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A Preliminary Study for the Use of Natural Fibers as Reinforcement in Starch-Gluten-Glycerol Matrix

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Summary: Mercerized and nonmercerized coconut, jute and sisal fibers were combined with a matrix of gluten/starch/glycerol to produce composite materials. All nonmercerized fibers improved the mechanical properties of the composites. After mercerization of the fibers, the composite reinforced with sisal fibers exhibited lower values of Young's modulus and ultimate tensile strength than composite with nonmercerized sisal fiber, whereas these properties were improved in the composites reinforced with mercerized coconut and jute fibers.

Keywords: composites; gluten; mercerization; natural fibers; starch

Introduction

Starch and gluten are interesting natural polymers to be used as matrix in biocomposite due to their biodegradability, low cost and availability.[1,2] Additionally, these polymers can be processed as a thermoplastic material in the presence of plasticizers with high boiling-points, such as trietylene glycol, glycerol, oleic acid, etc. by injection, extrusion or blow-molding, similarly to most conventional synthetic thermoplastic polymers.[3–5] Unfortunately, thermoplastics from natural polymers are very sensitive to water and have poor mechanical properties. Several attempts have been made to overcome these drawbacks, such as chemical modification,[6] blending of natural polymer and non-biodegradable commercial polymers,[7] reinforcement with inorganic materials[8] and natural fibers.[9,10] The use of natural fibers as reinforcement for biodegradable polymers presents a great potential for improving their perfomance and tecnological application, due to their low cost, abundance, biodegradation and high strength.[11–13] Properties of fiber-reinforced composites depend on many factors such as fiber-matrix adhesion, volume fraction of fiber, fiber orientation, etc.[14] Some approaches have been applied to enhance the fiber-matrix adhesion in natural fiber-reinforced composite by chemical or physical modification of the fibers.[15] The alkaline treatment or mercerization is one of most used because it is a simple and inexpensive method.[16–20] This method removes the artificial impurities thereby producing a rough surface topography, which make the contact with the matrix better and consequentely improve the mechanical properties of the matrix.[18,20]

In this study, sisal, jute and coconut fibers were used as reinforcement for a biodegradable polymer matrix of gluten/starch/glycerol. The mechanical properties of the composites and the effect of chemical modification (mercerization) of the fibers were evaluated.

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Experimental

Materials

Hybrid corn starch containing ca. 27% amylose (commercially known as “amisol 3408”) and corn gluten (60–70% protein, 20% starch and 4% lipids) were kindly supplied by Corn Products Brasil Ltda. Coconut, sisal and jute fibers were supplied by EMBRAPA Agroindústria de Alimentos, (Brazil, PE). Analytical grade glycerol and sodium hydroxide were purchased from Synth Ragents and used as received.

Mercerization of the Fibers

Coconut, sisal and jute fibers were washed in distilled water, prior to the chemical treatment. The fibers were immersed in a sodium hydroxide 10% aqueous solution at 70 °C, for a period of 3 hours. After this alkaline treatment, the fibers were washed in distilled water and dried.

Matrix and Composites Preparation

The composition of matrix was starch (35%, weight), gluten (35%, weight), glycerol (20%, weight) and water (10%, weight). The weight of fibers in the composites was 10% by weight of total weight of polymers (starch and gluten). The fibers used for preparation of composites were cut into ca. 7mm lengths. The composites were processed in a Haake torque rheometer at 120 °C, at 50 rpm for 10 min. The mixtures thus obtained were molded by hot compression in a hydraulic press equipped with heating plates and controlled temperature. The mold, which was placed between the plates, consisted of three 150 mm × 120 mm × 2.5 mm stainless steel plates. The material was transferred into the mold at a temperature of 120 °C, where it was left for 2 min without applying pressure in order to allow for its partial melting, after which a force of 5 tons was applied for 10 min. The mold was then allowed to cool down to 80 °C, after which the molded material was removed.

Characterization

The infrared spectra of nonmercerized and mercerized fibers were recorded from KBr pellets, using a Perkin Elmer FT-IR spectrometer model Paragon 1000.

The nonmercerized and mercerized fibers and composites were subjected to tensile tests in a universal testing machine (Instron, model 5569), following the ASTM D3379[20] standard. The testing conditions used for the fiber tests were: clamp displacement speed: 2.0 mm/min, load cell: 50N, fiber length: ca. 5.4 cm. At least 20 fibers were tested in each assay. Specimens used for the tensile tests of the composites were prepared acccording to the dimensions specified in the ASTM D638M, type II[21] standard. Prior to the tensile testing, the samples were conditioned in a relative humidity of 52% ± 2 and weighed at successive intervals until they reached absorption equilibrium. The tests were conducted with a 500N load cell and a clamp displacement speed of 5 mm/min.

The fibers and composites morphologies were analyzed by scanning electron microscopy (Zeiss DSM 960). The composites were fractured in liquid nitrogen.The samples were coated with a fine layer of silver and then metallized with gold in an argon plasma sputter coater (Balzers, model SCD 50).

Results and Discussion

Figure 1 shows the FTIR spectra of the mercerized and nonmercerized sisal, coconut and jute fibers.

The absorption bands in the spectra are typical of lignocellulose materials, which are constituted mainly of cellulose, hemicellulose and lignin.[17] Although the fibers possess the same constituents, these are present in different contents in the fibers, as shown in Table 1. The absorption bands at 1735 cm^{-1}, which were attributed to ester carbonyl stretching,[17] were present in the nonmercerized fibers but absent from the mercerized ones. The absorption intensity of CH angular deformation at 1240[17] diminished significantly in the mercerized coconut fiber spectrum, disappearing completely from the spectra of mercerized sisal

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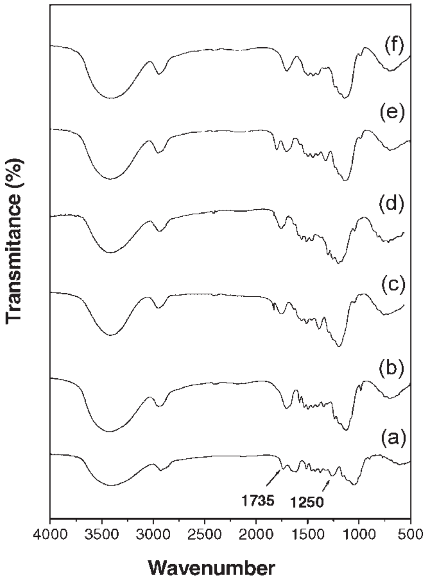

Figure 1.

FT-IR spectra of nonmercerized and mercerized fibers: (a) nonmercerized coconut fiber, (b) mercerized coconut fibers, (c) nonmercerized sisal fibers, (d) mercerized sisal fibers, (e) nonmercerized jute fibers, (f) mercerized jute fibers.

and jute fibers. These changes indicate the partial removal of lignin and hemicellulose from the fibers surfaces.

Figure 2 shows the SEM photomicrographs of the nonmercerized and mercerized fibers, showing the changes on the surfaces of mercerized fibers compared with nonmercerized ones. The surface of the nonmercerized coconut fiber (Figure 2a) shows that the fibrils that make up the fiber are covered with a layer of material called cuticle, which is identified as aliphatic wax.[22] The surface of the mercerized fiber (Figure 2b) presents modifications, indicating that the mercerization partially removed the cuticle layer, leaving the fibers more visible and with a few globular markings. The surface of the nonmercerized sisal fiber (Figure 2c) shows not only transversal markings originating from the parenchymal cells that surround the fiber but also the presence of impurities. After the alkaline treatment (Figure 2d), the impurities and parenchyma cells are partially removed and the fibrils that form the sisal fiber are separated. The nonmercerized jute fiber (Figure 2e) shows a smooth wax-coated surface while the mercerized jute fiber (Figure 2f) displays a rougher surface.

These results indicate that the alkaline treatment not only removed impurities from the surfaces of the fibers but also partially removed lignin and hemicellulose, thereby producing a rougher surface, which may contribute to increase the adhesion between the fibers and the matrix. The alkaline treatment of the fibers affects their mechanical properties by increasing the crystallinity of the cellulose, leading to an increase in tensile strength and modulus of elasticity.[23] However, depending on the conditions of the treatment, (concentration, time and temperature), this may cause intense defibrilation, decreasing the mechanical strength of the fibers, and consequently, the reinforcement of composites.[18,24]

Table 2 shows the mean values of Young's modulus (E), elongation at break (ε_r), and ultimate tensile strength (σ_r) obtained for the nonmercerized and mercerized fibers.

The higher E and σ_r values presented by the sisal fibers than those presented by coconut and jute fibers is attributed to their higher cellulose content, which is the main factor responsible for the mechanical strength of fibers, in addition to fiber

Table 1.

Principal constituents of sisal, coconut and jute fibers.[13,23]

Component	Sisal (wt.-%)	Coconut (wt.-%)	Jute (wt.-%)
Cellulose	67–78	36–43	61–71.5
Hemicellulose	10–14	0.15–0.25	13.6–20.4
Lignin	8–11	41–45	12–13

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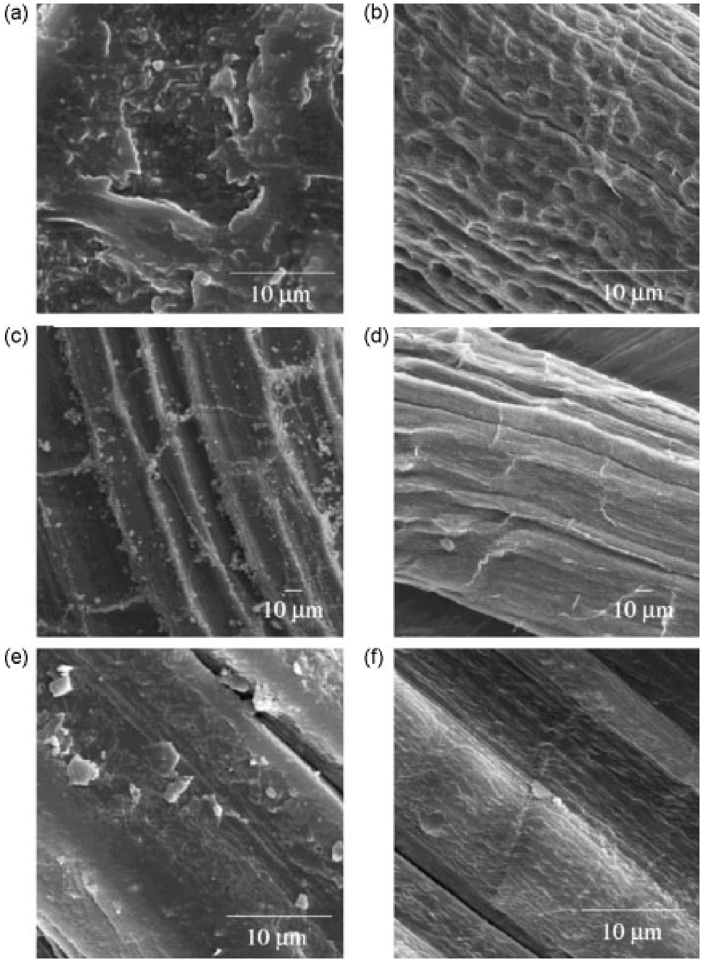

Figure 2.
SEM images of surface of fibers: (a) nonmercerized coconut fibers, (b) mercerized coconut fibers, (c) nonmercerized sisal fibers, (d) mercerized sisal fibers, (e) nonmercerized jute fibers, (f) mercerized jute fibers.

morphology.[25] On the other hand, the chemical treatment of mercerization of the sisal fibers caused a considerable reduction of the E e σ_r values. In the jute fibers, the chemical treatment also led to a reduction of the E, albeit less marked than in the case of the sisal fiber. The mechanical properties of the coconut fiber varied only slightly in response to the alkaline treatment. The different effects of the chemical treatment

Table 2.
Young's Modulus (E), ultimate tensile strength (σ_r) and elongation at break (ε_r) obtained for nonmercerized and mercerized fibers.

	E (GPa)	ε_r (%)	σ_r (GPa)
Nonmercerized sisal fibers	38.1 ± 12.1	3.2 ± 0.5	1.5 ± 0.3
Mercerized sisal fibers	25.2 ± 4.7	6.5 ± 0.8	1.2 ± 0.2
Nonmercerized jute fibers	15.4 ± 2.5	8.2 ± 0.8	0.4 ± 0.1
Mercerized jute fibers	9.6 ± 1.4	7.8 ± 1.5	0.3 ± 0.04
Nonmercerized coconut fibers	2.2 ± 0.98	19.9 ± 7.8	0.11 ± 0.02
Mercerized coconut fibers	1.8 ± 0.6	22.7 ± 5.8	0.14 ± 0.06

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Table 3.
Water absorption (WA), Young's Modulus (E), ultimate tensile strength (σ_r) and elongation at break (ε_r) of matrix (starch/gluten/glycerol) and of composites: (a) nonmercerized coconut fibers, (b) mercerized coconut fibers, (c) nonmercerized jute fibers, (d) mercerized jute fibers, (e) nonmercerized sisal fibers, (f) mercerized sisal fibers.

	WA(%)	E (MPa)	ε_r (%)	σ_r (MPa)
Matrix	9.2 ± 0.2	161 ± 22	3.30 ± 0.36	2.53 ± 0.23
(a)	7.8 ± 0.9	331 ± 55	2.19 ± 0.31	4.45 ± 0.30
(b)	7.5 ± 0.3	504 ± 47	1.43 ± 0.35	4.82 ± 0.59
(c)	7.2 ± 0.3	466 ± 45	1.49 ± 0.04	4.71 ± 0.39
(d)	7.6 ± 0.3	538 ± 54	1.48 ± 0.34	4.89 ± 0.66
(e)	7.2 ± 0.3	621 ± 54	1.08 ± 0.12	4.80 ± 0.43
(f)	7.6 ± 0.2	404 ± 58	1.49 ± 0.45	3.79 ± 0.52

on the fibers mechanical properties were probably due to the differences in the physical structure and chemical composition of the fibers.

Table 3 lists the mean values of water absorption (WA), Young's modulus (E), ultimate tensile strength (σ_r) and elongation at break (ε_r) of the composites reinforced with nonmercerized and mercerized fibers. It is observed that the slight reduction in water absorption due to the introduction of fibers into the matrix. This variation cannot be considered sufficiently significant to be attributed to an increase in the system's hydrophobicity.

The results obtained from the tensile tests of the composites reinforced with nonmercerized and mercerized fibers indicate that the values of E and σ_r were considerably higher than those obtained for the matrix, indicating the great potential of the fiber to be used as reinforcement for this system. The composites reinforced with mercerized coconut and jute fibers dis-

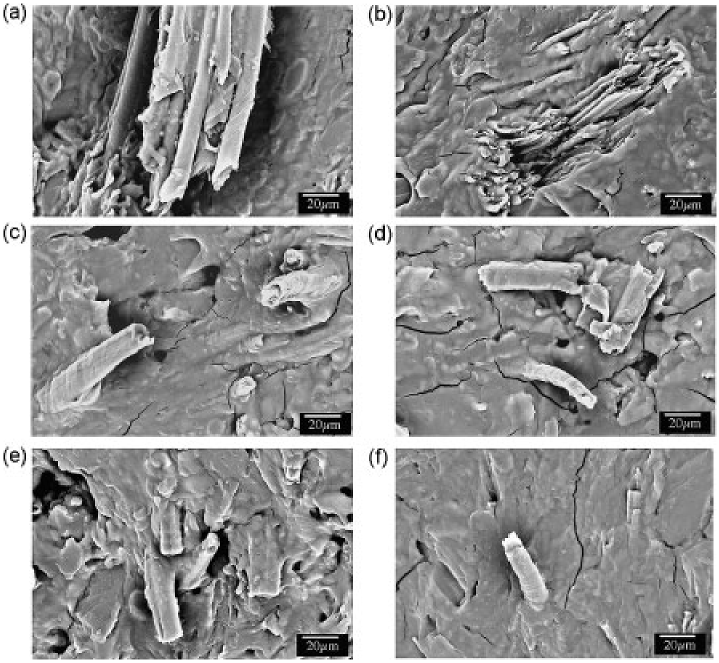

Figure 3.
SEM images of composites reinforced with mercerized and nonmercerized fibers: (a) nonmercerized coconut fibers, (b) mercerized coconut fibers, (c) nonmercerized sisal fibers, (d) mercerized sisal fibers, (e) nonmercerized jute fibers, (f) mercerized jute fibers.

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played higher E and σ_r values than those reinforced with nonmercerized coconut and jute fibers. On the other hand, the composites reinforced with mercerized sisal fibers showed lower E and σ_r values than those obtained for the composites reinforced with nonmercerized fibers. Although the alkaline treatment did not improve the mechanical properties of the coconut and jute fibers, it was an effective method to improve the properties of the composites reinforced with coconut and jute fibers. This indicates that the conditions of mercerization used led to modifications of the fibers surfaces, improving their adhesion to the matrix.

The adhesion between fibers and matrix was investigated based on images of the composites' fracture surfaces, which are depicted in Figure 3.

As it can be seen, the mercerization improved the interfacial adhesion between the matrix and coconut and jute fibers (Figures 3a–b and 3e–f), which was reflected in an increase in the E and σ_r values. In the case of the composites reinforced with sisal fibers, the chemical modification of those fibers apparently did not improve the fiber/matrix adhesion (Figure 3c–d). This behavior may be associated with the fact that the alkaline treatment altered the internal structure of the sisal fibers due to the conditions of the alkaline treatment, and hence significantly reduced their mechanical strength, in aggreement with the tensile tests which revealed that the value of E of the mercerized fibers dropped by 50% in comparison to the nonmercerized sisal fibers. Further studies will be conducted varying the conditions of the alkaline treatment of the fibers to optimize their performance as reinforcements in biodegradable starch/gluten/glycerol composites.

Conclusion

Sisal, coconut and jute fibers favored an improvement in mechanical properties, when used as reinforcement in the gluten/starch/glycerol composites. The chemical treatment of these fibers by mercerization affected the mechanical properties of the fibers themselves as well as those of composites produced. An improvement in Young's modulus and ultimate tensile strength of composites reinforced with treated coconut and jute composites was observed due to the increase on the surface roughness of the fiber.

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