



## Preparation and Characterization of Nanocrystalline Cellulose for Development of Nanocomposite Films

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Received: 22 May 2017;

Accepted: 22 July 2017;

Published online: 30 October 2017;

AJC-18616

Nanocrystalline cellulose crystals were synthesized from microcellulose crystals by physical method (ball milling) for being applied in the development of nanocomposite packaging films with improved barrier and mechanical properties. Structural evolution of nanocellulose crystals were investigated by a series of methods like particle size analysis, TEM, SEM, XRD, *etc.* The results showed the suitability of ball milling process as one of the techniques for nanocrystalline cellulose processing. Microcrystalline cellulose initially of particle size ranging from 40-30  $\mu\text{m}$  was reduced to size ranging between 200-300 nm by pulverizing process at 120 rpm for 8 h using ball mill.

**Keywords:** Microcellulose crystals, Nanocrystalline cellulose, Ball milling.

### INTRODUCTION

Cellulose application in the processing of polymer nanocomposites has increased drastically over a period of time. The application of celluloses or its derivatives like nanocrystalline cellulose (NCC) or nanocellulose fibers (NCF) in the development of nano composite packages have shown similar or better properties than the normal packaging materials. Nano crystalline cellulose are needle like crystals with a measure of 4-25 nm in diameter and length of 100-1000 nm [1]. The different processes involved in the by processing of nanocrystalline cellulose's involving chemical methods and physical methods. It is necessary to understand the behavior and characteristics of nano crystalline cellulose for engineering applications.

This paper emphasizes on conversion of microcrystalline cellulose to nano crystalline cellulose by using high energy planetary ball milling process which is a most commonly used method and works on the principle of size reduction caused due to energy released at the point of collision between balls as well as friction created between balls and the wall of cylinder [2]. As the mill rotates, due to centrifugal force, balls are picked up to the top most position by mill wall and they fall free due to gravity on top of the product. This process is repeated as per the set number of revolutions per minute for given time duration to create impact on the product which reduces the product to smaller size particles.

Use of nanocrystalline cellulose in the development of nanocomposite packaging has been described as the next great frontier of material science in packaging. Less work has been done on the application of nanocrystalline cellulose's in the synthetic polymers to improvise the morphological and barrier properties of the films. Linear low density polyethylene (LLDPE) and polypropylene (PP) packages are most commonly used films for food wrapping applications which have poor resistance to water vapor and gas transmission rates [3]. So LLDPE-NCC and PP-NCC hybrids are at the top priority to overcome the lacunas of virgin polymers. Hence the present study was carried out combine the nanocrystalline cellulose along with LLDPE and polypropylene for which structural, morphological and chemical properties of nanocrystalline celluloses were determined.

### EXPERIMENTAL

Microcrystalline cellulose (MCC-105) was obtained from Jukuochem, Chennai, India. All other chemicals (Sigma-Aldrich, India) for the study were of laboratory grade and used without further purification.

**Nanocrystalline cellulose (NCC) production:** Micro - crystalline cellulose (MCC) were first sieved using 0.420 mm (No. 40, Sigma Aldrich Chemicals) to ensure the lumps are broken and free flowing microcrystalline cellulose is obtained. Then the microcellulose crystals were pulverized for physical conversion into nanocrystalline cellulose (NCC). A high energy

planetary ball mill of Fritsch (Premium line) pulverisette 7 with sintered corundum container consisting of small zirconium balls of 10 mm diameter were used for converting microcrystalline cellulose into nanocrystalline cellulose. The BMR ratio (ball to material ratio) was maintained as 12:1 and the rotational speed (rpm) of the carriers was main-tained at 120 below the calculated critical speed (156 rpm). The equipment was given a pause for every 60 min and samples were collected and analyzed for particle size obtained.

**Nanocomposite film development:** The LLDPE granules, compatibilizer and nanocrystalline cellulose were taken as per the composition given in the experimental design (Table-1). The raw materials were thoroughly mixed for about 10 min before they were extruded. The mixture was then fed into a high-performance co-rotating twin screw extruder (ZV 20 model, Specific Engineering, Baroda, India) at a feed rate of 2 kg/h to get compounded materials of nanocomposites. The screw speed was set at 200 rpm. The temperature of five zones of extruder was set between 145-200 °C. Pale-yellow strands of the compounds were obtained through the die. The strands coming out of the die were immediately cooled in a water bath and then they were fed into the pelletizer (KVN Impex make, India). Small pellets of size not more than 5 mm were cut in the pelletizer and these pellets were further conditioned at 50 °C for 4 h in a hot air oven to remove excess moisture.

TABLE-1  
EXPERIMENTAL DESIGN FOR NANO COMPOSITE  
FILM DEVELOPMENT

Variables	Levels
Compatibilizer	5, 10, 15 %
Nanocrystalline cellulose	2, 4, 6 %
Essential oils	1, 2, 3 %

The dried granulated compounds were then fed into mono-layer blown film plant (KBFH/47-G, Konark, India) for fabricating nanocomposite films. A total of 17 types (treatments) of nanocomposite films along with control were fabricated. The prepared nanocomposite films wrapped in aluminum foil were stored at ambient condition (32 °C mean temperature and 60 % mean relative humidity) for further testing.

**Particle size analysis with zeta-potential value:** Cellulose (micro- and nanocrystalline cellulose) particle size analysis was analyzed using Horiba SZ100, Japan, with the following conditions: dispersant water, material refractive index 1.47, dispersion refractive index 1.33, viscosity 0.8872 cP, temperature 25 °C and general calculation model for irregular particles. Three measurements at duration of 10 s each were taken and the average was considered for further analysis.

Zeta-potential value for micro cellulose crystals and nano cellulose crystals were also analyzed using Horiba SZ100, Japan. Experiments were performed in a glass cuvette consisting of 4 mL approximately 0.1 wt% cellulose (micro- and nanocrystalline cellulose) suspension, solutions were all adjusted at pH values of 7.

**X-ray diffraction (XRD):** It is a known fact that the mechanical properties of cellulose products were strongly dependent on the crystallinity and its crystal structure. To determine the crystal structure XRD patterns of untreated (microcrystalline

cellulose and ball milled (nanocrystalline cellulose were measured by RIGAKU Ultima III, Japan automated powder X-ray diffractometer. The XRD data were generated by a diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) at 40 kV and current 30 mA over the range  $2\theta$ . Subsequently, the XRD raw data were analyzed using the Bragg's law to identify the peaks of the constituent phases and the interlayer spacing. The interlayer d-spacing for a single order of reflection for micro- and nanocrystalline cellulose can be determined from XRD data by Bragg's law using the following formula [4]:

$$2d \sin \theta = n\lambda \quad (1)$$

where, d = basal or interlayer spacing ( $\text{\AA}$ );  $\lambda$  = wavelength (1.54  $\text{\AA}$ ); n = order of reflection (1);  $\theta$  = peak angle.

The size of cellulose particles can be determined by the following Scherrer's equation:

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where, L = size of cellulose particles ( $\text{\AA}$ ); K = shape factor (0.9);  $\lambda$  = wavelength (1.54  $\text{\AA}$ );  $\beta$  = half-height width of diffraction peaks;  $\theta$  = Bragg's angle.

**Fourier transform infrared spectrometry (FTIR):** The (Fourier Transform- Infra Red (FT-IR) analysis was conducted to study any kinds of molecular interactions in the developed antimicrobial films. The JASCO FT-IR (Model no: 6800) spectrometer was used in the study.

**Transmission electron microscopy (TEM):** Internal feature observations of the cellulose particles (micro- and nanocrystalline cellulose) were performed using Transmission Electron Microscopy (Make: FEI Technai), operated at a voltage of 100 KeV. A drop of a highly diluted suspension of micro- and nanocrystalline cellulose particles were placed on two different copper grids coated with a thin carbon film. The samples were allowed to dry at room temperature after which the copper grids were stained with a 2 wt% solution of uranyl acetate for one minute and air dried.

**Scanning electron microscopy (SEM):** The morphology of the MCC and NCC samples was examined by a SEM (FEI Quanta<sup>TM</sup> 250, Oregon, USA) at an accelerating voltage of 3 kV. Before images were acquired, samples were mounted on SEM aluminum stubs with conductive carbon tape and sputter-coated with gold under vacuum at 20 mA for 2 min.

**Thermogravimetric analysis (TGA):** TGA was performed using a TA Instrument Exstar, TG/DTA 6300 thermal analyzer and the samples were heated from 0 to 700 °C at a heating rate of 10 °C min<sup>-1</sup> under a purging nitrogen atmosphere with a gas flow of 20 mL min<sup>-1</sup>.

## RESULTS AND DISCUSSION

Micro crystalline cellulose was ball milled for 8 h at 120 rpm and at every 1 h interval, the samples were taken and analyzed for change in particle size before and after ball milling. A comparative analysis of micro- and nanocrystalline cellulose (after 8 h of ball milling) was performed for different morphological characterizations.

**Particle size analysis with zeta-potential value:** The estimated surface charges or zeta potential of compounds can

be measured by taking into account the moving rate of positively or negatively charged particles in an electric field. Agglomeration of the samples is usually represented if the value is less than -15 mV and if the values are more than -30 mV it signifies that there is mutual repulsion and there in exists colloidal stability. The surface charges and analyzed particle size of micro- and nanocrystalline cellulose after 8 h of milling are given in Table-2.

Cellulose	Microcrystalline cellulose	Nanocrystalline cellulose (after 8 h of ball milling)
Particle size (nm)	~ 30-40 $\mu$ m	233.9
Zeta-potential (mV)	-8.3 $\pm$ 3	-32.8
Crystal size (L)-XRD (nm)	4.99	1.13
Crystallinity % (cr. I %)-XRD	73.60	18.11

Ball milled nanocrystalline cellulose samples possessed highly negative surface charges and this indicated that there is a high electrostatic repulsive force that is preventing the binding between nano crystals and thus giving a homogeneous nano-cellulose suspension.

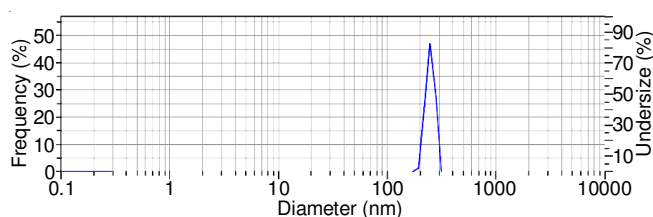


Fig. 1. Particle size distribution of nanocrystalline cellulose after 8 h of ball milling

**X-ray diffraction (XRD):** X-ray diffraction of micro- and nanocrystalline cellulose crystals (8<sup>th</sup> h sample) is given in Fig. 2.  $2\theta$  values for both the samples were analyzed and it was concluded from the graph that microcrystalline cellulose had the highest peak indicating it is more crystalline. Whereas, nanocrystalline cellulose showed low peak values indicating that after 8 h of ball milling, the samples lost its crystallinity and became more amorphous. Two crystallite sizes calculated for microcrystalline cellulose was found to be 4.99 nm and for nanocrystalline cellulose (8<sup>th</sup> hour sample) was found to be 1.13 nm. The crystallinity percent (Table-2) was found to be 73.6 and 18.11 % for micro- and nanocrystalline cellulose crystals, respectively. This showed that the crystalline nature of microcrystalline cellulose was reduced as the samples were ball milled for 8 h.

**Fourier transform infrared spectrometry (FTIR):** FTIR analysis of both micro- and nanocrystalline cellulose samples are given in Fig. 3. The FTIR band at  $3332\text{ cm}^{-1}$  represented O-H group stretching of O-H, H-bonded single bridge. In the region of  $2894\text{ cm}^{-1}$  is due to stretching vibrations of Ar-H, (-CH) several band at  $2341\text{ cm}^{-1}$  (C-H), 2 or 3 band of methyl group. The presence of aryl carboxylic group in the region  $1317\text{ cm}^{-1}$  represents C=O stretching vibration which was more in nanocrystalline cellulose sample. A band at  $1103\text{ cm}^{-1}$  represents presence of pyridine nucleus ring breathing. Etherial group is found at  $1024\text{ cm}^{-1}$ , where C-O-C shows very strong stretching.

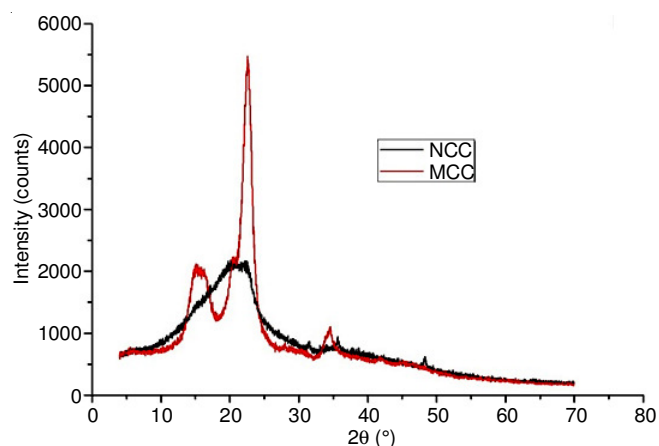


Fig. 2. X-ray diffraction pattern for microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) after 8 h of ball milling

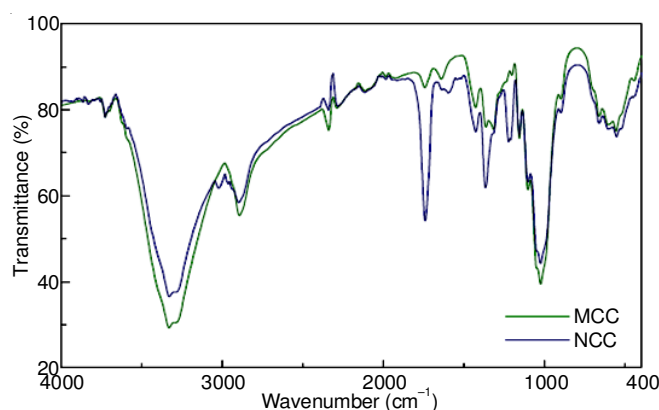


Fig. 3. FTIR graph of microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) (8<sup>th</sup> hour sample)

**Transmission electron microscopy (TEM):** Fig. 4(a) shows TEM images of microcrystalline cellulose which are much agglomerated and with very sharp and irregular edges. Whereas in Fig. 4(b) reflect the image of nanocrystalline cellulose after 8 h of ball milling in which nanocrystalline cellulose are dispersed and a lot of circular shaped particles with size ranging between 30 to 60 nm were formed.

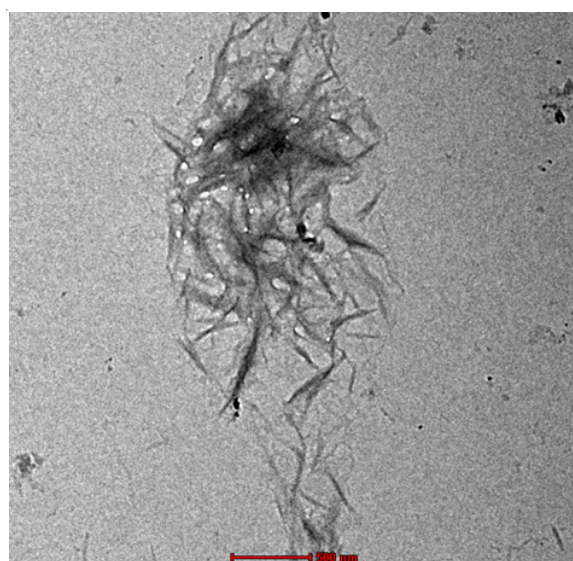


Fig. 4(a). TEM image of MCC at 500 nm



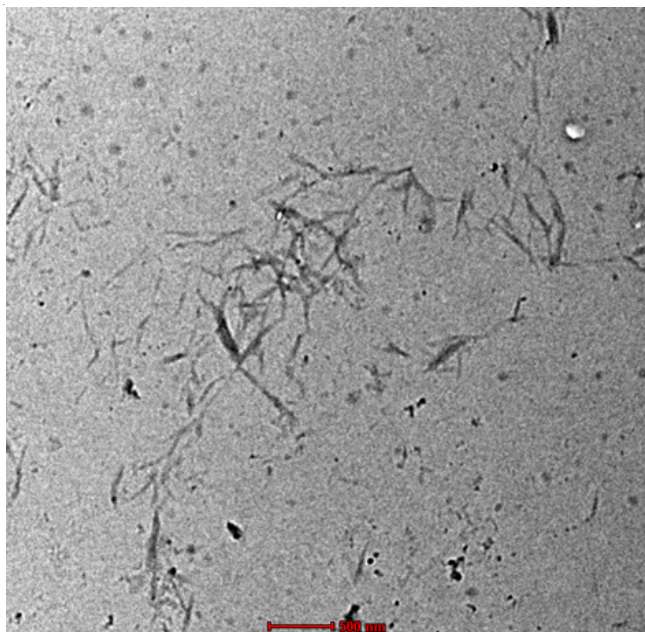


Fig. 4(b). TEM image of nanocrystalline cellulose at 500 nm

**Scanning electron microscopy (SEM):** The results got by SEM analysis were on par with those got in TEM and also were in agreement with the XRD results, which show clearly that microcrystalline cellulose had reduced to nano-size after ball milling microcrystalline cellulose for 8 h. The SEM images are presented in Fig. 5(a) and 5(b).

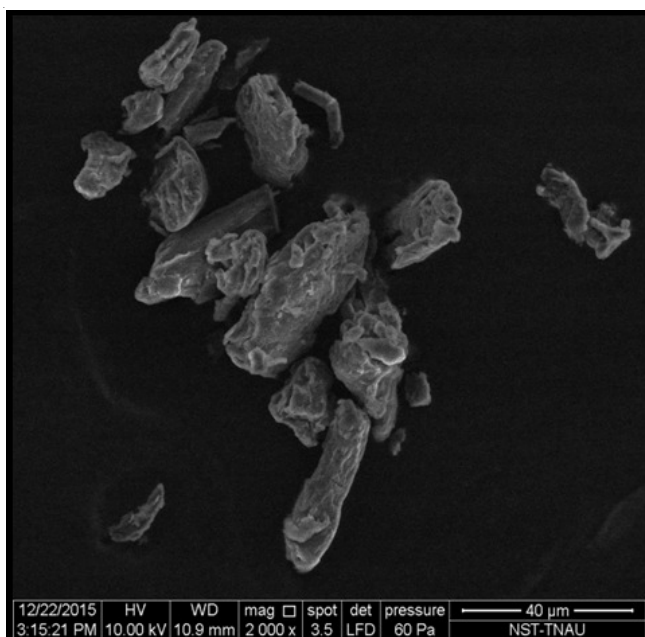


Fig. 5(a). SEM image of microcrystalline cellulose

**Thermogravimetric analysis (TGA):** Thermogravimetric analysis was performed to check the suitability of nanocrystalline cellulose for the development of nanocomposite films. Thermal behaviour of nanomaterials depends on their chemical composition, structure and degree of crystallinity [5]. The thermal decomposition curves for both micro- and nanocrystalline cellulose are shown in Fig. 6.

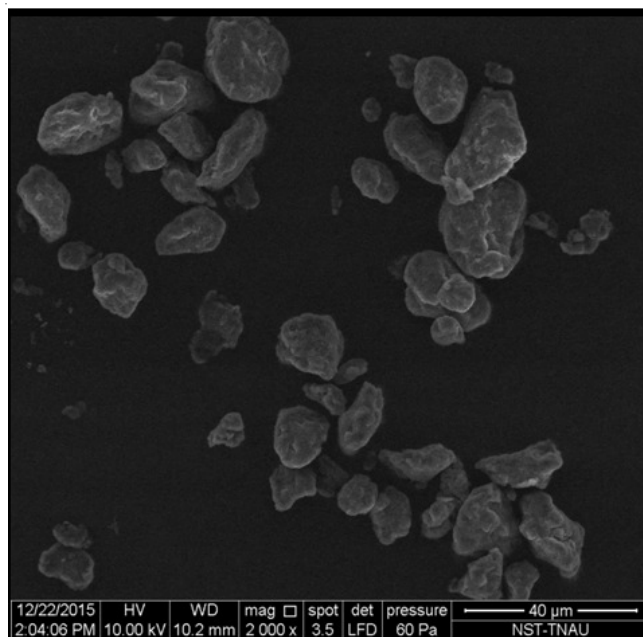
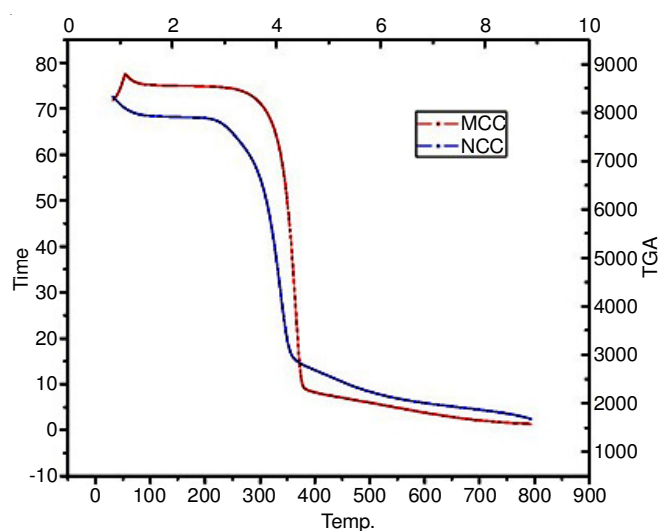


Fig. 5(b). SEM image of nanocrystalline cellulose

Fig. 6. TGA curves of microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) (after 8<sup>th</sup> hour of ball milling)

From Fig. 6, it can be seen that both micro- and nanocrystalline cellulose showed almost same trend of degradation and the degradation occurred at a temperature range of 350-400 °C, respectively. But comparatively microcrystalline cellulose degraded late as they have high crystallinity nature which results in high heat resistance [6].

## Conclusion

Ball milling is a suitable process for converting microcrystalline cellulose to nanocrystalline cellulose. With this method, nanocrystalline cellulose's with size smaller than 400 nm were produced. The determination of changes in nanocrystalline cellulose was demonstrated based on morphological, XRD, FTIR, and TGA analysis. Furthermore, this process can be modified for less time of operation by increasing the number of balls, increased ball diameter, by monitoring ball and material ratio and speed of rotation.

**ACKNOWLEDGEMENTS**

This work was supported by research grants from ICAR under the Nano Platform project. The authors also thank CBPST (a unit of CIPET), Kochi, India for their support during the study.

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