Defence Life Science Journal, Vol. 2, No. 4, October 2017, pp. 453-457, DOI : 10.14429/dlsj.2.12280

Physico-Chemical Characteristics of Fine Nano Scaled Carbon Fibres from Bacterial Cellulose

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ABSTRACT

Recently, carbon nanofibers have gained immense attention in research due to its tremendous application. Here, this work highlights a simple, cost effective and reliable method to develop carbon nanofibers (CNF) from biomass. The biomass used is bacterial cellulose (BC) synthesiSed using *Acetobacter xylinus*. CNF was developed by freeze drying of BC followed by pyrolysis at different temperatures (300 ºC - 900 ºC). The conversions of BC to CNF were characterised using SEM, FTIR, TGA and XRD respectively. The results exhibit three dimensional, lightweight, fine nanoscale fibers with a diameter of 10 nm which are tend to have hydrophobic and lipophilic characters, due to which it can be used in oil – water separation applications.

Keywords: Carbon nanofiber; Bacterial cellulose; Pyrolysis; Cost effective

1. INTRODUCTION

Carbonaceous materials are the new emerging excellent material which finds its application with multi functional properties. They have unique characteristics as catalysts, sensors, super capacitors, electrode material for batteries etc[1,2,3] The conventional methods used for the production of carbon aero gels involve a lot of chemicals and Resorcinol formaldehyde pyrolysis is the most followed method to obtain highly cross-linked carbon structure[4]. The major drawback of this kind of synthesis is the toxicity of the chemicals involved and formation of much dense carbon nanofibers. In recent years, challenges are addressed on the synthesis of carbon nanofibers with cost effective, reliable, simple, eco-friendly approach. Use of biomass, in the development of carbon nanofibers has gained attention to make it eco-friendly way of production and also it is cheap when compared to other methods. In the list of biomass, bacterial cellulose is considered as a new fascinating material for developing carbon nanofibers. Bacterial cellulose is produced by certain type of microorganisms like algae (*Vallonia sp.,*), fungi (*Saprolegnia sp.,, Dictystelium discoideum),* bacteria *(Acetobacter sp., Agrobacterium sp.,, Rhizobium sp.,* etc). Among these organisms *Acetobacter* sp., were explored well for the synthesis of bacterial cellulose and composites of bacterial cellulose, which had wider applications in biomedical field[5-8]. Bacterial cellulose are produced by certain type of microorganisms like algae (*Vallonia sp.,*), fungi (*Saprolegnia sp.,, Dictystelium discoideum),* bacteria *(Acetobacter sp., Agrobacterium sp.,, Rhizobium sp.,* etc). Among these organisms *Acetobacter sp.,* were explored well for the synthesis of bacterial cellulose and composites of bacterial cellulose which had wide applications in biomedical field[5-8]. Now a day apart from biomedical applications, bacterial cellulose proves itself in satisfying the requirement of other fields like environmental remediations, food industries, water purifications, fuel cells etc.[9-11].

Oil spills are difficult to remove from water, because of its dense nature. It forms thin layers all over water surfaces and spread vastly. A number of solutions have been developed to mitigate the impacts of oil spills, ranging from chemical dispersants similar to household detergents which are sprayed from planes or helicopters and help to break up oil spills, which again act as a pollutant and affects the wildlife and aquatic environment[12]. The traditional sorbents used for oil spill cleanup and organic pollutant removal are polypropylene webs, polyester foams and other polymeric compounds. Apart from polymers and traditional sorbents, bioremediation was also carried out to an extent in the removal of oil pollutants[13]. In this list, CNF was also studied by researchers to understand its efficiency in removing the oil spills and found that they possess excellent in separating oil and organic pollutants.[14-17].

In 2013, Shu-haung and group reported a facile route to produce ultra light, flexible, fire resistant carbon nanofiber (CNF) from BC pellicle and used as absorbent for removal of a wide range of organic solvents with reusability[4]. Also reported,

Received : 21 April 2017, Revised : 10 May 2017
Accepted : 15 July 2017, Online published : 09 November 2017

a simple route to fabricate carbon nanofiber (CNF) aerogels on a large scale from macroscopic-scale synthesised carbonaceous nanofiber hydrogels and the resulting CNF aerogels have a self-assembled, interconnected, three-dimensional (3D) network structure with a very low apparent density of 10 mg cm^{-3} and a high porosity of > 99 % [17].

Considering all these aspects, Carbon nanofibers were produced using eco-friendly biomass (Bacterial cellulose Pellicles) as the source. The BC pellicles are freeze dried and pyrolysed in a nitrogen atmosphere at higher temperature. The conversion from BC to CNF was investigated by understanding the physical and chemical characteristics like structure, chemical functionality, thermal stability and crystallinity of the material before and after pyrolysis.

2. MATERIALS AND METHODS

Mannitol, starch, glucose, sucrose, peptone, yeast extract, acetobacter agar (mannitol), acetobacter broth (mannitol), ethanol, glacial acetic acid, sodium hydroxide were purchased from Himedia Pvt. Ltd. *Acetobacter xylinum* (NCIM 2525) was obtained from National Chemical Laboratory (NCL), Pune, India. The bacterial cell suspension was stored at -80ºC in glycerol solution and cell culture was quadrant streaked in agar medium to get single colony. Pre-innoculum for all experiments was prepared by transferring a single *A. xylinum* colony grown on agar medium into 100 mL of liquid medium. Then, the flask was agitated at 30ºC for 24 h for culture growth and it was used as innoculum for further studies. The 100 ml medium for bacterial cellulose production contains mannitol (5 g), yeast extract (0.5 g) and peptone (0.5 g) with pH 5. 1 ml of cell suspension was inoculated into the above mentioned 100 ml culture media in a 250 ml Erlenmeyer flask and incubated at 30 ºC for 14 days under static conditions. The carbon source like rice starch, glucose, sucrose and mannitol was changed by keeping other component constant and synthesised under same conditions. The bacterial cellulose fibers were harvested and washed in distilled water to remove the medium components and boiled in 0.5 N NaOH to remove the cell debris and other impurities. It was continuously washed with water until the pH was neutral and autoclaved at 121 ºC. Upon subjecting the BC into air drying, hot air oven and freeze drying methods, freeze drying was selected as the suitable method to avoid the shrinkage of the fibers.

2.1 Pyrolysis Process

By choosing appropriate medium for the production of BC pellicles, the obtained BC was freeze dried to form aerogels and then pyrolysis was done using tubular furnace. The samples were cut into uniform size and weighed before pyrolysis. The pyrolysis was carried out in an inert atmosphere using nitrogen gas flow in bubble rate. The temperatures range was 300ºC to 900ºC.The weight loss was checked for all samples after pyrolysis. The sample pyrolysed at 900ºC were fragile. Further for characterisation sample processed at 700 **ºC** was considered.

2.2 Characterisation

Physical and chemical properties of CNF obtained were characterised by different techniques. A small piece of sample was sputter coated with metallic gold (Emitech sputter coater) for SEM imaging. Size and morphology of all the nanofibers were obtained using Quanta 200 Scanning electron microscope (ICON Analytical). Powder X-ray diffraction (XRD) patterns of the samples were recorded on a PANalytical X-Ray diffractometer by monitoring the diffraction angle from 10° to 60° at 40 keV. The samples were exposed for a period of 5min in room temperature for X-ray diffraction analysis. The functional groups were verified by Nicolet Avatar FT-IR instrument. Pyrolysis process was carried out using Tubular furnace, Technico Pvt. Ltd. Instrument consist of cylindrical cavity surrounded by heating coils that are embedded in a thermally insulating matrix. Temperature can be controlled via feedback from a thermocouple. Thermal characterisation was done using Simultaneous thermal analyser NETZSCH STA 449F3.

3. RESULTS AND DISCUSSION

3.1 Gravimetric Analysis

The samples subjected to pyrolysis were weighed before and after the process to obtain the weight loss of the samples. The initial weight of the bacterial cellulose pellicle was 600 mg, 700 mg and 1000 mg respectively. After pyrolysis process the weight was 60 mg, 72 mg and 96 mg. 90 percent weight loss was observed in all the samples. The remained 10 percent CNF derived from this process are less dense and flexible in nature.

3.2 Morphological Characteristics Before Pyrolysis Process

The fiber size and structure of BC synthesized from different carbon sources was characterized by placing a piece of each samples in sputter coater and the samples were checked for the morphological characterisation at various magnification. Figure 1: represent the structure, size and morphology of BC. Carbon sources influenced the fiber formation as well as the yield of the fibers. In case of rice starch the fibers were loosely packed. Fiber from glucose showed a randomly arranged fibers with the width of 50-70 nm in diameter. In case of sucrose, the yield was comparatively less and also the fiber orientation were damaged which is upon alkaline treatment. Whereas in case of mannitol, the fibers were in the range of 20-50 nm and the arrangement was much entangled with dense fibers. The width of the fibers and the porosity of the networked BC were increased upon the lyophilisation technique, which is evident in the SEM images of the BC samples. Upon various carbon source utilised, mannitol was chosen for the further processing of CNF.

3.3 Thermo Gravimetric Analysis

Thermo gravimetric analysis was done in order to understand the temperature at which the weight loss is observed and to fix the temperature for pyrolysis process. Fig.2 represents the weight loss observed exactly at three points. First mass change was at 190 º C which corresponds to the moisture content present in the freeze dried samples. The second major mass change was at 376.8 ºC, where BC starts decomposing and about 70 percent of weight loss was observed. The final weight loss of 10 percent was observed at 560 ºC. Based on the thermal analysis of BC, the pyrolysis temperature was chosen.

3.4 Morphological Characteristics After Pyrolysis Process

BC fibers obtained from mannitol media show a well

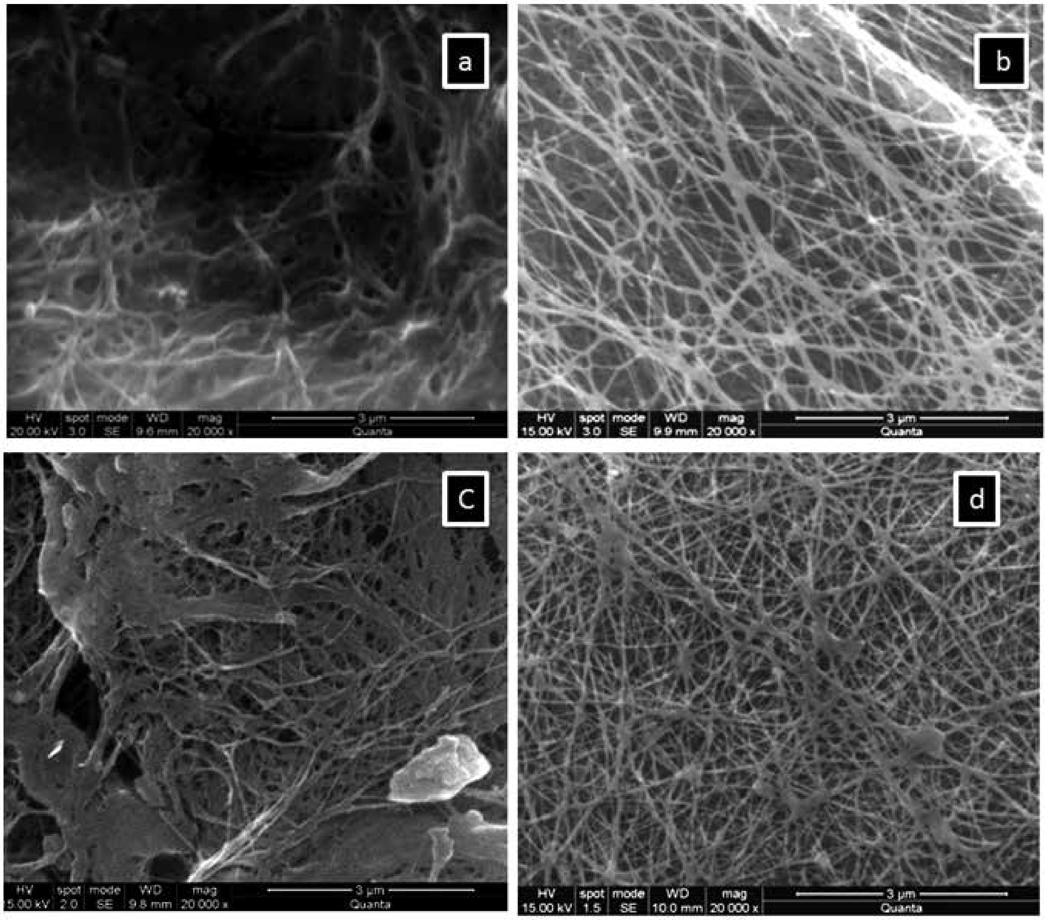

Figure 1. Scanning electron microscopic images of BC from different carbon source a) Rice starch, b) Glucose c) Sucrose d) Mannitol.

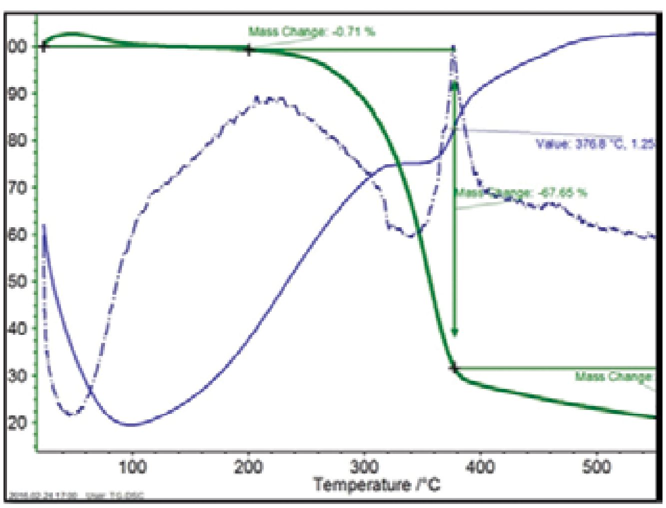

Figure 2. Termo gravimetric analysis of BC.

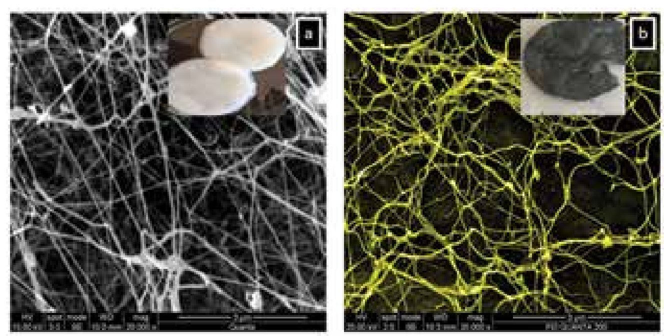

Figure 3. Scanning electron microscopic images of a) BC and b) CNF

organized, porous, 3D network interconnected with narrow size of fiber around 50 nm. After pyrolysis process, the formed CNF reveals that the structure of the BC fiber was maintained as such and the junctions and network were undisturbed upon the pyrolysis treatment. Also the width of the fibers got reduced in the range of 10 nm-20 nm in diameter. Pyrolysis of BC has not damaged the interconnection of fibers and the 3D network remained the same. While comparing with BC, CNF have more void space. The main evidence for the size reduction upon pyrolysis is the SEM images

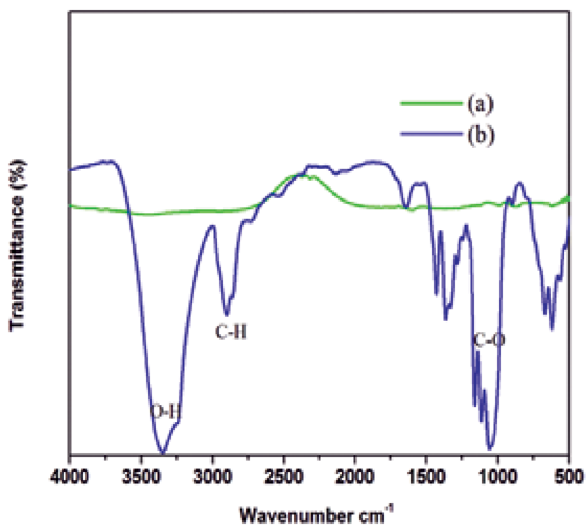

Figure 4. FTIR Spectrum of a) CNF and b) BC.

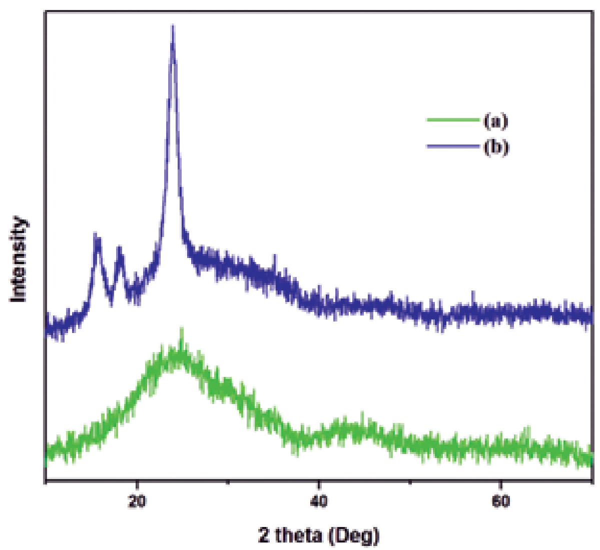

Figure 5. XRD Pattern a) CNF b) BC.

(Fig. 3). This fine size reduction is not observed in much of the other methodologies followed for the carbon nanofiber synthesis.

3.5 Chemical Characterisation

The FTIR analysis revealed the effect of pyrolysis. BC showed the main absorption bands at 3400cm^{-1} which corresponds to the O-H stretching due to the presence of abundant surface hydroxyl group. The other main band was at 2900 cm^{-1} which is of C-H stretching and the C-O angular bending absorption at 1060 cm^{-1}. (Fig. 4) After pyrolysis, this peak disappears as the carbon nanofibers are inactive at IR region, which indicate the complete carbonisation[4].

3.6 XRD Analysis

BC shows sharp peaks at three planes 100, 010 and 110 in correspondence with cellulose of type-I allomorph with 2 theta values of 14º, 17º and 22.7º respectively. After pyrolysis, the peak completely disappears and an amorphous peak appears which indicates the carbonisation. The broad amorphous peaks correspond to the amorphous carbon (Fig. 5).

Crystallinity index have been calculated by the reflecting intensity data using the method of Segal *et al.* C.I = $I_{020}-I_{am}/I_{020}$, Where I_{020} is the maximum intensity of the lattice diffraction and I_{am} is the intensity of the amorphous region[19]. The crystallinity index obtained were 76 in case of BC. The highly crystalline peak gets destroyed upon pyrolysis and amorphous carbon peak centred at 22.4º was observed in CNF. As reported previously by Wu, Zhen□Yu, *et al.* (2013).

4. CONCLUSIONS

I. The nanosize of the BC pellicles influenced in the development of template mediated formation of CNF.
II. The formed CNF were found to be very fine in diameter of 10nm in size.
III. The 3D structure and inter connection with several junctions got maintained after the process of pyrolysis.
IV. The CNF obtained from BC were found to be reliable and simple approach.
V. This can be further utilised in the cleanup of oil spills based on the characteristics of the CNF like fine nanofibers, light weight, hydrophobicity etc.

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ACKNOWLEDGEMENTS

Author Jiji S. is grateful to Defence Research and Development Organisation (DRDO) for funding Junior Research Fellowship under Phase-II programme and also thanks J.A. Allen and K. P. Thiruppathi for SEM and XRD analysis.

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His contribution also includes the guidance throughout the work and the correction of manuscript.

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