

# Preparation and Alkylation of Carbon Nanofibers from Polymethyl Methacrylate

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## Abstract

Carbon nanofibers have revolutionized nanotechnology due to their potential applications in emerging frontiers of research and industrial sectors. This can be attributed to their superior properties such as higher mechanical strength, unique surface characteristics, and improved adherence that is transmitted into the polymer matrix to form a nanocomposite with improved properties. Polymethyl methacrylate is a common carbon source for the synthesis of carbon nanofibres of its high mechanical strength, thermal stability, and low moisture and water absorbing capacity that allows its products to have several applications. In this work, we report the successful electrospinning of carbon nanofibres from Poly methyl methacrylate and functionalizing the resulting carbon nanofibres. The functionalized carbon nanofibres were analyzed to determine their solubility/dispersion in selected organic solvents, then characterized using Fourier transform infra-red spectroscopy, Raman spectroscopy and Thermalgravimetric analysis.

## **Keywords**

Polymethyl Methacrylate, Electrospinning Carbon Nanofibres, Alkylation

## **1. Introduction**

Since their discovery in 1879, carbon fibers (CFs) have found several applications in energy technology, modification of mechanical and physical properties of composites, and manufacturing of sensors [1]. An important difference between the

CFs and carbon nanofibers (CNFs) is their diameters. Conventional CFs have a diameter range of several micrometers while that of CNFs is 50 - 200 nanometers. The two-phase method of generating CNFs involving catalytic vapor deposition growth followed by electro-spinning confers unique properties to them compared to conventional CFs that are typically prepared from high-strength Polyacrylonitrile (PAN) and mesophase pitch (MP) by varying preparation conditions, choice of precursors and adjusting treatment temperature [1] [2]. Previous studies have documented the possibility of electro-spinning appropriate precursors to generate CNFs. For instance, electro-spinning of polyacrylonitrile before oxidative stabilization was reported to result in CNFs with a diameter range of 200 - 300 nm and improved physio-chemical properties compared to conventional CFs [3] [4]. Polymethyl methacrylate and its modified forms have been used as precursor units to produce carbon nanofibers with various physical and mechanical properties such as higher thermal stability [5] and improved and a higher Young's modulus [5] [6] [7]. Recent studies on the production of nanofibres have focused on the enhancement of the surface area to improve the morphology of the nanofibers so that they can be well impeded in the polymer matrix as depicted in Scheme 1 below [8], This includes the treatment process [9]-[11], coupling of precursor materials before electrospinning [12] [13], adjusting precursor solution concentration, choice of solvent to be used [14], adjusting the production conditions including solvent flow rate, applied voltage, distance to the collector, have been extensively applied to vary the morphology of the nanofibres.





Functionalization of carbon nanotubes mainly through mechanical, acid treatment, and alkylation methods has been widely reported [15]. However, not much has been reported on the alkylation of carbon nanofibres mainly due to their structure. The addition of the alkyl group to carbon nanofibers is called alkylation and it is a two-stage process where an alkyl group is attached to the surface of CNF via reductive alkylation using lithium and alkyl halides in liquid ammonia, this is a SN2 reaction mechanism where the bonds of two bimolecular reactants are broken and another formed synchronously to form two new products as shown in **Scheme 2**.



Scheme 2. Functionalization of carbon nanofibers by Alkylation.

In this work, we report the electro spinning functionalization of carbon nanofibres from Polymethyl methacrylate, with *n*-butyl, dodecyl, and acetyl moieties and the solubility, thermal strength, and surface characteristics of the functionalized carbon nanofibers.

## 2. Materials and Methods

All chemical reagents and solvents used in the research work were sourced from reputable supplies such as Sigma-Aldrich (U.S.A) and were of analar grade. The chemicals included PMMA, Li, DMF, DCM, CH<sub>3</sub>CH<sub>2</sub>OH, CHCl<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>I, CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>I, and H<sub>2</sub>NCOCH<sub>2</sub>I.

## 2.1. Preparation of Carbon Nanofibers

The preparation of carbon nanofibers was carried out as previously described with slight modifications [16] [17]. Exactly 80 mg of analytical grade polymethyl methyl acrylate (Sigma Aldrich) was dissolved in 10 ml of a dichloromethane/dimethylformamide mixture in a ratio of 2:3 and stirred using a magnetic stirrer for 3 hours. The polymer solution was electrospun at 18 K v, 22°C, and 45% humidity (BK precision 1901 32V/30a), and fibers were deposited on an aluminum foil placed 15 cm away from the tip of the pipette [17]. The resulting white fibers were allowed to dry at room temperature for 2 hrs and calcinated at 400°C in an inert environment to yield black carbonized nanofibers.

### 2.2. Functionalization of the Carbon Nanofibers

#### 2.2.1. Preparation of Butyl Derivatives of Carbon Nanofibers

Butyl derivatization was carried out as previously described with slight modifications [15]. Exactly 2.0 grams of carbon nanofiber, 120 ml of 30% ammonia solution in water, 1.68 grams of metallic lithium, and 14.5 ml of Butyl iodide was added to a dry 500 ml one-neck round-bottomed flask and the mixture was stirred for 12 hrs with the slow evaporation of ammonia gas. The mixture was cooled in an ice bath with a slow addition of 100 ml methanol, followed by 200 ml of distilled water. The resulting mixture was acidified with 50 ml of 10% HCl, before the addition of 250 ml of n-hexane, on shaking the functionalized carbon nanofibers were extracted into the *n*-hexane, filtered, and washed with distilled water. The nanofibres were oven-dried at 80°C to yield 1.382 g (69.1%) of *n*-butyl functionalized carbon nanofibers.

#### 2.2.2. Preparation of Acetyl Derivatives of Carbon Nanofibers

Acetyl derivatives of carbon nanofibers were prepared as previously described with slight modifications [18]. Exactly 1.4273 grams of carbon nanofibres, 120 ml of 30% ammonia solution in water, 1.24 g of metallic lithium, and 22 grams of Iodo acetyl were added to a dry 500 ml one-neck round-bottomed flask and the reaction mixture stirred for 12 hrs with the slow evaporation of ammonia gas. The mixture was cooled in an ice bath with slow addition of 100 ml of methanol followed by 200 ml of distilled water. The resulting mixture was acidified with 50 ml of 10% HCl, before the addition of 250 ml of n-hexane, on shaking the functionalized carbon nanofibers were extracted into the n-hexane, filtered, and washed with distilled water. The nanofibres were oven-dried at 80°C to yield 1.045 g, (73.21%) of Acetyl-functionalized carbon nanofiber.

#### 2.2.3. Preparation of Dodecyl Derivatives of Carbon Nanofibers

Dodecyl derivatives of carbon nanofibers were prepared as previously described with slight modifications [15]. About 1.0127 g of carbon nanofibres, 120 ml of 30% ammonia solution in water, 0.8787 g of metallic lithium and 25 g of Iodododecane were added to a dry 500 ml one-neck round-bottomed flask and the reaction mixture stirred for 12 h with the slow evaporation of NH<sub>3</sub>. The mixture was cooled on an ice bath with a slow addition of 100 ml of methanol followed by 200 ml of distilled water. The resulting mixture was acidified with 50 ml of 10% HCl, before the addition of 250 ml of n-hexane, on shaking the functionalized carbon nanofibers were extracted into the n-hexane, filtered, and washed with distilled water. The nanofibres were oven-dried at 80°C to yield 0.88 g (86.89%) of the dodecyl nanofiber.

## 2.3. Solubility/Dispersion of Unfunctionalized and Functionalized Carbon Nanofibers

The unfunctionalized and alkylated carbon nanofibres were tested for solubility in acetone, chloroform, dichloromethane, hexane, and *N*, *N*-dimethylformamide

by dissolving 2.0 mg of sample in the 100 ml of solvent at room temperature [19] [20].

#### 2.4. Characterization of the Nanofibers

#### 2.4.1. The Infrared Spectroscopy Analysis

The Fourier transform-infrared (FT-IR) data for both unfunctionalized and alkylated carbon nanofibers was acquired on an FT-IR 600 spectrophotometer in the range of 400 to 4000/cm. Potassium bromide crystals were dried at 105°C and ground to a fine powder using a mortar and pestle. 10% of the sample was combined with the fine KBr powder, and the mixture was further ground to give a uniform fine powder. The mixture was put in a cylindrical press and compressed at a pressure of 25 MPa to form sample pellets. The pellets were mounted and 20 scans per sample were recorded.

#### 2.4.2. Raman Spectroscopy Analysis

Raman scattering analysis of unfunctionalized and alkylated carbon nanofibers was measured in backscattering configuration using a WITec alpha300 RAS+ confocal Raman microscope with a 532 nm laser and laser power of 1mW. The WITec alpha300 RAS+ had an optical microscope able to focus the incident laser and record the illuminated area at the same time.

## 2.4.3. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDS)

Scanning Electron Microscopy observation and Energy Dispersive X-ray (EDX) measurements of unfunctionalized and alkylated carbon nanofibers was done using a Zeiss EVO LS15 Scanning Electron Microscope, with an accelerating voltage of 5 or 8 kV. The samples were dissolved in acetone and sonicated. A drop of the resulting solution was put on a microscope slide and dried in a vacuum. The slide was gold coated in a vacuum and mounted on the sample holder using double-sided sticky carbon tape to increase the conductivity of the sample and avoid decomposition at high temperatures.

#### 2.4.4. Thermogravimetric Analysis

Thermogravimetric analysis was carried out on a TGAQ/DSCI Thermogravimeter under  $N_2$  gas, using 20 mg of sample. Analysis temperature was increased from 30°C to 800°C at a rate of 10°C/min while the gas flow rate was 20 ml/min.

#### 3. Results and Discussions

## 3.1. Solubility/Dispersion in Different Solvents

A comparison of the solubility/dispersion of functionalized and unfunctionalized carbon nanofibers in selected solvents revealed important differences (Table 1).

Functionalization of carbon nanofibers with n-butyl and Acetyl moieties induced their good dispersion/solubility in acetone, chloroform, hexane, and N, Ndimethyl formamide. However Dodecyl functionalized nanofibers did not dissolve/disperse uniformly in the solvents except in the N, N-dimethyl formamide, could be due to the large structure of the dodecyl that could not make it polar and more dispersible than the others.

 Table 1. Solubility/dispersion of functionalized and unfunctionalized carbon nanofibers in selected solvents.

Sample	Acetone	Chloroform	Hexane	DMF
Butyl f-cnf	Soluble	Soluble	soluble	Soluble
Acetyl f-cnf	Soluble	Soluble	soluble	Soluble
Dodecyl f-cnf	Not Soluble	Not soluble	Not soluble	Soluble
Un f-cnf	Not soluble	Not soluble	Not soluble	Not soluble

#### 3.2. Fourier Transform-IR

Evidence of functionalization of the carbon nanofibers was determined/tested using FT-IR, Raman spectroscopy, scanning electron microscopy, energy dispersive spectroscopy, and thermal gravimetric Analysis.

The IR radiation was used to induce vibrations of the bonds with the nanofibers causing them to absorb the light at a specific wavelength giving us several peaks. The absorption peak at 3500 cm<sup>-1</sup> in the acetyl functionalized nanofiber was associated with N-H amide stretch. Absorption peaks in the range of 2800 - 2932 cm<sup>-1</sup> were associated with the C-H stretching vibrations of alkyl groups while those at 1590 - 1620 cm<sup>-1</sup> were linked to the stretching vibrations of the C=O bond of Polymethyl methacrylate backbone. The peak at 1410 cm<sup>-1</sup> was associated with CH<sub>2</sub> symmetric bending while C-H wagging vibrations were associated with peaks in the region of 1106 - 1112 cm<sup>-1</sup>. The peak at 700 cm<sup>-1</sup> revealed skeletal vibrations of Polymethylmethacrylate. The summary of absorption peaks and sample spectra are given in **Table 2** and **Figure 1** below.

#### 3.3. Raman Spectroscopy

FT-IR data on its own was not sufficient to confirm functionalization. Hence, further techniques that could reveal the extent of functionalization of carbon nanofibres were required. The Raman spectrum of carbon nanofibres and functionalized derivatives revealed two overlapping peaks at 1350 - 1580 cm<sup>-1</sup> and

Sample	PMMA Structure	C-O-C	C-C	PMMA C=O	С-Н	О-Н
Un-cnf	705.8	1106.94	1398	1590.9	2800	3197.3
Butyl f-cnf	696.171	1112.7	1409.7	1600.2	2938	3220
Acetyl f-cnf	707.75	1106.95	1398.1	1598.07	2931	3200
Dodecyl f-cnf	714.6	1110.23	1398.1	1612.19	2809	3203.1

Table 2. FT-IR absorption of carbon nanofibres and functionalized derivatives.



Figure 1. FT-IR spectrum of carbon nanofibers and functionalized derivatives.

1580 cm<sup>-1</sup>. The D-band peak, (1348 - 1354 cm<sup>-1</sup>), revealed defects in carbon nanofibres caused by distortion of sp3-hybridized carbon in the hexagonal framework of the CNF wall. The G-band peak (1580 cm<sup>-1</sup>) pointed to in-plane vibration of the six-membered ring common to carbon-based compounds. The extent of distortion in the parent CNF skeleton was estimated using the intensity ratio of the G to D band peaks. When the CNFs were functionalized, the number of structural defects increased and the sp3 hybridized carbon distortion disrupted the hexagonal carbon order, which led to an increase in the relative intensity of the disordered mode. The increase in the ratio of intensity (I) and area (A) of D and G bands confirmed successful functionalization. The summary of Raman spectroscopy of the unfunctionalized and functionalized carbon nanofibres is shown in **Table 3** and **Figure 2** & **Figure 3**.

Tab	le 3.	Raman	absorption	1 data of	f carł	oon n	anofibres	and	functional	derivatives
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Sample	D band	G band	G'	$A_G/A_D$	$I_G/I_D$
Un f-cnf	1348.98	1577.24	2686.74		
Area	$17,761.2 \pm 344.01$	14,599.3 ± 270.3	3367.9 ± 253.7	0.878	0.842
Butyl f-cnf	1355.28	1582.40	2695.30		
Area	18,271.7 ± 340.5	$15,461.1 \pm 257.02$	5259.4 ± 246.7	0.802	0.8018
Acetyl f-cnf	1353.92	1575.83	2699.0		
Area	9190.3 ± 753.9	7099.4 ± 577.6		0.772	0.794
Dodecyl f-cnf	1352.32	1579.16	2689.02		
Area	23,602.7 ± 728.3	17,351.9 ± 546.9	2778.5 ± 421.5	0.726	0.765



Figure 2. Raman spectrum unfunctionalized carbon nanofibers.



Figure 3. Raman spectrum of Dodecyl functionalized carbon nanofibers.

## 3.4. Scanning Electron Microscopy and Energy Dispersion Spectroscopy

Surface characteristics of carbon nanofibres and functionalized derivatives were investigated by use of scanning electron microscopy.

The surface of unfunctionalized carbon nanofibres **Figure 4**, displayed a smooth, long, and non-woven morphology with an average diameter of  $152 \pm 26$  nm. The functionalized carbon nanofibers, **Figure 5** were short, with rougher surfaces compared to the unfunctionalized, and with nodule/beads-like structures with an increased average diameter of  $156 \pm 14$  nm probably because of functionalization [21]. This had a net effect of increasing the surface area of the nanofibers and higher interfacial area for adherence when mixed with polymer. This suggested the successful functionalization of the fibers [22].



Figure 4. Scanning electron microscopy image of Unfunctionalized carbon nanofibers.



Figure 5. Scanning electron microscopy image of functionalized Dodecyl nanofibers.

The EDX of the carbon nanofiber **Figure 6** was almost 98 wt% made of the carbon while the functionalized derivative of acetyl **Figure 7** showed some traces of oxygen 8 wt% and gold metal, less than 1 wt% that was used in coating the







Figure 7. EDS spectra of n-butyl functionalized carbon nanofibres (cps/eV/KeV).

sample to prevent charging of surface and uniform emission of secondary electrons.

## **3.5. Thermal Analysis**

The composition and quantitative content of the unfunctionalized and the functionalized carbon nanofibres were determined by thermogravimetric analysis and the derivative thermal gravimetric. The decomposition pattern of carbon nanofibres and functionalized derives revealed important differences **Figure 8** & **Figure 9**. Thermogravimetric analysis of carbon nanofibres showed three stages, the



Figure 8. Decomposition pattern of unfunctionalized carbon nanofibres.



Figure 9. Decomposition pattern of Acetyl functionalized carbon nanofibres.

first part of the curve with a temperature up to 280°C showed a stable compound with very minimal loss in weight as the temperature increased. From 280°C onwards there was a steady loss in weight as the temperature increased towards 700°C, this could represent the decomposition and amorphous carbon, and the gradual breakdown of the backbone of the carbon nanofiber. The TG derivative of carbon nanofibres has several peaks between 280°C and 700°C showing that several exothermic processes are taking place as the temperature increases this linked with the decomposition and breakdown of the CNF backbone theory. Generally, the loss in weight was less than 5% showing a very stable nanofiber. This can be attributed to the structure of the polymethyl methacrylate which is also thermally stable. Decomposition temperature above 600°C was characteristic of crystalline graphitic carbon.

The functionalized carbon nanofibres had almost the same TGA curve as the unfunctionalized ones, however, they had a sharp decrease in weight loss of weight of about 1% most likely related to the release of moisture/water molecules that were in the structures of the functionalized CNF. The functionalized carbon nanofibers had two distinct peaks, one just before 100°C and another one beyond 600°C. The weight remained constant between 100°C and 540°C then gradually decreased by an average of 4% as the temperature increased towards 800°C, only two peaks were observed on the derivative of the thermograph, just before the 100°C temperature mark associated with the loss of water and at 524°C probably due to the breakdown of the backbone and or functionalized moieties, its noted that other small peaks probably associated with the burning of amorphous carbon are absent due to the cleaning and drying process of the functionalized Carbon nanofibres. Decomposition beyond 600°C is associated with an increase in adhesion of the CNF groups indicating that the functionalized derivative has higher thermal stability compared to unfunctionalized nanofiber. The changes observed provided additional evidence of successful functionalization of the carbon nanofibres.

## 4. Conclusion

Electro-spinning of carbon nanofibres from various sources has been widely reported. Herein, through optimization of various factors, we were able to electrospin and calcinate carbon nanofibres from PMMA. Functionalization of carbon nanofibres through the introduction of butyl, acetyl and dodecyl moieties was achieved in the presence of metallic lithium, this had only been reported with the carbon nanotubes. The functionalized carbon nanofibers had an increased solubility in selected organic solvents and had higher thermal strength, with distorted surface characteristics that could increase their adherence during the fabrication of nanocomposites for different applications. This work contributes to the increasing body of knowledge showing that alkylation may be used to functionalize carbon nanofibres. Functionalized nanofibres that have unique chemical and physical properties can subsequently be used in the synthesis of novel nanocomposites that have a wide range of applications.

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## **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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