

BIODEGRADABLE NANOCOMPOSITES FROM WHEAT STRAW

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Abstract

We investigate the mechanical and thermal properties of cellulose nanofiber reinforced starch based thermoplastic composites. Cellulose nanofibers were isolated from wheat straw by a chemi-mechanical technique. Their morphology, physicochemical and thermal properties were investigated to examine potential applications as reinforcement fibers in biocomposites. Transmission electron microscopy results showed that almost 60% of them have a diameter within a range of 30-40 nm and lengths of several thousand nanometers. Their average aspect ratio was found to be 95. Chemical characterization of the nanofibers confirmed that an applied alkali and acid treatment resulted in increased cellulose content from 43% to 85%. FT-IR spectroscopic analysis of the fibers demonstrated that this chemical treatment also led to partial removal of hemicelluloses and lignin from the nanofibers' structure. PXRD measurements revealed that this resulted in an improved crystallinity of the fibers. After mechanical treatments, thermal properties of the nanofibers were studied by the TGA technique and found to increase dramatically. The nanocomposites were prepared by a solution casting method. The tensile strength and modulus of the reinforced starch films were compared with those of pure starch and were found to have considerably improved, even at 5% nanofiber loading.

Introduction

Ecological concerns and the impending depletion of fossil fuels are driving the development of new bio-based, green products. Over the past few decades, research has explored the possibility of exploiting natural fibers (bio-fibers) as load bearing constituents in composite materials and produced encouraging results. Industrial use of these natural fiber-reinforced composites is increasing due to their relative cheapness compared to conventional materials and their potential to be recycled. The abundance of natural fibers is evidently advantageous to manufacturing industry.

Generally, cellulose-based fibers (obtained from plants), including cotton, flax, hemp, jute and sisal, and wood fibers are used to reinforce plastics. With their relative high strength, high stiffness and low density, these reinforced plastics are of interest as a replacement for synthetic fiber reinforced plastics in an increasing number of industrial sectors including the automotive industry, packaging, and furniture production,

In the 1990s the novel idea was explored of manufacturing entirely natural and biodegradable nanocomposites from cellulose nanofibers (rather than fibers) and biopolymers (1,2). These nanocomposites have excellent properties of rigidity, strength and resistance to high temperatures. The size of the fibers is crucial in allowing these biocomposites to be as strong as a pure cellulose crystal. Theoretical calculations of the elastic modulus of cellulose chains give a value of up to 250 GPa, which is to be compared to bulk natural fibers having an elastic modulus of 10 GPa (3). Although, the technology of extraction of the cellulose crystal from natural sources is deficient, it is still possible to

isolate nanofibers with a diameter between 5-80 nm by a chemi-mechanical treatment (1,2, 4,5).

In this work wheat straw was chosen as a nanofiber source due to its abundance in agriculture. Tons of unused wheat straw residues are generated every year, with only a small percentage being used in applications such as feedstock and energy production. Biocomposites are a prospective commercial application that would unlock the potential of these underutilized renewable materials and provide a non-food based market for agricultural industry.

The main goal of the present work is to isolate cellulose nanofibers from the wheat straw with a chemi-mechanical technique and characterize them in order to evaluate their suitability as reinforcement for biocomposite applications. The structural and physicochemical properties of the nanofibers were studied by scanning and transmission electron microscopy, FTIR spectroscopy and powder X-ray diffraction (PXRD) techniques. The thermal properties of the nanofibers were investigated by TGA. The mechanical performance of the nanocomposites containing cellulose nanofibers and thermoplastic starch were evaluated by tensile testing.

Experimental Procedure

Isolation of the Nanofibers

The nanofibers were isolated from wheat straw obtained from local sources (Ontario farms). A patented method for the isolation of cellulose from crop-based fibers was adopted (6). The wheat straw was cut into 4-5 cm lengths before a pre-treatment was applied. The cut wheat straw was soaked in a concentrated sodium hydroxide solution and then washed several times with distilled water. The pre-treated pulp was hydrolyzed by diluted HCl and then washed with distilled water repeatedly. The pulp was treated once more with the 2 % w/w of NaOH solution. The alkali treated pulp was washed several times with distilled water until the pH of the fibers became neutral before being vacuum filtered and dried at room temperature.

To individualize the microfibrils from the cell walls a mechanical treatment was applied to the chemically treated fibers. The mechanical treatment procedure includes cryocrushing, disintegration and defibrillation steps.

Processing of the Nanocomposites

The nanocomposites were prepared from the wheat straw nanofibers with thermoplastic starch polymer as the matrix and glycerol as the plasticizer. The wheat straw nanofiber suspension was first mixed with thermoplastic starch, then cast in Petri dishes and left to dry at room temperature for 2 days. The resulting films were placed in an oven at 37 °C for a week. The dry amount of the thermoplastic starch is 4g in each composite film. The nanofiber content was varied between 0 and 10 % of the dry weight of the composites.

Characterization

The composition (α -cellulose, hemicelluloses and lignin contents) of the untreated and chemically treated fibers was analyzed according to the procedure pioneered by Zobel and McElvee, 1966 and the TAPPI standards. The holocellulose content (α -cellulose + hemicelluloses) of the fibers was determined by treating them with a NaClO₃ and NaOH mixture solution (7). The cellulose content of the fibers was then determined after extracting hemicelluloses from the holocellulose by NaOH treatment. The difference between the values of holocellulose and α -cellulose gives the hemicelluloses content of the fibers. The lignin content of the fibers was found by treating them with a sulphuric acid solution according to TAPPI procedure 250UM-85 and TAPPI standard T222 om-83.

The fibers' morphology was characterized using a scanning electron microscope (SEM) and transmission electron microscope (TEM). Fibers were mounted on metal stubs by double-faced tape and the surface was coated by carbon. Images were taken at 15 kV by JEOL JSM-840 model SEM. A Philips CM201 model TEM operating at 60 kV was used.

FT-IR spectroscopy was used to examine any changes in the structure of the fibers which arose after chemical treatment of the fibers. A Perkin Elmer spectrum 1000 was used to obtain the spectra of each sample. Fibers were ground and mixed with KBr. They were then pressed into transparent thin pellets. FT-IR spectra of each sample were obtained in the range of 4000-400 cm^{-1} . Spectral outputs were recorded in the transmittance mode as a function of wave number.

The crystallinity of the untreated and chemically treated cellulose fibers was examined using a Bruker AXS D8 Discovery Diffraction System equipped with a high power point focus (1x1mm) Cu- $k\alpha$ target, graphite monochromator (2 θ = 26.53 $^\circ$) for elimination of Cu- $k\beta$ lines, and a Hi-Star GADDS area detector for 2-D images. High-resolution frames (1024x1024 pixels) for accurate integration of the diffraction images were recorded. The frames from the analyzed cellulose materials were taken with a 0.5 mm pinhole collimator at 600 s (5 min) using a transmission mode with $2\theta = 21^\circ$ and $\omega(\theta) = 10.5^\circ$.

Thermogravimetric analysis was performed to compare the degradation characteristics of the chemically treated fibers with the untreated ones. Thermal stability of each sample was determined using a TGA Q 500 series Thermogravimetric analyzer (TA Instruments) with a heating rate of 10 $^\circ\text{C}/\text{min}$ in a nitrogen environment.

Tensile testing of the composites was carried out using a Sintech-1 tensile machine with a load cell of 50 lb and following ASTM D 638. The crosshead speed was set to 2.5 mm/min. The samples were cut in a dumbbell shape with an ASTM D 638 (type V) die and at least 6 specimens were tested for each sample.

Results and Discussion

Chemical Composition and Morphology of Chemi-mechanically Treated Wheat Straw

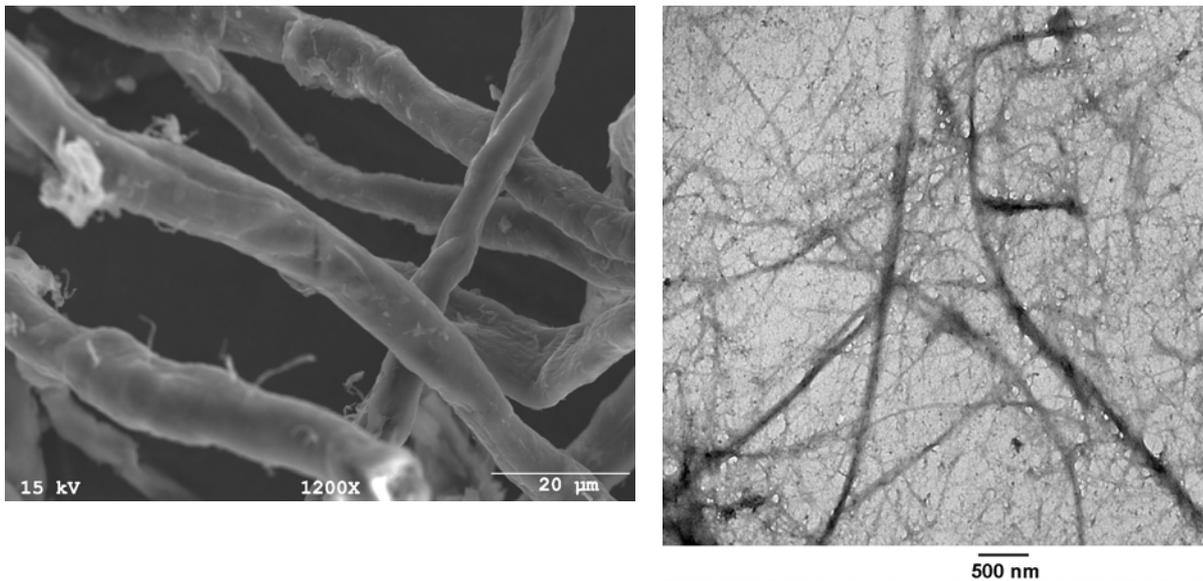
Table 1 shows the chemical composition of the wheat straw after each stage of the chemical treatment. It was found that at the end of the chemical treatment the α -cellulose content was increased from 43.2 % to 84.6 % while hemicellulose and lignin content were significantly decreased to 6% and 9.4 % respectively.

Table 1. Chemical composition of the wheat straw fibers after each step of the chemical treatment

Wheat straw fibers	α -cellulose (%)	Hemicelluloses (%)	Total lignin (%)
Untreated fibers	43.2	34.1	22.0
Acid treated fibers	61.8	19.0	14.1
Acid and alkali treated fibers	84.6	6.0	9.4

* All values are reported as mean (N \geq 3)

The chemical treatments result in structural changes as well as chemical changes to the fiber surfaces. SEM pictures of the wheat straw fibers were taken to investigate the structure of these fibers and are shown in figure 1a. These pictures visually suggest the partial removal of hemicelluloses, lignin and pectin after chemical treatment, which are the cementing materials around the fiber-bundles. It is clear from the pictures that the average diameter of the fibers is about 10-15 μm , which is lower than the average size of fiber bundles, 25-125 μm (8) before chemical treatment.



(a)

(b)

Figure 1. (a) SEM and, (b) TEM pictures of the wheat straw fibers

Figure 1b shows the TEM pictures for the wheat straw nanofibers obtained after the chemi-mechanical treatment. The mechanical treatment of the fibers resulted in defibrillation of nanofibers from the cell walls and the TEM picture of the cellulose fibers shows the separation of the nanofibers from the micro-sized fibers. The diameters of the fibers after chemical and mechanical treatments were calculated by an image processing analysis program, UTHSCSA Image tool, using the SEM and TEM images. The diameters of 75% of the wheat straw fibers obtained after chemical treatment were smaller than 9 μm . The maximum diameters were between 6 and 7 μm , with 25% of the total in this range. It was found that the diameters of the wheat straw fibers after mechanical treatment decrease. Almost 60% of them have a diameter within a range of 30-40 nm and lengths of several thousand nanometers. The aspect ratio of the wheat straw nanofibers was found to be between 90 and 110.

Spectroscopic Analysis

Fig. 2 shows the FT-IR spectra of untreated and chemically treated wheat straw fibers. The dominant peaks in the region between 3600 and 2800 cm^{-1} are due to stretching vibrations of CH and OH. The prominent peak at 1737 cm^{-1} in the untreated wheat straw is attributed to either the acetyl and uronic ester groups of the hemicelluloses or the ester linkage of carboxylic group of the ferulic and p-coumeric acids of lignin and/or hemicelluloses (9,10). This peak disappeared completely in the chemically treated wheat straw because of the removal of most of the hemicelluloses and lignin from the wheat straw by applied chemical extraction.

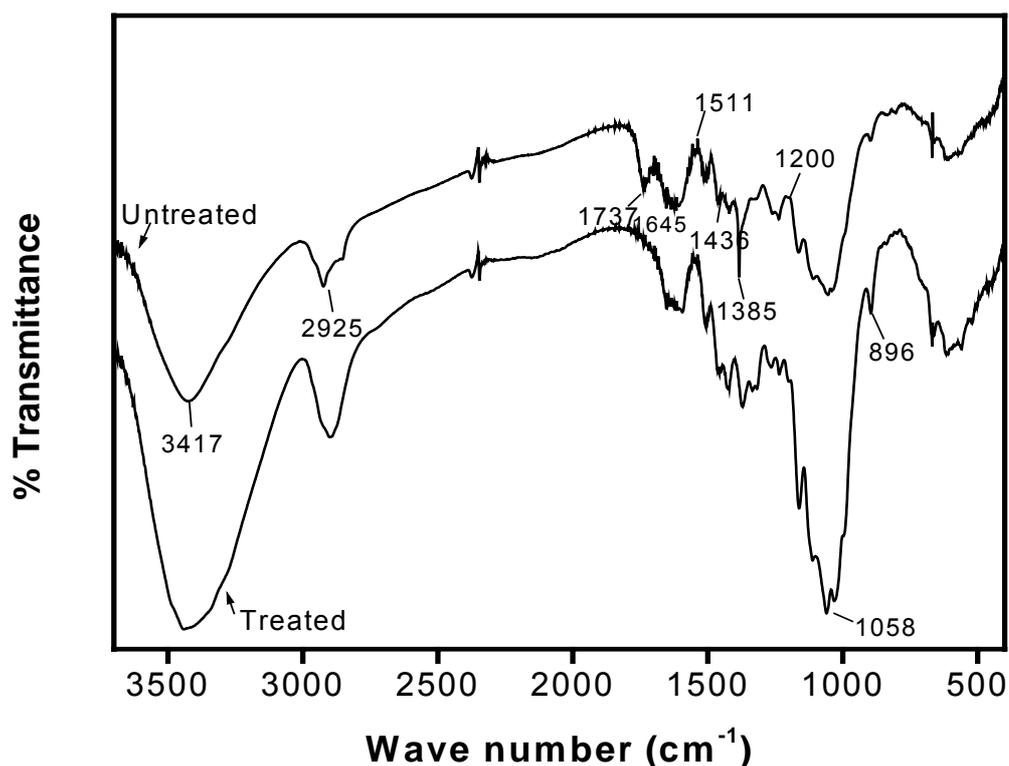


Figure 2. FT-IR spectrum of the untreated and treated wheat straw fibers

The peaks at 1507 and 1436 cm^{-1} in the untreated wheat straw represent the aromatic C=C stretch of aromatic rings of lignin (9-11). The intensity of these peaks decreased in the chemically treated wheat straw, which was attributed to the partial removal of lignin. The sharp peak at 1385 cm^{-1} reflects C-H asymmetric deformations (10). The peaks in the region 1200-950 cm^{-1} are due to C-O stretching (11). The increase of the band at 896 cm^{-1} in the chemically treated wheat straw indicates the typical structure of cellulose.

Crystallinity of Untreated and Treated Fibers

The hydrogen bonds between cellulose molecules are arranged in a regular system resulting in an ordered system with crystal-like properties. The crystalline lattice of cellulose is monoclinic. Individual fibrillar units consist of long periods of ordered regions (crystallites) interrupted by completely disordered regions. In native cellulose the length of the crystallites can be 100-250 nm with cross-sections an average of 3 x 10 nm. The cellulose molecule continues through several crystallites. Chemical and mechanical treatments affect the crystallinity of the cellulosic fibers.

Crystallinity is commonly measured as a ratio between the diffraction portion from the crystalline part of the sample, and the total diffraction from the same sample. Figure 3 shows the PXRD patterns of the untreated and treated cellulose fibers. The peak at $2\theta = 22^\circ$ is sharper for chemically treated wheat straw than untreated cellulose fibers. The sharper diffraction peak is an indication of higher crystallinity degree in the structure of the treated fibers. The crystallinity values were estimated as 57.5% and 77.8%, for the untreated wheat straw and chemically treated wheat straw fibers respectively. In all cases the portion of crystalline cellulose was found to be higher for chemically treated cellulose fibers than for untreated fibers due to partial removal of the hemicelluloses and lignin during chemical treatment. The increase in the number of crystallinity regions increases the rigidity of cellulose. Higher crystallinity in the chemically treated cellulose fibers is associated with higher tensile strength of the fibers.

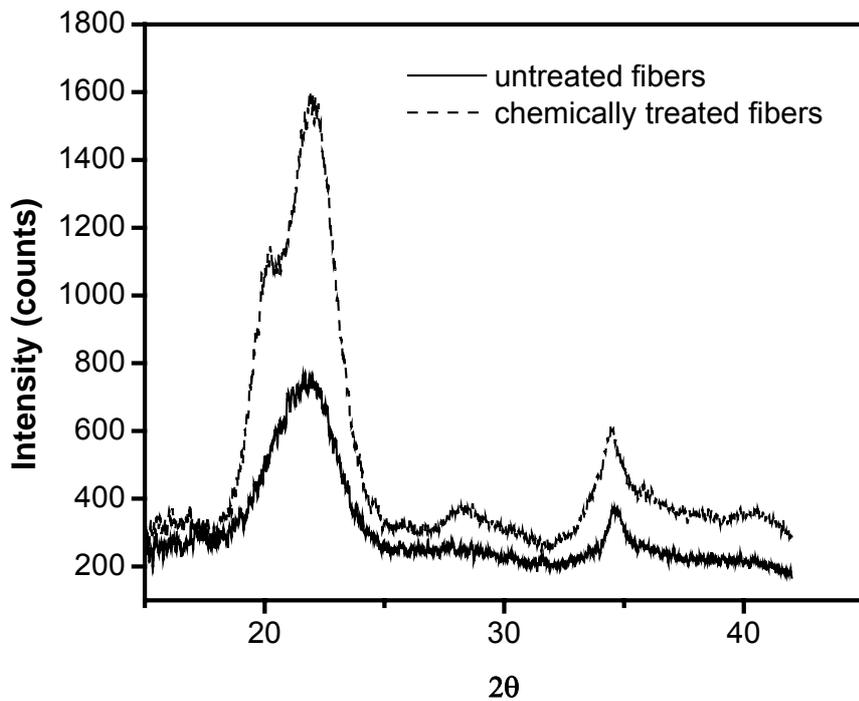


Figure 3. PXRD diffraction patterns of the untreated and treated wheat straw fibers

Thermal Properties

Investigation of the thermal properties of the natural fibers is important in order to gauge their applicability for biocomposite processing. Figure 4 and Table 2 show the TGA results obtained from wheat straw fibers. These results clearly illustrate that the thermal stability of the wheat straw fibers increases after chemical and further increases after mechanical treatments. The degradation temperature of the nanofibers was increased. There is also a distinction between the amounts of the residues of the fibers remaining after 550 °C heating for untreated, treated, and nanofibers.

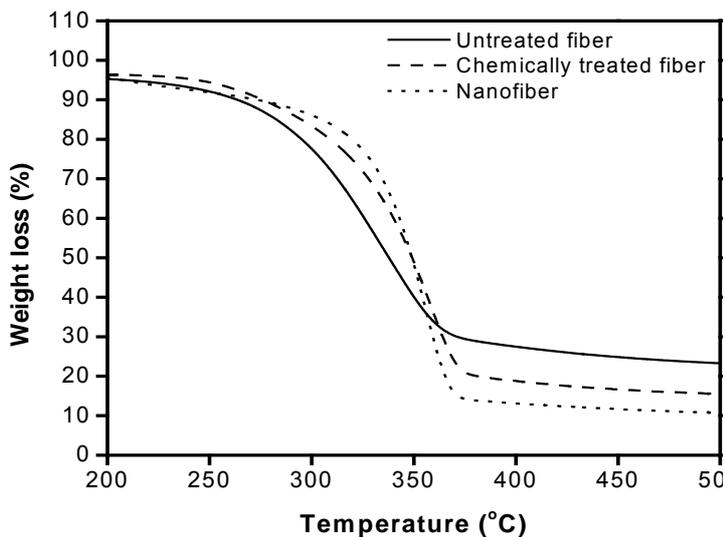


Table 2. Degradation Characteristics of the wheat straw fibers

Wheat straw fibers	Onset of degradation (°C)	Residue after 550 °C (%)
Untreated	215	22.3
Chemically treated	232	13.6
Nanofibers	296	10.2

Figure4. TGA thermograms of the wheat straw fibers.

Mechanical Properties of the Nanocomposites

Figure 5 shows the reinforcing ability of the wheat straw nanofibers by means of modulus and tensile strength. The tensile strength and modulus of the nanocomposites films were increased linearly while the nanofiber content was increased. The tensile strength of the composite film with 10% nanofibers loading showed a 36% increase compare to the pure thermoplastic starch polymer film. A two-fold increase in the modulus was observed in the composite with 10% nanofiber loading.

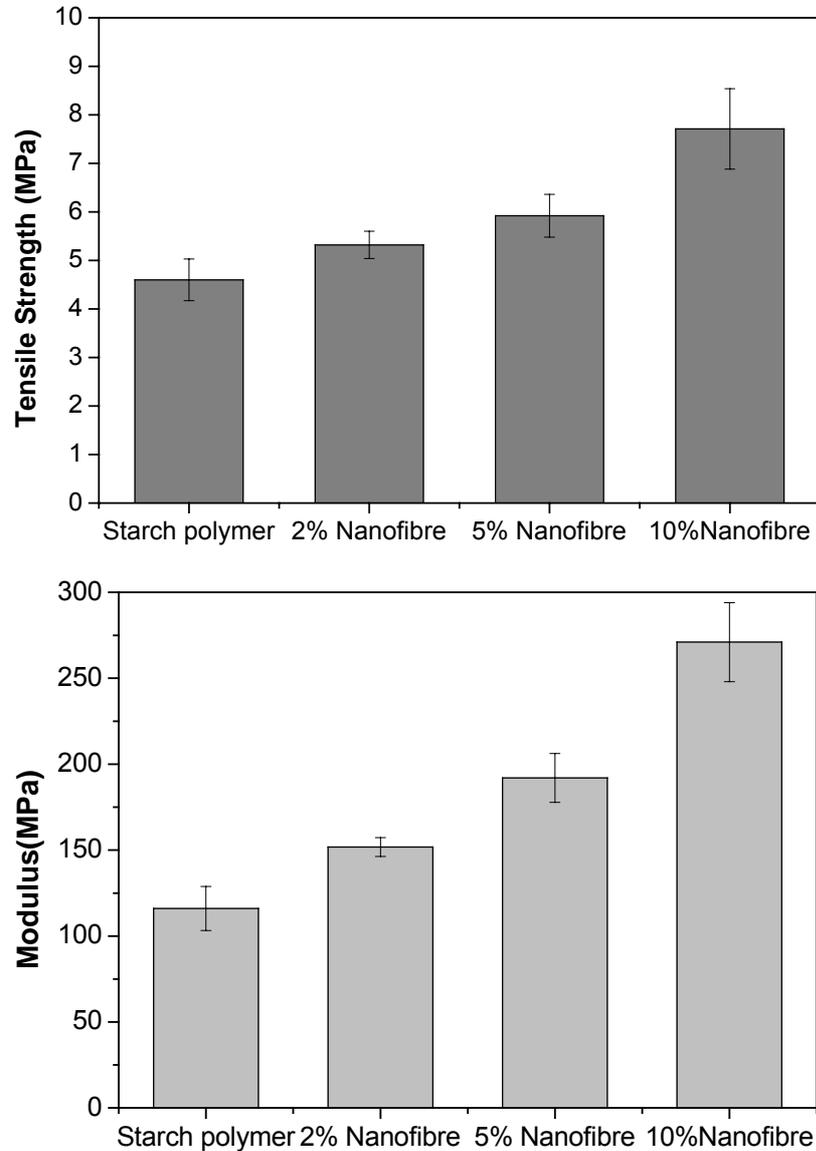


Figure 5. Mechanical performance comparison of nanocomposite films with different loading

Conclusions

In this work, cellulose nanofibers were extracted from wheat straw by chemical treatment followed by a mechanical treatment. Chemical composition, morphology and physical and thermal properties of the nanofibers were characterized to investigate their usability in biocomposite applications. Experimental results showed that the resulting wheat straw nanofibers' diameters are within the range of 10-80 nm with lengths of a few thousand nanometers. Chemical analysis and FTIR measurements of the fibers revealed

the partial removal of hemicelluloses and lignin due to the success of the chemical treatment applied. The crystallinity of the nanofibers was increased by 35% for the wheat straw nanofibers relative to the untreated wheat straw. The nanofibers showed enhanced thermal properties, with thermal degradation temperatures increased by 45%. The mechanical tests showed that nanocomposites had slight improvement in tensile strength and modulus, 2-fold increase, compared to pure thermoplastic starch. Results showed that the cellulose nanofibers obtained from wheat straw can find potential application in biocomposite production such areas of medical and automotive industry.

Acknowledgements

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