Properties of Thermoplastic Corn Starch Based Green Composites Reinforced with Barley (*Hordeum vulgare* L.) Straw Particles Obtained by Thermal Compression

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Abstract: Currently, greater environmental awareness promotes research and development advances in biodegradable materials; they represent an alternative that decreases the environmental impact caused by traditional synthetic plastics. This study consists of the development and characterization of thermoplastic corn starch-based composites, reinforced with barley straw particles made by thermal compression. The study materials were prepared by using three particle concentrations (5, 10, and 15 %), while the matrix (0 %) was used as a reference. A mechanical evaluation of all samples was carried out, as well as that of their water absorption properties. They were also characterized by scanning electron microscopy (SEM), infrared spectroscopy (FTIR), X-ray diffraction (XRD), and flammability tests. The inclusion of straw in the thermoplastic matrix increased water absorption and quickened carbon formation, although it also increased its tensile strength (7 MPa) and the Young's modulus of activity (MOE) (420 MPa) with a 15 % reinforcement. The FTIR analysis highlights the presence of a carbonyl signal (1720 cm^{-1}) caused by a thermal breakdown (caramelization) linked to barley particles. Moreover, X-ray diffraction demonstrated a V_A-type crystallinity pattern (anhydrous) within the biocomposites and an increase of the crystallinity index, through incorporating barley particles in the thermoplastic corn starch-based matrix.

Keywords: Thermoplastic starch, Barley straw, Green composites, Thermal compression

Introduction

Synthetic polymers have been widely used in the application of human products, the petroleum-derived plastics representing around a fifth of household waste in cities. During the last few decades, the plastic volume and related issues about its disposal and prolonged degradation time have caused several environmental problems [1].

Conversely, the increasing demand for technologies (and products that cause less environmental impact) has driven ecologic awareness and an interest in studying and applying biodegradable and renewable raw materials. Research in the material engineering field has developed easily degradable packaging materials that are less harmful to the environment [2]. The adaptation of composite materials, classified in the scope of sustainable development and included in ecological projects, is a philosophy being applied in both technology and new materials development.

Starch is the second most abundant polymer in the world after cellulose, and it is obtained from renewable resources [3]. Plants synthesize and store starch within their seeds (corn grain, wheat, rice, sorghum, barley, and beans) as well as within their tubercles and roots (potato, cassava, yucca), used as an energy reserve by the plant. Starch is considered a promising candidate for sustainable materials development, as it (i) is a natural occurring polymer, (ii) economical, (iii) abundant, and (iv) biodegradable. It can be turned into plastic through temperature change and shearing. A partial substitution of the original hydrogen bonds between amylose and amylopectin macromolecules with other hydrogen bonds and the plasticizer is needed [4]. Thermoplastic starch materials (TPSs) may be reinforced with lignocellulosic fibers to produce biocomposites or "green" composites, a special class of composite materials that are currently quite relevant. As every component is biologically- or naturally-derived, it is considered completely biodegradable. Generally, all composite materials made from thermoplastic starch display low mechanical properties. As such, the inclusion of lignocellulosic fibers has been proposed, as they may improve its mechanical performance [5]. There is no limitation regarding the use of natural fibers as a reinforcement for a thermoplastic starch matrix, including non-timber fibers (kenaf, jute, sisal, coconut, banana, sugarcane bagasse, etc.) and wood particles (hard and soft woods). All vegetable resources may be used directly from the production process or in the form of residues from a number of agricultural activities.

Several studies have demonstrated improved properties of thermoplastic starch [6-8] by including several types, along with lignocellulosic fiber materials. The use of natural fibers is considered to be renewable, biodegradable, and less of a pollutant on the environment, and may be obtained from several plant species. The use of vegetable fibers as composite reinforcement has the following advantages: abundance, low cost, low density, lack of toxicity, non-abrasive, biodegradable, anisotropic, viscoelastic, reactive, renewable, recyclable,

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and compostable: their handling is also safer in comparison with synthetic fibers. High-resistance products are obtained with a highly specific modulus, as well as suitable thermal stability, high electric resistance, and good acoustic properties [9]. Barley is an agricultural waste that is increasingly produced in large amounts, but has no intended use. According to reports by the Food and Agriculture Organization (FAO) in 2014, it is the fourth most harvested cereal worldwide, with approximately 145.5 million tons produced [10]. Barley straw represents an important source of lignocelluose material that may be used as raw material in several industrial processes or as a reinforcement of polymeric matrices [11,12].

Thermoplastic starch (TPS) is a sustainable component that incorporates reinforcements of natural origin to form biocomposites that are completely biodegradable. Most of them are obtained following a typical injection-extrusion process of several steps; every step involves time and energy consumption. On the other hand, biocomposites prepared by thermal compression offer several advantages in comparison to the traditional injection-extrusion process: (i) the process is relatively new, (ii) fibers are used as a reinforcement to be better distributed in the matrix, (iii) they are economically profitable, since the complete process of plasticization takes place in one step, saving energy and preparation time.

Thus, this study aims to develop biocomposites from thermoplastic corn starch by incorporating barley straw particles to act as a reinforcement by thermal compression (within the scope of producing environment-friendly materials). Mechanical, structural, and chemical evaluations of the matrix and biocomposites (related to different amounts of barley straw) assess tensile strength, water absorption, and use a flammability test (knowing the combustible properties of biocomposites are an important parameter), optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD) and infrared spectroscopy (FTIR).

Experimental

Materials

Native corn starch was supplied by Indumex, Monterrey N.L., barley straw (Financiera Cebaderos S.A de C.V del Valle de Apan, Hidalgo, Mexico) and glycerol reactive degree (Golden Bell) were used for preparing the TPS matrix and the composites.

Samples Preparation

The barley straw was dried, milled and sieved to obtain particles of length of mostly 425 μc. The cornstarch was mixed thoroughly with 30 wt. % glycerol in a plastic bag until attaining a homogeneous mixture. Then, the particles of barley straw were added in different proportions to prepare the composites with 5, 10 and 15 %, they were compared with the thermoplastic matrix (0 %). These

mixtures were transferred to a stainless steel mold (170 mm ×170 mm×3 mm) to process composite. A hydraulic press (Smart Steel model HI-TR2014) with a heating system and controlled cooling was used to obtain the laminates of both the thermoplastic starch (TPS) matrix and composites. The processing conditions used were: temperature 160 $^{\mathrm{o}}$C with applied pressure 100-150 bar and pressurization time of 50 min. From the resulted laminated biocomposites were obtained the specimens for mechanical testing, water absorption, X-ray diffraction, behavior to the flame and chemical characterization by FTIR.

Water Absorption Test

The percentage of water absorption was evaluated following the EN 317 standard (EN 317-1993) [13]. For this test, specimens measuring 30×30×3 mm cut from the laminates plaques were first dried in an air-circulating oven at 60 $^{\mathrm{o}}$C and then immersed in water at room temperature (23 $^{\mathrm{o}}$C) for 2 and 24 h respectively. To determine the percentage of water absorption, the samples were weighed before and after immersion.

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

$$\% \ WA = [(M_1 - M_0/M_0) \times 100] \tag{1}$$

where, M_0 and M_1 are the masses of the sample before and after immersion in water.

Tensile Strength

Tensile samples of the matrix and the composites were cut from respective laminates (plaques) using a laser cutting machine (Guian Modelo GN 600 LS). The samples obtained were tested in a universal testing machine (Instron model 4411), following ASTM standard D 638M [14] (specimen type 1). All the specimens were tested after of thermal treatment of which consisted of placing them in a drying oven at 50 $^{\mathrm{o}}$C for 5 hours. Seven specimens were tested for each sample and the average values of the tensile strength, Young's modulus and percentage of elongation were recorded.

Flammability Test

The behavior to the composite specimens to flame was made based on the ASTM D-635 [15]. For this assay, the samples are approached to a flame of a Bunsen burner for 10 seconds to start burning. The parameters that were measured were the amount and color of smoke, the color of the flame, the kind of combustion, the odor, if fire is self- extinguished, the possible deformation of the test and combustion rate (mm/s).

Infrared Spectroscopy with Attenuated Total Reflectance (ATR)

The FTIR analyses of the native starch and the bio-

composites samples were performed in a Perkin-Elmer (model Spectrum GX) spectrophotometer by means of ATR (Attenuated Total Reflectance) technique. All IR spectra were the average of 64 scans with a resolution of 4 cm^{-1} within a frequency of 4000-700 cm^{-1}.

Optical Microscopy

A Motic stereoscope microscope (model K-400L) equipped with a Moticam camera was used to observe the transparency obtained in the composites, porosity and the distribution of the particles of barley straw in the matrix of thermoplastic starch. The composites were observed with no previous preparation.

Scanning Electron Microscopy (SEM)

Through a Hitachi (model TM 1000) scanning electron microscope was observed the fracture surface of the specimens used in the tensile strength test, without gold addition.

X-ray Diffraction (XRD)

X-ray diffraction (XRD) studies were carried out using a Shimadzu diffractometer (Model XRD 7000), with monochromatic Cu Kα radiation (k=1.5418 Å), at operation conditions of 40 KeV and 20 mA to determine the crystallinity of the materials. All samples were dried at 60 °C during 8 h, composites specimen used had dimensions of 40×20×0.3 mm, while the starch sample was in the powder form. The analysis was carried out in the 2θ angle range of 2.5° to 60° with a scanning speed of 1°/min. The relative crystallinity of starch and composites was calculated according to equation (1) [16], based on the deconvolution calculus of amorphous and crystalline areas calculated with the aid of the computer program ORIGIN 8.5.

$$IRC = (AC/AC + AA) \qquad (2)$$

where, RC is the index relative crystallinity, AC is the crystalline area and AA is the amorphous area in the XRD pattern obtained.

Results and Discussion

Water Absorption

Water sensitivity is an important criterion for many practical applications of starch-based thermoplastic products: their water absorption in high humidity or in direct contact with water is very important, because it determines their integrity and performance under adverse conditions [17,18]. Thermoplastic starch composites have a hydrophilic character due to their chemical composition of starch (amylopectin and amylose), and the hydroxyl groups and oxygen form hydrogen bonds with water [18]. In addition, a plasticizer increases the affinity to moisture [19]. Table 1 shows the percentage of water uptake by the composites containing

Table 1. Water absorption in matrix (0 %) and the biocomposites

Material	Water absorption	
	2 hr (%)	24 hr (%)
0 %	41.6 (4.9)	95.1 (9.0)
5 %	48.3 (3.4)	105.0 (5.6)
10 %	86.3 (4.2)	113.9 (5.1)
15 %	100.6 (4.5)	116.9 (6.4)

different amounts of particles of barley. After 2 h, the TPS matrix showed 41.6 % of water uptake, while incorporation of barley straw increased this amount up to 100 %, in the composite with 15 %. Incorporation of barley particles in the starch matrix with water uptake was more evident after 24 h. The thermoplastic starch matrix absorbed water up to 95.1 %, while all composites (5, 10, and 15 % barley straw) showed water absorption above 100 %. Increased incorporation of barley straw particles in the starch matrix also increases water uptake. This may be because barley straw has a great deal of parenchyma, and a hydrophilic character. Saetun *et al.* [6] reported an increase of water absorption with 12 wt% rubber wood sawdust in TPS composites. However, several authors report a less hydrophilic nature of composites when lignocellulosic fibers are included in the matrix, as biocomposite water absorption decreases when cellulose fiber is added with its crystalline features [18].

Tensile Strength

Figure 1 shows the matrix tensile strength (0 % particles), as well as that displayed by biocomposites containing 5, 10, and 15 % barley particles. It is noticeable that only 10 and 15 % concentrations show significant differences for increased tensile strength by including a reinforcement. Shah *et al.* [21] and Müller *et al.* [22] point out that the
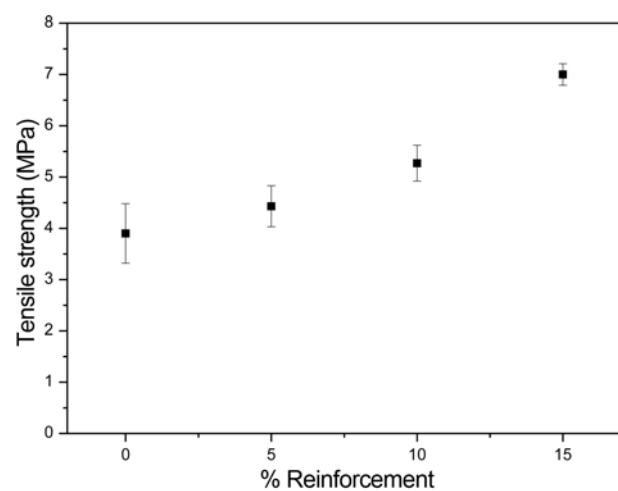

Figure 1. Results of tensile strength of matrix (0 % barley straw particles) and the biocomposites (5-15 %).

enhanced mechanical properties (e.g., tensile strength) of starch-based composite materials compared to those of the matrix (0 %) confirm the interfacial attachment and improved interactions between the matrix and lignocellulosic fibers. These results are favored by chemical similarities between starch and cellulose fibers. In addition to the type and amount of reinforcement, the starch type (native or modified) used, the amount and type of plasticizer, and the thermoplastic starch processing method also impacts the resistance properties. For instance, with the tensile strength, Müller *et al.* [23] reported values ranging between 1.59 and 26.6 MPa by using cellulose fibers (eucalyptus) with the casting method. Guimarães *et al.* [24] found 1.73-4.34 MPa by using sugarcane bagasse with the thermal conformation method, and Texeira *et al.* [25] reported 1.6-4.6 MPa by using cellulose nanofibers by Haake's rheometer; Corradini *et al.* [26] used coconut fibers to reinforce a starch matrix processed with Haake's rheometer and reported a 4.45 MPa value, whereas Ma *et al.* [18] found values between 5 and 15 MPa using cotton textile fibers in biocomposites, processed by extrusion. The results obtained for tensile strength, caused by the inclusion of barley particles, are within the expected range for thermoplastic starch-based composites by other authors. Prachayawarakorn *et al.* [27] reported lower values of 3, 4, and 5 MPa for tensile strength by studying 5, 10, and 15 % jute and kapoc reinforcements. Saetun *et al.* [6] found tension values of 1.2 MPa for thermoplastic starch biocomposites, containing 12 % wood sawdust and 0.7 MPa when a 12 % reinforcement with thermal compression of commercially available cellulose was used. Previously, Lomelí *et al.* [8] evaluated the tensile strength of composites made from cassava starch, reinforced with different concentrations of green coconut fiber. The tensile strength values were 3.5, 5.8, 7.9, and 9 for biocomposites with 0, 5, 10, and 15 % reinforcements, respectively. These are slightly higher than in the present study associated with mechanical properties of coconut fibers used as reinforcement.

Sarsari *et al.* [9] examined walnut shell composites through three compatibilization processes: (i) haake rheometer, (ii) extrusion, and (iii) pellets processed by injection, as well as by powdered maleated anhydride grafted polypropylene (MAPP) as a coupling agent to improve the interface between components. Although the process involved shear and chemical compatibilization, the tensile strength obtained with 0 and 30 % reinforcement was not in accordance with the values of 5 and 6 MPa, respectively. Recently, Guleria *et al.* [10] evaluated the properties of thermoplastic starch crosslinked with urea formaldehyde and reinforced with okra cellulosic fiber through thermocompression. The values of tensile strength reported were 11.2, 12.1, 14.8, and 17.7 MPa with 0, 5, 10, and 15 % reinforcement, respectively. These results are higher due to the type of reinforcement used, as well as the crosslinking of the starch, which
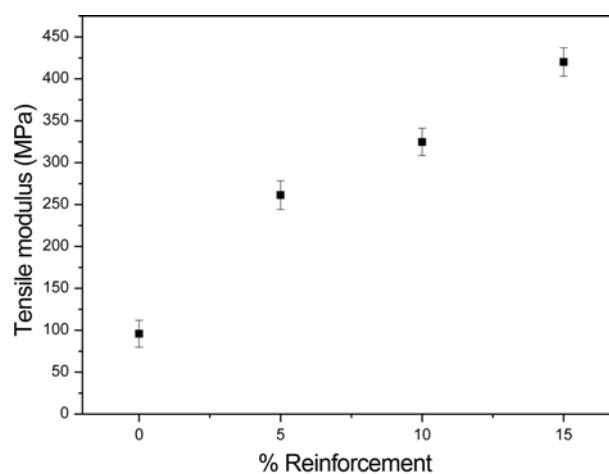

Figure 2. Tensile modulus of the matrix (0 %) and the biocomposites (with 5, 10 and 15 % barley straw particles).

improves the mechanical properties.

Figure 2 shows the modulus of elasticity (MOE) of the study materials. All composite MOEs exhibited statistical differences with a 95 % confidence level. Elasticity modulus concomitantly increased with the barley particle percentage. It is well known that the fiber/particle geometry, orientation, volume and density are factors that greatly impact on the mechanical properties [22]. The elasticity or Young's modulus is a parameter that defines the tenacity and rigidity of a given material. Müller *et al.* [23] reported values ranging from 11-1047 MPa for the elasticity modulus, Guimarães *et al.* [24] obtained 24.6-484.0 MPa, Texeira *et al.* [25] reported 16.8-84.3 MPa, Corradini *et al.* [26] observed 331 MPa, and Ma *et al.* [18] reported values ranging from 40 to 140 MPa. The MOE values here were higher compared to those obtained by Kaushik *et al.* [28], using thermoplastic starch bio-composites reinforced with barley straw nanofibers. The observed values were 76, 107, 175, and 224 MPa for the matrix and a concentration of 5, 10, and 15 % nanofibers, respectively. Wattanakornsiri *et al.* [29] reported a 17 MPa MOE by using a cellulose reinforcement obtained from recycled paper.

Lopez-Gil *et al.* [7] also assessed the properties of biocomposites, based on thermoplastic starch and barley straw fibers with plasticizers at high temperatures and shear forces applied by extrusion. The results obtained showed that tensile strength values are comparable to those obtained in this work; however, the MOE values are at the same concentrations: 0 % (90 MPa), 5 % (150 MPa), 10 % (250 MPa), and 15 % (310 MPa), and are much lower than those obtained by thermal compression.

Sarsari *et al.* [9] report MOE results for composites with corn thermoplastic starch of 1 GPa with 0 % and 1.2 GPa with 30 % of walnut shells. However, the authors did not explain the direct contribution of the 3 stages and the
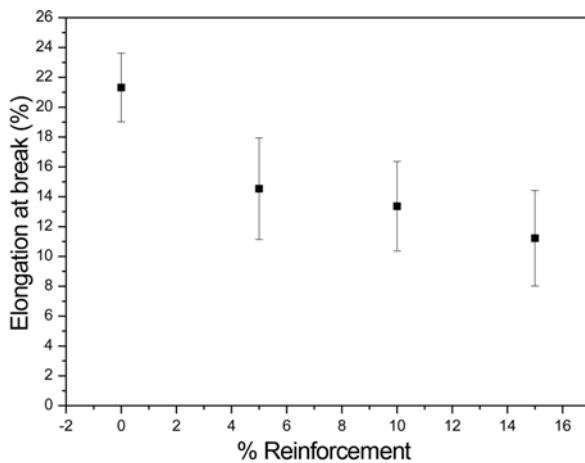
Figure 3. Percentage of elongation at break of matrix and the biocomposites.

Figure 4. Stress-strain curves compared the matrix (0 %) and the biocomposites (5, 10 and 15 %).

coupling agent in the process over enhanced mechanical properties of biocomposites. Guleria *et al.* [10] also reported high values of MOEs in biocomposites reinforced with 0 % (0.5 GPa), 5 % (1.1 GPa), 10 % (1.2 GPa), and 15 % (2.5 GPa) of okra fiber by crosslinking.

Figure 3 presents the results for the deformation percentage with different concentrations of reinforcement barley straw particles: increasing the number of particles within the matrix causes an elongation decrease. Fibers restrict the thermoplastic corn starch-based matrix elongation during the tension test. Saetun *et al.* [6] reported deformation percentage values for thermoplastic starch biocomposites of 20 % with wood sawdust and 30 % with a commercially available cellulose reinforcement. Shah *et al.* [21] showed that the waste cellulose fiber of biodegradable composites include thermoplastic starch (containing waste cellulose fiber), which increased the composite's stiffness, thereby increasing its tensile strength, although its elongations were reduced. Müller *et al*. [23] reported elongation values ranging from 13-101 %, Guimarães *et al.* [24] observed 1.2-75.5 %, Texeira *et al*. [25] obtained 29.8-92.4 %, Corradini *et al.* [26] found 2.2 %, whereas Ma *et al.* [18] reported values between 20 and 115 %. Guleria *et al.* [10] reported that the elongation percentage decreased according to the amount of okra fiber added in the thermoplastic starch matrix. All results shown here are in agreement with earlier reports on starch composites with different reinforcements.

Figure 4 shows typical stress vs strain curves in this study for tensile strength tests of matrix (0 % fiber) and bio-composites with 5, 10, and 30 % barley straw particles. The curves of the matrix with and without reinforcement show differences: typical curves of ductile material reveal large deformation and low stress strain. In contrast, biocomposites show typical curves of ductile materials with less deformation. Increasing the reinforcement in the samples also increases
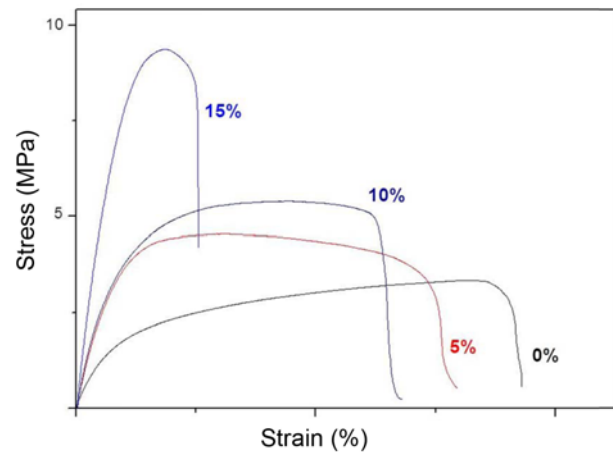
the stress-strain.

Flammability Test

There are few studies on the behavior of biocomposites exposed to fire. Some, however, have established that certain combinations of matrix and fiber may reduce flammability, while others state that the incorporation of fiber increases the combustibility of composite material [30,31]. In general, incorporating lignocellulosic fibers into thermoplastic starch matrix improves its properties, but in the case of flammable behavior, it can be a drawback: vegetable fibers have little fire resistance. Thus, the flammability of a composite material depends not only on the polymer matrix and fiber type, but also on the interaction between them [32].

Table 2 shows the flammability test of the matrix and biocomposites. During this process, carbon appeared in most of the composites, although no leak was observed for the thermoplastic starch matrix. It has been found that these materials produced scarce but clear-colored smoke, with an orange flame and slightly sweet odor during combustion. The matrix tends to self-extinguish while the composites do not. The test specimens are not deformed, as they only burned, in turn forming carbon (Figure 5). The carbonized layer created during combustion is an important criterion in assessing a polymer's flammability, as the produced carbon may serve as a barrier between the ignition source and internal unburned polymer layers. A carbon-forming polymer may possess low flammability, which is a desirable quality for a polymeric matrix [32].

TPS exhibits a low burning time and high burning rate due to its flammable nature, although combustion is very slow [31]. The progressive increase of barley particles in the starch matrix causes a faster ignition. The combustion rate (mm/s) was 0.20, 0.24, 0.34, and 0.81 for the matrix and composites of barley particles, at a concentration of 5 %,

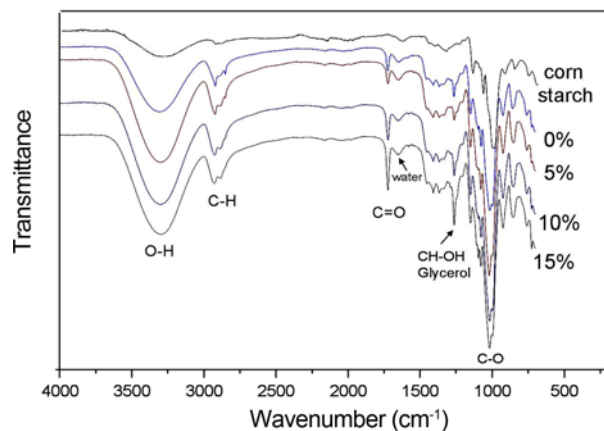**Table 2.** Flammability test of the different materials evaluated

Material	Smoke		Flame hue	Self-extinguish	Carbon formation	Burning speed (mm/s)	Deformation of the specimen
	Amount	Color		Yes/Not			Yes/Not
0 %	*		Orange	Yes	*	0.20	
5 %	*	White			**	0.24	
10 %	**	White	Blue/orange	Not	**	0.34	Not
15 %	***				***	0.81	

Figure 5. Behavior evaluation by flame test of matrix and biocomposites.

Figure 6. FTIR-ATR spectra of corn starch, matrix (0 %) and biocomposites (with 5, 10 and 15 % of barley straw particles).

10 %, and 15 %, respectively. This agrees with data reported by Bocz *et al*. [30], having identified that the natural fiber inclusion in the thermoplastic starch matrix increases flammability. Thus, a retardant was needed to decrease combustion.

FTIR Analysis

The chemical composition and differences of thermoplastic biocomposites, prepared with native and modified starch, have been extensively measured by FTIR spectroscopy [7,18,33-36]. Figure 6 shows the FTIR spectra of the corn starch samples, TPS, and biocomposites of 5, 10, and 15 % barley straw particles with an average size of 425 μ. All samples depict a similar spectroscopic pattern of signals, with a broad signal of around 3300 cm^{-1} originating from OH groups in the hydrogen bond system and stretching vibrations of 2970 and 2850 cm^{-1} of C-H aliphatic chains; this includes the water signal of 1650 cm^{-1}, since signals between 1500 to 900 cm^{-1} are attributed to C-H bending as well as C-C and C-O stretching vibrations. These signals also corroborate alcohol, ether, and aliphatic composition from the starch and glycerol matrix (TPS) of biomaterials. Spectroscopic changes are observed in samples of TPS with 5, 10, and 15 % of barley straw with signals of 1720 cm^{-1} and 1240 cm^{-1}-which are not appreciated in the corn starch

spectrum. In the signal of 1720 cm^{-1}, this can be attributed to C=O stretching vibrations of carbonyl groups such as aldehydes, ketones, and carboxylic acids formed by starch decomposition in the thermal treatment of TPS lamination. On the other hand, the signal of 1240 cm^{-1} is associated with CH-OH groups from glycerol in the TPS matrix. We previously reported those signals in similar TPS biocomposites [9]. Furthermore, the intensity of those signals increased when the amount of barley straw increased in the TPS matrix. In the carbonyl signal (1720 cm^{-1}), it increased as a consequence of thermal decomposition in the biomaterials, associated with the amount of barley straw particles. However, this thermal decomposition (known as caramelization) only occurs on the surface of samples without affecting their mechanical properties, as we earlier reported [8]. This can be explained by the molecular organization of the starch and the glycerol changes when the barley straw particles are added to the matrix, thus exposing more OH groups to thermal oxidation. In addition, the molecular organization of OH groups is also observed in the glycerol signal (1240 cm^{-1}), which increased according to the barley straw particles in the biocomposite; this is due to the hydrogen bond system in the TPS being disturbed.

Optical Microscopy

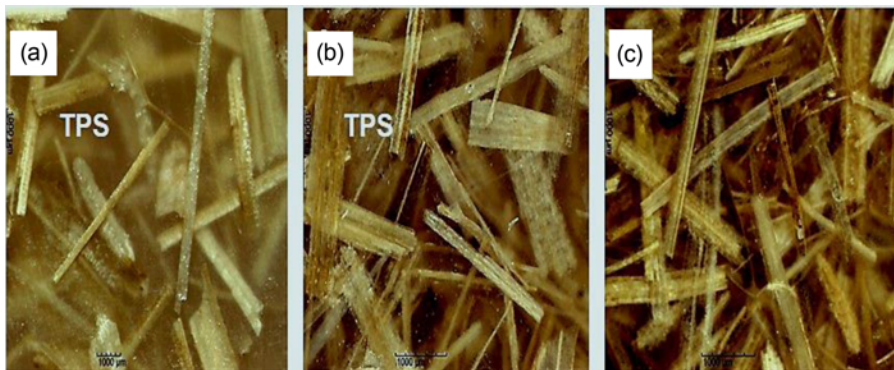Figure 7(a, b, and c) shows photographs of corn starch-

Figure 7. Images of the biocomposites with 5 % (a), 10 % (b) and 15 % (c) of barley particles.

glycerol biocomposites with 5, 10, and 15 % barley particles observed under a stereomicroscope. When the original semi-crystalline structure of the starch granule is completely disorganized by heat, shearing, and pressure, it becomes a thermoplastic starch characterized by amorphousness, transparency, and low crystallinity. A main feature of amorphous polymers is their transparency [37], especially in the polymeric phase (TPS matrix in Figure 7), allowing for observation of the parenchymal tissue characteristic of the

barley straw. The uniform and homogenous distribution of particles within the matrix is also observed. Vallejos *et al.* [38] reported poor dispersion of fibers during preparation of thermoplasticized cassava starch composites with 10 % sugarcane bagasse, processed in a rheometer (Haake). Oniszczuk and Janssen [39] point out that the size of the fiber or particle is a limiting factor for extrusion and injection methods. Very long fibers or those in high amounts may cause an excessive increase in viscosity that induces
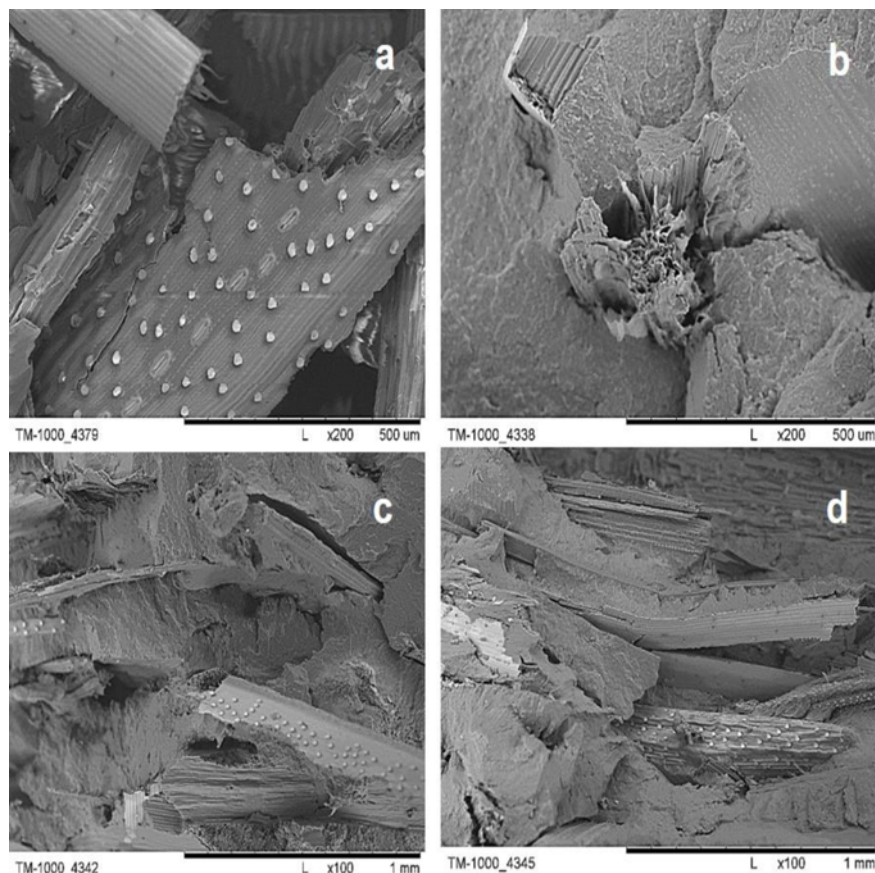

Figure 8. SEM micrographs of barley straw (a), and composites 5 % (b), 10 % (c), 15 % (d).

aggregation and may increase mechanical energy during processing. Small-sized fibrous materials are used for these processes, with images showing no air bubbles or unplasticized parts during the thermal plasticizing process.

Scanning Electron Microscopy

Figure 8(a) shows a SEM micrograph of barley straw. Stomata arranged in rows (straw veins) can be observed, as well as wax accumulation on the barley straws. The presence of epicuticular waxes is common in monocotyledonous plants, which appear as rods, granules, clusters, scales, and several other forms that may reach 3.9 mm [40,41]. Wisniewska *et al.* [42] similarly found various granules of wax, with an approximate 5 mm diameter in the barley straw.

Figure 8(b-d) shows the surface of the studied cylinders, evaluated by traction of composites containing 5 %, 10 %, and 15 % of barley particles, respectively. The images show an interaction between barley particles and the thermoplastic matrix during tensile stress. Some barley particles are separated during the mechanical test, although there are other particles that remain well attached to the thermoplastic starch matrix, demonstrating the effect of the reinforcement. The composites containing 15 % of barley particles were deformed during the stress as a function of the tension test. The reinforcement theory establishes that its effect is reflected when a suitable interface (optimal attachment) occurs during the mechanical test, as the tensile stress is transferred to the matrix with an increased tensile resistance [39]. Figure 8(c,d) shows wax granules on the barley particle during the thermal compression process.

X-ray Diffraction

The crystallinity of corn starch was calculated according to equation (2) at 33 %. Srichuwong *et al.* [43] reported a 31-37 value for corn, whereas Avérous and Halley [44] observed it at 39 %. Figure 9 shows the X-ray diffractograms for native starch, the matrix, and biocomposites. The particular type-A crystallinity pattern of most cereals (corn, rice, wheat, and oat) is observed on the diffractograms. It has previously been described as amylopectin chains of the type-A structure, and 23-29 glucose-units long, forming a highly condensed and crystalline monocyclic cell unit that harbors 4 water molecules between its helixes [45,46]. Native corn starch displayed particular diffraction peaks at 2θ 15°, a doublet at 18°, along with an additional peak at 23° [25,47]. Figure 9 shows the diffractograms of the TPS matrix and its composites. The direct plasticization process in the press, and the combined action of temperature, pressure, and the plasticizer caused granular disruption, leading to a change in the characteristic profile of native starch from type-A to type V_A. However, a change is observed when diffractogram profiles of the studied materials are compared to those of granular starch. This is caused by disorganization of the
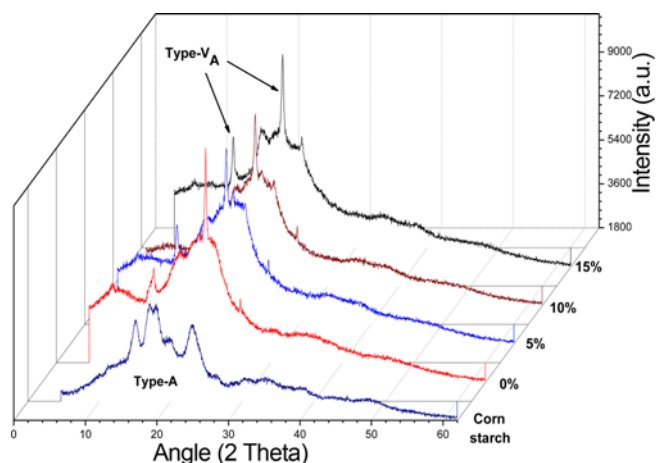

Figure 9. X-ray diffractograms of native starch, matrix (0 %) and biocomposites.

starch granule (semi-crystalline structure) during the plasticizing process, as the interaction between the hydroxyl groups in amylose and amylopectin are modified, with new interactions occurring between the plasticizing agent (glycerin) and the starch chains. Furthermore, the combined action of temperature, time, and applied pressure must be taken into account [48]. The type-A crystallinity of corn starch disappeared and a V_A polymorphic was formed. The identification of the peaks on the diffractogram was based on the data reported by Van Soest *et al.* [49], Teixeira *et al.* [24], and Corradini *et al.* [26]. At 2θ $\sim$13.5°, a strong signal is observed, whereas at 2θ $\sim$17.5° the signal is intermediate, and at 2θ $\sim$20.9° a very pronounced peak occurs for both the matrix and composites. According to Van Soest *et al.* [49], these peaks match type-V_A crystallinity (anhydrous). Lu *et al.* [2] reported that the content of the plasticizer agent, the temperature, and the processing method, including the residence time and cooling rate, are factors impacting the material's final crystallographic pattern. The V_A lattice has more contracted amylose helices and less water than the V_H lattice [49]. Dai *et al.* [50] also found a V_A-type crystallinity for thermoplastic corn starch at the same angles as seen in this study. The crystallinity index is an important parameter, as it impacts physical, mechanical, chemical, and technological properties of materials. The crystallinity index observed for the matrix was 0.56, whereas the values for 5 %, 10 %, and 15 % composites were 0.63, 0.68, and 0.74, respectively. These values are higher in comparison to those we reported previously [9].

Conclusion

It is possible to prepare thermoplastic corn starch-based composites with the thermal compression method, reinforced with 5 to 15 % of particles from barley straw residues. The

materials had optimal transparency, enabling the observation of homogeneous distribution of barley particles in the thermoplastic matrix. The inclusion of barley particles quickened combustion and carbon formation, as well as water absorption. Although barley straw is a material displaying high parenchyma and less fiber, its inclusion in the thermoplastic starch matrix increased mechanical performance of biocomposites. The SEM micrographs showed the attachment of the particles to the thermoplastic starch matrix and demonstrates the mechanical reinforcement effect. The infrared analysis exhibited a carbonyl signal (1720 cm^{-1}) caused by thermal decomposition (caramelization) of biomaterials related to the amount of barley straw particles. However, this decomposition did not affect the materials or their mechanical properties. The composites' crystallinity pattern was of the V_A type (anhydrous) and the crystallinity index increased concomitantly with the barley straw content in the corn starch matrix. Finally, the present work assessed the possibility of producing renewable and sustainable materials, such as biocomposites, with attractive mechanical and physicochemical properties, acting as an alternative to classical synthetic polymers.

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