Digest Journal of Nanomaterials and Biostructures Vol. 14, No. 2, April - June 2019, p. 419 - 425

INVESTIGATION ON THE THERMAL DECOMPOSITION AND THE MORPHOLOGICAL PROPERTIES OF CRYOGENICALLY TREATED MWCNTs

N. MANIKANDAN[a*], C. SABARINATHAN[b]
[a*]*Department of Mechanical Engineering, P.A. College of Engineering and Technology, Pollachi, Tamilnadu, India- 642002*
[b] *Department of Mechanical Engineering ,Hindusthan College of Engineering and Technology, Coimbatore, Tamilnadu, India - 641032*

Carbon nanotubes being a major vital role player in nanocomposites, due to their versatility and ability to improve and enhance the properties of the matrix which is used in the composite, it is necessary to study the properties and the changes of the morphology in the carbon nanotubes with respect to different working conditions. Since nano composites were widely used in aerospace applications, where the thermal cycles are very extreme. So, it is necessary to study the change in morphology and properties of the carbon nanotubes after introduction in these extremities. This research on carbon nanotubes involves the cryogenic treatment of carbon nanotubes at 77K (Cryogenic Temperature) followed by the study of the morphology by Field emission Scanning electron microscopy, thermal decomposition by DSC/TGA till the temperature of 550°C and analyzing the XRD results and comparing the results with that of untreated carbon nanotubes.

(Received November 20, 2018; Accepted May 22, 2019)

Keywords: Carbon nanotubes, Cryogenic treatment, Field emission scanning electron microscope, DSC/TGA

1. Introduction

Carbon nanotubes being synthesized accidentally by SumioIijimaat his laboratory instead of synthesizing fullerenes in Japan, it has been widely used for different purposes and it is found to enhance properties in almost all the applications. And this wide range of application led to the research on carbon nanotubes and its application in various fields. One such evident application is the use of CNT nanocomposites in aerospace applications due to their light weight and enhanced properties. The temperature cycles out in space are very extreme and hence the nano composite would experience thermal fatigue and may end in failure and thus it becomes necessary to study the impact on the morphology and properties of carbon nanotubes after deep cryogenic treatment (i.e., below77K).

The budding requirements of the aerospace applications demand the implementation of innovative and effective methods of treatment of materials to enhance of the properties. The aerospace components are prominently manufactured using composite materials. The immense mechanical, thermal and electrical properties of the Carbon nanotubes had made it an evident candidate in the nano composite fabrication. The aerospace components mostly are employed in extreme temperatures in the space. So it is necessary to study the influence of the properties of the main reinforcement i.e., Carbon nanotubes by the cryogenic temperatures persisting in space. Cryogenics is a recently developed simple, effective and environmentally friend domain to improve the properties of materials (mostly on metals) by using mainly liquid nitrogen at very low temperatures with materials immersed in it. The primary categorization of Cryogenic treatment includes two main classifications based on the Temperature reached in a cycle as the parameter. They are:

[*] Corresponding author: manipacet@gmail.com

Sub-zero Cryogenic Treatment (SCT): The materials are treated at 193K and brought back to room temperature.
Deep Cryogenic Treatment (DCT): The materials are gradually cooled to 77K and held for many hours and brought down to room temperature.

This research includes the treatment of the carbon nanotube powder by cryogenic methods and studying the transformation in microstructure and other properties in a sequence of tests including Field emission Scanning electron microscopy, differential scanning calorimetry, thermogravimetry and Xray diffraction.

2. Experimental data

2.1. Synthesis and purification

Carbon Nanotubes is produced by the CVD method [1]. This product is suitable as reinforcement filler in base polymers for the fabrication Nano-composites/bio-Nano-composite. It is a black powder in form and has an outer diameter of 60-80 nm which was characterized by SEM and TEM. The length of the carbon nanotubes is 5 micron and purity of the nanotubes is 96%. Metal particles are less than 4% and amorphous carbon is less than 1% and its specific surface area is 330 m^2/g, bulk density is about 0.04 – 0.06 g/cm^3.

The synthesis of CNTs was finished by catalytic disintegration of C_2H_2 utilizing CVD technique. A steady flow rate of nitrogen gas was kept up during heating. A mix of Fe, Ni, and Cr was utilized as catalyst for the synthesis of Carbon Nanotubes [2]. Catalyst preparation method was employed using Liquid phase impregnation. Improved measure of Chromium acetic acid derivation, Nickel Nitrate, and Iron Oxide was dissolved in conc. HCl, and heating was done at 70˚C for 60 minutes. The catalyst substrate was put at the focal point of horizontal quartz tube in the tube furnace. The heater temperature was kept up at 850˚C for 30 minutes in the N_2 flow to actuate the catalyst. The synthesis was done at various increasing temperatures (600-750˚C), keeping the proportion of C_2H_2: N_2 at 1:10 sqcm. After the conclusion of reaction, the flow of C_2H_2 was halted and the reaction temperature was kept up in the reactor for an hour in flowing nitrogen. At that point the reactor was chilled off to the room temperature under a similar flow rate of N_2. The synthesized multi walled carbon nanotubes were heat treated at 400˚C for 1 hr in ambient atmosphere for purification [3].

To purify the produced multi walled carbon nanotubes, and 0.5 g of multi walled carbon nanotubes was placed in a ceramic boat and afterward inserted inside the heater at 450˚C for two hours to oxidize the amorphous carbon. The MWCNTs were then plunged in 250 ml acidic solution and mixed for 1 hour at 90˚C. The MWCNTs was then expelled from acidic solution utilizing a rotator. The rest of the MWCNTs were washed with deionized water and after that centrifuged for an additional 10 minute at 3000 rpm. This procedure was rehashed 3-4 times until the point that the pH of the arrangement moves toward becoming 7. The MWCNTs were then dried in an oven at 90˚C for 2 hr [4, 5].

2.2. Cryogenic treatment and characterization

By using the cryogenic treatment equipment, the air tight packed MWCNT sample was placed in the cryo box of the cryogenic treatment equipment and then the box is closed and the liquid nitrogen is passed from the external storage through the inlet tube to the cryo box [6, 7]. The temperature of the cryo box is maintained by the electronic temperature controller which operates a solenoid valve to obtain the required temperature by regulating the liquid nitrogen supply. The fan in the cryobox rotates by using an external motor to circulate the liquid nitrogen evenly to maintain uniform temperature inside the box, later the gas gets out through the outlet tube. The Schematic illustration of cryogenic treatment as show in fig.1.

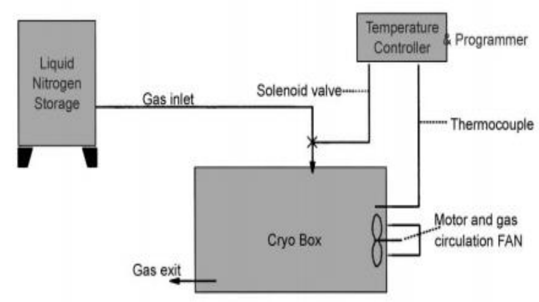


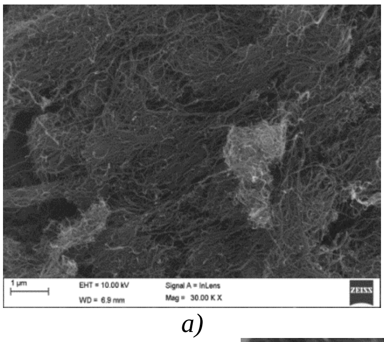
Fig. 1 Schematic illustration of the process of cryogenic treatment

2.3. Field emission scanning electron microscopy

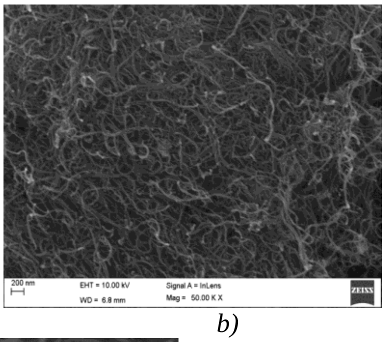
The morphological analysis of the cryogenically untreated (Fig.2 (a-c)) and cryogenically treated (Fig. 3(a-c)) carbon nanotubes were studied by Field emission scanning electron microscopy. The powder sample was prepared for FESEM by passing a calculated current which causes an arc and eventually making the carbon nanotube powder to get coated.

The process of imaging was carried out with Zeiss sigma FESEM with Schottky Field Emission (FE) source and GEMINI electron optical column. The imaging conditions that were followed are working distance (WD) = 6.8m, current of 80µA with a standard aperture size of 30µm and the imaging was obtained on an on-screen Polaroid display at various magnifications with an in-lens detector at 10kV.

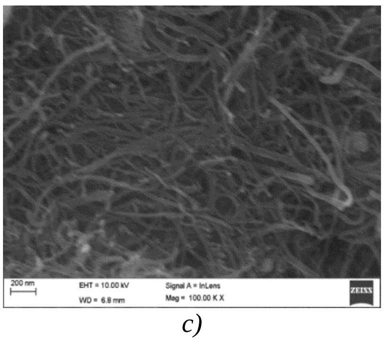
The image result analysis showed that the number of particles per unit area has increased thus resulting in close arrangement of the carbon Nanotubes structures in the FESEM study [8, 13]. This closer and fine distribution of the particles shows significant improvement in perimeter of the carbon Nanotubes and also the easy tendency of carbon Nanotubes to form agglomerates due to the Vanderwaal'sforces [8, 9] in the carbon atoms is prevented. This prevents the entanglement and agglomeration of the Nanotubes and thus helping it to disperse finely in the polymer matrix [10, 11]. This distinct characterized carbon Nanotubes has more surface area exposed and bonds better with the polymer matrix i.e., the bonding area of the polymer matrix and the carbon Nanotubes increases [12].



a)

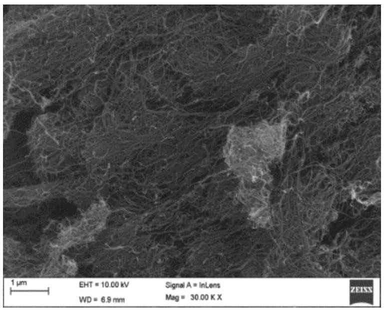


b)

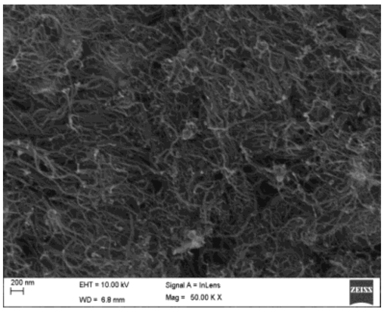


c)

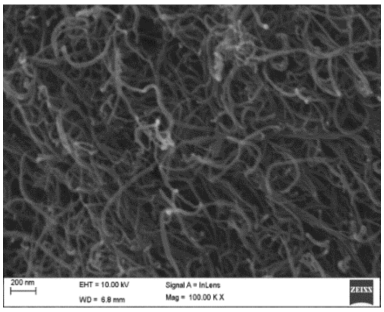
Fig. 2 SEM Image of cryogenic untreated MWCNTs with various magnification factor (a) 30KX, (b) 50KX, (c) 100KX



a)



b)



c)

Fig. 3 SEM Image of cryogenic treated MWCNTs with various magnification factor (a) 30KX, (b) 50KX, (c) 100KX

2.4. Differential scanning calorimetry and thermogravimetry

The thermal decomposition of MWCNTs was studied by the Differential scanning calorimeter (DSC) and Thermogravimetry (TGA) Principles. NETZCH Germany & STA 449 F3 Jupiter was used to analyze the measurement of mass changes and the thermal effects for the temperatures ranging from the room temperature to 550°C.The standards that were maintained are DIN 51006, ASTM D3418 and ASTM E793. The temperature was raised in the order of 30°C/10 min (K/min).

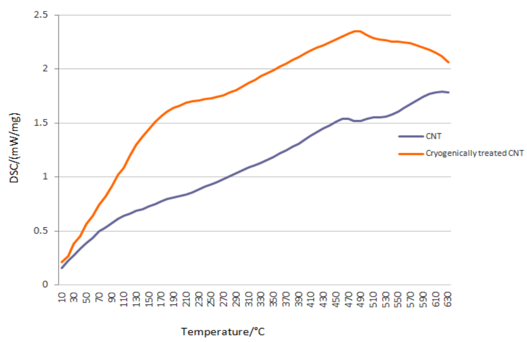


Fig 4 Thermogravimetric behavior of cryogenic treated and untreated MWCNTs for heat absorption

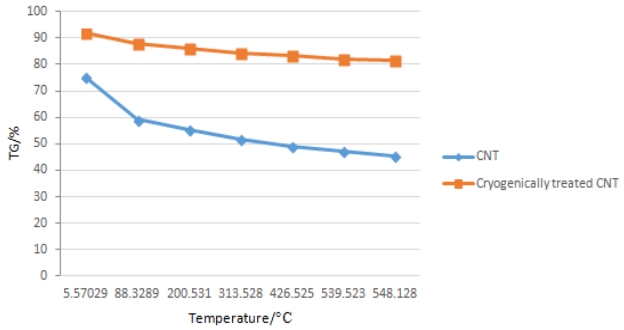


Fig 5 Thermogravimetric behavior of cryogenic treated and untreated MWCNTs for residual mass

The sample is placed on a constant base with a chromel wafer underneath it in an inert N_2 atmosphere. The Chromel-Alumel thermocouple is used to measure the temperature and the heat is measured by the difference in temperatures across the sample and the reference chromel wafer. The results of DSC can be interpreted as the heat capacity variation of the material with respect to the change in temperature or in other words, it can be used to measure the amount of heat absorbed with respect to the temperature applied. The test results were studied and the comparison with the untreated MWCNTs and the cryogenically treated MWCNTs revealed that the thermal heat absorption of the cryogenically treated sample was found to be higher than that of the ordinary MWCNTs [14].

The cryogenically treated sample showed an average of 61.17% increased heat absorption than the untreated sample. The maximum value of heat absorption occurred at 200°C with 102.29% increased heat absorption than that of the untreated sample and the minimum value was at 630°C with 15.63% increase in heat absorption that the untreated sample.

In thermogravimetric analysis, the Phase transition, absorption, desorption, thermal decompositions, oxidation and reduction can be studied. The testing setup includes an apparatus to measure the mass change with respect to the temperature change in an inert (N_2) atmosphere.

In detail this test results can be used to determine which specimen of carbon nanotubes has slow decomposition with temperature. The figure 5 shows that the untreated carbon nanotube sample showed a decomposition of the sample with a residual mass of 87.04% and the cryogenically treated sample with a residual mass of 95.05%. These results show that the untreated pure MWCNTs are not thermally stable as the cryogenically treated MWCNTs. The untreated sample had 12.96% of its sample decomposed and the cryogenically treated sample had only 4.95% of its mass decomposed at a Temperature of 548.12°C. Thus, the results infer that the cryogenic treatment enhances the thermal stability of the sample [14, 15].

2.5. XRD

XRD is one of the popular methods to determine the phase analysis and orientation of a crystalline material without doing any harm to the specimen. Xray Diffraction are designed for obtaining the ultimate quality diffraction data, combined with ease of use and flexibility to quickly switch to different applications[16]. The machine used for testing is X'Pert Powder provided by PANALYTICAL, MWCNT powder of 10 mg and cryogenically treated MWCNT of 10 mg was tested with x ray diffraction. The test results suggest formation of Bragg peak (002) was appeared for cryogenically treated as well as untreated multi walled carbon nanotubes at 25.8170 Å and 25.8037 Å. This difference might be due to the impurities between tubular layers of both samples, which have a d- spacing of 3.45101nm and 3.45276nm respectively[17].

The peak (100) appeared at 2θ= 30.3916and 30.3879 for cryogenically treated MWCNTs and untreated MWCNTs, this variation is due to the presence of impurities and debris which also can increase the roughness on the surface of carbon nanotubes lattice structure. From the figure 6 and 7 shows the intensities at plane (100) are 10.37 and 10.19[18],this shows that cryogenically treated MWCNT has good crystallinity than the untreated MWCNT which is due the elimination of Copper Gallium Selenide Telluride and Zinc Antimony that has a crystalline structure Monoclinic and Anorthic[18].

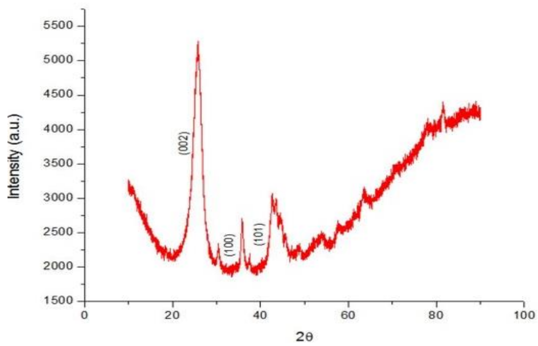


Fig. 6. XRD pattern of untreated MWCNTs

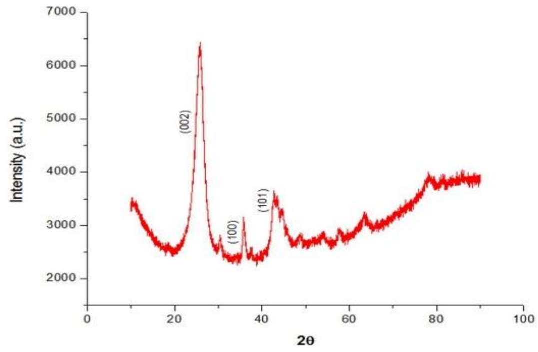


Fig. 7. XRD pattern of cryogenically treated MWCNTs

3. Results and discussion

The above study on the cryogenically treated MWCNTs showed an immense leap in the thermal properties and phase transition. The increase in the amount of heat absorbed by the sample which was studied in Differential scanning calorimetry and the phase transition resistance at higher temperatures has increased. This increase in energy absorption up to 102.29% than the untreated sample can be due to the finer arrangement of the MWCNTs per unit area which was characterized by the FESEM analysis. The improvement in perimeter of MWCNTs also contributes to the increased heat absorption by the sample. This increased amount of heat absorption increases the threshold temperature of the sample. Thus, the phase transition of cryogenically treated sample at higher temperatures is extremely low (4.95%) when compared with the untreated MWCNT sample (12.96%).

4. Conclusion

The above research on the cryogenic treatment of carbon nanotubes has revealed that the amount of heat absorption per sample has increased drastically corresponding to decreased decomposition or phase transition of the carbon nanotube sample which evidently encouraged the usage of MWCNT nanocomposites in aerospace applications and also where the thermal cycles are extreme.

References

[1] K. Takeuchi, T. Hayashi, Y. A. Kim, K. Fujisawa, M. Endo, The state-of-the-art science and applications of carbon nanotubes **5**(1), 15 (2014)

[2] KalpanaAwasthi, AnchalSrivastava, O. N. Srivastava, Journal of Nanoscience and Nanotechnology **5**(10), 1616 (2005).

[3] NobuhitoInami, MohdAmbri Mohamed,EijiShikoh, Akihiko Fujiwara, Sci. Technol. Adv. Mater.**8**(4): 292 (2007),Bibcode:2007STAdM.8.292I. doi:10.1016/j.stam.2007.volume g number 4.

[4] M. Kumar, MJournal of Nanoscience and Nanotechnology**10**(6), 3739 (2010).

[5] Jianwei Liu, Mingwang Shao, Xiangying Chen, WeichaoYu, Xianming Liu, Yitai Qian, J. Am. Chem. Soc. **125**(27), 8088 (2003), DOI: 10.1021/ja035763b

[6] Jiao-Ping Yang, Zhen-Kun Chen, Qing-Ping Feng, Yin-Hu Deng, Yu Liu, Qing-Qing Ni, Shao-Yun Fu, Cryogenic mechanical behaviors of carbon nanotube reinforced composites based on modified epoxy by poly(ethersulfone) **43**(1), 22 (2011).

[7] Yiqin Shao, Fujun Xu, Wei Liu, Mengjie Zhou, Wei Li, David Hui, YipingQiu, JCOMB 5100**125**, 195 (2017).

[8] Myung-GonKim, Jin-Bum Moon, Chun-Gon Kim, Effect of CNT functionalization on crack resistance of a carbon/epoxy compositeat a cryogenic temperature**43**(9), 1620 (2012).

[9] Zhen-Kun Chen, Jiao-Ping Yang, Qing-Qing Ni, Shao-Yun Fu, Yong-Gang Huang, Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties **50**(19), 4753 (2009).

[10] Qing-Ping Feng, Yin-Hu Deng, Hong-Mei Xiao, Yu Liu, Cheng-Bing Qu, Yang Zhao, Shao-Yun Fu, Enhanced cryogenic interfacial normal bond property between carbon fibers and epoxy matrix by carbon nanotubes**104**, 59 (2014)

[11] Jiangtao Hu, Min Ouyang, Peidong Yang, Charles M. Lieber, Nature **399**, 48 (1999), doi:10.1038/19941.

[12] A.Esawia, K.Morsib. Dispersion of carbon nanotubes (CNTs) in aluminum powder **38**(2), 646 007)

[13] K.C.Hoa, Y.H.Teowab, A.W.Mohammadab, W.L.Angab, P.H.Leec. Development of graphene oxide (GO)/multi-walled carbon nanotubes (MWCNTs) nanocomposite conductive membranes for electrically enhanced fouling mitigation **552**, 189 (2018), https://doi.org/10.1016/j.carbon.2008.02.01

[14] B. Schartel, U. Braun, U. Knoll, M. Bartholmai, H. Goering, D. Neubert, P. Pötschke. Mechanical, thermal, and fire behavior of bisphenol a polycarbonate/multiwall carbon nanotube nanocomposites **48**(1), 149 (2008).

[15] M. Geoffrey, SpinksaSu, RyonShinb, G. Gordon, WallaceaPhilip, G.Whittena I. Sun, KimbSeon,JeongKimb, Mechanical properties of chitosan/CNT microfibers obtained with improved dispersion **115**(2), 678 (2006), https://doi.org/10.1016/j.snb.2005.10.047.

[16] PeterR.Changa,PengwuZhengb,BaoxiangLiuc, DebbieP.Andersoa,JiugaoYuc, XiaofeiMac, Characterization of magnetic soluble starch-functionalized carbon nanotubes and its application for the adsorption of the dyes **186**(2–3), 2144 (2011), https://doi.org/10.1016/j.jhazmat.2010.12.119.

[17] Liming Zhou, Shaoming Fang, Jiayou Tang, LijunGao, Junya Yang, Polymer composites Pg.1866-1873,DOI 10.1002/pc.22305.

[18] Byeong-Joo Kim, Biplab K. Deka,Il-Joon Bae, Dong-Hyuk Choi, Dong-Il Son, Young-Bin Park, Polymer composites.Pg.1-7, DOI 10.1002/pc.24835.

[19] E.Y.Malikov, M.B.Muradov, O.H.Akperov, G.M.Eyvazova, R.Puskás, D.Madarász, L. Nagy, Á.Kukovecz, Z.Kónya, Synthesis and characterization of polyvinyl alcohol based multiwalled carbon nanotubes nanocomposites.