

# **BIONANOCOMPOSITES BASED ON UNMODIFIED AND SURFACE MODIFIED NANOFIBRILLATED CELLULOSE EXTRACTED FROM WHEAT STRAW**

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**Keywords:** Nanocomposites, cellulose nanofibers, thermoplastic starch, thermal degradation

## **Abstract**

Cellulose nanofibers have gained importance due to their unique characteristics like large surface to volume ratio, high surface area, good mechanical properties and low coefficient of thermal expansion. The present study involves isolation of cellulose nanofibers from wheat straw, their surface modification and synthesis of bionanocomposites with thermoplastic starch (TPS). Cellulose nanofibrils were isolated using alkaline steam explosion coupled with high shear homogenization. The chemical composition of fibers at different stages was analyzed according to the ASTM standards. Structural analysis of fibers carried out by FTIR, TEM, SEM, AFM and XRD revealed nanodimensions of the fibers. Aggregates of microfibrillated cellulose isolated were subjected to propionylation in heterogeneous phase to render the surface hydrophobic which was confirmed by TEM, SEM and contact analysis. WA-XRD analysis reported slight variation in the crystalline nature of the fibers. The extent of reaction between the propionyl groups and surface hydroxyl groups of cellulose were thoroughly studied with degree of substitution analysis. The modified and pristine nanofibers were used to make TPS nanocomposites. The nanocomposite films were analyzed using SEM, WAXRD, TGA, DSC and barrier properties. Thermal properties improved significantly for the nanocomposites as reflected in TGA and DSC analysis. Barrier properties also improved with addition of nanofillers up to 10% but deteriorated further due to fiber agglomeration.

## **1. Introduction**

Agro-residues are the important source for production of biopolymers based green nanocomposites. These are also called next generation materials that are environmental friendly and possess great tendency to replace non-degradable plastic composites. These bio-nanocomposites have prospective commercial applications that would unlock the potential of these underutilized renewable materials and provide a non-food based market for polymer industry [3].

Biopolymers such as starch produced from agro-residues are one of the limited alternatives to the petroleum plastics used for the food packaging applications. But, the starch based films possess brittle nature as well as poor thermal and mechanical properties hence making them unsuitable for commercial applications. There are several strategies that can be investigated in order to improve different properties

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of the starch. Blending starch with other polymers such as polylactic acid, polyethylene and polyvinyl alcohol is one of the common strategies. In recent years, impregnation of natural nanofillers such as cellulose nanofibrils in the pristine thermally plasticized starch biopolymer matrix has come out as an excellent opportunity for obtaining advanced bionanocomposite with improved barrier and mechanical properties [4]–[6]. The nanofibrillated cellulose further allows modification of their surfaces therefore using this strategy, reinforcing potential of these nanofibrils in the biopolymer matrix can be improved tremendously.

This research work is aimed at development of thermoplastic starch based bionanocomposites by modifying the surface of nanofibrillated cellulose and reinforcing them in starch biopolymer matrix. The pristine nanofibrillated cellulose was isolated from wheat straw fibers using alkaline steam explosion coupled with high shear homogenization. The surface of pristine nanofibrils was modified using an indirect method. Finally, the effect of impregnation of these two types of nanofibers in thermoplastic starch matrix has been investigated using different characterization techniques.

## 2. Materials and methods

Wheat straw is abundantly available and was taken as such. For preparation of the thermoplastic starch (TPS) the regular maize starch (10% moisture content) of Labochem. India Pvt. Ltd. (Art. No. 6117) along with plasticizer (glycerol) were supplied by Swan Scientific, Chandigarh (India).

The pristine nanofibrillated cellulose from wheat straw fibers were isolated using physico-chemical treatments coupled with high shear mechanical treatment. The physico-chemical treatment involves alkaline steam explosion, bleaching and acid hydrolysis of wheat straw fibers for successive removal of lignin, hemicellulose and pectin from cellulosic fibers to obtain microfibrillated aggregates of cellulose called MFCs. The mechanical treatment using high shear homogenizer further separates the fine nanofibrils of cellulose from MFCs. These treatments have been thoroughly discussed in author's previous work [7].

The microfibrillated aggregates of cellulose fibers (MFCs) of wheat straw fibers procured in previous section were subjected to additional esterification treatment using propionic anhydride to obtain cellulose nanofibers with activated surface. In this indirect method, reaction was carried out in a toluene and pyridine medium containing 2-3 drops of concentrated H<sub>2</sub>SO<sub>4</sub>. The fibers to propionic anhydride ratio were taken in 1:2 (w/v) proportions and treatment was carried out at 80°C constant temperature for 90 minutes in an oil bath. Finally, cellulosic fibers were removed from the solution mixture and then repeatedly vacuum filtered using ethanol and water and dried at 50°C for 24 hrs. Then these modified fibers were disintegrated mechanically using Fluko FA25 homogenizer operating at 10,000 RPM to obtain surface modified nanofibers.

Finally, Bionanocomposite films of thermoplastic starch reinforced with nanofibrillated cellulose (NFCs) extracted from wheat straw fibers were prepared using solvent casting method and has been described in author's previous work [8].

Different techniques were used to characterize the pristine and surface modified cellulosic nanofibers and their reinforced thermoplastic starch bionanocomposites. Chemical composition analysis of wheat straw

fibers and extracted MFCs was conducted using ASTM standards for  $\alpha$ -cellulose (ASTM D1103-55T), lignin (ASTM D1106-56) and holocellulose (ASTM D1104-56). A Perkin Elmer RX -FTIR spectrophotometer was used to identify variations in the functional groups as a result of different chemical treatments. A Perkin-Elmer 240C CHNSO-Elemental Analytical Instrument (USA) was used to conduct elemental analysis of unmodified and surface modified MFCs of wheat straw fibers. To collect the morphological information about the pristine and surface modified nanofiber transmission electron microscope (TEM) model Hitachi-2100 was used at 80KV accelerating voltage. Scanning electron microscope (SEM) model JSM JEOL-6100 was used for microstructural analysis of pristine and propionylated MFCs. The model was also used for cross sectional analysis of the nanofibers reinforced TPS nanocomposite films. Atomic force microscopy (AFM) model Bioscope II AFM, VEECO was used to investigate the topography of pristine nanofibrils. Samples of pristine and modified NFCs in powdered form and nanocomposites in form films were analyzed using a Philips X'Pert- Pro X-ray diffractometer. Crystallinity index (CrI) of the nanofibrils was calculated using Segal empirical method [7]. The surface properties of propionylated MFCs and its NFCs were estimated for static & dynamic contact angles (DCA) measurements for a check time of 0.2 seconds using a Dynamic Absorption Tester DAT 1100 at 23 °C and 50% RH. Thermo-gravimetric analysis of pristine and surface modified cellulose nanofibers and TPS bionanocomposites was done using TGA of type PERKIN ELMER STA-6000 in nitrogen environment and at heating rate of 10 °C/min. Differential scanning calorimeter (DSC) analysis of TPS nanocomposites were also done using a General DSC-2910 TA instrument in temperature range 0-250 °C at scanning rate of 10°C/min in nitrogen environment. Finally, TPS nanocomposites prepared using pristine and surface modified nanofibers were subjected to moisture absorption experiment by maintaining 75% relative humidity (NaCl) at 25°C. The moisture uptake at any point of time was determined using below mentioned equation in which Wh and Wo denote the weight of humid specimens at time 't' and initial dry sample, respectively.

$$\text{Percentage moisture uptake} = \frac{W_h - W_o}{W_o} \times 100 \quad (1)$$

### 3. Results and discussions

#### 3.1 Characterization of nanofibrillated cellulose (pristine and surface modified)

Table 1 shows the chemical composition of raw, alkaline steam exploded, bleached and hydrolyzed wheat straw fibers. The raw fiber contains the highest percentage of hemicellulose and lignin and the lowest percentage of  $\alpha$ -cellulose while the same content increases from 45.7% in raw fiber

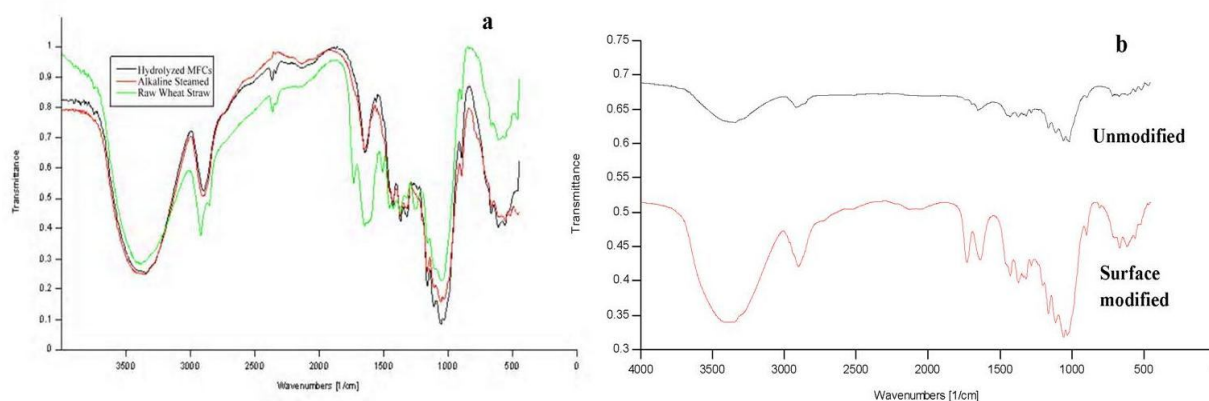
**Table 1:** Chemical composition of raw, alkaline steam exploded, bleached and hydrolyzed wheat straw fibers.

Material	Percentage of $\alpha$ -cellulose	Percentage of Hemi-cellulose	Percentage of lignin
Untreated Wheat straw	45.70±0.18	37.12±0.9	17.43±2.1
Alkaline steam exploded	65.29±2.51	22.22±1.12	10.27±1.67
Bleached fibers	75.28±2.37	12.34±1.18	8.12±1.35
Hydrolyzed fibers or MFCs	86.38±3.12	8.13±0.8	6.34±1.25

to 86.38% in finally hydrolyzed MFCs. Figure 1(a) shows the ATR-FTIR spectrum of the raw wheat straw fibers, alkaline steamed and hydrolyzed MFCs. The peaks in area 3369 cm<sup>-1</sup> correspond to O-H stretch band i.e. due to vibrations of the hydrogen bonded hydroxyl (OH) group. The peaks at 2922 cm<sup>-1</sup> are due to the aliphatic saturated C-H stretching

vibration in lignin polysaccharides. Peak at  $1734\text{ cm}^{-1}$  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]–[11]. It can be seen in figure 1 that this peak is almost absent in the spectra of acid hydrolyzed MFCs. The aromatic C=C stretch from aromatic ring of lignin gives two peaks at  $1510$  and  $1426\text{ cm}^{-1}$  that can be observed in raw wheat straw fibers [9]. Peak at  $1510\text{ cm}^{-1}$  has almost vanished and the intensity of peak at  $1426\text{ cm}^{-1}$  has significantly decreased in chemically treated fibers attributing partial removal of lignin. The intensity of the peak at  $1258\text{ cm}^{-1}$  has sharply decreased after chemical treatment indicating the removal of hemicelluloses. The increase of band at  $897\text{ cm}^{-1}$  in final acid hydrolyzed MFCs of wheat straw indicates the typical structure of cellulose. The ATR-FTIR spectra (figure 1 b) of pristine and propionylated MFCs show significant differences in each other evidencing the effect of propionylation. For instance, a new band was observed in the ester carbonyl area ( $1720$  to  $1745\text{ cm}^{-1}$ ). The esterification of hydroxyl groups of cellulose is confirmed with the emergence of this new carbonyl peak area. This is due to the formation of the ester bonds on the surface of the fibers. The strong band in the region near  $1642\text{ cm}^{-1}$  in the figure 1(b) attributes to H-O-H bending of adsorbed water [11]–[13].

The CHNSO elemental analysis of pristine MFCs depicted concentration of carbon, hydrogen and oxygen around 41.94%, 6.54% and 43.49%, respectively. While propionylated MFCs have shown marginal variations in the concentration of carbon (42.14%), hydrogen (6.67%) and oxygen (46.19%). The marginal variations in the carbon, hydrogen and oxygen concentrations may be possibly due to absorbed moisture content or truncation of certain error during the elemental analysis [12], [13]. Figure 2a and b showing the SEM images of wheat straw fibers taken to examine microstructure analysis of the cellulose fibers after final hydrolysis and propionylation treatments. It is clear from the figures that the size of the fiber bundles is around  $10\text{--}15\text{ }\mu\text{m}$  level. Figure 2 c shows the topographical images of the pristine



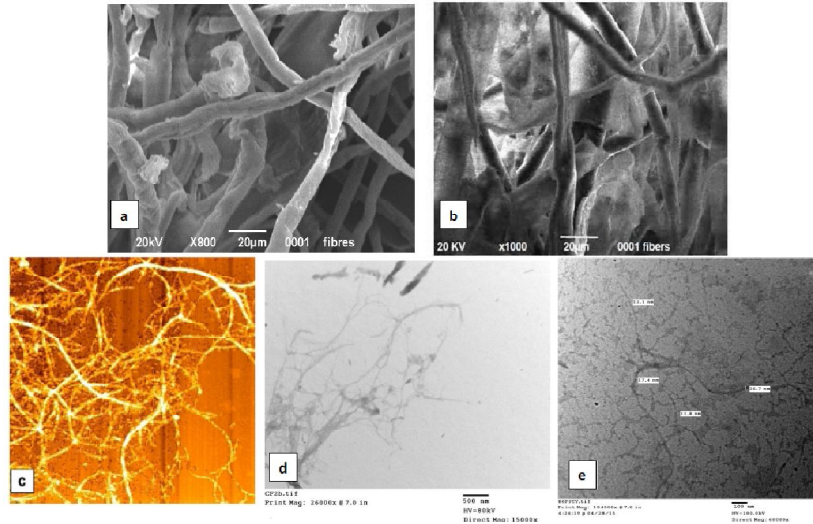
**Figure 1:** FTIR spectroscopy analysis of (a) wheat straw, steam exploded and finally hydrolyzed MFCs; (b) simple MFCs and surface modified (propionylated) MFCs.

nanofibers of cellulose confirming that diameter of the fibers has been reduced to the nanometer range after high shear mechanical treatment. The fibers with unmodified surface are found to be slightly agglomerated. Figure 2 c and d show TEM images of the pristine and surface modified cellulose nanofibers. Mechanical treatment resulted in defibrillation of the cellulose nanofibers from the cell wall and TEM images reveal the separation of these nanofibers from the microsized fiber bundles. Diameter of the

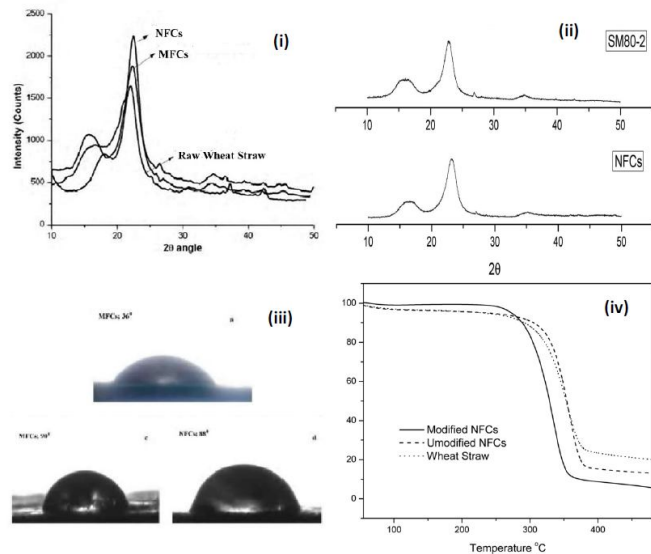
fibers is found in the range of 10-60 nm for unmodified fibers while it is between 10-40nm for surface modified nanofibers. A tendency of agglomeration for surface modified nanofibers could also be observed to be reduced as compared to the pristine nanofibers.

Figure 3(i) depicts XRD profiles of the raw fibers, acid hydrolyzed MFCs and mechanically treated pristine nanofibers of wheat straw. Cellulose nanofibrils show highly crystalline nature. The peak intensity at  $2\theta=22.6^\circ$  corresponding 002 lattice plane increases with the reduction in size as well as impurities from the cellulosic fibers. It reported a sharp increase with high shear mechanical treatment of the MFCs. A narrow peak at  $26.5^\circ$  has also been observed in the XRD spectra that indicates heavy loading of the chemicals [10]. The results also confirm that hydrolysis takes place mostly in the amorphous region due to acidic dissolution while crystalline regions are more stable towards chemical attack [10], [14]. Figure 3 (ii) shows the XRD spectra of pristine and surface modified NFCs. The spectra reveal that surface modification treatment has not distorted the native crystalline nature of the cellulose. The crystallinity Index estimated from these spectra reveal increase in CI percentage of raw fibers increases from 54.42% to 66.60% for acid hydrolyzed MFCs and it further increases to 84% and 79.87% for pristine and modified NFCs.

The water contact angle results of fibers shown in figure 3(iii) evidenced the reduced penetration of water liquid in surface modified NFCs signifying the fact that nanomaterial has gained a stable and good level of hydrophobicity ( $80^\circ$ ).



**Figure 2:** (a and b) SEM images simple MFCs and propionylated MFCs; (c) AFM of unmodified nanofibrils (NFCs); (d and e) TEM of unmodified and modified NFCs).



**Figure 3:** (i and ii) XRD analysis of raw wheat straw, its pristine MFCs, NFCs and surface modified (SM80-2) NFCs; (iii) Static contact angle of simple MFCs and modified MFCs and its NFCs; (iv) TGA plots of raw, pristine and modified NFCs.

TGA profile shown in figure 3(iv) depicts that all types of fibers suffered maximum degradation at offset temperature region 350 to 380 °C respectively. Surface modified nanofibrils were found to be less thermally stable but their weight loss characteristics have been improved due to surface treatments. This behavior can be due introduction of ester bonds in the cellulose structure or due to slight decrease in crystallinity of the samples obtained after the esterification [15], [16].

### 3.2 Characterization of pristine and surface modified NFCs filled TPS nanocomposites

Figure 4 (a and b) show SEM images of starch/cellulose nanocomposites taken from their cryo-fractured edges. From the images, it is clear that the 10% surface modified nanofibers are well dispersed and covered by the TPS matrix as compared to 10% pristine cellulose nanofibrils reinforced TPS bionanocomposites. No fiber pull-out or debonding was observed because of the fine adhesion between the surface modified nanofibers and the biopolymer matrix.

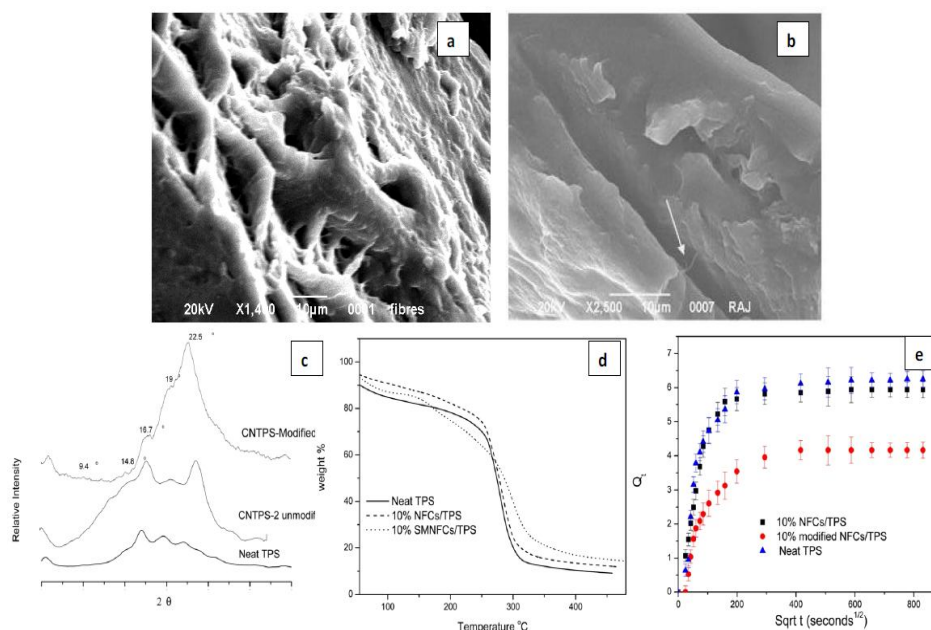
The figure 4 (c) exhibit WA-XRD spectra of neat, pristine and surface modified nanofibrils reinforced TPS films. The spectra shows that surface modified nanofibrils have overpowered the amorphous profile of starch matrix and resultant composites are significantly different in their crystalline structures. The spectra give a strong peak at diffraction angle around 22.5° which is also a characteristic diffraction angle for crystalline cellulose, therefore, growth of the peak near this region in composite film exhibit high quality of dispersion between the matrix and surface modified nanofibers.

The preliminary DSC analysis exhibited larger enthalpy of fusion for composites filled with preliminary nanofibers than neat TPS film, for neat TPS film  $\Delta H_m$  (heat of fusion) was 171 J/g while it was 190 J/g for TPS nanocomposites. The incorporation of two types of nanofibers influenced thermal characteristics of resultant TPS nanocomposites. Figure 4(d) shows that surface of modified TPS nanocomposites exhibit decrease in onset degradation temperature to 251°C which is close to onset degradation temperature of modified NFCs.

The moisture uptake characteristics (figure 4 e) for bionanocomposites filled with surface modified nanofibrils were surprisingly decreased to 4.79% as compared to unmodified nanofibrils reinforced TPS bionanocomposites. The modified hydroxyl groups present at the surface of the nanofibrils with 10% concentration in TPS biopolymer matrix would have possibly contributed in three ways for improving the moisture resistance capability of the TPS bionanocomposites (i) introducing hydrophobic groups in TPS biopolymer thereby making it less hygroscopic, (ii) preventing agglomeration of the nanofibrils in the biopolymer matrix and (iii) generating good entangled network of the fibrils in the TPS matrix.

## 4. Conclusion

Corn starch based TPS bionanocomposites were prepared by reinforcing unmodified and surface modified cellulose nanofibrils. FTIR and contact angle studies confirmed the surface modification of the nanofibrils extracted from wheat straw fibers. TEM, SEM and AFM confirmed the effect of surface modification and nano-size of the fibers. The bionanocomposites filled with surface modified nanofibrils confirmed good dispersion of these nanofibers in TPS matrix. XRD results of bionanocomposites reveal overall improvement in crystallinity with addition of two types of nanofibrils. The results of TGA and DSC



**Figure 4:** SEM images of cryo-crushed edges of (a) 10% pristine nanofibrils and (b) 10% surface modified nanofibrils filled TPS bionanocomposites; (c, d and e) XRD, TGA and Barrier characteristics of neat, 10% pristine nanofibrils and 10% surface modified nanofibrils filled TPS bionanocomposites.

experiments indicated an interaction between the fiber and the plasticizer, causing the reduction in onset of degradation temperatures. A reduction in water uptake ability of the bionanocomposites was observed as compared to the neat TPS. The surface modified nanofibrils reinforced TPS bionanocomposites indicated considerable improvement in their barrier properties.

### Acknowledgements

We are grateful to acknowledge financial support rendered by Council for Scientific Instrumentation & Research (CSIR), India, Technical Education Quality Improvement Program (TEQIP-II) of HRD ministry, India, All India Council of Technical Education (AICTE), India and University Grants Commission (UGC), India for the research work.

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