

Reinforcing thermoplastic starch composites with cellulose nanofibers

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Cellulose from sugarcane bagasse can be used to improve the mechanical and barrier properties of bionanocomposites.

Thermoplastic starch (TPS) is starch that has been plasticized with the use of a variety of plasticizer materials (such as glycerol or sorbitol). In recent years, it has gained popularity as an alternative to synthetic polymers¹ because starch is easily available, inexpensive, and completely biodegradable. In addition, TPS polymers exhibit a range of desirable properties, e.g., ranging from flexibility (polyethylene) to rigidity (polystyrene). TPS therefore has potential applications in the food industry, medical field, and agriculture. However, TPS also exhibits a number of problems that need to be addressed before it can be fully adopted as a suitable alternative to traditional synthetic polymers. Such problems include low impact resistance, low water absorption, a lack of interfacial adhesion, and very poor mechanical properties.²

Previous studies have shown that the limitations of native TPS can be overcome by blending it with other polymers or using it to make nanocomposites. For example, a blend of starch and polycaprolactone (PCL) has been synthesized.³ The application of starch-PCL blends, however, is limited because this material has a melting point of only 60°C and it therefore softens at temperatures above 40°C. It has also been demonstrated that the addition of other biopolymers—e.g., polylactic acid (PLA), polybutylene succinate, and polyhydroxybutyrate—increases the resistance to water absorption of TPS and improves the mechanical properties of the resultant products. In another study,⁴ starch/clay nanocomposites (with good dispersion) were prepared. These nanocomposites exhibited improved tensile modulus and strength with a clay loading of 5wt% in the starch matrix. In addition, TPS/PLA/montmorillonite nanocomposites were prepared via twin-screw extrusion and were found to have stable mechanical properties over a period of 300 days.⁵ Nanocomposite technology can therefore be used to circumvent some of the main problems associated with starch-based plastics (namely, water resistance and poor mechanical properties).

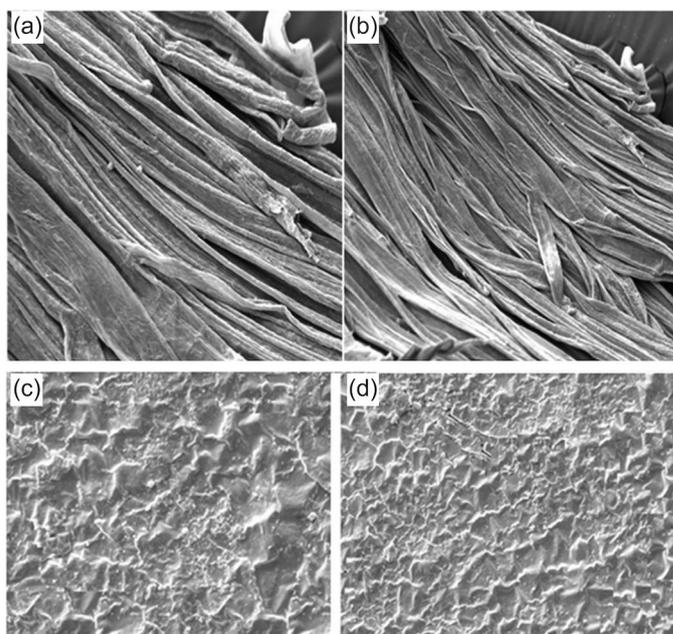


Figure 1. Scanning electron microscope images of (a) and (b) cellulose nanofibers (CNFs), with an average diameter of about 20µm, and (c) and (d) the thermoplastic starch (TPS) nanocomposite film reinforced with 12% CNFs.

In this work,⁶ we have therefore tried to overcome the current limitations of TPS by reinforcing the starch with cellulose nanofibers (CNFs). Because the structures of cellulose and starch are broadly similar, we expected a good interface between the two materials and to thus produce synergistic properties.⁷ For our work, we used a series of chemical-mechanical treatments to extract the CNFs from sugarcane bagasse. We also performed comprehensive characterizations of the nanofibrils, in terms of their morphology, composition, size, and crystallinity, before using them to reinforce the TPS. In the next step of our work, we used a solvent casting (with the reinforced

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Table 1. Chemical composition of the extracted nanofibrils from untreated sugarcane bagasse, steam-exploded, bleached, and acid-hydrolyzed cellulose. α -cellulose: Cellulose portion that does not dissolve in a sodium hydroxide solution.

Material	α -cellulose content (%)	Hemicellulose content (%)	Lignin content (%)	Solid yield (%)
Untreated sugarcane bagasse	46.50 \pm 0.18	23.9 \pm 0.9	22.14 \pm 2.1	100
Alkaline-steam-exploded fibers	65.59 \pm 1.51	13.45 \pm 1.22	17.27 \pm 1.27	67.59
Bleached fibers	77.28 \pm 2.37	10.34 \pm 1.18	12.12 \pm 1.35	50.22
Acid-treated fibers	82.38 \pm 3.12	8.18 \pm 0.8	9.34 \pm 1.25	36.59

TPS in an aqueous phase) method to obtain biodegradable nanocomposites. Finally, we evaluated the mechanical and transport properties of our prepared nanocomposites to establish their practical utility.

Our procedure for the extraction of the CNFs from the sugarcane bagasse is based on a previously reported technique.⁸ In this approach, we first thoroughly washed and dried the raw bagasse, before soaking it overnight in a 2% solution of sodium hydroxide to remove the extraneous impurities. We then conducted an alkaline steam explosion, at a pressure of about 15lb for five hours. This resulted in the explosive defibrillation of the cellulose, with the removal of lignin and hemicellulose coverings. We then bleached the washed bagasse pulp by immersing it in an 8% solution of hydrogen peroxide for 24 hours. Following this step, we performed sonication and high-shear homogenization to completely disperse and defibrillate the fibers down to nanosize dimensions. We added a dispersion of CNFs in distilled water to a mixture of maize starch and sorbitol, and then high-sheared this mixture to form a viscous solution that we then cast into thin films of varying CNF concentration.

Our measurements of the chemical composition of the cellulose nanofibrils (see Table 1) show that the content of α -cellulose (i.e., the portion that does not dissolve in a sodium hydroxide solution) increases from 46.5% in the raw (untreated) bagasse to 82.33% in the final, treated fibers. In contrast, the contents of hemicellulose and lignin decrease in the same samples from 23.9% to 8.81%, and from 22.14% to 9.34%, respectively.

Our scanning electron microscope (SEM) images—see Figure 1(a)—of micrometer-sized cellulose show that the fibers have smooth surfaces and average diameters of about 20 μ m. In addition, the SEM images of the TPS film reinforced with 12% CNFs—see Figure 1(b)—reveal that there are no agglomerations. This indicates that we achieved uniform dispersion of the nanofibers. The mesh-like structure of the fibers is also clearly observed in the transmission electron microscope images we obtained after conducting the chemical-mechanical treatment. We find that these fibers have diameters in the range of 30–40nm.

The presence of a peak at 1733cm⁻¹ in the Fourier transform IR (FTIR) spectrum of the untreated bagasse—see Figure 2(a)—

Table 2. Mechanical properties of TPS/CNF nanocomposites.

Sample (% CNF)	Tensile modulus (MPa)	Elongation at break (%)	Yield strength (MPa)
0	4.81 \pm 0.190	24 \pm 0.600	0.298 \pm 0.008
4	6.46 \pm 0.250	23 \pm 0.570	0.442 \pm 0.013
8	8.61 \pm 0.340	21 \pm 0.520	0.502 \pm 0.015
12	9.98 \pm 0.390	19 \pm 0.470	0.582 \pm 0.017
16	11.2 \pm 0.450	17 \pm 0.420	0.631 \pm 0.018
20	12.8 \pm 0.510	16 \pm 0.400	0.724 \pm 0.020

Table 3. Barrier properties of TPS/CNF nanocomposites, measured at 98% relative humidity and 25°C. M_{∞} : Moisture uptake at equilibrium.

Sample (% CNF)	M_{∞} (%)	Diffusivity (cm ² /s) $\times 10^{-6}$	Sorption (g/g)	Permeability (cm ² /s) $\times 10^{-6}$
0	2.39 \pm 0.11	9.93 \pm 0.10	0.43 \pm 0.11	4.28 \pm 0.09
4	1.91 \pm 0.16	6.23 \pm 0.16	0.35 \pm 0.18	2.11 \pm 0.11
8	1.62 \pm 0.09	5.13 \pm 0.22	0.29 \pm 0.21	1.43 \pm 0.08
12	1.42 \pm 0.13	4.25 \pm 0.19	0.25 \pm 0.17	1.06 \pm 0.17
16	1.26 \pm 0.15	3.82 \pm 0.12	0.22 \pm 0.11	0.86 \pm 0.19
20	1.07 \pm 0.23	3.23 \pm 0.21	0.19 \pm 0.22	0.61 \pm 0.21

corresponds to acetyl and uronic ester groups of hemicellulose, or to ester linkage of carboxylic groups in ferulic and p-coumeric acids of lignin or hemicellulose. In addition, peaks in the spectrum at 1514 and 1252cm⁻¹ represent the carbon-carbon double-bond stretch of lignin aromatic rings. Our FTIR spectrum of a final, treated CNF, however, does not contain these peaks. This indicates that most of the hemicellulose and lignin were successfully removed from the bagasse.⁹ We also find that the FTIR spectra for our reinforced TPS films—see Figure 2(b)—exhibit some peaks in common with the CNFs. This is because of the chemical similarities between starch and cellulose.

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From x-ray diffraction (XRD) patterns of the cellulose nanofibrils—see Figure 3(a)—we find that the average cellulose crystallite has a size of 7.13nm. In addition, the high crystallinity index (80.17%) clearly indicates substantial decomposition of a disordered region of raw materials (i.e., lignin and hemicellulose). We also observe—see Figure 3(b)—that with increasing CNF content the sharpness of the XRD peaks

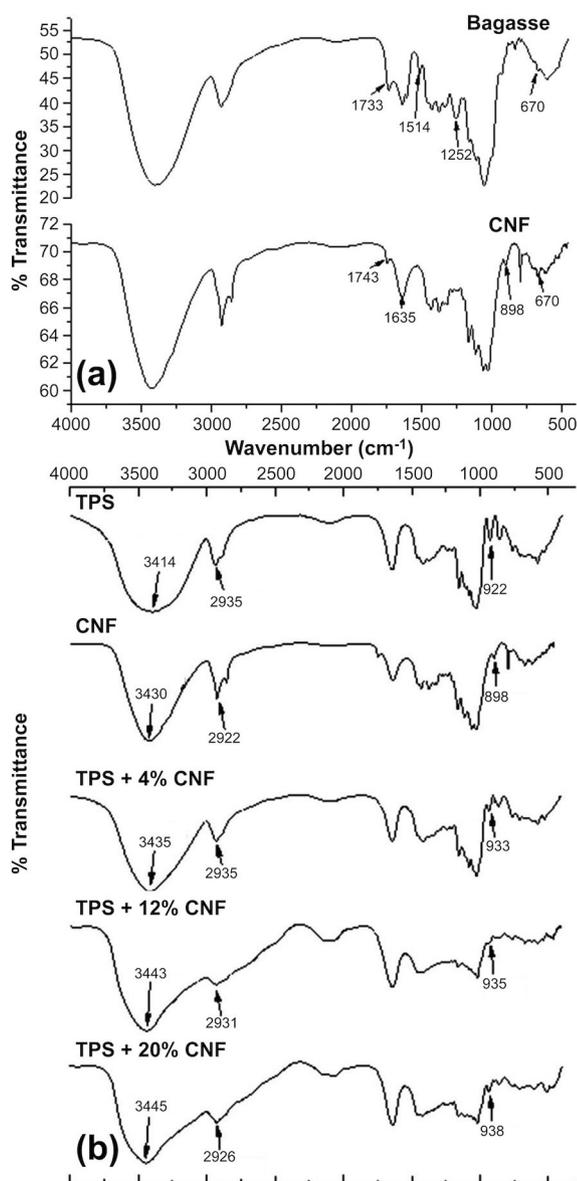


Figure 2. (a) Fourier transform IR (FTIR) spectra of (top) untreated sugarcane bagasse and (bottom) final, treated CNF. (b) FTIR spectra of TPS, CNF, and TPS reinforced with 4, 12, and 20% CNFs. Numbered labels denote the wavenumber of characteristic peaks.

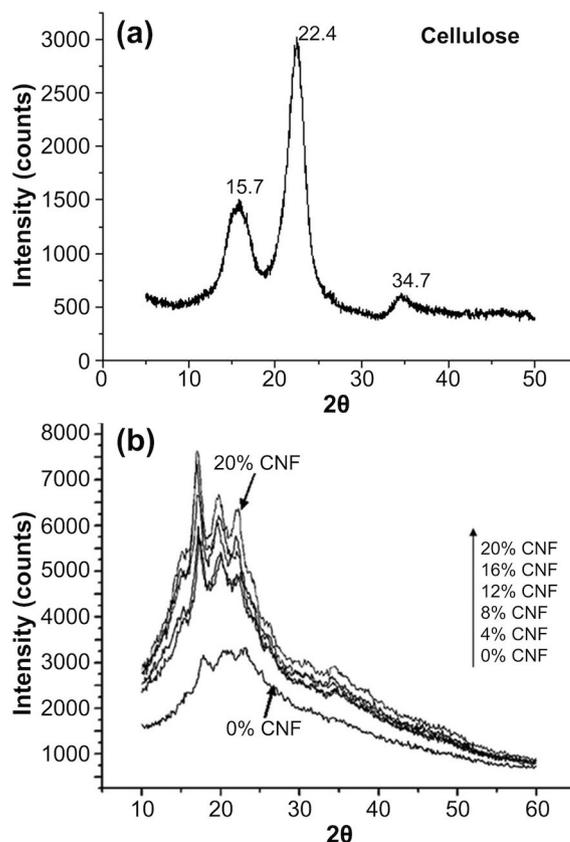


Figure 3. X-ray diffraction patterns of (a) cellulose nanofibrils and (b) TPS nanocomposites containing different (0–20%) CNF contents. θ : Measured angle of diffraction.

increases. This is indicative of an increase in the degree of crystallinity of the nanocomposites.

We have also performed tensile testing (according to the ASTM D638 standard test method) and moisture absorption measurements at 98% relative humidity (using potassium sulfate salt, according to the ASTM D570 standard test method) to assess the mechanical properties and establish the potential practical applications of our nanocomposite films. The results of our tests (see Table 2) indicate that there is an increase of about 267% in the tensile modulus of the 20% CNF-reinforced composite compared with the neat TPS film. Furthermore, our moisture absorption results (see Table 3) show that the moisture uptake of the TPS/CNF nanocomposites at equilibrium decreases considerably (from 2.4 to 1.1%) with increased CNF loading (from 0 to 20%). The high tensile strength and very low moisture

uptake properties of our composites mean that they are suitable for packaging materials.

In summary, we have synthesized thermoplastic starch/cellulose nanofiber nanocomposites. Our in-depth characterization of the samples indicates that the reinforcing cellulose fibers have nanoscale dimensions and high crystallinity, and that they are uniformly dispersed within the starch matrix. We have also examined the mechanical and barrier properties of the nanocomposites, and we conclude that the materials have the potential to be used as packaging materials. Our future work will involve the synthesis and characterization of TPS-based nanocomposites with different nanofillers, as well as an exploration of their potential applications.

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