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Thermoplastic Starch (TPS)-Cellulosic Fibers Composites: Mechanical Properties and Water Vapor Barrier: A Review

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Additional information is available at the end of the chapter

Abstract

Current research studies have been focusing on the procurement of environmentally friendly materials, with the aim of resolving the problems created by materials derived from petroleum. Starch is a promising biopolymer for producing biocomposite materials because it is renewable, completely biodegradable, and easily available at a low cost. Thermoplastic starch (TPS), by itself, exhibits poor mechanical properties such as low tensile strength and severe deformations, which limits its application in packaging or films. In addition, TPS presents high hygroscopicity. The use of reinforcing agents in the starch matrix is an effective means to overcome these drawbacks and several types of biodegradable reinforcements, such as cellulosic fibers, whiskers, and nanofibers, have been utilized to develop new and inexpensive starch biocomposites. This chapter provides the latest advances in green composite materials based on TPS and cellulose fibers and includes information on compositions, preparations, and the properties of "green" composite materials elaborated from TPS and cellulose fibers, with the focus on using undervalued natural resources.

Keywords: Thermoplastic Starch, Cellulose Fibers, Sustainable Green, Biopolymer, Natural Resource

1. Introduction

Current research studies have been focusing on the procurement of environmentally friendly materials with the aim of resolving the problems created by materials derived from petroleum. Starch is a promising biopolymer used in the production of biocomposite materials because it is renewable, completely biodegradable, and easily available at a low cost. Starch, in the form of its thermoplastic derivate (TPS), has been revealed as an appropriate candidate to be employed as a substitute of synthetic polymers traditionally used for packaging. Starch is not a real thermoplastic polymer, but can be processed after its gelatinization by mixing it with enough water and/or plasticizers [1, 2]. In most investigations the plasticization of the material is carried out by casting a dispersion of starch with glycerol [1, 3].

TPS films are reported to have low permeability to gases, poor water vapor barrier properties, and must resist the tensions arising from their use in packaging [4].

Therefore, improving the resistance of TPS films to traction forces is a factor that must be taken into consideration for their use [5, 6]. The use of reinforcing agents in the starch matrix is an effective means of overcoming these drawbacks and several types of biodegradable reinforcements such as cellulosic fibers, whiskers, and cellulose nanofibers (CNF) have been utilized to develop new and inexpensive starch biocomposites. Cellulose is the most abundant, renewable polymer in the world; it is found in plant cell walls and it can also be synthesized by some bacteria. Its reinforcing property is remarkable [7]. Basically two types of nanoreinforcements can be obtained from cellulose: microfibrils (or CNF) and whiskers.

Improving the mechanical and water barrier properties by the addition of CNF (extracted from different botanical sources) can depend on the correct dispersion and the generation of an active nanoreinforcement/matrix interface.

This chapter provides the latest advances in green composite materials based on TPS and cellulose fibers and includes information on compositions, preparations, and the properties of "green" composite materials elaborated from TPS and cellulose fibers, with the focus on using undervalued natural resources.

2. Starch

Starch is a biodegradable and widely available natural resource [8], and constitutes the main source of carbohydrate reserves in plants. This polysaccharide is found in different parts of the plants and can be isolated from seeds, fruits, leaves, tubers, and roots [9].

The functionality of starch is largely due to its two components of high molecular weight: amylose and amylopectin. Most of the starches contain between 20 and 30% of amylose and 70 and 80% of amylopectin; these proportions depend on the plant source. Amylose molecules consist of approximately 200–20,000 glucose units joined by α-1,4 glycoside bonds (**Figure 1**) in unbranched chains or coiled helix [10].
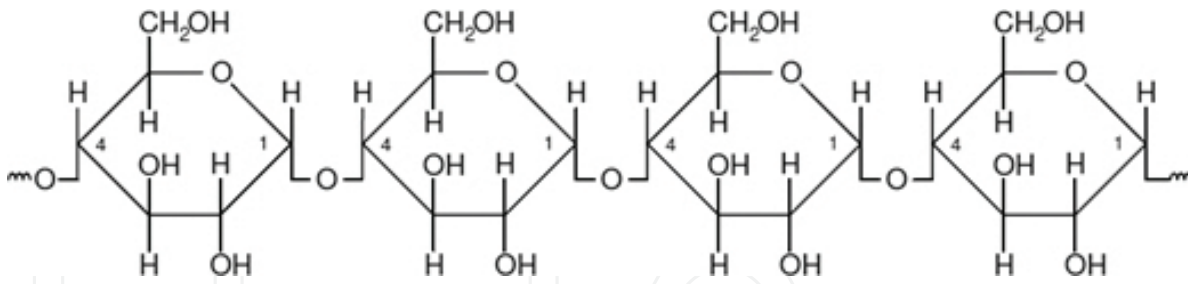
Figure 1. Segment of an amylose molecule [10].

The structure of amylopectin is different from that of amylose; amylopectin molecules contain α-1,4 and α-1,6 glycosidic bonds, as can be seen in **Figure 2**. The glycosidic bonds join the glucose molecules in the main amylopectin chain. Branches of the main chain are often found, which are due to the α-1,6 glycosidic bonds with other glucose molecules.
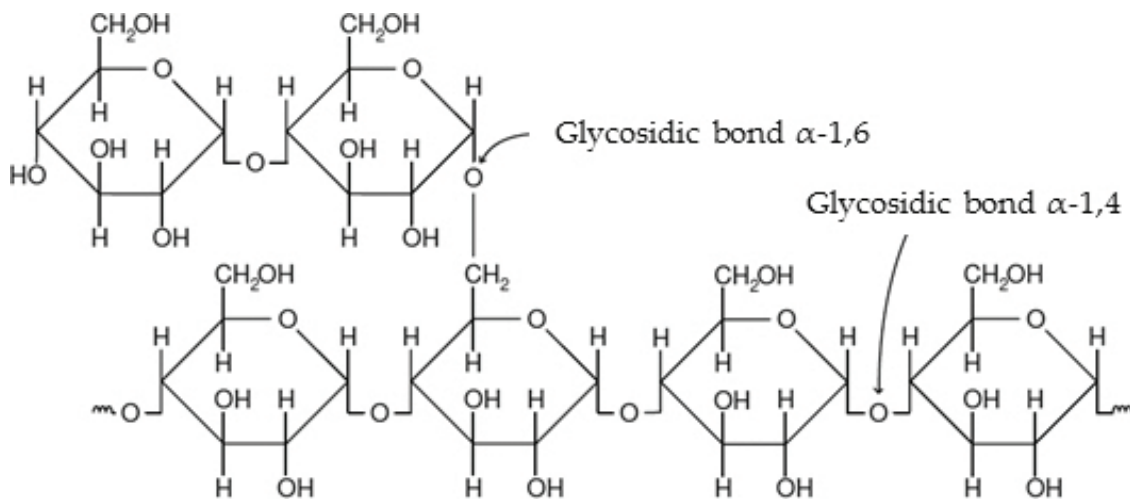
Figure 2. Segment of an amylopectin molecule [10].

The bonding points of the branches constitute between 4 and 5% of all the bonds [11]. Amylopectin molecules are significantly larger than the amylase molecules; some contain between 10,000 and 20,000,000 glucose units. The molecular weight of amylose is between 0.1 and 1 million g/mol while that of amylopectin ranges between 10,000 and 1000 million g/mol [10].

One of the most important properties of natural starch is its semicrystallinity and amylopectin is the dominant component for crystallization in most starches. The significant commercial properties of starch, such as mechanical resistance and flexibility, depend on the resistance and character of the crystalline region, which in turn depend on the amylose/amylopectin ratio and thus on the type of plant; these properties also depend on the distribution of molecular weight, degree of branching, and the conformation process of each polymeric component [12].

Starch is versatile due to its variety of uses; it is also one of the most important ingredients at an industrial level. In the food industry, starch is used to provide a wide range of functional

properties and is probably the most utilized hydrocolloid [13]. It can be used in flavor encapsulation, as a thickening agent or a filling agent, in bakery products, production of syrups, etc. Starch is also included in many other industries such as textiles, paper, cosmetics, plastics, pharmaceutical, and adhesives.

Currently, the negative environmental impact caused by synthetic polymer wastes, denominated plastic materials, is well known and there is now a growing interest in biodegradable materials like starch to substitute the conventional plastic materials, such as polyethylene and polystyrene. A number of studies have reported the use of starch in the manufacture of fast food utensils and packaging material [14].

It is clear that one of the alternatives is the use of starch from nonconventional sources, particularly in countries where there is a high production of raw material for the production of this polymer. Nonconventional sources of starch have attracted much attention, given their diversity of properties, which allow their application in different industries, including the food industry.

Table 1 shows the amylose content, granule size, and gelatinization temperature of a few starches from nonconventional sources such as chestnut [15], kudzu [16], ramon [17], chayote [18], -parota [19], makal [20], sorghum [21], mango [22], and okenia [23], which could be considered for the production of biodegradable materials. In general, the new botanical sources are always widely available in the countries, which produce them.

Type of starch	Amylose (%)	Granule size (μm)	Gelatinization temperature (°C)	Reference
Chestnut	26.6	4–21	61.9	[15]
Kudzu	22	2–20	64-83	[16]
Ramon	25.3	6.5–15	83.05	[17]
Chayote	12.9	7–50	67.7	[18]
Parota	17.5–21.3	20–28	76-78	[19]
Makal	23.6	12.4	78.4	[20]
Sorghum	11.2–28.5	Not reported	70–75	[21]
Mango	9–16	7-28	77–80	[22]
Okenia	26	Not reported	71.3	[23]

Table 1. Characteristics of starches from different botanical sources.

3. Thermoplastic starch (TPS)

To produce a film based on starch, a high content of water or plasticizer is required (glycerol, sorbitol). These plasticized materials (application of mechanical and thermal energy) are known as thermoplastic starches [8].

The development and production of TPS is considered to be important for the reduction of the total quantity of synthetic plastic wastes in the world [24].

TPS is a material which is obtained through the structural disruption (modification) occurring inside the starch granule when it is processed with a low water content and the action of shear force and temperature in the presence of plasticizers which do not evaporate easily during the processing [25].

To date, it is known that the techniques (extrusion, injection molding, and film casting) for processing starch-based materials are similar to those used for conventional polymers. However, it is important to note that although the processing of starch is complicated, it can be achieved successfully if an appropriate formulation is developed and adequate processing conditions are established [26].

A simple and well-established technique for producing sheets or films by extrusion is the use of a twin-screw extruder with a slit or flat film die, followed by a takeoff device for orientation and collection [27, 28].

Foaming extrusion has mainly been used to produce loose-fill packaging materials, in a similar way to the production of extruded expanded snack foods [29].

Twin-screw extrusion is the most widely used and is preferred because of its ease of feeding, longer residence time, more extensive shear, and more flexible temperature control [30, 31].

The high viscosity and poor flow properties of starch-based materials present difficulties during injection molding, while the lack of reliable parameters makes it difficult to design the optimum processing conditions [26].

Compression molding has been intensively investigated for processing starch-based plastics, particularly in the production of foamed containers, and generally involves starch gelatinization, expanding, and drying. Apart from gelatinization agents, mold-releasing agents such as magnesium stearate and stearic acid are also often used in formulations to prevent the starch sticking to the mold [26].

The casting technique for preparing starch films includes the preparation of a dispersion, gelatinization at 95°C, casting in acrylic or Teflon plates, and a drying period of approximately 24 h at 40–75°C [32–34]. Glycerol is the most used plastifier in the preparation of starch films. The resulting starch film can have a thickness between 0.02 and 0.10 mm [26].

Over the last few years, much research has focused on the modification of the starch in the production of a good thermoplastic material [35, 36]. A number of mixtures of TPS with biopolymers based on thermoplastic starch are being commercialized with a certain degree of success, by companies such as Mater Bi® (Novamont S.P.A., Italia) in Italy [www.mater-bi.com], Carghill-Down® in the U.S., and by others in Spain, Germany, France, Japan, Denmark, and Canada [37].

4. Cellulose

Cellulose is the most abundant renewable biomass material in nature and is also a major component of plant cell walls. It has been widely used in the form of wood and plant fibers as an energy source, for building materials, and for clothing. Cellulose can be used as feedstocks for producing biofuels, bio-based chemicals, and high value-added bio-based materials. In the past, much attention has been given to the conversion of cellulose-to-cellulose-based composites due to its properties relating to mechanical strength, biocompatibility, biodegradation, and bioactivity, as well as its potential applications which include biomedical, antibacterial, water pretreatment, and in the field of functional materials for photocatalysis [38].

The basic building block of cellulose is β-D-glucose ($C_6H_{12}O_6$) (**Figure 3**). To form the "cellobiose" molecule, one water molecule is eliminated for every two glucose molecules. Then, from the condensation of various cellobiose molecules, the cellulose molecule is formed. The cellulose chains are found very close to each other due to their hydrophilic character [39].
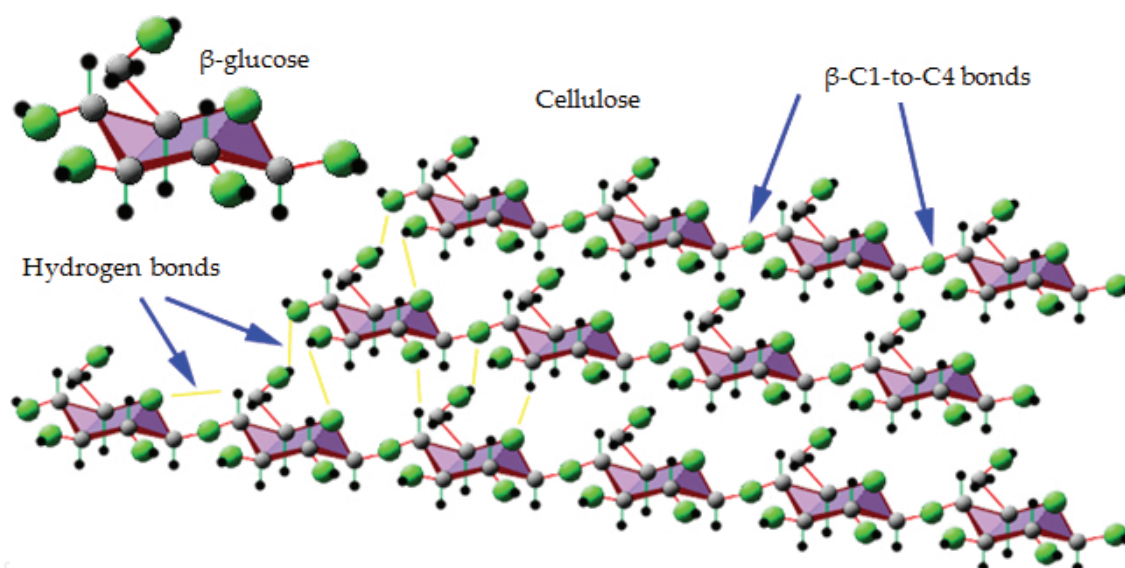

Figure 3. Segment of a cellulose molecule.

The elemental composition of cellulose was discovered in 1842 by the French chemist Anselme Payen [40] and cellulose consists of: 44.0–45.0% carbon (C), 6.0–6.5% hydrogen (H), and 48.5–50.0% oxygen (O).

Table 2 presents a list of the chemical composition of several materials containing cellulose [41].

In plants, cellulose can be found in the form of microfibers in the primary, secondary, and tertiary cell walls, organized either unidirectional or as a woven mesh. Cellulose microfibers are 5 nm thick strands of glucopyranose molecular chains, whose Young's module is 134 GPa, with a density of 1.5 g/cm^3, and a tensile strength (TS) estimated at approximately 2 GPa. Cellulose microfibers have a diameter of 20–200 Å, while the length can reach several dozen microns. These characteristics are responsible for the interesting mechanical properties of the

microfibers, which are extracted from the biomass by means of a chemical treatment followed by a mechanical treatment; the aim being to obtain a homogenous suspension of individual microfibers [42, 43].

Composition (%)				
Source	Cellulose	Hemicellulose	Lignin	Extract
Hardwood	43–47	25–35	16–24	2–8
Softwood	40–44	25–29	25–31	1–5
Cotton	95	2	1	0.4
Bagasse	40	30	20	10
Coconut fiber (coir)	32–43	10–20	43–49	4
Corn cobs	45	35	15	5
Corn stalks	35	25	35	5
China grass (ramie)	76	17	1	6
Flax (unretted)	63	12	3	13
Flax (retted)	71	21	2	6
Hemp	70	22	6	2
Jute	71	14	13	2
Sisal	73	14	11	2
Kenaf	36	21	18	2
Sunn	80	10	6	3

Table 2. Chemical composition of materials containing cellulose [41].

In this process, the disintegration of the cellulose was achieved by the generation of high shear forces. As a consequence of the above, the microfibers detach from the surrounding material and remain united to other microfibers, thereby forming a network of fibers with nanometric dimensions. The cellulose obtained from this procedure is denominated cellulose nanofibers. These CNF are packages of fibers on a nanometric scale. It has been determined that, within the plant, these CNF are capable of supporting the pressure exerted by the water contained in the plant cells and thus the interest in using cellulose in this form for nanocomposites, based on the concept of introducing nanometric loads (fillings) in a polymeric matrix [44].

4.1. Extraction of cellulose nanofillers

Several processes have been used to extract highly purified CNF from cellulosic materials. All these methods lead to different types of magnesium stearate and stearic acid, depending on the cellulose raw material and its pretreatment, and more importantly, depending on the disintegration process itself [45]. CNF extraction can be divided into: chemical hydrolysis and extraction by mechanical force.

4.1.1. Extraction by chemical hydrolysis

A commonly used extraction methodology of CNF is acidic hydrolysis of the amorphous regions surrounding the embedded CNF and cleavage of the bundles, followed by filtration or centrifugation to exclude dissolved noncrystalline elements [46, 47]. The methodology is beneficial in that it can be performed on very small quantities of cellulose, it requires only the simplest laboratory equipment, and the CNF can be obtained without any induced imperfections caused by mechanical processing. The conditions typically involve the use of aqueous solutions of sulfuric acid, stirred at 45–60°C at atmospheric pressure until a homogeneous beige solution is obtained [48, 49]. After acid hydrolysis, the suspension is diluted with water in order to stop the chemical reaction. This suspension is subjected to centrifugation to obtain the cellulose and eliminate excess acids. The resulting cellulose is washed with water using centrifugation and is finally dialyzed using membranes to reach a neutral pH [50].

This procedure results in CNF having anionic groups on the surfaces (leading to electrostatic stabilization of the nanocrystals in suspension) with the ability to form chiral nematic liquid crystalline phases in concentrated solutions [51]. The form of cellulose obtained was denoted microcrystalline cellulose (MCC) by Battista in 1975 [52].

Exaggerated hydrolysis can typically be noted as the solutions turn dark or black in color as the degradation of the CNF occurs. This phenomenon was reported by Roman et al. in 2004 [53], who assigned the crystal degradation to potential induced thermal degradation related to the sulfate groups, introduced as a functional surface on the CNF when sulfuric acid is used for hydrolysis.

4.1.2. Extraction by mechanical force

The mechanical methods to extract CNF from wood pulp and parenchyma cells typically involve a high-pressure homogenizer treatment [42, 54], a microfluidizer [55, 56], a high-pressure refiner, a super-grinder treatment [57], or ultrasonication [58]. The form of cellulose obtained was denoted microfibrillated cellulose (MFC) by Herrick et al. and Turbak et al. in 1983 [42, 43]. These processing methodologies have in common the fact that they rely on the application of high shear forces on cellulose fiber suspensions in order to mechanically liberate the CNF from the original plant cell wall structure. In a high-pressure homogenizer this is achieved by allowing a cellulose suspension to pass under high pressure through a thin slit where it is subjected to high shear forces. The shear forces serve to disintegrate the microfibrils or microfibril bundles in the plant cell wall, resulting in CNF with diameters of about 5–100 nm [59].

High-intensity ultrasonication consists of a combination of chemical pretreatment and high-intensity ultrasonication. To obtain the cellulose fiber, first, the lignin is eliminated from the samples by immersion for 1 h at 75°C in a solution of sodium chlorite, previously acidified [60, 61]. After the bleaching, the samples are treated with potassium hydroxide (3%) at boiling point for 2 h. After which, they are subjected once again to a treatment with potassium hydroxide at a different concentration (6%), the aim being to eliminate hemicellulose, residual starch, and pectin. After the application of the chemical treatment, the samples are washed

with distilled water and the resulting cellulose fibers are immersed in distilled water. A total of 120 ml of this solution containing purified cellulose fibers is placed in an ultrasound generator of 20–25 kHz in frequency equipped with a cylindrical titanium alloy probe tip of 1.5 cm in diameter. The subsequent ultrasonication is conducted for 30 min to isolate the CNF.

4.2. Green composites of TPS and cellulose fibers

Human beings are known to be highly dependent on synthetic polymers derived from petroleum for the elaboration of diverse packaging and utensils, giving rise to environmental problems [45]. However, reports have been published of the combination of natural fibers, which are completely biodegradable, for the development of green composites. These materials are environmentally friendly and their use can reduce contamination on a global level [45].

Nanocomposites contain materials with a nanometric dimension ranging between 1 and 100 nm. These materials surpass conventional composite materials due to their superior thermal, mechanical, and barrier properties [62, 63]. Biodegradable polymers, in particular, may require improvement in terms of brittleness, low thermal stability, and poor barrier properties [63].

The physical and mechanical properties of the polymeric material reinforced with cellulose are strongly dependent on their structure, relaxation, and morphological processes, as well as a good dispersion of the fiber in order to achieve the minimization of holes. Indeed, a good dispersion of fibers in the polymer matrix has been reported as something very difficult to achieve [64].

The processing of TPS reinforced with cellulose fibers processing is similar to most conventional synthetic thermoplastic processing [65]. Most thermoplastic operations involve heating and forming into desired shapes, and then cooling. Processing techniques used on thermoplastics can also be used in the TPS reinforced with cellulose fibers. These include extrusion, injection molding, internal mixing, compression molding, and others [66].

4.3. Preparation of green composites: mechanical properties and water vapor barrier

From a tensile test, basic mechanical properties of a TPS can be obtained such as tensile strength (the maximum tensile stress a TPS can withstand before it breaks), percentage of elongation at breakage (E) (flexibility), percentage of elongation at yield (EY), and modulus of elasticity (EM) (stiffness) [67, 68].

It has been reported that the mechanical properties of a starch film is affected by the glass transition temperature, degree of crystallinity of the films, amylose content, plastifier type, and content and the storage conditions.

Studies of the barrier properties of starch films are important in order to estimate the shelf life of a food product. This barrier property depends on the starch source, and on the quantity and type of plastifier used, among the most important. Gas barrier properties for a TPS film include water vapor permeability (WVP), oxygen permeability [14], and aroma permeability. WVP is used to describe the ability of the film to control water vapor transportation between a food system and its surrounding. TPS films are not considered good water vapor barriers [68].

The use of CNF has shown to be a viable option for the improvement of mechanical and barrier properties of TPS films. **Table 3** presents a number of studies on the use of starch from different botanical sources to obtain TPS films reinforced with CNF from different materials. However, there are in fact very few reports relating to the use of CNF as reinforcement materials in TPS films. A number of studies have researched the use of undervalued residues as source material for the procurement of cellulose fibers or CNF such as cassava bagasse, barley husk, and sugarcane bagasse, as shown in **Table 3**.

Type of starch	Type of fiber	Preparation of CNF or isolation of cellulose fiber	Preparation of TPS reinforced with CNF or cellulose fibers	Most important results	Reference
Cassava	Cassava bagasse	Acidic hydrolysis with sulfuric acid (H_2SO_4) at 60°C for 40 min. Excess acid was removed by centrifugation. Dialysis of the suspension and ultrasonic treatment	A mixture containing starch, glycerol or a mixture of glycerol with sorbitol, stearic acid and different quantities of CNF from cassava bagasse. The films were prepared by compression molding at 140°C	The addition of 10% and 20% of CNF significantly reduced the elastic module of the TPS films	[49]
Barley grain	Barley husk	Removal of lipids from the barley husk. Removal of lignin and hemicellulose by alkaline treatment at 80°C for 4 h. Bleaching to remove residual lignin in sodium acetate buffer and a solution of sodium chlorite at 95°C for 4 h	The films were prepared by *casting*. A suspension containing 3% starch in distilled water, 0.30 g of glycerol/g dry starch, 0.01 g of guar gum/g dry starch, 10 and 20 g of cellulose fiber/100 g dry starch.The solution was heated at 90°C for 10 min and poured onto acrylic plaques	The addition of cellulose fibers in the films increased the TS and decreased elongation. The WVP of the starch film with 20% of cellulose fibers was lower than that of the film without fibers	[72]
Potato	Wood flour	To obtain the cellulose, the wood flour was treated with acetic acid and sodium chlorite between 70 and 75°C for 58 h.The CNF were obtained from delignified wood flour through mechanical fibrillation	A mixture of starch, sorbitol, stearic acid and CNF (5, 10, 15, and 20 g/100 g dry starch). The TPS films with CNF were manufactured using a twin screw extruder. Pieces of the extruded materials were compression molded into thin films with a thickness of 0.3 mm	An increase in TS of TPS films was observed with the addition of CNF	[74]

Type of starch	Type of fiber	Preparation of CNF or isolation of cellulose fiber	Preparation of TPS reinforced with CNF or cellulose fibers	Most important results	Reference
Cassava	Wood cellulose fibers	Not reported	The films were prepared by casting. Film-forming solutions were prepared with 3% w/w of cassava starch, 0.30 g glycerol/g dry starch, 0.01 g guar gum/g dry starch (to avoid fiber sedimentation) and three concentrations of cellulose fibers: 0.10, 0.30, and 0.50 g of fiber/g dry starch. The film forming solution was placed in a Petri dish and dried at 40°C for 16 h	The incorporation of cellulose fibers mechanically reinforces the films, resulting in high TS, low deformation and low WVP	[4]
Corn	Eucalyptus wood fiber	Acid hydrolysis of eucalyptus wood fiber at 50°C for 50 min. The hydrolyzed material was subjected to centrifugation, washing, dialysis, and ultrasonication	The films were prepared by *casting*. The filmogenic solution was composed of 3% starch, 20% glycerol, gelatin, and CNF. The solution was placed in Petri dishes and dried at 25°C to 50% relative humidity (RH)	The films with gelatin and CNF have greater resistance.	[75]
Chayote	Starch	Acid hydrolysis of the cellulose fiber (H_2SO_4, 60%) at 45°C for 30 min	The films were prepared by *casting*. The filmogenic solution consisted of 4% starch, 2% glycerol, cellulose, or CNF and water. The solution was heated to 90°C for 10 min. The solution was placed in Petri dishes and dried at 40°C for 24 h. The films were placed at 25°C and 57% RH	The addition of CNF reinforced the film matrix, improving TS, EM, and E. The mechanical properties of the starch films with CNF were better than those for films with cellulose. Starch films added with CNF presented the lowest WVP values	[48]
Tamarind seeds	Sugarcane bagasse	Not reported	A mixture of tamarind starch (12%, w/v) and cellulose	The cellulose used	[77]

Type of starch	Type of fiber	Preparation of CNF or isolation of cellulose fiber	Preparation of TPS reinforced with CNF or cellulose fibers	Most important results	Reference
			(4% w/v) in 100 ml of deionized water. 1.5% of acetic acid and 2.5% of glycerol were added. The mixture was gelatinized at 105°C for a period of 15–20 min. The mixture was placed on glass trays at 50°C, for 6 h	as filler improves the mechanical properties of the film (TS and E)	
Potato tuber	Potato tuber	Potato pulp was treated with NaOH (2%) at 80°C for 2.5 h. The cellulose was submitted to a bleaching process with a solution of sodium chlorite (NaClO$_2$). The resultant cellulose was washed with distilled water and lyophilized. The cellulose microfibrils were obtained by submitting the cellulose to a homogenization process with distilled water at 500 bars and 90–95°C	A suspension of cellulose microfibrils (3.3%) was mixed with a gelatinized solution of starch (3.1%). Glycerol was used as plasticizer. The mixture was homogenized and air bubbles were eliminated at reduced pressure. The suspension was poured into a Teflon mold.	The cellulose microfibrils reinforce the starch matrix in the film (greater tension module in comparison with the film without cellulose microfibrils)	[73]
Corn	–	Extraction of the crystalline region of the cellulose was carried out by acid hydrolysis (H$_2$SO$_4$, 64%) for 30 min at 45°C. The CNF obtained was washed and neutralized by dialysis. Finally, the	The nanocomposites were obtained by *casting*. A solution was prepared containing 3.58 g of normal corn starch, 1.93 g glycerol, 35 g of distilled water, and different quantities of waxy corn starch nanocrystals (0, 50, and 100%) and CNF (0, 50, and 100%). The solution was gelatinized at 90°C. The mixture	The addition of waxy starch nanocrystals and CNF increased the TS and reduced WVP of TPS films. Moreover, with the addition of the CNF, deformation values decreased and	[76]

Type of starch	Type of fiber	Preparation of CNF or isolation of cellulose fiber	Preparation of TPS reinforced with CNF or cellulose fibers	Most important results	Reference
		suspension was sonicated for 15 min	was placed in Petri dishes and dried at 55°C. The samples were stored at 43% RH for 2 weeks	Young's module increased	
Wheat	Cotton	The cotton CNF were obtained by acid hydrolysis with H_2SO_4 (64%) at 45°C for 4 h. After hydrolysis, the suspension was neutralized and washed by dialysis	A suspension was prepared containing 7% wheat starch, 3% glycerol, and 90% water. The suspension was gelatinized at 100°C for 20 min. After gelatinization, a dispersion of CNF (0, 2.5, 5, 10, 15, 20, 25, and 30%) was added to the suspension and mixed for 20 min. The mixture was degassed in a vacuum and placed in a polystyrene mold. The nanocomposites were dried at 40°C with 50% RH	As the CNF content increased, deformation diminished and both Young's module and TS of TPS films increased	[78]

Table 3. Research work on the use of starch from different botanical sources to obtain TPS films reinforced with CNF.

Table 3 presents information regarding the isolation of cellulose fibers, CNF preparation, the preparation of TPS films reinforced with CNF or with cellulose fibers, and indicates the most significant results.

In general, one can observe that the isolation of cellulose fiber consists in exposing the plant material to high temperatures by means of an alkaline treatment, with the purpose of eliminating lignin and hemicellulose. In addition, the material is exposed to a bleaching process at high temperatures with a solution of sodium chlorite.

For the procurement of CNF, the cellulose fibers are treated with hydrolysis between 45 and 60°C. After hydrolysis, the CNF are recovered by centrifugation, dialysis, and subsequent treatment with ultrasonic bath.

Diverse studies are available which report the use of the casting technique for the production of biodegradable starch films. The most commonly used plasticizer is glycerol. To prepare the solution used to form the films, the starch is mixed with glycerol, water, and different quantities of CNF (between 2.5 and 50% with respect to the starch) as reinforcing agents. In some cases, guar gum is used to avoid sedimentation of the fibers. The solution for film formation is heated in order to achieve gelatinization of the starch for a specific period of time. After gelatinization,

the solution is poured into Petri dishes for the formation of the films, and conditioned for evaluation. Very few studies have been published reporting on the use of injection molding and extrusion to obtain TPS films reinforced with CNF.

The mechanical properties and water barrier properties of TPS films reinforced with CNF have been reported in a number of publications. In general, CNF facilitates an increase in tensile strength, a decrease in deformation values, an increase in Young's module, and a decrease in WVP of TPS films. The chemical structure of cellulose and starch is similar. When they are mixed to produce a filmogenic solution, interactions among the OH groups of both polymers are produced by hydrogen bridges, producing a rigid network that increases the TS [4, 5, 69]. The addition of CNF favors high values of TS for TPS films. This may be due to the fact that a greater contact surface is produced between CNF and the starch chains [70].

The nanometric size of CNF allows a low WVP value of the starch films, which favors the generation of a network of hydrogen bridges between the starch chains and the CNF, causing the water molecule to follow a path with many "curves and bends" and thus reducing its diffusion through the starch films [71]. In addition, the cellulose is less hydrophilic than starch, due to its higher crystallinity and compact microfibrillar arrangement, making it more hydrophobic [69].

Table 3 shows research works on the use of starch from different botanical sources, such as cassava [4, 49], barley grain [72], potato [73, 74], corn [75, 76], chayote [48], tamarind seeds [77], and wheat [78], to obtain TPS films reinforced with CNF.

5. Conclusions

The knowledge that the ecosystem is already considerably contaminated as a consequence of the use of synthetic polymers derived from petroleum, environmental initiatives have now been put in place to promote research work on new products which will be compatible with the environment. The development of biocomposites of TPS with cellulose can reduce the dependency on oil reserves.

In recent times, science and technology has centered on the use of more environmentally friendly, raw materials; emphasizing the importance of the advances in such research on "green" composite materials and cellulose fibers for use in the industry.

It is important to mention that cellulose on a nanometric scale is used as a biodegradable reinforced material to improve the mechanical properties as well as the water barrier properties of the TPS.

According to reports in the literature, the technique for the preparation of cellulose fibers from different materials is very similar, whereas the technique for the preparation of TPS reinforced with CNF presents some differences depending on the type of material processed.

Starches from different sources which do not include corn and potato are used in the development of the green composite material, while the cellulose fibers are obtained from waste

material produced by the industries, the aim being to attain the sustainability of natural resources.

Extrusion is one of the most promising methods for processing "green" composite materials and cellulose fibers (TPS-cellulose); however, very little information is available with respect to this.

Based on information found in the literature, it is reported that the incorporation of CNF mechanically reinforces the films, which display high tensile strength, low deformation, and low WVP.

Within the next few years, it is highly likely that the production of biocomposites of TPS films-cellulose will intensify with techniques that are normally used in synthetic polymer processing.

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