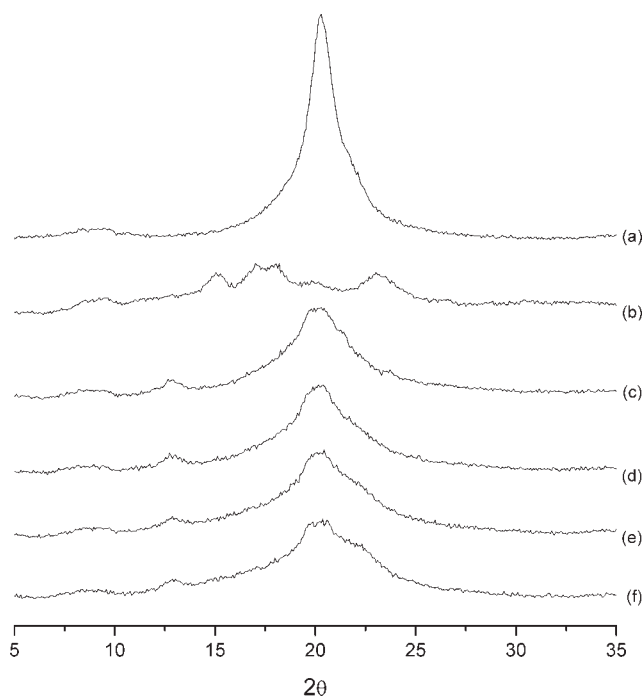


Figure 6 X-ray powder diffraction scans of starch/EVOH/glycerol composites at different content of fibers. (a) EVOH, (b) starch, (c) starch/EVOH/glycerol, (d) starch/EVOH/glycerol/5% coconut fiber, (e) starch/EVOH/glycerol/10% coconut fiber, and (f) starch/EVOH/glycerol/15% coconut fiber.

of fiber in any amount had no impact on the degradation of starch/EVOH/glycerol composites.

X-ray diffraction

X-ray powder diffraction patterns of starch, EVOH, and composites with different fiber contents are shown in Figure 6. The starch/EVOH/glycerol blend consists mainly of the combination of the diffraction peaks of both components and some other changes including the disappearance of three peaks at $2\theta = 15$, 17 , and 23° and appearance of another peak at $\sim 12.7^\circ$. This behavior can be attributed, respectively, to partial destruction of the starch crystalline phase, including the amylose–lipids complex formation, which appears in diffraction patterns at $2\theta = 23^\circ$ ²⁵ and cocrystallization of starch and EVOH into a more imperfect crystalline phase. Results of Figure 6(c–f) also show that composites with fiber exhibited basically the same crystalline pattern when compared with starch/EVOH/glycerol blend without fibers, but with a slight appearance of a shoulder for 2θ values between 21° and 23° , which is associated with the addition of crystalline coconut fibers as reported by Tomczac et al.¹⁹ These minor modification upon fiber addition are also supported by DSC results that showed minor changes in baseline and some inflections between 166 and 173°C for composites loaded with 15% of fibers.

CONCLUSIONS

The effects of coconut fiber content on the tensile, thermal, structural, and biodegradability properties of starch/EVOH/glycerol blends were characterized in this study. The data indicated that an increase in coconut fiber content resulted in a decrease in TS and ϵ , but a significant improvement in E . SEM results showed that tensile properties of composites were influenced mainly by lack of adhesion between the matrix and fibers. The results also indicated that size and shape irregularities might play a dominant role in the ultimate properties. It was found that the fiber content slightly influenced thermal stability of the resulting composites, but did not lead to major changes in crystallinity and biodegradability of the materials. The coconut fiber represents an additional source of renewable biomass with attractive properties. Additionally, it is also inexpensive and available in abundance and remains mostly unexploited. Its incorporation into biocomposites as fillers can

provide substantial cost saving without critically compromising the properties of the composites.

The authors thank the technical support given by EMBRAPA, Labex/program, CNPq, FINEP, CAPES, and ARS/USDA. They also thank Tina G. Williams for assistance with the scanning electron microscopy.

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