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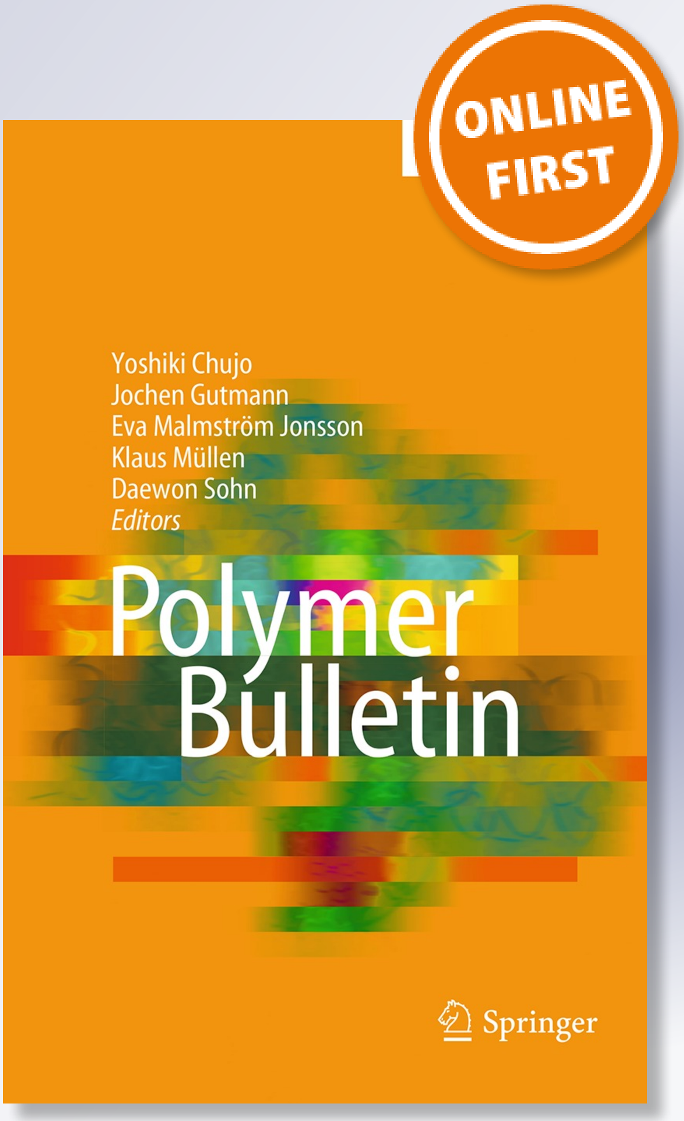

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REVIEW

Cellulosic materials as natural fillers in starch-containing matrix-based films: a review

Tomy J. Gutiérrez[1,2,3] · **Vera A. Alvarez**[3]

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Abstract In this work, the different cellulosic materials, namely cellulose and lignin are analyzed. In addition, the starch-containing matrices (isolated starch and flour) reinforced with cellulosic materials to be used in packaging applications are described. Many efforts have been exerted to develop biopackaging based on renewable polymers, since these could reduce the environmental impact caused by petrochemical resources. Special attention has had the starch as macromolecule for forming biodegradable packaging. For these reasons, shall also be subject of this review the effect of each type of cellulosic material on the starch-containing matrix-based thermoplastic materials. In this manner, this review contains a description of films based on starch-containing matrices and biocomposites, and then has a review of cellulosic material-based fillers. In the same way, this review contains an analysis of the works carried out on starch-containing matrices reinforced with cellulose and lignin. Finally, the manufacturing processes of starch/cellulose composites are provided as well as the conclusions and the outlook for future works.

Keywords Cellulosic materials · Food packaging · Starch · Biocomposites

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Abbreviation

CNCs	Cellulose nanocrystals
CNFs	Cellulose nanofibers
CNPs	Cellulose nanoparticles
REx	Reactive extrusion
T_g	Glass transition temperature
TPS	Thermoplastic starch

Introduction

The increase of waste from the synthetic polymers used for packaging has been a key factor for the development of new biodegradable materials for such application [1, 2]. Several biodegradable polymers, both synthetic and natural, for example proteins and polysaccharides, are promising materials for environmentally-friendly packaging [3, 4]. Starch can be highlighted as one of the most widely studied polysaccharides; this is because of its competitiveness as a result of its low cost and high production compared to other biopolymers. Nonetheless, the use of flours with high starch content as amylaceous matrix in the film formulation has gained relevance recently [5–7]. This is because flours are cheaper compared to starch; besides, flours have the advantage containing cellulosic material (cellulose, hemicellulose and lignin), which strengthens the internal structure of flour-based films. In this context, Gutiérrez et al. [5] reported that chemical modification of plantain flour increased relatively its fiber content due to leaching of other constituents of the flour during the modification process, which led to an increase in the Young's modulus and tension to break in films based on modified plantain flour. Thus, flours with high starch content are a potential source for the development of self-reinforced thermoplastic films. Additionally, the flours have in their chemical composition, sugars and proteins, which enhance the plastic characteristics of these materials, i.e., the materials obtained have higher elongation and, therefore, its glass transition temperature (T_g) is lower [5–7]. Nevertheless, these materials have some drawbacks; among them, we can mention their high sensitivity to water due to their hydrophilic character and their poor barrier properties to gases (water, ethylene, carbon dioxide, oxygen).

On the other hand, several natural fillers, particularly cellulosic materials are mixed with starch-based polymers to improve their mechanical and physicochemical properties, in particular Young's modulus and toughness. For preparation of fiber composites, various techniques have been used, and the same have effects on characteristics of these composites. The following review aims to address the different factors that influence the production of these composite materials. In addition, highlight the advantage of taking flours as starch-containing matrix in formulation of biodegradable and edible films.

Films based on starch-containing matrices

Starch-containing matrices mean any of the forms of starch or flour from tubers, rhizomes, cereals and seeds, e.g., wheat, corn, sorghum, potato, cassava, taro, yam, sagu, zulu, etc., which contain mixtures of amylose/amylopectin in different proportions or contain some of these macromolecules in a majority relationship, as is the case of the "waxy" starch that has very low amylose content, or the starches with high amylose content, which are obtained from genetic modifications of the vegetal material or by isolation of the macromolecule.

Several studies based on the use of starch from different sources have been published. Nevertheless, only few studies on the utilization of flour as raw material for the production of films have been carried out.

The behavior of flours still needs to be studied and analyzed as there are just few works related to this topic [5–7]. The results on the use of flour as biodegradable matrix are really promising [5–7]. In addition, flour as a feedstock is much more interesting because it is cheaper to obtain than commercial starches, which is related with the higher efficiency and performance.

However, thermoplastic starch (TPS) has been extensively studied worldwide, since it is the most economical biopolymer in market [8–13]. Besides, TPS shows similar properties and processing conditions to those of polyolefins. For this reason, many of the studies performed on the effect of incorporating cellulosic material have been evaluated on starch-based films. Nonetheless, this review also intended to include some recent studies in films made from flour.

Films based on starch-containing matrices/natural fillers blend

Due to the accumulation of waste at the end of the life cycle of traditional polymeric products, the development of biopolymeric materials which are environmentally friendly has attracted extensive interest [14], with starch being one of the most important ones. Nevertheless, the mechanical, physicochemical and barrier properties of such kind of biopolymer are lower when compared to traditional polymers. To improve the properties and performance of the biopolymer materials, natural fillers may be incorporated to produce biocomposites [15–43]. TPS has been mainly reinforced by filler materials such as cellulosic materials, clays and inorganic nanoparticles. However, strong tendency for obtaining natural and biodegradable materials has led to focus efforts on the development of composite materials from natural fillers such as cellulosic materials. Hence, we extend the analysis on cellulosic materials incorporated into films based on starch and flour.

Natural filler: cellulosic materials

Cellulose-based composites have received great attention in the last years since cellulose can be used as reinforcing fillers in biopolymers based on starch. Likewise, low cost, availability, renewability, light weight, nanoscale dimension, low density, low coefficient of thermal expansion, non-toxicity, unique morphology, sustainability and biodegradability of these biomaterials allow to continue stimulating the development of different structural materials from a renewable natural resource [44–46].

Cellulose is an important polysaccharide that helps in maintenance of cell structure of plants, bacteria, fungi, algae, amoebas, and even animals. Each of the layers in cell wall contains cellulose that is embedded in matrix of lignin and hemicellulose [47, 48]. In other words, microfibrils consisting of cellulose are glued by lignin and hemicellulose. A schematic graph of cellulose strands surrounded by hemicellulose and lignin is shown in Fig. 1. Likewise, cellulose is a high molecular weight homopolysaccharide composed of β-1,4-anhydro-D-glucopyranose units [$C_{6n}H_{10n}O_{2(5n+1)}$ (n = degree of polymerization of glucose)] and is considered to be the most abundant polymer [46, 49, 50]. In nature, cellulose chains have a degree of polymerization (DP) of approximately 10,000 glucopyranose units in wood and 15,000 in native cotton [51]. It has also been reported that cellulose can be considered as a string of cellulose crystallites linked along the chain axis by amorphous domains (Fig. 2). Their structure consists of a predominantly crystalline cellulosic core which is covered with a sheath of paracrystalline polyglucosan material surrounded by hemicelluloses [52, 53]. It is worth noting that frequent increase in hydrolysis time destroys the amorphous phase and leads to the increase of crystalline phase. Besides, peaks at $2\theta = 15°$, 16.5°, 20.1°, 22.5°, and 35.2°

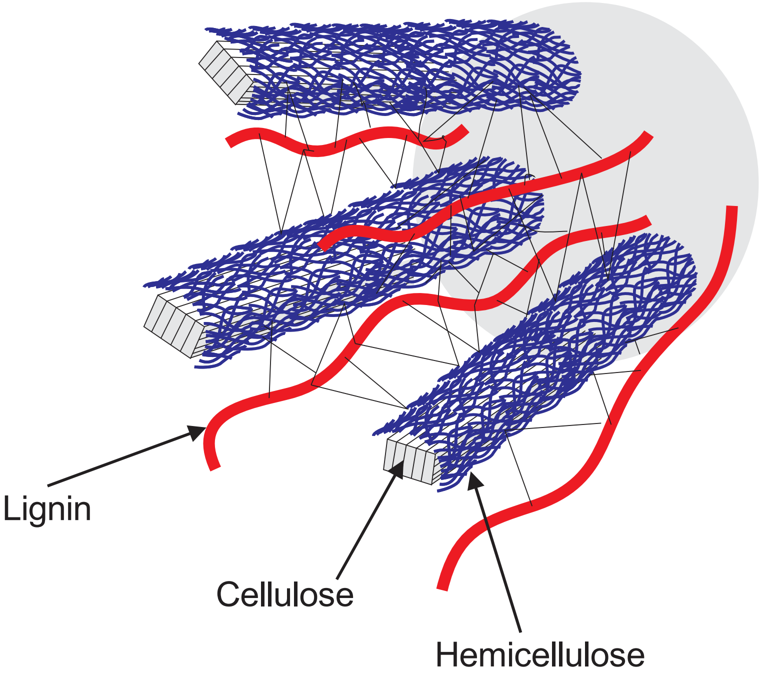

Fig. 1 Cellulose strands surrounded by hemicellulose and lignin

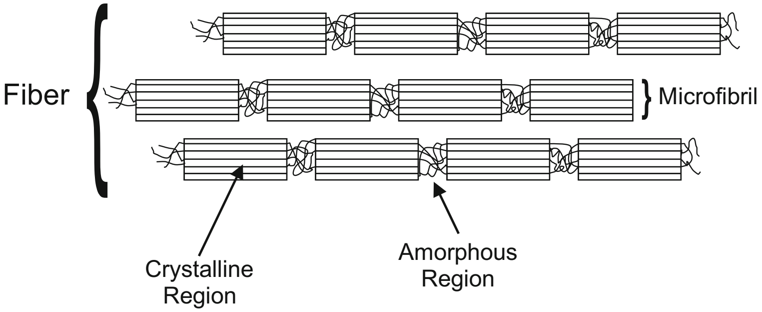

Fig. 2 Schematic diagram of the physical structure of a semicrystalline cellulose fiber

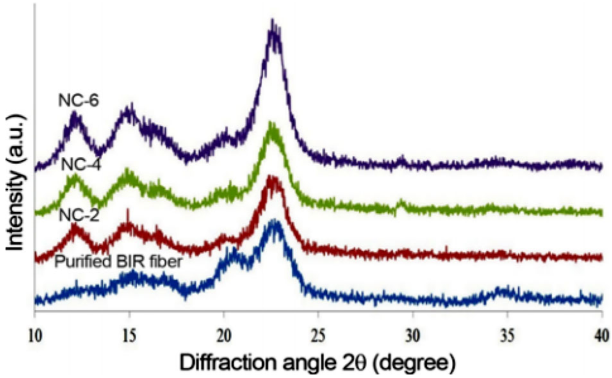

Fig. 3 XRD profiles of beer industrial residuals (BIR) fibers and nanocellulose (NCs) prepared with different hydrolysis times [46]

could be attributed to [101], [101], [021], [002] and [040] atomic planes, respectively (Fig. 3) [46].

Crystalline cellulose can be isolated by treatment of cotton, sisal, and wood with strong acids such as hydrochloric acid and sulfuric acid to remove the amorphous parts yielding crystals with diameters in the range 5–20 nm and aspect ratio of about 1–100 times (Fig. 4) [49, 54–56]. As a result of acid treatment used to obtain cellulose, cellulose nanocrystals (CNCs) often have electronegative charges on their surface [57].

Shafiei-Sabet el al. [58–60] investigated the influence of ultrasound energy, surface charges, and ionic strength on the rheological properties of CNC suspensions. They found that the critical transition concentrations were shifted to higher values when more ultrasound energy was applied or when the CNCs had higher surface charges or when more NaCl was added.

Li et al. [55] investigated the structure–morphology–rheology relationships for cellulose nanoparticles (CNPs), including CNF and CNC. The mechanical disintegrated CNFs showed inactive surface characteristics (e.g., low zeta potential value and fewer hydroxyl groups), larger aspect ratios (>80), and high flexibility. In

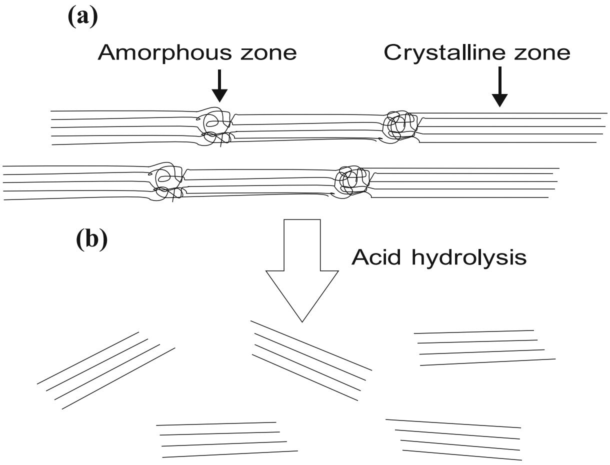

Fig. 4 Isolation of cellulose nanofibers: **a** schematic representation of the isolation process used to obtain cellulose microfibrils; **b** disintegration of microfibrils by acid attack forming nanofibrils

contrast, the sulfuric acid-hydrolyzed CNCs carried negatively charged sulfate groups and a large number of hydroxyl groups on the surface. The concentration, aspect ratio and surface charges of CNCs had significant influences on the network of CNC suspensions. In addition, the introduction of sulfate groups on the surface of CNCs generated strong electrostatic repulsion between CNCs, reducing the interparticle interactions, which also contributed to the observed liquid-like rheological behavior.

Likewise, hemicellulose is the second most abundant family of naturally occurring polymers [61, 62]. Hemicellulose comprises a group of polysaccharides (excluding pectin), which are formed from different highly branched polysaccharides of much lower molecular weight than cellulose, such as glucose, galactose, mannose, xylose and others [61–64]. Hemicellulose has been found to remain associated with cellulose after removal of lignin. Hemicellulose is generally used as gelling agents, tablet binders viscosity modifiers, etc. [50].

Among other three major natural lignocellulosic components of vegetal cell wall is found the lignin, which is a highly branched polymer [61, 62, 65]. One difference between hemicellulose and lignin is that the latter is composed of aliphatic and aromatic hydrocarbons [53]. Therefore, lignin is hydrophobic in nature thus making cell wall impermeable to water ensuring an efficient water and nutrition transport in vegetal cells [66]. Likewise, lignin structure is very complex although it is well known as a cross-linked macromolecular material based on a phenylpropanoid monomer structure organized into a three-dimensional skeleton [47, 53, 67–70]. However, these structures differ in the degree of oxygen substitution on phenyl ring [53]. In lignin, both the carbon–carbon and carbon–oxygen bond occur between monomers. The carbon–oxygen link between a p-hydroxy moiety and the β-end of propenyl group (β-O-4) accounts for most of the bonds between monomer units in the lignin from most resources [53]. Figure 5 shows the carbon–carbon and carbon–

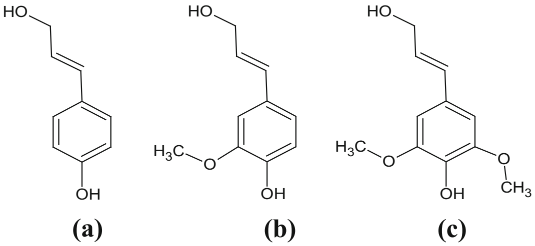

Fig. 5 Monolignol monomer species: **a** p-coumaryl alcohol (4-hydroxyl phenyl, H), **b** coniferyl alcohol (guaiacyl, G) and **c** sinapyl alcohol (syringyl, S)

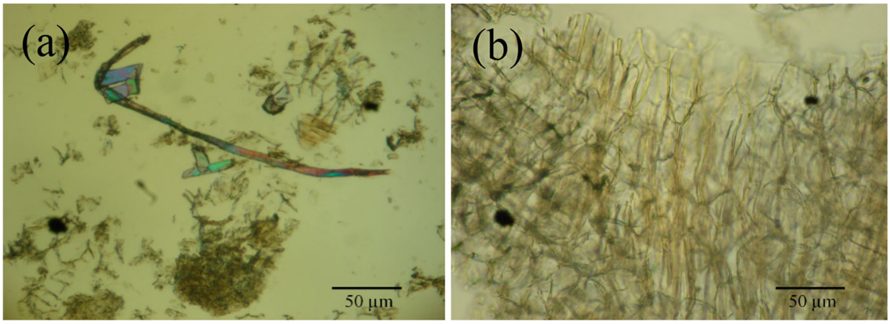

Fig. 6 Optical micrographs with polarized light of: **a** lignin fragments belonging to the wall of the sclerenchyma of beet and **b** cellulose associated to the wall of the cell parenchyma of the beet, at 20× of magnification [5]

oxygen bonds formed between different monomer units in the lignin [53]. Depending on the type of lignin (whether it is procured from soft wood/hard wood), the degree of cross-linking varies in the lignin, and depending on the degree of substitution, rigidity of structures varies [53], i.e., different phenylpropanoid units in lignin are linked together through various types of carbon–carbon and ether bonds as opposed to linear or branched chains as in carbohydrates.

Lignin has been found to play a major role in protecting the cellulose/ hemicellulose from harsh environmental conditions such as water [50]. In a given lignocellulosic material (e.g., natural fibers), cellulose provides the strength and thermal resistance to materials and hemicellulose on the other hand is responsible for the largest biodegradation and moisture absorption [71, 72]. Figure 6a shows a lignin strand obtained from beet flour and Fig. 6b shows the walls of the cells of beet, which are found in beet flour.

The impressive properties of lignin, such as its high abundance, low weight, environmental friendliness, antioxidant, antimicrobial and biodegradable nature, along with its CO_2 neutrality and reinforcing capability, make it an ideal candidate for the development of novel polymer composite materials [53, 73–75]. Nevertheless, there are only few studies on polymer composites reinforced with lignin; therefore, the research on lignin-based polymer composites is still in its infancy [65].

Cellulosic particles are distinguished by their liquid crystal behavior when suspended in water, presenting birefringence phenomena under polarized light

(Fig. 6a). One of the most specific characteristics of cellulose is that each of its monomer bears three hydroxyl groups. These hydroxyl groups and their ability to hydrogen bond play a major role in directing crystalline packing and in governing important physical properties of these highly cohesive materials [76]. Likewise, due to strong hydrogen bonds that occur between cellulose chains, cellulose does not melt or dissolve in common solvents.

On the basis of their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing conditions, cellulosic materials are classified into three main subcategories according to Khalil et al. [45] (see Table 1).

Moreover, cellulose obtained from nature is known as cellulose I, or native cellulose. In this type of cellulose, the chains within unit cell are in a parallel conformation [77], making it an unstable form. Special treatments of native cellulose result in other forms of cellulose, namely cellulose II, III, and IV [78]. This conversion also allows possibility of conversion from one form to another [79]. For this reason, several modifications have been carried out on cellulose to improve its stability and fiber–polymer compatibility, since it is also well known that without such treatment, stress applied to the fiber–polymer composite is not efficiently transferred from the matrix to the fiber, and beneficial reinforcement effect of fiber remains underexploited [80, 81].

Table 1 The family of cellulose materials classified into three main subcategories

Type of cellulose	Selected references and synonyms	Typical sources	Formation an average size
Microfibrillated cellulose	Microfibrillated cellulose, nanofibrils and microfibrils, nanofibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax, cotton, sisal, cellulose from algae and bacteria, etc	Delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment diameter: 5–60 nm length, several micrometers
Nanocrystalline cellulose	Cellulose nanocrystals, nanocrystals, crystallites, whiskers, rodlike cellulose microcrystals	Wood, cotton, hemp, flax, wheat straw, mulberry bark, ramie, Avicel, tunicin, cellulose from algae and bacteria	Acid hydrolysis of cellulose from many sources diameter: 5–70 nm length; 100–250 nm (from plant celluloses); 100 nm to several micrometers (from celluloses of tunicates, algae, bacteria). There are also studies where nanocrystalline cellulose has been obtained from mechanical methods
Bacterial nanocellulose	Bacterial cellulose, microbial cellulose and biocellulose	Low-molecular-weight sugars and alcohols	Bacterial synthesis diameter: 20–100 nm; different types of nanofiber networks

Some cellulose derivatives that can be indicated are: cellulose acetate, cellulose propionate, cellulose acetate/butyrate, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellose, methyl cellulose, ethyl cellulose, hydroxypropyl methylcellulose and cellulose nitrate.

So far, this has allowed to obtain different cellulose derivatives, which are important commercial products for plastics, textiles, packaging, films, lacquers, food, pharmaceutical and explosives [82]. In addition, the use of cellulose can also extend and improve quality and food shelf life as they can serve as carriers of some active substances, such as antioxidants and antimicrobials [83].

Films based on starch-containing matrices with cellulose Cellulose fibrils have been the most studied organic reinforcement in starch-based composites due to their remarkable mechanical properties. The affinity between starch and cellulose due to their structural similarity can be exploited not only to enhance the mechanical properties of composites but also to produce biodegradable materials [49, 84, 85].

In starch-based composites, the mechanical properties are strongly related to moisture content and humidity conditions and the addition of cellulose in starch composite materials can reduce water adsorption.

The application of nanocellulose compared to the microcellulose has had great interest because of its increased surface area, thus allowing to improve cohesive forces between matrix and cellulose. In this sense, in studies on glycerol-plasticized starch nanocomposites reinforced with nanocellulose from wheat straw, Alemdar and Sain [86] found that the addition of 10 wt% of cellulose nanofibrils improved the tensile strength and Young's modulus of nanocomposites. Nanocomposites based on wheat starch plasticized with glycerol and reinforced with cellulose nanofibrils extracted from ramie fibers by acid hydrolysis [87] showed improvement in water resistance, good dispersion, good adhesion between components, an increase in Young's modulus (from 56 to 480 MPa), and improvement in tensile strength (from 2.8 to 6.9 MPa) with increasing filler content from 0 to 40 wt%.

In the same way, the addition of cellulose microfibrils extracted from cotton, softwood, or bacterial cellulose at low concentrations to wheat or potato starch blended with pectin has a significant effect on their mechanical properties [88]. Young's modulus of wheat starch nanocomposites reinforced with cotton nanofibrils increased by five times with the addition of only 2.1 wt% of nanofibrils.

Likewise, strong interactions between cellulose nanofibers (CNFs) prepared from cottonseed linters and between the filler and the glycerol-plasticized starch matrix were reported to play a key role in reinforcing properties [89]. In nonpercolating systems for instance, for materials processed from freeze-dried CNCs, strong matrix/filler interactions enhance the reinforcing effect of the filler.

More recently, Rodney et al. [90] evaluated the addition of 5 % (v/v) tea tree fiber as a filler, which improves the tensile strength of the tapioca starch composites (TS) up to 34.39 % in tea tree leaf-reinforced TS composites (TTL/TS), 82.80 % in tea tree branch-reinforced TS composites (TTB/TS) and 203.18 % in tea tree trunk-reinforced TS composites (TTT/TS) (Fig. 7).

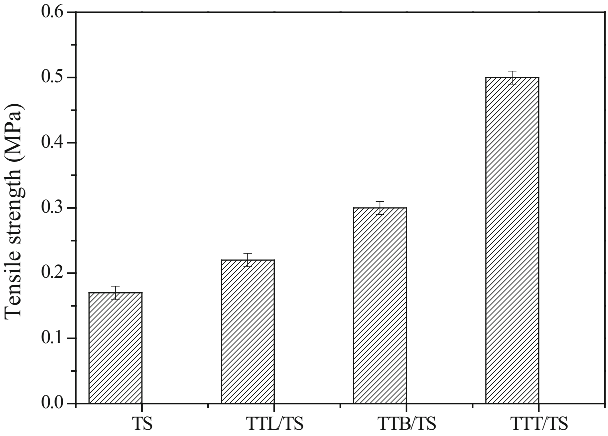

Fig. 7 Tensile strength of the tea tree fiber-reinforced TS composites [90]

In addition, according to Anglès and Dufresne [91, 92] and Dufresne et al. [93], the mechanical properties of nanocomposites based on glycerol-plasticized waxy maize starch and cellulose whiskers show a relationship between plasticizer content and relative humidity conditions during storage. Wherefore, mechanical properties of these nanocomposites are more dependent on plasticizer and moisture content than on the addition of nanocellulose. Example of this was the accumulation of plasticizer at interface, which increased the ability of amylopectin chains to crystallize, thus leading to the formation of a transcrystalline zone around cellulose whiskers. Such crystalline zones accounted for the lower water adsorption of the nanocomposites with increasing filler content. A very low reinforcing effect was observed upon the addition of tunicin cellulose whiskers as a consequence of this plasticizer accumulation at the interfacial zone. Therefore, the accumulation of glycerol on the cellulose whisker surface led to increased antiplasticization effects [91, 93] and thus poor mechanical properties. Based on these studies, it can be said that films based on starch with high amylose content avoid the antiplasticization effect in the presence of cellulose whiskers. In this way, polymer composites based on cellulose whiskers/starch blends have a better performance when amylose content in the starch used is higher.

Besides, Sonkaew et al. [94] who evaluated antioxidant activity of curcumin on cellulose-based films found an antioxidant effect developed on the films due to the presence of curcumin. However, the effect on the mechanical properties of these nanocomposites has not been evaluated; therefore, it remains an interesting study for the future.

Finally, the major factors that govern the properties of fiber–starch thermoplastic composites are fiber volume fraction, fiber dispersion, fiber aspect ratio and length distribution, fiber orientation and fiber–matrix adhesion [95]. Each of these parameters is briefly discussed below.

Fiber volume fraction

Fiber-based nanocomposites can transfer the stress from the matrix to the fiber by means of shear. When it is stressed in tension, both the fiber and the matrix are elongated equally according to the principle of combined action [96]. Therefore, the mechanical properties of nanocomposite can be evaluated on the basis of the properties of individual constituents. For a given elongation of the composite, both constituents (starch and fiber), may be in elastic deformation; the fiber may be in elastic deformation whereas the matrix may be in plastic deformation, or both the fiber and the matrix may be in plastic deformation (Fig. 8).

Additionally, the properties of starch–fiber nanocomposites are strongly determined by fiber concentration. At low fiber volume fraction, a decrease in tensile strength is usually observed. This is ascribed to the dilution of matrix and introduction of flaws at fiber ends, whereas a high stress concentration occurs causing the bond between fiber and matrix to break. At high volume fraction, stress is more evenly distributed and a reinforcement effect is observed. Nevertheless, this occurs until a threshold is determined by inherent properties of cellulose fibers; since as is well known, to exceed this threshold the cellulose fibers are flocculated and percolated, giving rise to weak points in structures. However, all values of strain in composites are given by a simple mixing rule balanced by the volume fraction of each constituent before the threshold point. This means that there exists a critical volume to observe the effect of reinforcement on the matrix, which decreases with increasing strength of fibers. Likewise, below this value, the behavior of composite is only governed by the matrix.

Moreover, these fillers generally increase stiffness of the nanocomposites [97]. Alvarez et al. [34] reported that Young's modulus of MaterBi-Y ® starch nanocomposites (a commercial starch) reinforced with sisal nanofibrils increased at

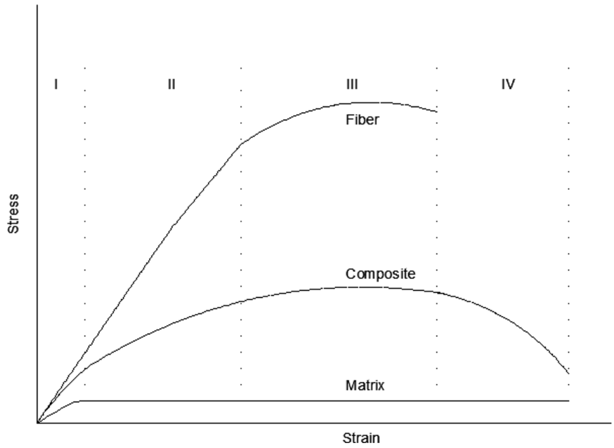

Fig. 8 Illustration of four stages of stress–strain curves of fibers, matrix and composite. *Stage I* elastic deformation of both fibers and matrix; *stage II* elastic deformation of fibers and plastic deformation of matrix; *stage III* plastic deformation of both fibers and matrix; *stage IV* failure of both fibers and matrix [96]

least two times with the addition of only 20 wt% of nanofibrils. In this example, the source of cellulose nanofibrils influences the mechanical properties of composites; composites reinforced with sisal. On the other hand, the addition of a third component such as pectin, proteins, chitosan, polyphenolic extracts, among others, can give rise to complex interactions between components, often resulting in poorer mechanical properties (Fig. 9) [98]. As pointed out by Anglès and Dufresne [92], the addition of microfibrils to multicomponent systems can completely change the trends in mechanical properties. Likewise, microfibrils have a particular infinity to one particular component over another phase, promoting partitioning and blend immiscibility.

Mechanical, dynamic mechanical and thermal properties of nanocomposites of potato starch reinforced with cellulose nanofibrils and plasticized with water and sorbitol with 5 wt% of cellulose nanofibrils showed well-distributed reinforcements in the starch matrix with a significant improvement in tensile properties compared to the pure matrix [99].

Alemdar and Sain [86] found that the addition of 10 wt% of cellulose nanofibrils improved the tensile strength and Young's modulus of starch nanocomposites reinforced with cellulose nanofibrils from wheat straw and plasticized with glycerol. Likewise, Lu et al. [87] showed improvement in water resistance, good dispersion, good adhesion between components, an increase in Young's modulus (from 56 to 480 MPa), and improvement in tensile strength (from 2.8 to 6.9 MPa) with increasing filler content from 0 to 40 wt% (Fig. 10).

Babaee et al. [81] who evaluated the addition of modified and native cellulose in films based on cassava starch found that the CNFs improved the mechanical properties of these starch-based nanocomposites. In addition, the modification of cellulose using anhydride acetic allowed to obtain strong starch–fiber interactions, which decreased the water adsorption and the water vapor permeability, this because polar groups were blocked. Nevertheless, other authors have reported an anchoring effect of the lignocellulosic filler acting as nucleating agent for polymeric chains has been reported resulting in an increase in the degree of crystallinity of the matrix [100]. This effect seems to be strongly influenced by lignin content and the surface aspect of fiber [101, 102].

Fiber dispersion

The primary requirement for obtaining good performances from short-fiber composites is a good dispersion level in the host polymer matrix, which is obtained if fibers are separated from each other and, therefore, each fiber is surrounded by the matrix, since if fibers are equally dispersed in the matrix, the stress can be transferred equally to the whole composite and vice versa [90]. In this sense, there are many studies in which wetting and adhesion between a reinforcing material and a matrix are so poor that electron micrographs show spaces between the phases and "pull-out" of reinforcing fibers upon breakage of a composite structure. Clumping and agglomeration must, therefore, be avoided. Insufficient fiber dispersion results in an inhomogeneous mixture composed of matrix-rich and fiber-rich domains.

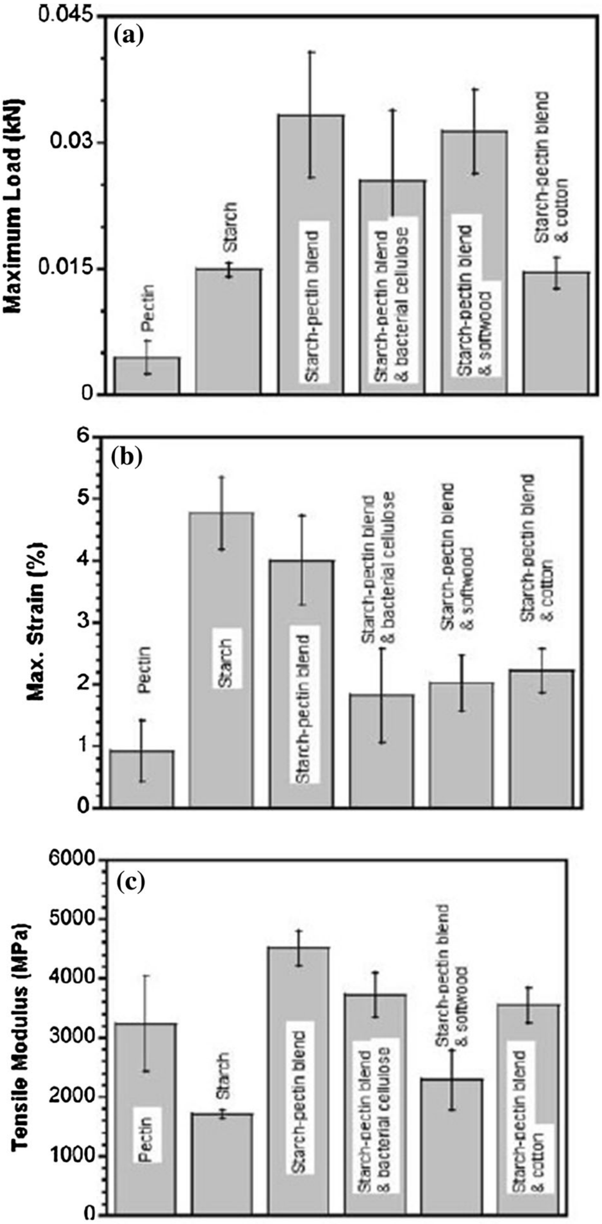

Fig. 9 Mechanical properties—maximum load (*top*), maximum strain (*middle*) and modulus (*bottom*)—of 50:50 starch–pectin blended films. Microfibrils derived from various sources, as noted have been added to the starch–pectin blend at 3 % (w/w) concentrations [88]

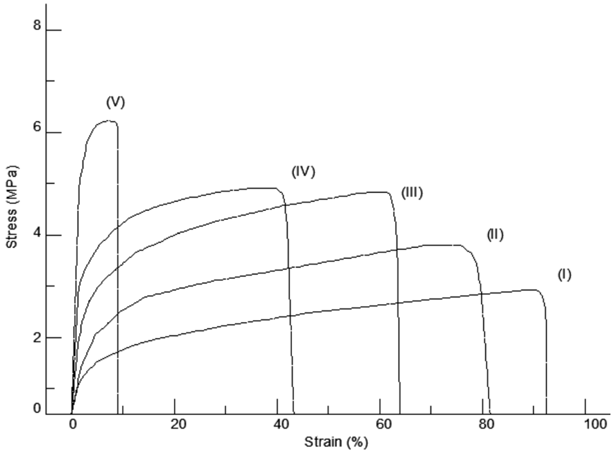

Fig. 10 The stress–strain curves for nanocomposites of starch reinforced with ramie nanofibrils: *i* glycerol-plasticized starch, and composites with *ii* 5, *iii* 10, *iv* 25, and *v* 40 wt% of ramie nanofibrils [87]

Mixing the polar and hydrophilic fibers with a non-polar and hydrophobic matrix can result in dispersion difficulties [94].

There are two major factors affecting the extent of fiber dispersion: fiber–fiber interaction, such as hydrogen bonding between the fibers, and fiber length, because of the possibility of entanglements. As mentioned above, one of the specificities of cellulose fibers as reinforcement materials is their poor dispersion characteristics in many thermoplastic melts, due to their hydrophilic nature. Several methods have been suggested and described in the literature to overcome this problem and improve the dispersion [94]. Among them are:

1. Fiber surface modification: the surface energy is closely related to hydrophilicity of lignocellulosic fibers. Surface modification of nanofibrillated cellulose is crucial to improve compatibility and homogeneous dispersion within polymer matrices [103]. Different methods such as esterification, cationization, silylation, polymer grafting and TEMPO oxidation have been reported for the surface modification of nano-sized cellulose [104–107].
2. Use of dispersing agents, such as stearic acid: the dispersion of lignocellulosic fibers can be improved by pretreatment with lubricants or thermoplastic polymers. An addition of 1–3 % stearic acid is sufficient to achieve a maximum reduction in size and number of aggregates [108].
3. Use of a coupling agent: according to Trejo-O'reilly et al. [109] cellulose fibers have problems of compatibility with the thermoplastic starch; therefore, the coupling agents may be necessary. In this sense, cellulose offers the possibility of various coupling reactions, due to the three hydroxyl groups in each glucose residue [110]. The main idea is to use a simple coupling reaction between hydroxyl groups in cellulose fibers and molecular or macromolecular agents bearing one or more –OH reactive functional groups. Some commonly used coupling agents can be indicated: alkenyl succinic anhydride (ASA), phenyl

isocyanate (PI), silane, 3-isopropenyl-α,α dimethylbenzyl isocyanate (TMI), among others [110–112]. Bledzki et al. [113] reported that coupling agent treatments of cellulose fiber had better effects on the mechanical properties of cellulose composites, but mechanisms or explanations were not mentioned. Lu et al. [111] indicated that coupling agent (silane) improved the tensile strength and the values of elongation at break.

4. Increased shear force and mixing time. The best processing method involves twin-screw extruder. Hietala et al. [114] investigated if cellulose nanofiber gels with high water content can be processed to nanocomposites with starch powder using continuous twin-screw extrusion. The results showed that the addition of cellulose nanofiber improved the mechanical properties and had a positive effect on moisture adsorption of the TPS.

Some physical methods have also been suggested to improve the dispersion of short fibers within the matrix.

Treatments such as stretching, calendering, thermotreatment and the production of hybrid yarns do not change the chemical composition of fiber, but modify their structural and surface properties and thus influence their mechanical bonding with polymers.

Fiber aspect ratio and length distribution

The efficiency of a composite also depends on amount of stress transferred from the matrix to the fibers. This can be maximized by improving interaction and adhesion between both phases and also by maximizing length of fibers retained in the final composite. However, long fibers sometimes increase the amount of clumping resulting in poor dispersion of the reinforcing phase within the host matrix. The ultimate fiber length present in the composite depends on the type of compounding and molding equipment used and processing conditions. Several factors contribute to fiber attrition, such as the shearing forces generated in the compounding equipment, the residence time, the temperature and the viscosity of the compound.

The fiber aspect ratio, which is its length to diameter ratio, is a critical parameter in a composite. A relationship has been proposed by Cox to relate the critical fiber aspect ratio, l_c/d, to the interfacial shear stress, τ_y, viz.,

$$\frac{l_c}{d} = \frac{\sigma_{fu}}{2\tau_y} \tag{1}$$

where σ_{fu} is the fiber ultimate strength in tension. At controlled fiber ultimate strength in tension, this equation shows an inverse relationship between the critical aspect ratio and the interfacial shear stress, where the former decreases as the latter increases, because of efficient transfer. This means that, for each short-fiber composite system, there is a critical fiber ratio that corresponds to its maximum value for which the maximum allowable stress can be achieved for a given load. This parameter is determined by the fiber properties, the matrix properties and the quality of the fiber–matrix interface.

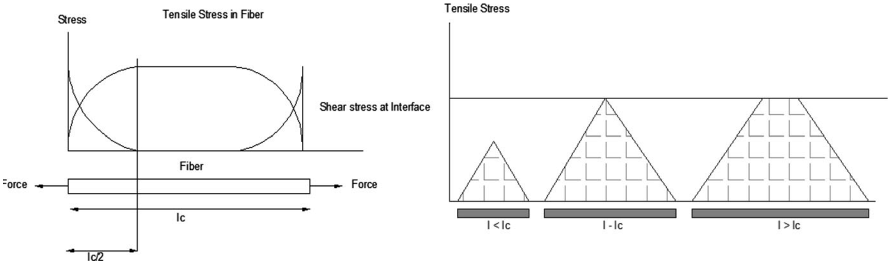

Fig. 11 Variation of tensile stress in fiber and shear stress at interface occurring along the fiber length. If the length is lower than its critical value, l_c, the fibers are not loaded to their maximum stress value [95]

The condition for maximum reinforcement, that is the condition ensuring maximum stress transfer to fibers before the composite fails, is to have a length higher than the critical length *lc* (Fig. 11). If the fiber aspect ratio is lower than its critical value, the fibers are not loaded to their maximum stress value. A specificity of cellulose fibers is their flexibility compared to glass fibers which allows a desirable fiber aspect ratio to be maintained after processing, which is around 100 or 200 for high-performance short-fiber composites.

Fiber orientation

Fiber orientation is another important parameter that influences mechanical behavior of short-fiber composites. This is because fibers in such composites are rarely oriented in a single direction, which is necessary to obtain the maximum reinforcement effects. During processing of short-fiber composites, a continuous and progressive orientation of individual fibers occurs (Fig. 12). This change is related to geometrical properties of fibers, the viscoelastic properties of the matrix and the change in shape produced by processing. In these operations, the polymer melt undergoes both elongation and shear flow [95].

A schematic diagram of the organization of the cellulose fiber is given in Fig. 13. According to Dufresne [115], at low concentration of CNC suspensions are isotropic, with a random arrangement of rods, while at high concentration the suspensions are anisotropic, with the cellulose rods packed in a chiral nematic arrangement. Just beyond the critical concentration for anisotropic phase formation is a biphasic region in which the isotropic and anisotropic phases coexist [116].

Rod-shaped species have been demonstrated to display nematic order, whereas suspensions of cellulose crystallites spontaneously form a chiral nematic phase

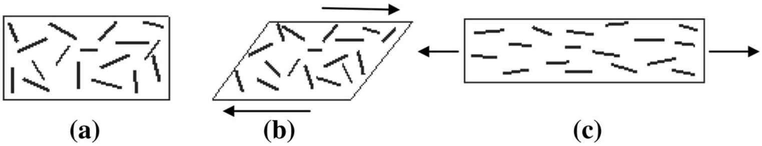

Fig. 12 Orientation of individual fibers during processing: **a** initial random distribution, **b** rotation during shear flow and **c** alignment during elongational flow

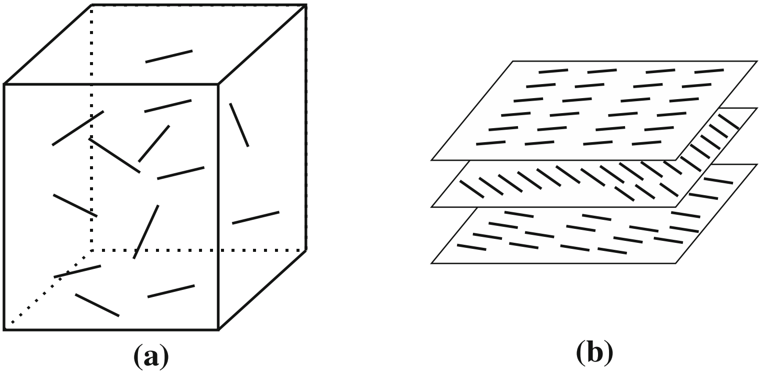

Fig. 13 Schematic representation of rod orientation in both the **a** isotropic and **b** chiral nematic phases

[117]. The chiral nematic or cholesteric phase consists of stacked planes of molecules aligned along a director, with the orientation of each director rotated about perpendicular axis from one plane to next [118].

In 1959, Marchessault et al. [119] reported the birefringent character of acid-treated cellulose and chitin monocrystals. The birefringence of aqueous suspensions can be observed through a pair of cross-nicols. This birefringence results from two origins: (1) a structural form anisotropy of cellulose ($\Delta n \approx 0.05$), and (2) a flow anisotropy resulting from alignment of nanoparticles under flow generally operated before observation [76].

According to the prediction of Onsager [120], the cellulose whiskers can undergo an orientational disorder–order phase transition from a disordered isotropic phase to an orientationally ordered phase. Rod-like nanoparticles point with equal probability towards each direction in isotropic phase. However, they cluster around a preferred direction in anisotropic phase. Suspensions divided into isotropic and anisotropic phases when a critical concentration was reached [116]. This phase transition depends on geometrical axial ratio of whiskers [120], their surface charge [116, 121], and their length polydispersity [122]. Dong et al. [123] reported an increase in critical concentration at phase transition in the presence of counterions. The latter influences also in stability of the cellulose whisker suspensions and modifies the temperature dependence of the phase separation.

The rheological behavior of tunicin whisker (an animal cellulose from tunicate—a sea animal) aqueous suspensions was studied by Bercea and Navard [124]. They observed two different behaviors according to whisker concentration. In the isotropic phase ($c < 0.8$ wt%), where whiskers are randomly oriented, a decrease of viscosity in relation to shear rate increase was explained by the whiskers alignment. In the anisotropic phase ($c > 0.8$ wt%), the behavior is similar to that of liquid crystal polymers with a weak shear-thinning region surrounded by two other shear-thinning regions.

Anisotropic magnetic susceptibility of the individual C–C, C–O, C–H, and O–H bonds and their relative orientation in the crystal were suggested to originate from the magnetic orientation [125, 126], opening up the possibility to control the degree

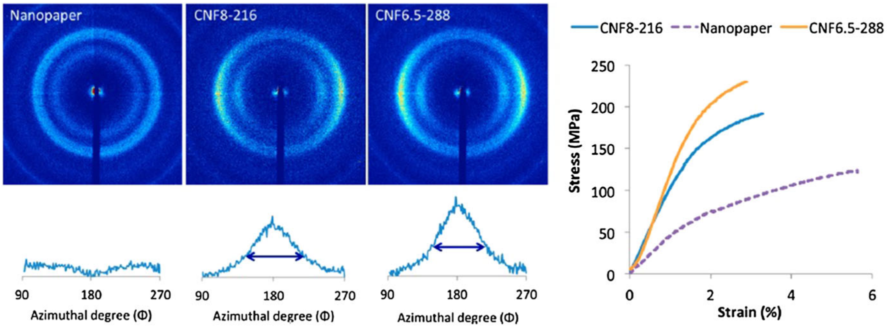

Fig. 14 X-ray diffractograms and representative stress–strain curves of the prepared CNF-nanopaper, CNF8-216, and CNF6.5-288 [131]

of orientation during processing. One example is the extrusion blow-molding of packaging films and electric or magnetic devices with orientation in film processing [94]. However, a negligible role in alignment has been attributed to ester groups at the whiskers surface. Owing to viscosity of cellulose crystallite suspensions, the process of magnetic alignment occurs over a period of hours to days. When a magnetic field is applied to chiral nematic suspensions, an overall orientation is achieved where the cholesteric axis becomes parallel to the magnetic field [127]. Magnetic alignment of the chiral nematic phase of tunicin whisker suspensions was also reported by Kimura et al. [128]. It was shown that the helical axis of the chiral nematic phase aligned in the direction of the applied static field, resulting in highly regular monodomains, whereas exposure to a rotating magnetic field caused unwinding of the helical axes to form nematic-like alignment. Besides, the orientation of the deposited CNCs has been observed, but only after long exposure (24 h) to the field [129, 130].

On the other hand, more recently Hooshmand et al. [131] reported the diffractograms of the CNF nanopaper; they showed a ring pattern (Fig. 14), indicating random orientation, while diagrams for both filaments based on CNF indicated equatorial arcs corresponding to (110) and (200) confirming the partial orientation of the CNF. Probably, the corresponding arc to (110) is merged with (110) on the diffractogram because of their very close scattering angles. The orientation index of the new filament was calculated to be 0.67. Whereby, it is clearly seen in representative stress–strain curves (Fig. 14) that the spun filaments have better mechanical properties when compared to randomly orientated CNF–nanopaper. It is also seen that CNF6.5-288 has better mechanical properties than CNF8-216, i.e., a better orientation of CNF allows to improve the properties of filaments.

Fiber–matrix adhesion

Fiber to matrix adhesion plays a very important role in reinforcement of composites with short fibers. It is necessary to have an effective load transfer from the matrix to the fibers for the ensuing composites to have good mechanical properties. This requires good interaction as well as adhesion between fibers and matrix, i.e., strong and efficient fiber–matrix interface [132, 133].

One way of applying this concept to the present context is to impregnate the fibers with a polymer compatible with the matrix and, in general, this is achieved using low-viscosity polymer solutions or dispersion. For a number of interesting polymers, however, the lack of solvents limits the use of this method. The compatibilization of two components by specific chemical or physical treatments has been the most common approach to this problem as frequent. Although, another less frequent approach to improve the starch matrix–fiber compatibility has been based on the use of a surface modifier that bears a structure very close to that of the matrix, but which has been appropriately modified so that its macromolecules can react at the fibers surface.

In fact, generating covalent bonds across the interface improved the adhesion between matrix and fibers, and both Young modulus and tensile strength were found to be higher than those obtained with the untreated fibers [134].

It has also been found that moisture absorbance of the natural fiber–polymer composite can be prevented if the fiber–matrix adhesion is optimized [134, 135].

According to Valadez-Gonzalez et al. [132], the interfacial shear strength between natural fibers and a thermoplastic matrix has been improved by morphological modification of the fiber surface. The level of fiber–matrix adhesion was further enhanced by the presence of a silane–coupling agent. The alkaline treatment has two effects on the fiber: (1) it increases the surface roughness that results in a better mechanical interlocking; (2) it increments the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites. The fiber preimpregnation allows a better fiber wetting which in a normal fiber–polymer mixing procedure would not be possible because of the high polymer viscosity. Thus, the preimpregnation enhances the mechanical interlocking between fiber and matrix. The fiber-surface silanization results in a better interfacial load transfer efficiency but do not seem to improve the wetting of the fiber.

Similarly, acetylation can reduce the hygroscopic nature of natural fibers and increases the dimensional stability of composites. Acetylation has been used in surface treatments of fiber for use in fiber-reinforced composites. Acetylation treatment of sisal fiber has improved the fiber–matrix adhesion. The procedure included an alkaline treatment initially, followed by acetylation [136].

Juntaro et al. [137, 138] developed a technique for modifying natural fiber (hemp and sisal) surfaces to improve the interaction between the fibers and polymers by attaching bacterial nanocellulose to the fiber surfaces. Unidirectional natural fiber reinforced composites were manufactured to investigate the impact of the surface modification on the fiber and the interface-dominated composite properties. It was reported that both the tensile strength parallel to and perpendicular to the bacterial nanocellulose-modified natural fibers increased significantly. The explanation for these improvements was that the presence of the nanofibers enhanced the interfacial adhesion between the primary fibers and the polymer. Water absorption was also reduced by bacterial nanocellulose grafting onto sisal fibers. In principle, this approach could be successfully applied to any natural fibers (hemp, flax, jute), provided their surfaces are sufficiently hydrophilic [138].

Lu et al. [139] successfully modified microfibrillated cellulose by applying three different coupling agents, namely 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, and a titanate coupling agent (Lica 38), to enhance the adhesion between microfibrils and polymer matrix. The surface modification modified the character of microfibrillated cellulose from hydrophilic to hydrophobic while the crystalline structure of the cellulose microfibrils remained intact. Among the tested coupling agents, the titanate gave the most hydrophobic surface, possibly due to the lower polarity of the titanate modifier alkyl chain. Unlike silane coupling, titanate coupling is thought to occur via alcoholysis, surface chelation or coordination exchange. When there are hydroxyl groups present on the surface of the substrate, the monoalkoxy- and neoalkoxy-type titanium-derived coupling agents react with the hydroxyl groups to form a monomolecular layer.

Films based on starch-containing matrices with lignin

Çalgeris et al. [140] prepared lignin-reinforced starch-based biocomposites. Lignin was extracted from hazelnut shells and used as a potential additive in different ratios in the preparation of starch composite films. It was observed that the lignin content in the starch-based films improved the mechanical and thermal properties in a considerable extent depending on load. Furthermore, it was concluded that these films have the potential to be used in a number of fields such as in coatings, food packaging and drug delivery systems [140].

Spiridon et al. [141] have also reported their study on the preparation of lignin-reinforced starch-based composites. In this study, glycerol-plasticized corn starch (GCS) prepared using a casting process was used as the polymer matrix, while adipic acid (AA)-modified starch microparticles (AASM) were used as the reinforcing materials.

Subsequently, the effect of two different types of lignin on the morphology, mechanical, thermal, and surface properties, along with water sorption, was investigated. It was observed that thermal stability and surface water resistance of the composite materials significantly improved through the addition of lignin [141].

Moreover, despite being well known that lignin is the only cellulosic material with oxidant activity, this effect has not been taken into account on starch-based films reinforced with lignin.

Manufacturing processes of films based on starch-containing matrices/cellulose blend

Most of the works found in the literature related to starch materials have been based on films obtained by casting method. However, processing methods such as blown extrusion, compression or injection molding are less reported. Solvent casting has been the most used method at small scale for the preparation films based on starch-containing matrices, which involves solubilization, casting, and drying steps. Despite being a good and adequate technique at laboratory scale, it is considered as a high-energy-consuming procedure.

Therefore, high levels and efficient biodegradable films production are required by industrial area. In this sense, scaling up processing methods using equipments designed for synthetic polymers is indispensable [142, 143]. In this context, extrusion, blowing, injection and thermo-compression are viable alternatives due to their energy efficiency combined with their high productivity [144–146]. Particularly, extrusion followed by thermo-compression is useful as a processing method because of its simplicity. These biomaterials could have feasible applications to develop economic and ecological materials [147]. In this sense, below will be indicated the manufacturing processes that are studied in starch/cellulose composites:

Solution casting method

Recently, nanocomposites from wheat straw CNFs and TPS from modified potato starch were prepared by the solution casting method [86]. Thermal and mechanical performance of the composites was compared with the pure TPS using thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and tensile testing. The tensile strength and modulus were significantly enhanced in the nanocomposite films, which could be explained by the uniform dispersion of CNFs in the polymer matrix. The modulus of the TPS increased from 111 to 271 MPa with maximum (10 wt%) nanofiber filling. In addition, the T_g of the nanocomposites was shifted to higher temperatures with respect to the pure TPS.

Mondragón et al. [148] applied glyceryl monostearate (GMS) as surfactant in TPS-microfibrillated cellulose nanocomposites prepared by solution casting. As expected, CNF derived from husks and corncobs increased the Young‘s modulus and tensile strength of TPS films due to the strong interactions between the starch matrix and the high aspect ratio CNFs. It was also noticed that mechanical properties could be further improved by the application of GMS surfactant. This was attributed to the formation of amylose–GMS complexes, which could increase the V-type crystallinity and interact with the hydroxyl groups of cellulose. Although the relative increase of Young’s modulus was higher than that reported by Alemdar & Sain [86], the absolute values were significantly lower in the study by Mondragón et al. [148]. This might be explained by the difference both in TPS and in microfibrillated cellulose sources.

Melt mixing followed by thermo-compression

Besides solution casting, the dispersion of CNFs in TPS has been also performed via melt mixing by Chakraborty et al. [149]. Microfibrillated cellulose suspension was poured into molten TPS to obtain fiber loadings up to 2 wt% and then composites were compression molded into thin films. A maximum of 20 % increase in tensile strength and a 100 % increase in stiffness due to cellulose reinforcement was reported.

Takagi and Asano [150] investigated the effect of processing conditions on the mechanical properties and internal microstructures of composites consisting of a dispersion-type biodegradable resin made from esterified starch and CNF. All samples with nanofiber loading of 70 wt% were prepared by hot pressing at 140 °C and pressures of 10–50 MPa. It was found that the density of the composites increased with increased molding pressure. Moreover, both extra stirring and vacuum drying of the dispersion before molding resulted in the removal of voids. Density was used as an indicator for the mechanical strength of the composites. Although similar densities were measured for vacuum-treated and extra-stirred samples, the latter showed significantly higher flexural strength, which was explained by differences between their internal microstructure and fiber dispersion.

Bottom-up method

A different approach to achieve starch–nanocellulose composites has been presented by Grande et al. [151]. In their study, starch was added to the culture medium of cellulose-producing bacteria (*Acetobacter* sp.) to introduce the granules into the forming network of cellulose. The application of such a bottom-up technique allowed the preservation of the natural ordered structure of CNF. The bacterial cellulose–starch mats were hot pressed to obtain nanocomposite sheets. Atomic force microscopy and environmental scanning electron microscopy (ESEM) revealed that starch acted as a matrix which filled the voids in the bacterial cellulose network. The gelatinized starch formed a homogenous layer on bacterial cellulose fibers and a typical brittle fracture surface of the composites was observed. Using microfibrillated cellulose, a molded product with a bending strength of 250 MPa was obtained by Yano and Nakahara [152] without the use of binders. When 2 wt% oxidized tapioca starch was added, the yield strain doubled and the bending strength reached 310 MPa.

Reactive extrusion method

Reactive extrusion (REx) is a process that combines mass and heat transport operations with simultaneous chemical reactions taking place inside an extruder with the purpose of modifying the properties of existing polymers or for producing new others. In this sense, extruding mixtures of corn starch/microcrystalline cellulose in the presence or absence of plasticizers (polyols) was studied by Psomiadou et al. [153]. The authors found an increase in breaking strength in the films obtained by extrusion reactive with cellulose, while elongation at break and water vapor permeability was reduced. Furthermore, starch may be thermodynamically compatible with the carboxymethylcellulose (CMC) when starch content is below 25 % by mass in REx processes. In the same way, these films can be biodegradable in the presence of microorganisms [154]. It is worth noting that very few studies have been reported concerning the processing of CNF-reinforced nanocomposites by extrusion methods.

Finally, starch/cellulose blends can be cross-linked by REx, which allows obtaining innovative materials with improved properties and one hundred percent biodegradable from natural resources. In this context, recently Rodríguez-Castellanos et al. [155] reported this behavior for different cellulose-reinforced starch–gelatin polymer composites. Tests showed an increase of 163 % in hardness and

123 % of elastic modulus enhancement after recycled cellulose inclusion. Atomic force acoustic microscopy showed that distribution of recycled cellulose in the polymer matrix is rather homogeneous at nanoscale, which improved load transfer. According to the authors [155], thermogravimetric analysis indicated an increase in thermal stability of the cellulose-reinforced polymer matrix samples.

Conclusions and outlook

In the last two decades, diverse amylaceous sources, particularly starch, have been evaluated for their film-forming ability in applications in area of food packaging. But, due to the known drawbacks of this type of matrices (mainly poor mechanical properties, low water resistance and higher water absorption from the environment), these should preferably be reinforced with natural fillers to produce biocomposites. This is commonly done to improve their physical–chemical and mechanical properties but maintaining the biodegradability of these materials. Cellulosic materials have been proposed as natural, economic, biodegradable and high-performance fillers to be incorporated in starch-based films, since bio-based materials are highly desired in many diverse areas, especially if they are abundant and readily obtainable. Nonetheless, recently films made from flour matrices have attracted the attention of many scientists worldwide as well as the technologists, since this type of matrices contains fiber in its chemical composition, which has improved the properties of these materials; therefore, it can be said that these are self-reinforced matrices.

On the other hand, since the yield for obtaining this amylaceous matrix is much higher compared to starch production, this has allowed it to be very economical, which allows to improve competitiveness of these materials against materials elaborated from non-renewable resources obtained from the petroleum industry. In this regard, greater efforts must be taken in the processing of cellulose (reactive extrusion, homogenizer and microfluidizer, grinding process, cryocrushing, electrospinning, among others) as well as in the manufacturing processes of starch/cellulose composite materials (extrusion, blowing, bottom-up, injection and thermo-compression) to that they can be massified by the industrial sector, since until now, its use in industrial scale is limited as to displace synthetic polymers from the petrochemical industry.

The power to solve these challenges could revolutionize the future market, because would be feasible the development of packaging materials, flexible displays, electronic display materials, solar cells, electronic paper, security paper, panel sensors and actuators. Although, it is worth noting that these applications are more feasible for use as packaging or other short-lived applications such as catering, sport, agriculture, and hygiene, where long-lasting polymers are not entirely adequate.

It is also highly recommended that future works at laboratory level should be oriented to grafting the antimicrobial compounds or chromophoric groups, which allow the development of active and intelligent (A&I) materials with improved properties. Similarly, it is still required to study the effects of cellulosic materials in the migration of active compounds not only in starch matrices but also in other biopolymers. In this sense, the study of surface modification of cellulosic materials is a field that is in full swing. Therefore, more efforts should be taken in this direction to insert these starch-based materials in the market in the near future. Finally, this review contains an analysis of the works carried out on starch-containing matrices reinforced with cellulose and lignin.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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