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PREPARATION AND CHARACTERIZATION OF GRAFT COPOLYMER OF BUTYL ACRYLATE ON CELLULOSE NANO CRYSTALS (CNCs) FROM BANANA FIBER

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ABSTRACT

In this present work a novel material of Cellulose Nano Crystals (CNCs) grafted with butyl acrylate with ceric ammonium nitrate as initiator was prepared. The graft copolymerisation was done by changing the conditions like monomer (Butyl acrylate), amount of initiator concentration and temperature. The yield of grafted copolymer was observed in each case. Cellulose Nano Crystals was prepared by steam explosion method using banana fiber. The CNCs, grafted copolymer is then subjected to various analytical techniques such as FT-IR, XRD, SEM and TEM. From the FT-IR, the CH_2 type of linkages was observed in the grafted copolymer showing increased transmittance of the polymers. From the X-ray diffraction method (XRD) the Crystalline and amorphous areas are calculated by Scherrer equation. The morphology of the prepared Cellulose Nano Crystals were evaluated using SEM and TEM.

KEYWORDS: Cellulose Nano crystals, banana fiber, butyl acrylate, SEM, TEM.

1. INTRODUCTION

The developing global environmental concern, the depletion of petroleum resources growing environmental problems related to search for new materials. This leads to new growing materials developed from various bio based resources, particularly cellulose is a most popular. Now a present days cellulose and their composites a highly attractive in research line. The most important sources of cellulose fibers are plant and wood. The plant based cellulose nanofibers has produced significant source of nanometre sized fillers since sustainability, abundant availability, and the related characteristics such as a very large surface to volume ratio, high tensile strength, high stiffness, high flexibility, good dynamic mechanical, electrical and thermal properties as compared with other commercial fibers.[1-4] The basic structural units of all plants and cellulose are cellulosenanofibrills, the world's most abundant natural, renewable, biodegradable polymer. It has been estimated that globally, 10^{10}–10^{11} tonnes are synthesized and destroyed each year.[5] Cellulose is a polydispersed linear polymer of poly-β (1, 4)-D-glucose with a syndiotactic configuration. The CNCs have a width ranging from 5-30 nm are highly crystalline materials formed by the aggregation of long thread like bundles of molecules stabilized laterally by hydrogen bonds between hydroxyl groups and oxygen's of adjacent molecules.[5,6]

The CNCs are extracted from several methods are used from plant cell wall. They are generally through on chemical and mechanical treatments such as steam explosion method is a pre-treatment of lingo cellulosic fibers.[7,8] The steam explosion process was first introduced by Mason in 1927 to defibrate wood into fiber for board production.[9] Bibin Mathew Cherian et al. was first reported by synthesis of cellulose Nano fibril whiskers from banana fibers.[10] Generally, the graft copolymer referred to as the backbone polymer of a long sequence of one monomer (main chain) with one or more branches (grafts) of long sequences of a different monomer.[11] The graft copolymerisation of many monomers onto cellulose and onto cellulose derivatives has been carried out by different methods that can be generally classified into three major groups: (i) free radical polymerisation, (ii) ionic and ring opening polymerisation and (iii) living radical polymerization. The methods of cellulose graft copolymerisation are based on one or more of three approaches, ‘‘grafting-to’’ the cellulose, ‘‘grafting-from’’ the cellulose, and ‘‘grafting through’’ the cellulose. Among these three approaches of grafting, the ‘‘grafting from’’ approach is the most commonly used procedure. One of the major advantages of this approach is that a high graft density can be achieved due to the easy access of the reactive groups to the chain ends of the growing polymers.[12]

In this work Cellulose Nano Crystals are extracted from banana fibers by applying steam explosion method. The converted CNCs grafted with monomer butyl acrylate. The grafted copolymer can be prepared with same monomer and initiator (ceric ammonium nitrate) taken in different weight proportions. The grafted copolymer yield was observed in each case. The isolated CNCs are characterized by different modern techniques such as FTIR, XRD, SEM and TEM.

2. MATERIALS AND METHODS

2.1 MATERIALS

The materials used for the study includes banana fibers (collected from local farms), NaOH (commercial grade), acetic acid (commercial grade), sodium hypochlorite (commercial grade), oxalic acid (commercial grade). Analytical grade butyl acrylate, Ceric ammonium nitrate were used.

2.2 Preparation of Steam Exploded Banana Fibers. (Stage-1)

30 gms of Banana fibers were chopped into uniform size of approximately 10 cm. The fibers were treated with 2% NaOH (fiber to liquor ratio 1:10) in an autoclave and kept under 20 lb. pressure for a period of 1h. Pressure was released immediately. The fibers were removed from the autoclave, and the fibers were washed in water till they were rid of alkali. The washed fibers were allowed to drain off free flowing water.

2.3 Preparation of Steam Exploded Bleached Banana Fibers. (Stage-2)

The steam exploded fibers were bleached using a mixture of NaOH and acetic acid (27 and 78.8 g, respectively) and a mixture of 1:3 sodium hypochlorite solution. The bleaching was repeated six times. After bleaching, the fibers were thoroughly washed in distilled water and dried.

2.4 Preparation of Steam Exploded Fibers in Acidic Medium. (Stage-3)

The steam exploded bleached fibers were treated with oxalic acid (9%) in an autoclave till it attained a pressure of 20 lb. The pressure was released immediately. The autoclave was again set to reach a pressure of 20 lb., and the fibers were kept under that pressure for 15 min. The pressure was released and the process repeated 8 times. The fibers were taken out, washed till the washings no longer decolorized $KMnO_4$ solution to make sure that the washings were free from acid.

2.5 Mechanical Treatment of the Processed Banana Fibers (Stage-4)

The fibers were suspended in water and under continuous stirring with a mechanical stirrer of type RQ – 1.27 A and 8000 R.P.M. for 4 h. The suspension was kept in an oven at 90°C till it was dry.

Stage-1 **Stage-2** **Stage-3** **Stage-4**

Figure-A Photograph of steam exploded banana fibers at various stages

2.6 Preparation of grafted co-polymer

A required amount of cellulose (0.5g) was dissolved in water (100ml) with constant stirring forming a homogeneous solution. The 1ml of butyl acrylate monomer dissolved in 10 ml of ethanol was then added to that homogenous solution then to initiate the polymerization process, the initiator ceric ammonium nitrate (10 ml) was added.

After all the addition was over the above mixture was heated to 70°C simultaneously the stirring of that mixture was performed using a magnetic stirrer. This solution was then poured into excess sodium hydroxide solution to precipitate the graft copolymer. It was then filtered, dried and weighed.

The graft copolymerization was done by changing the conditions like different monomer (butyl acrylate) ratios, initiator concentration and various temperature. The yield of the graft copolymer was observed in each case.

3. CHARACTERIZATION

3.1 FTIR Spectroscopy

Measurements were performed with Thermo Nicolet AVATAR 330 Spectrometer in 4000 – 400 cm^{-1} ranging using KBr pellet at DKM College for women, Vellore.

3.2 X – ray powder Diffractometer (XRD)

In order to observe the molecular packing of the processed Banana fibers (4 stages) and grafted copolymers X – ray powder diffractometer (XRD – SHIMADZU XD –D1) using a Ni – filtered Cu Kα X – ray radiation source.

3.3 SCANNING ELECTRON MICROSCOPE (SEM)

The surface morphology of the processed Banana fibers (4 stages) the surface and cross section topography were analyzed with a Cambridge stero scan 440 (scanning electron microscope (SEM Leica Cambridge UK) operated at an acceleration voltage at 20 kV.

3.4 TRANSMISSION ELECTRON MICROSCOPE (TEM)

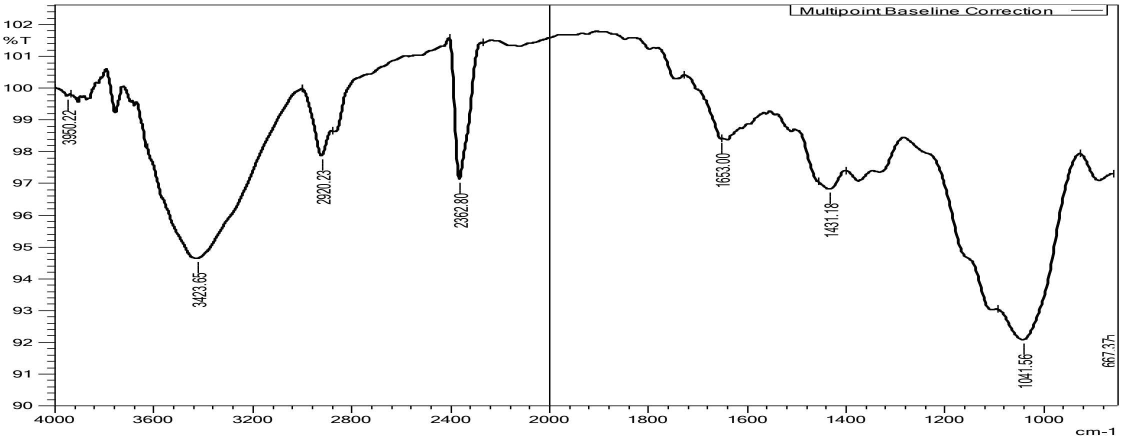
Transmission electron micrographs was used to study the structure and size of CNCs produced from Banana fiber. TEM of CNCs were taken with a Hitachi-600 transmission electron microscope with an acceleration voltage of 75kV. CNCs were deposited from an aqueous dispersion on a microgrid covered with a thin carbon film (≈ 200 nm). The deposited CNCs were subsequently stained with a 2% uranyl acetate solution to enhance the microscopic resolution.

4. RESULTS AND DISSCUSSION

4.1 Fourier transform infrared spectroscopy

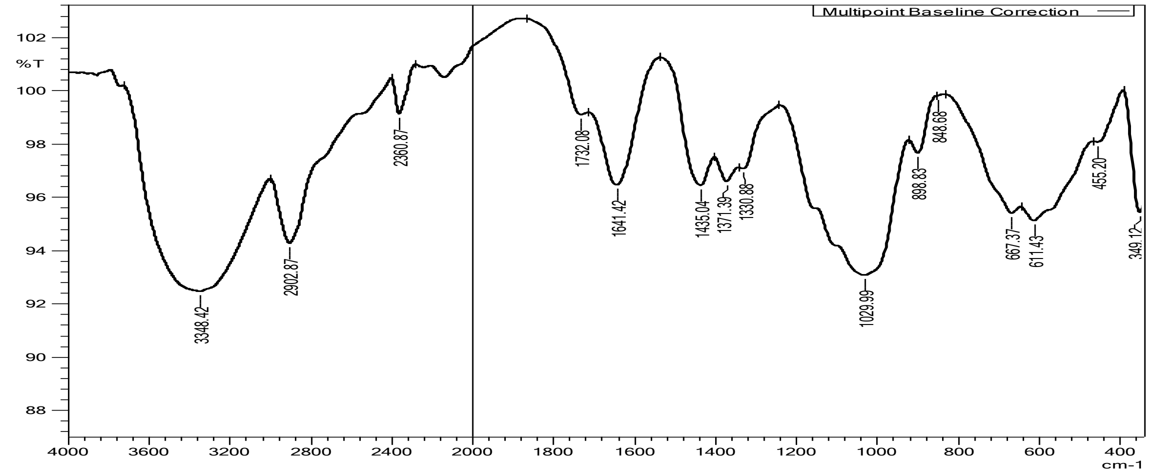
FTIR is mainly used to determine of functional groups in frequency range from 400 cm^{-1} to 4000 cm^{-1}. The FTIR Spectral details of first four stages in banana fibers were represented in Fig (1) – (4).

Figure-1



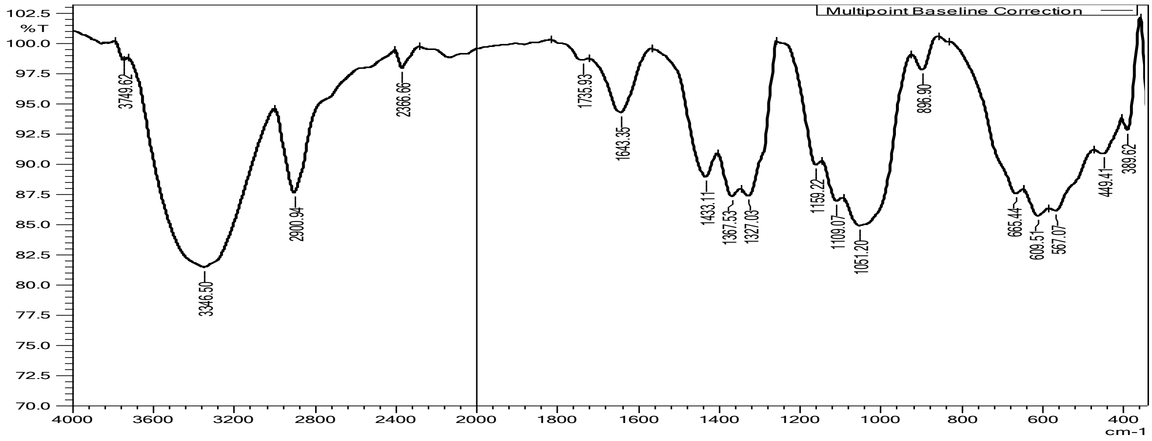
Stage-1 Preparation of Steam Exploded Banana Fibers.

Figure-2.



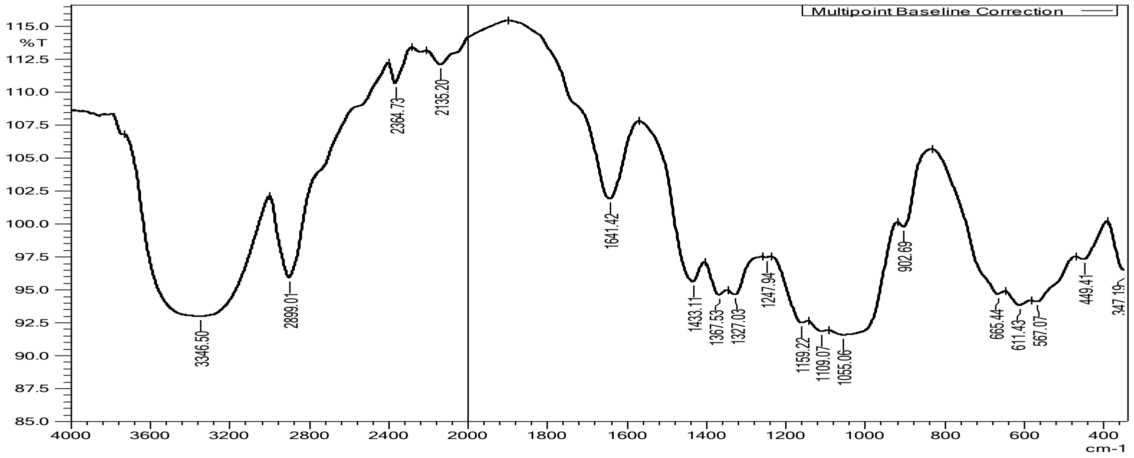
Stage-2 Preparation of Steam Exploded Bleached Banana Fibers.

Figure-3.



Stage-3 Preparation of Steam Exploded Fibers in Acidic Medium.

Figure-4



Stage-4 Mechanical Treatment of the Processed Banana Fibers.

The FTIR spectra of alkaline, steam exploded and bleached banana fibers shows the peaks in the area 3423 cm^{-1} arise due to O-H stretching vibrations of hydrogen bonded hydroxyl (OH) group. The hydrophilic tendency of the steam exploded and bleached banana fibers in the broad absorption band in the 3700-3100 cm^{-1} region, which is related to the –OH groups present in their main components. The peaks at 2920 cm^{-1} are due to the aliphatic saturated C-H stretching vibration in cellulose and hemicellulose. The peak at 1732 cm^{-1} due to C=O stretching of the acetyl and uronic ester groups of residual hemicelluloses or the ester linkage of carboxylic group of the ferulic acids of lignin.[13] This peak is absent in the steam exploded and bleached banana fiber due to the dissolution of the hemicellulose component present in the banana fiber during the process of steam explosion and bleaching. This peak may have also arisen because of the C=O stretching of methyl ester and carboxylic acid in pectin. In steam exploded and bleached banana fibers, this peak is absent, the partial removal of carboxylic groups by alkali treatment throughout a process called de-esterification.[14, 15]

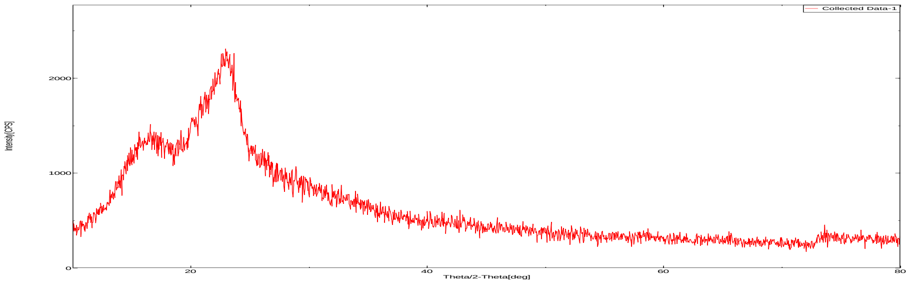
Peaks at 1641 cm^{-1} and 1643 cm^{-1} are indicative of the presence of lignin and attributed to the C=C vibration.[16] The peak 1630 cm^{-1} the bending mode of the absorbed water with some contribution from carboxylate groups.[13] The peaks in the region 1250-1056 cm^{-1} involve the C-O stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicellulose, lignin and extractives.[17] The peaks in the region 1430 cm^{-1} are due to various lignin components.[18] The broad peaks at 1050 cm^{-1} are assigned to ether linkage (C-O-C) from lignin or hemicellulose, while the peak at 898 cm^{-1} is due to β-glycosidic linkages of glucose ring of cellulose.[19]

Stage-3 and Stage-4 the sharpening of the peak in the area 2920 cm^{-1} takes place. This is due to the increase in the crystallinity in the fibers, showing the increase in the percentage of cellulose components.

4.2 X-ray Diffraction Studies

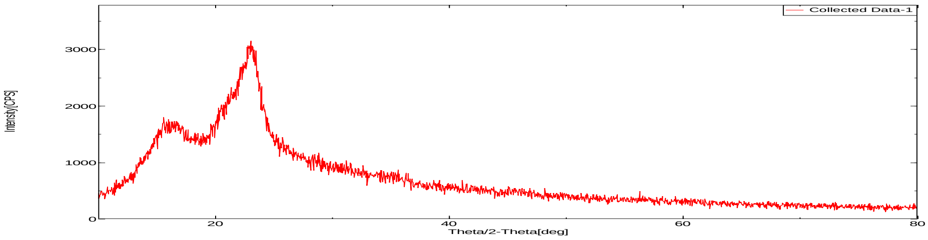
XRD studies of the steam exploded banana fibers were done to investigate the crystalline behaviour and size of the fibers. From the XRD graphs, it is clear that the treated banana fibers show a crystalline nature. The steam exploded banana fibers show increasing orientation along a particular axis under different processing conditions.

Figure-5



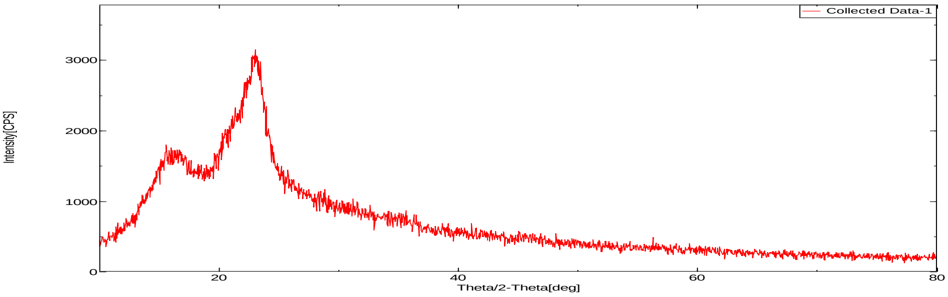
Stage-1 Preparation of Steam Exploded Banana Fibers.

Figure-6



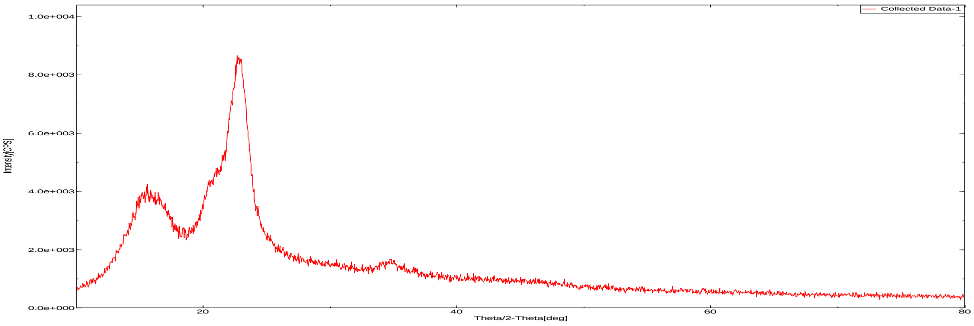
Stage-2 Preparation of Steam Exploded Bleached Banana Fibers.

Figure-7



Stage-3 Preparation of Steam Exploded Fibers in Acidic Medium.

Figure-8



Stage-4 Mechanical Treatment of the Processed Banana Fibers.

The XRD pattern of a steam exploded banana fibers (Stage-1) intense peak at $2\theta=23.075^0$. From the (Fig-5) shows the fiber is almost amorphous with very little crystallinity in it. The XRD pattern of a steam exploded bleached banana fibers (Stage-2). From the (Fig-6) shows slight crystallinity is evident that intense peak at $2\theta=22.930^0$. The XRD pattern of a steam exploded banana fibers in acidic medium (Stage-3) the crystallinity is increased gives a relatively intense peak at $2\theta=23.015^0$. The XRD pattern of a mechanical treatment of the processed banana fibers (Stage-4) intense peak at $2\theta=22.868^0$ respectively. Based on the results sharp peak in the X-ray diffraction method of the acid treated fibers exhibits a higher crystallinity compare with other stages. The removal of noncellulosic polysaccharides and dissolution of amorphous zones. Accordingly the above results indicates that hydrolysis took place more favourably in the amorphous region. This increase of crystallinity after acid treatment has been reported by several authors.[20, 21] Figure 6, 7 and 8, shows the broadening of the peak at maximum 2θ. This shows the evidence for the decrease in banana fiber diameter.

The fiber diameters (D) of variously treated banana fibers are calculated using the scherrer formula.[22]

$$D= \frac{0.89\lambda}{BCos\theta}$$

Where K is a constant dependent on crystallite shape (0.89)

λ = X-ray wave length,

B = fwhm (full width at half-max) or integral breadth,

θ = Bragg angle.

The fiber diameter of different stages of steam exploded banana fiber converted to CNCs calculated diameter = 4.4nm it is clear that there is a decrease in fiber diameter during crystalline in nature.

The degree of crystallinity can be expressed as follows

$$Xc\ (\%) = \frac{Ac}{Ac+Aa} \times 100$$

where Xc=Degree of crystallinity; Ac=Crystalline area on the X-ray diffraction and Aa= Amorphous area on the X-ray diffraction TABLE-1 shows the X-ray diffractogram details of the steam exploded banana fibers of various stages.

Table-1 XRD details of treated banana fibers.

Stages (1-4)	**2θ**	**Degree of crystallinity (%)**
Preparation of steam exploded banana fibers.	23.07^{o}	35.93
Preparation of Steam Exploded Bleached Banana Fibers.	22.93^{o}	55.40
Preparation of steam exploded fibers in acidic medium	23.01^{o}	67.73
Mechanical treatment of the processed banana fibers.	22.87^{o}	73.52

Steam explosion process based on results, cellulose content is increased degree of crystallinity and crystals of higher perfection and size, as shown by the width of the X-ray reflections before and after the steam explosion process.[23] Table-1 shows crystallinity of different stages of steam exploded banana fibers. We can see that the increased percentage crystallinity in the banana fibers this is due to the fact that during acid treatment the amorphous regions are readily attacked by dilute acid while the crystalline regions are most resistant to attack.

4.3 Scanning electron microscopic (SEM) studies

SEM was used to investigate the surface morphology of the steam exploded banana fibers the results reveal that fiber diameter can be reduced to the nanometre range.

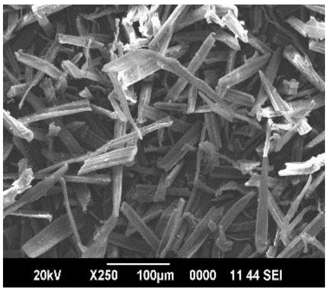


Figure-9

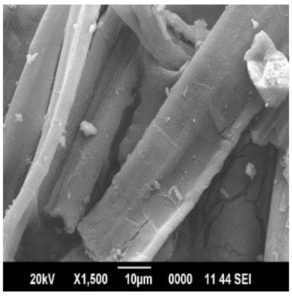


Figure-10

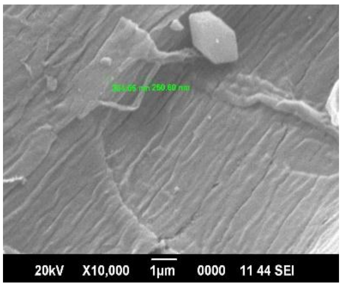


Figure-11

SEM Micrograph of CNC extracted from banana fiber

The banana fibers converted to CNCs by applying steam explosion process of various stages (1-4) affect the fiber morphology, exposing its surface due to removal of some non-cellulosic, macromolecular components such as hemicelluloses, lignin, pectin, and other impurities. Figure (9-11) shows banana fibers converted to cellulose Nano crystals (CNCs). These images shows reduced the roughness due to the removal of impurities from the banana fiber surface. The surface of the fibers is found to be smooth from the SEM images.[24] The steam exploded banana fibers shows the alkaline treatment and bleaching process have broken the lignocellulosic complex, solubilized the lignin and hemicellulose to expose more porosity and surface area of the hidden cellulose. Based on the results ligno cellulosic fibers aligning and distributing individually between each other, making them more accessible for the cellulose Nano crystal extraction process.

4.4 Transmission Electron Microscopy (TEM)

TEM was very useful tool to study the morphology and nanometre scale of CNC. The banana fiber converted to CNCs using steam explosion process such as acid hydrolysis process to reduce the amorphous part of cellulosic fibers, increase the crystalline region and reducing the size of the fiber to nanometre scale. The CNCs had an average diameter 4.4nm. From the micrographs CNCs have a needle-like or rod-like structure.[25] The average diameter of the Nano fibrils were found to be between 4-5nm, and the average length of the Nano fibrils were found to be between 200-250nm.

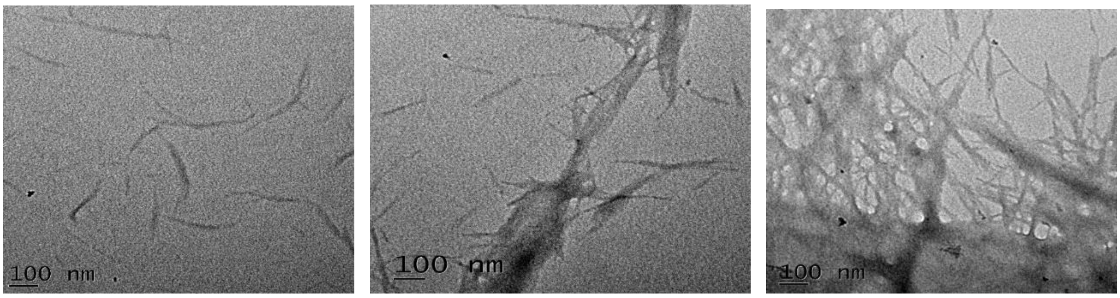


Figure-12 **Figure-13** **Figure-14**

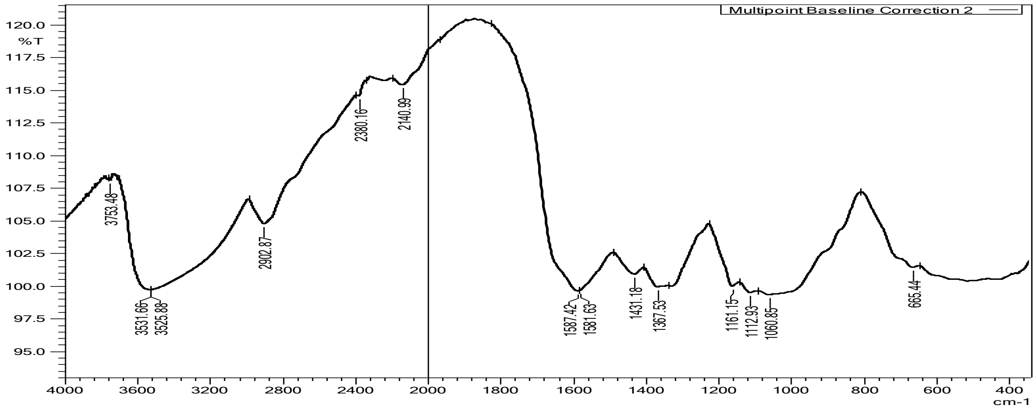
TEM Micrograph of CNC extracted from banana fiber

4.5 FTIR SPECTRAL ANALYSIS OF GRAFTED COPOLYMER

Figure-15

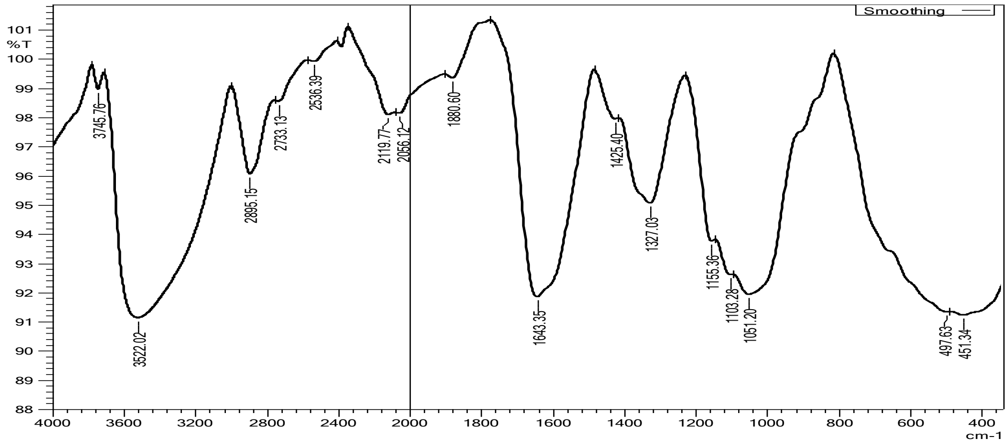
CNCs grafted butyl acrylate at different Initiator concentration.

Figure-16



CNCs grafted butyl acrylate at different monomer concentration.

Figure-17



CNCs grafted butyl acrylate at different temperature concentration.

The formation of graft copolymer of Cellulose Nano Crystals (CNCs) grafted butyl acrylate monomer was confirmed through FT-IR analysis. The FT-IR Spectrum of CNC-g-butyl acrylate prepared under different monomer (butyl acrylate) ratios, initiator concentration and various temperature. The yield of the graft copolymer was observed in each case. The maximum grafting yield shows the better result of graft copolymer. Figure (15-17) shows maximum yield of different monomer (butyl acrylate) ratios, initiator concentration and various temperature.

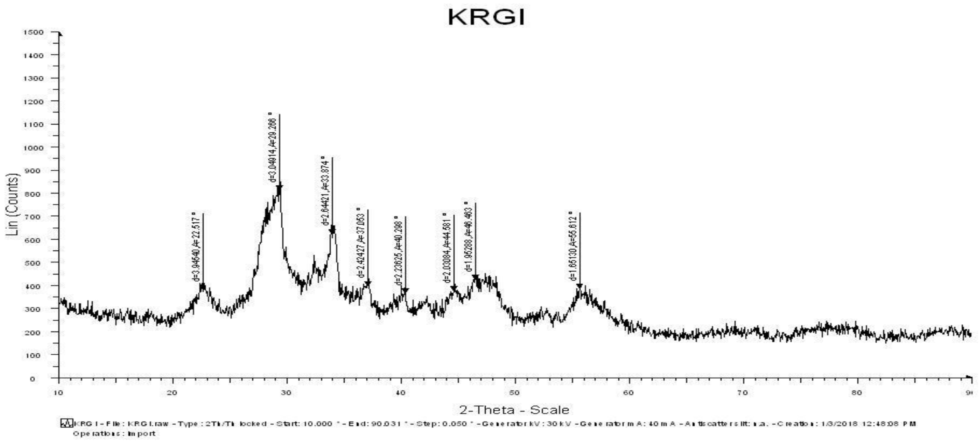
The FTIR the peaks in the area 3522 and 3462 cm^{-1} arise due to O-H stretching vibrations of hydrogen bonded hydroxyl (OH) group. The broad absorption band in the 3700-3100 cm^{-1} region, which is related to the –OH groups present in their main components. The peaks at 2895 and 2902 cm^{-1} are due to the aliphatic saturated C-H stretching vibration in cellulose.[13]

Also successful grafting of butyl acrylate at the surface CNC is proven by strong carbonyl band 1689 cm-1 and 1643 cm^{-1}.[26,27] In comparison with the FTIR spectra of free CNC and CNC-grafted butyl acrylate shows an increase in C-H stretching vibration area at 2902-2056 cm^{-1} which can be described to the methylene groups are increased.[28, 29] As a result of polymer grafting at the surface of CNC, the hydroxyl band area at 3700-3100 cm^{-1} is decreased.[30] Appearance of the characteristic bands spectra of the polymer-modified CNCs shows that grafting reactions have been appropriately done. Increase of peak area of CH_2 groups at 2800-2500 cm^{-1} is observed for CNC grafted block copolymers by increase of block co- polymer length.

4.6 XRD Diffraction studies

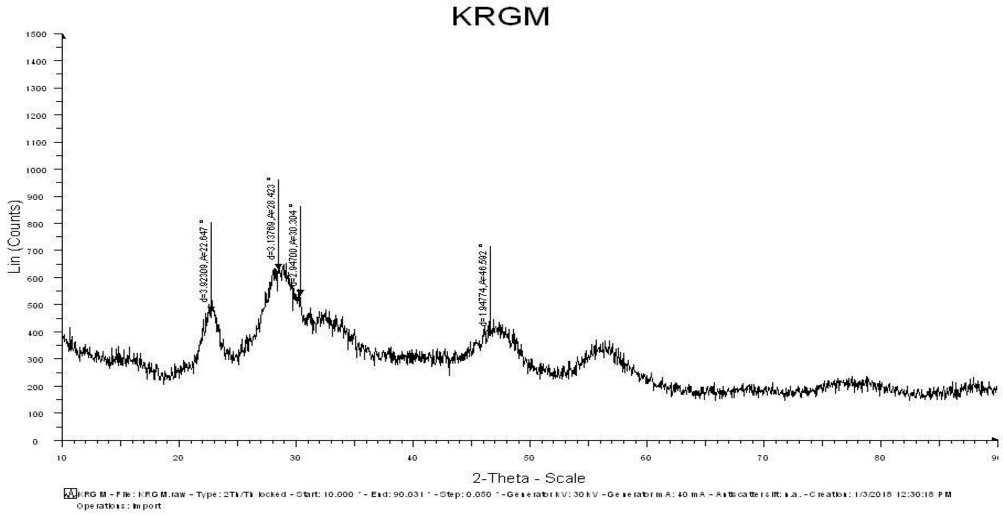
X-ray diffraction (XRD) analysis is an important tool in determining the structure and crystallization of polymer matrices.[31] X-ray diffraction patterns of CNC-g-Butyl acrylate copolymer were measured to investigate the change of crystalline nature of CNC after polymerization. The X-ray diffraction patterns of different monomer (butyl acrylate) ratios, initiator (CAN) concentration and various temperature. The yield of the graft copolymer was observed in each case. The maximum grafting yield shows the better result of graft copolymer. Figure (18-20) shows maximum yield of different monomer (butyl acrylate) ratios, initiator concentration and various temperature.

Figure-18



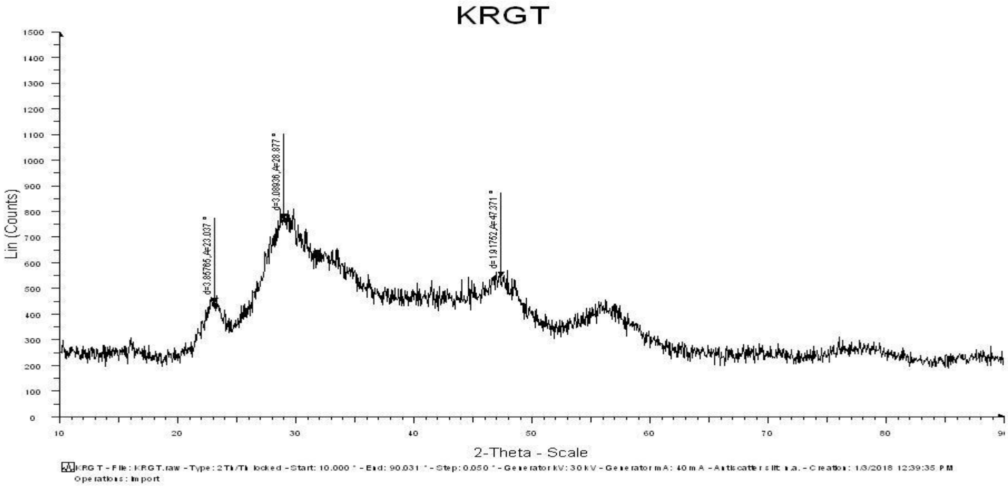
CNCs grafted butyl acrylate at different Initiator concentration.

Figure-19



CNCs grafted butyl acrylate at different monomer concentration.

Figure-20



CNCs grafted butyl acrylate at different temperature concentration.

The X-ray diffractogram of pure CNCs shows only one sharp peak at 22^0 and 23^0 but CNC-g-butyl acrylate at different monomer (butyl acrylate) ratios shows the intensity of peak at 22^0, 28^0, 30^0, and 46^0. The different initiator (CAN) concentration shows the intensity of peak at 22^0, 29^0, 33^0, 37^0, 40^0, 44^0, 46^0 and 55^0. The different temperature shows the intensity of peak at 23^0, 28^0 and 47^0. From the number of peaks obtained it was concluded that decreased crystallinity compared with CNCs. Generally, the graft process does not affect the crystalline structure of CNCs and the observed results indicate that the graft copolymer of CNC-g-butyl acrylate has more number of crystalline forms when compared to the pure CNC. The changes in the graft copolymer indicates clearly there is an interaction between the CNC and the butyl acrylate monomer.

5. CONCLUSION

CNCs have been successfully isolated from banana fiber by steam explosion method. The non-cellulosic materials of banana fiber such as lignin and hemicellulose were successfully removed after chemical treatments (Stages1-4). Characterization of the synthesized CNCs was done by different modern techniques such as FTIR, XRD, SEM and TEM. FTIR spectral details revealed that the sharpening of the peak in the area 2920 cm^{-1} at stage 3&4 due to the increase in the crystallinity in the fibers, showing the increase in the percentage of cellulose components. The XRD studies of the treated banana fibers were done to investigate the crystalline behaviour and size of the fibers. SEM images was used to investigate the surface morphology of the steam exploded banana fiber and the surface of the fibers is found to be smooth. The TEM images shows that isolated CNCs displayed their rod-like shape and further confirmed the size reduction of banana fiber to a nanometre scale of 4.4nm in diameter.

The extracted CNCs grafted with the butyl acrylate monomer using ceric ammonium nitrate as an initiator. The proof of grafting was obtained from FT-IR analysis. In comparison with the FTIR spectra of CNC and CNC-grafted butyl acrylate shows an increase in C-H stretching vibration area at 2895-2056 cm^{-1} which can be described to the methylene groups are increased. The changes in crystalline nature of CNC-g-butyl acrylate due to polymerization were confirmed using X-ray diffraction patterns.

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