TEMPO mediated synthesis of Nanocellulose from *Terminalia Elliptica*

Madhuri R[1], Virupaxappa S Betageri[1], Onkarappa H S[1], Latha M S[2*]

[1]Research Centre, Department of Chemistry, G M Institute of Technology, Davangere, Karnataka, India.

[2] R L Science Institute (Autonomous), Belagavi, Karnataka, India.

Abstract

In the current work, a natural residue *Terminalia Elliptica*is processed into cellulose by pre-treating it with NaOH (5%) & $NaClO_2$ (5%). Further, the cellulose has been converted to nanocellulose through the acid hydrolysis method followed by ultra sonication. The Crystallinity and functional group analysis was studied using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR), respectively. The surface morphological investigation of prepared nanocellulose was carried out using scanning electron microscope (SEM) transmission electron microscope (TEM). The thermal stability was investigated using thermogravimetric and derivative thermal analysis (TGA/DTA). The obtained results revealed semicrystallinity nature, good thermal stability, and fibrous nanocellulose nature with agglomeration.

Keywords: Nanocellulose, Terminalia Elliptica, Cellulose, Fibrous, Thermal stability

1. Introduction

Intense research has been going on in recent years for search of materials which can be produced in nano-terms but also to have capability to direct the society that is sustainably sound [1, 2]. Cellulose, a biopolymer exists in nature, which possesses many properties. It has great specific strength, good stiffness, good aspect ratio, low toxicity, surface tunability. It is less costly and is biodegradable in nature [4-6] thus, making it a good considerate material for green-nanotechnology. Any material having the source as a lignocellulosic mass, is highly recommended for the preparation of cellulose using it as a starting material. Many varieties of plants are included in Ligno cellulosic mass which adds up to the vast availability of the starting material. But wood and agricultural wastages are majorly considered as the starting raw materials for the synthesis of nanocellulose. Many unconventional sources of cellulose are cotton linter, olive tree, banana plant, cereal straw

etc., have been utilized as raw compound to synthesis nanocellulose from its innate form of cellulose [7].

This naturally existing cellulose is made up of homo-polysaccharide which have D-AGU (D- anhydrous glucopyranose units) that are connected together by the aid of β-1, 4-glycosidic bonds. It is also a naturally existing biopolymer that is hydrophilic in nature [8]. The formation of hydrogen bonding is permitted by the existence of the hydroxyl groups (-OH) making it strong [9]. It is polymer that is semi-crystalline because it has both crystalline and amorphous phases in it [10]. Over the years, this important ancient polymer is being explored in many ways and is being called by new name i.e., Nano Cellulose which had marked its place in the fast-growing field of nano technology and engineering.

It was applied as a starting compound for variety of applications viz., sensor devices[11,12],foams formulation[13-17], composites [18-21], emulsion [22], in packaging[23], biomedical tools[24-27], modifiers in rheology [28-29], hydrogels [30], films of biocomposite [31], xerogels, super capacitors [32] etc. Latter mentioned applications have evidently proven their importance and future of cellulose in nanotechnology.

Nanocellulose can be isolated in many different ways. i.e, chemical and mechanical method. Mechanical method includes high-intensity ultra-sonication method [33] or high-pressure homogenization method and in Chemical method it includes TEMPO, AH (Acid Hydrolysis) and IL (Ionic Liquid). TEMPO, an oxidation approach is highly considerable for its selective oxidation of carboxyl groups present on C-6 along with preserving of its spatial arrangement [34]. TEMPO is generally used for selective oxidation of p-hydroxyl groups and its activation which eventually coverts hydroxyl groups into carboxylic acid. By using the prepared activated TEMPO-Oxidized nanoparticles, supplementary reactions are done.

In the present work Terminalia Elliptica (TE) is the raw materials taken for the isolation of its respective nanocellulose. It is suggested for the production of NC due to its high strength and stiffness [35-37]. Hence NC have prepared by TEMPO oxidation method followed by high intensity ultra-sonication. The effects of synthetic approaches on functionality, surface morphology, crystallinity &thermal stability of the prepared NC were noted using SEM, XRD, FTIR, TEM, and TGA/DTA.

2. Materials and Methodolgy

Terminalia Elliptica was gathered from the saw mills in Davangere. TEMPO, $NaClO_2$, NaBr, NaClO, CH_3COOH, and NaOH, procured from SD-fine chemicals (purity 98.0 percent) and used without further purification as received.

2.1. Alkali treatment

The sufficient exposure of the fibres for TEMPO and bleaching is done with the help of alkali pre-treatment of the fibers. Which proved to be an effective way for the surface modification and is also cost-efficient.10g of finely grinded, sieved starting material powder was treated with 5% NaOH solution for 2 hours at 80^0C-100^0C to remove hemicellulose. Followed by filtration and washed with distilled water to achieve the pH of the effluent as neutral.

2.2. Bleaching treatment

Alkali treated fibers were then subjected to bleaching. The bleaching treatment with $NaClO_2$ solution was performed to eliminate the residual lignin. 5% Sodium chlorite solution was added to alkali treated samples. The mixture was heated at 80°C to 100°C with magnetic stirrer for 2-3 hrs by maintaining an acidic pH with acetic acid. On washing repetitively using distilled water, to remove remaining lignin. Further, with the help of deionized water, the pulp is filtered until its pH is neutral. Next, the gained cellulose was kept in the oven to dry for a day and was stored in a dry place until further use or preparations.

2.3. Preparation of TO-TENC from TEMPO Oxidation

2, 2, 6, 6-Tetra methyl piperidine-1-oxyl radical shortly referred to as TEMPO is commonly used to oxidize the hydroxyl groups which is accompanied with a primary oxidant. This leads to oxidation of -OH groups into carboxylic groups present in the cellulose [38]. After the oxidation, the attained nanocellulose was found to contain carboxylic acid surface with micro and nanometre length and diameter [39-41]. On oxidizing with TEMPO / NaBr and NaClO in water by maintaining the pH of 10-11, the p-hydroxyl groups existing in the C6 of the cellulose molecule expectantly oxidises to the carboxylate groups. Based on the consumption of the aq. NaOH, the oxidation process of the reaction can be studied and monitored, and the NaOH is regularly adding to the reaction mixture to attain its pH to 10 [42-45].

Terminalia Elliptica nanocellulose (TO-TENC) was obtained by treating 1gm of the respective cellulose contained in a beaker with 100 ml double distilled water 0.06 gm

Tempo & 0.1 gm NaBr were mixed separately into 50 ml water. Tempo mixture & NaBr were blend together with the help of stirrer. Reaction was initiated by adding 10% NaClO using NaOH to attain pH of about 10. The solution is washed with water, & 0.5m HCl to set the pH to neutral. The suspension volume is set for 200ml, and then homogenized at 10000 rpm, followed by 10 mins ultra sonication. Finally, the product was washed at 40°C to obtain TO-TENC. The yield from this form of nanocellulose is found to be 95%.

Charaterization

TO-TENC were measured as KBr pellets to infer the Fourier transform infrared spectra (FT-IR) by NICOLET 370 model in the range 4000-400 cm-1. Rigaku Miniflex 600 (5th gen) was used to record X-Ray Diffractogram. Scanning electron microscopy (SEM) images were recorded on JOEL JSM 6390LV, with an acceleration voltage of 10 kV and a Secondary Electron (SE) detector was used to capture the images. Thermal analysis was done by using Perkin Elmer STA 6000 instrument for Differential Thermal Analysis and Thermogravimetric analysis. Model-Perkin Elmer, diamond TG/DTA.

3. Results and Discussion

3.1 FT-IR

The FT-IR spectra of TO-TENC outline the existence of functional group. The FT-IR spectra of cellulose, TO-TENC is shown in Fig.3.1 which disclosed the exhistance of organic groups. The broad absorption peaks observed at 3313 to 3319cm^{-1} is assigned to -OH groups of cellulose. Peak at 2886-2890 cm^{-1} represents C-H stretching vibrations. There are no broad peaks observed like in other NCs. Bending mode of adsorbed water and conjugated C=O stretch vibrations were appeared at 1631-1623cm^{-1}. The appearance of a peak at 1310-1314cm^{-1} is attributed to C-H deformation (asymmetric) and shifts to low wave number. Cellulose characteristic peaks observed at 1032-1036cm^{-1}attributed to C-O stretching & C-H rocking.The transition from cellulose I to II observed by absorption of peaks shifted to higher wave numbers.The results conform that no other derivational reaction occurred during the hydrolysis process.

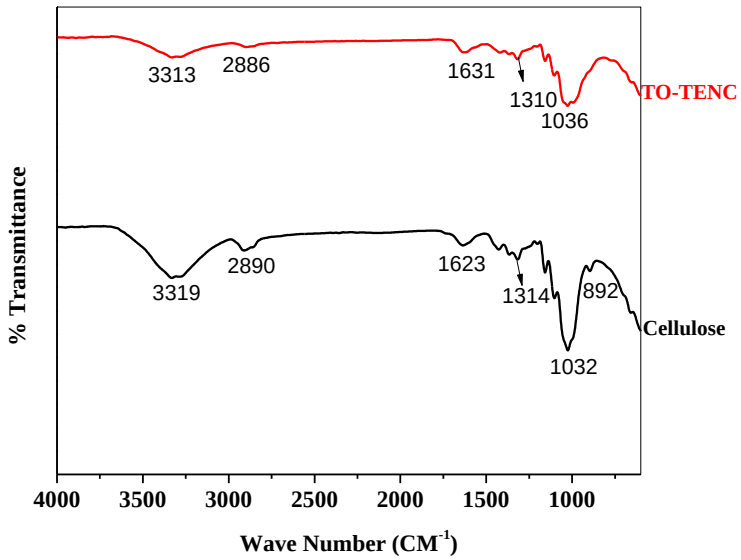

Fig.1. FT-IR spectra of Cellulose, TO-TENC

3.2. X-Ray Diffractometer

The determination of the mechanical & thermal properties of nano cellulose is studied based on its crystallinity, hence making it a key feature. To study the synthetic effects, thermal & mechanical properties and crystallinity of the synthesized nanocellulose XRD was used. XRD of TO-TENC is presented in Fig.2. The sample shows intensity peak at 22.98^0. The intense peaks observed at TO-TENC remarks that TEMPO oxidation followed by ultrasonicityhas no effect on the parent cellulose.TO-TENC denotes at 7083.3cps intensity. The sample shows broad peaks with less intensity because during the ultrasonicity, the cavitation effect has noselectivity, which acts on crystalline & amorphous domains of nanocellulose, causing some damage on crystal. Thus, the TO-TENC crystallinity decreases. As crystalline domains are more resistant to chemical treatments, only amorphous regions regions are eliminated during TEMPO oxidation, resulting an increament in crystallinity of TO-TENC.

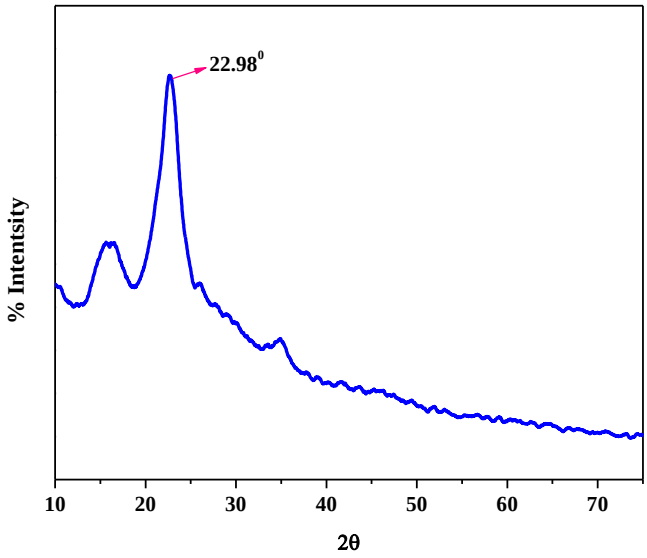

Fig 2. XRD pattern of TO-TENC

3.3. SEM

SEM data feeds us the high resoluted images to study the sample based on its morphology and the topographical information. SEM monographs obtained for TO-TENC show that synthesized NCis crystalline and fibrous along with good agglomeration leading to the confirmation of their sizes which are in dissimilar shapes yet in nano scale. Hence, it confirms the affect on the surface and distribution of size when prepared by a synthetic approach. TEMPO, a hybrid chemo-mechanical process keeps amorphous domains undamaged partly, leading to fibrillar nature. The surface morphology of the product shows the fibrillar nature and it exhibits cellulose nanofibers. It can also be concluded that the fibers are entangled in a regular fashion and doesn't have uniform surface.TO-TENC surface showcases that there is no entanglement of the fibers rather one can notice a uniform suface that is soomth and no fibers extruding can be noticed. However, one can notice there is the accumulation of the fiber crytsals. From the above analysis, it can be settled that the methods of the extraction employed have particularly affect the size distribution & morphology of NC.

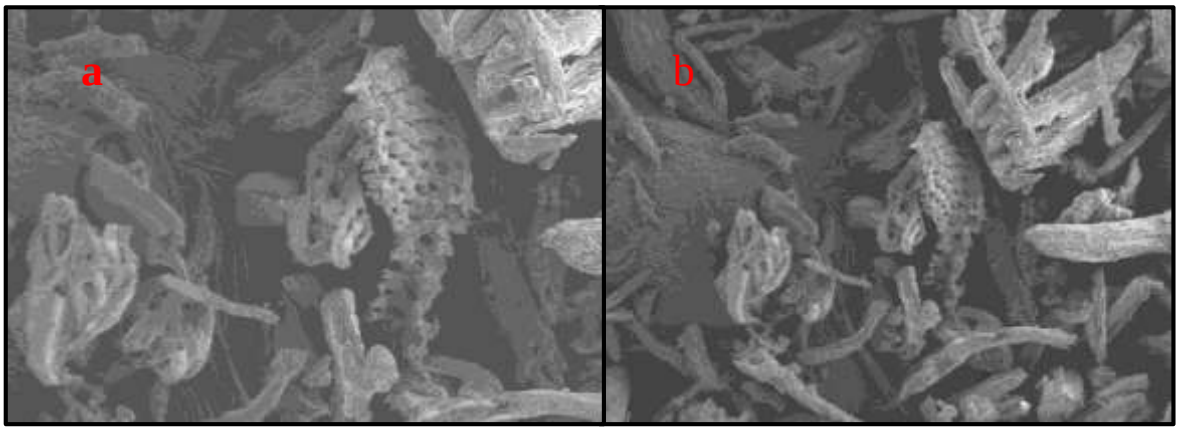

Fig.3SEM Monographs of (a & b) TO-TENC.

3.4. TEM

TEM monograph of TO-TENC have been depicted in Fig.4 (a-b) respectively. TO-TENC has fibrous shaped bundles with average size 38-45nm. It displays relative less size dispersion. The shapes of nanofibers are fine and clear and are varied with diameter distribution in nano size. Also noted that nanofibers are entangled with each other.

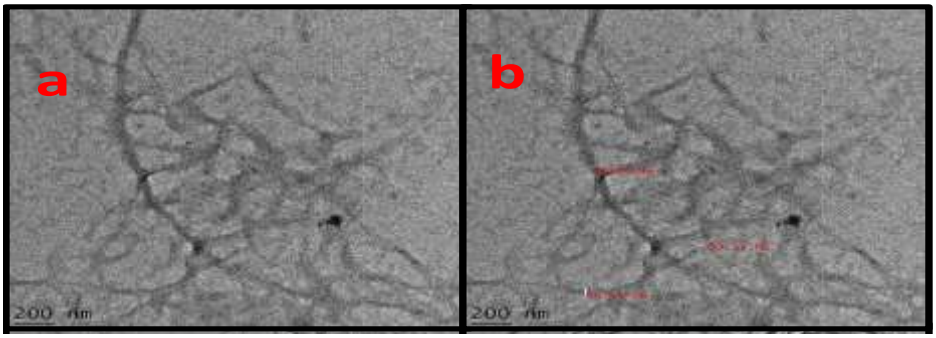

Fig.4 TEM Monographs of (a & b) TO-TENC.

3.5. TGA and DTA

Thermal stability of TO-TENC was examined by using TGA and DTA whose curvesare shown in **Fig.5 & 6** respectively. The moisture evaporation in all the NCs leads to weight loss at 100^{o}C. The degradation temperature of the nanocellulose TO-TENC-277°C, the loss of weight at 100°C is probably credited the water's evaporation. It was noticed as a small trough on left side of DTA plot. The onset degradation temperatures of the obtained nanocellulose are TO-TENC enter the degradation tempearature, as shown in sharp troughs in DTA plot. The thermal stability shown by the sample is considerably low when compared to other TEMPO synthesized products. The variation in degradation temperature of TO-TENC around 360^{0}C is due to impurities present in the tempo oxidised nanocellulose.

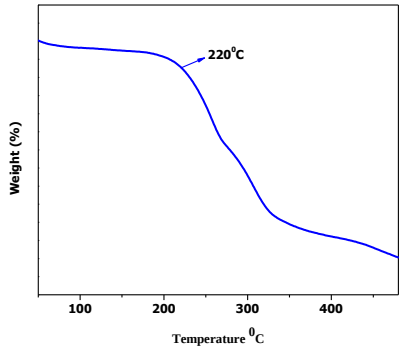

Fig.5 TGA of TO-TENC

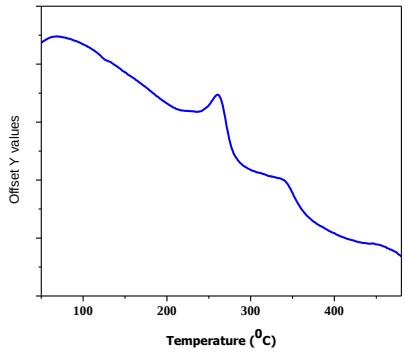

Fig.6. DTA Thermogram of TO-TENC

5. Conclusion

The present works revolves over the renewable agricultural resource to obtain TO-TENC. Tempo oxidation method was employed. FTIR spectra reveal TO-TENC show the cellulose characteristic peaks. The result indicates that no other derivational reaction occurred during the processes of dissolution. XRD spectral patterns are typical of semicrystalline in nature with crystallinity index. SEM images exhibit varied shapes of nonuniform surface, lumens, irregular cross-section, and large number of fibrous crystalline and translucent surface morphology.TEM monograph shows that prepared nanocellulose are in the nanoscale dimension. The size of the cellulose nanofibers is in the range of 38-45nm. TGA/DTA analysis indicates that samples show less loss of weight around 100°C, which is attributed to water evaporation. TENC have good thermal stability. .

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