REINFORCEMENT OF COMPOSITE MATERIALS USING ARCHITURED CARBON NANOTUBES – CARBON FIBERS.

Fabrice LAURENT, Hanae OULANTI, Thang LEHUU, Gildas L'HOSTIS, Basma HASIAOUI, Bernard DURAND[1]

Laboratory of Physics and Mechanic Textiles (LPMT), University of Haute Alsace, 11 rue Alfred Werner, 68093 Mulhouse Cedex, France
Email: fabrice.laurent@uha.fr, Web Page: http://www.uha.fr

Keywords: Multi Walled Carbon Nanotubes, flame method, architectured fibers, composite materials, mechanical and electrical properties.

Abstract
In this paper, we present carbon nanotube (CNT) growth, using an oxyacetylene flame method, on carbon fibers, a method developed in the laboratory. The goal of this development is the "scaling-up" of the process in order to bring new properties to the reinforcements and the composite materials. After studying and tuning all the process parameters, we operated growth of CNTs on commercial carbon fiber tapes (CF). Microscopic examinations at different scales are presented. The CNT structures differ considerably according to the localization of the tape: straight and hollow in the middle, and compartmentalized on the edges. The composite materials were hand lay-up molded. TGA measurements showed that the CNT and CF volume fractions were 46 % for the reference and 39 % for CF-CNT specimens. Mechanical tests highlighted a significant improvement in tensile and bending moduli and contrasted results in strength and elongation at breaks. The electrical longitudinal conductivity of the composite specimens was multiplied by 4 to 8. A few hypotheses have been proposed in the conclusion.

1. Introduction

Since the discovery of fullerenes by Kroto, Curl and Smalley in 1985 [1], research into carbon nanostructures has continued to increase. The first carbon nanotubes (CNT), synthesized by electrical arc discharge method, were highlighted by Ijima [2,3]. Since then, a large number of CNT production processes have been developed, in particular those permitting growth by chemical vapor deposition (CVD). This well researched method allows production of multi-walled nanotubes (MWCNTs) or single-walled nanotubes (SWCNT) according to the operating conditions. Dresselhauss et al. [4], and Dai. [5] provide a comprehensive description of the means of production and the CNTs formed. The structure and quality of CNTs depend on growth conditions (temperature, gas flow, gas type, nature of the substrate, surface area of the substrate, type of catalyst, catalyst particle size, and presence of a carrier gas). Naturally, several teams had the idea of growing CNTs on carbon fibers, alumina and glass by CVD. The number of publications on the subject has increased significantly over the past ten years. Several names characterize this material: Fuzzy fiber, Hierarchical structures, NTC infusion, Grafting.

This research presents a potential response to the "massive" mix of CNTs in resin in order to obtain composite materials with high mechanical and electrical performances. The principle is to grow CNT directly on the fibers to prevent their agglomeration and significantly improve the properties of the composites made from these fibers [6-8]. The growth conditions are very similar to those described above. Many patents describing a continuous process CNT growth on S2 glass and carbon fibers were deposited by the company Applied Nanostructures Solutions between 2010 and today [9-11]. CNT growth takes place at atmospheric pressure and at temperatures of between 550 and 800 ° C. The predicted growth rate is of the order of one second, thereby treating fibers at speeds of 0.1 m / min to 10 m / min. According to the catalysts and precursors used, CNTs are dense and long at low speed and rather short and sparsely distributed on fibers at maximum speed. Storck et al. [12] reported a significant improvement in mechanical properties, and in particular the interlaminar shear properties of composites reinforced with glass fibers or carbon fibers infused CNT. The energy release rate measured (G_{IC}) is

Excerpt from ISBN 978-3-00-053387-7

twice as high for composites infused CNT composite fibers that for reference composite. The highest values are obtained when CNTs are very dense and very long.

Another CNT growth technique on fibers is to use a flame as a growth initiator [13-17]. This flame acts as the vector of the precursor gas, combustion of which ensures temperature elevation. This process with high potential due to the ease of manufacturing and growing CNTs on glass or carbon fibers has been far less studied than the CVD method.

These works have given priority to process development and to understanding growth mechanisms. This is very complex, which is why we chose a complete raw material characterization rather than a fine characterization of the composite material which is still at its beginning.

2. Experimentations

The device we developed in the laboratory has 4 main parts: The gas supply, the burner, the support, and the process control. It is presented in Figure 1.

- A mobile table, made of copper, in all three spatial directions, cooled by water-glycol mixture maintained at 18°C.
- A burner generating the flame (commercial oxyacetylene burner with a 0.8 mm orifice).
- A deflector more or less inside the flame in order to regulate the exposition (exposure ?) temperature of the carbon fibers.
- A pyrometer (Raytek) focused on the flame measuring temperature.
- Two mass flow MKS Instruments (0-10 l/min) equipped with their control box.
- K-type thermocouples emerging at the surface of the plate and in the center of the flame.
- A National Instrument data acquisition system (Labview and acquisition cards associated).

The detailed operation of the system is described in a paper we published in 2015 [18] and in the patent protecting the principle [19]. The strength of our process is linked to the fact that CNT growth takes place in ambient environment without any neutral gas or particular atmosphere surrounding the flame and also continuously.

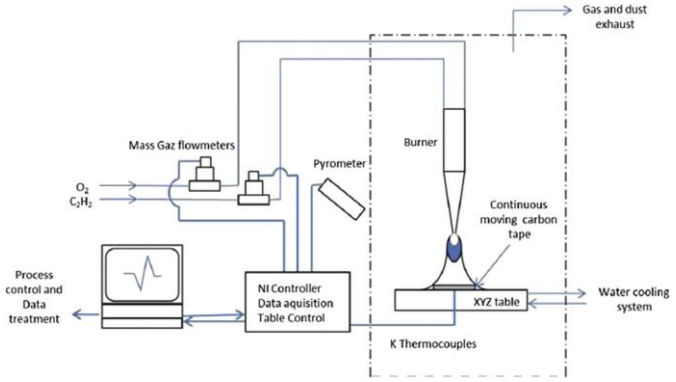

Figure 1: Device for the growing process flame method.

The catalyst used for these experiments was a mixture of ferrocene (Iron dicyclopentadienyl $Fe(C_5H_5)_2$) concentrated at 0.15mol/l in ethanol deposited by pulverization. Unidirectional carbon fiber tape HTA 40 E 13 6k (Toho Tenax), 295 g/m^2, 10 mm wide, 7 threads linked together with a fine glass frame of 28g/m² were utilized as growth support and reinforcements. The microscopic examination was conducted on a Scanning Electron Microscope (High resolution SEM XL30 FEG XL Series Philips). CNT quality was analyzed by Raman spectroscopy (Jobin Yvon Type Labram). The Transmission Electronic Microscopy used for CNT structure analyses is a Jeol JEM-ARM200F Cold FEG, allowing examination of samples at atomic scale. For this examination, the CNTs were extracted by sonication in ether for 1h. A droplet filled with CNTs was deposited on the grid for analysis purposes. Raman spectra were recorded using an argon ion laser Raman microprobe. The analyses were conducted on 6 different areas of the tapes. Excitation laser wavelength is 632.8 nm with a laser power of 1 mW. The instrument

Excerpt from ISBN 978-3-00-053387-7

was operated in the multichannel mode with the beam focused on a spot diameter of approximately 1 mm. The samples were scanned between 250 and 3800 cm^{-1}. The mechanical tests were carried out on a test machine Instron 5985L 250 kN, class 0.5, where each specimen was equipped with an extensometer determining elongation. Tensile and flexural tests were carried out according to NF EN ISO 527-5 and NF EN ISO 14 125. Tensile tests were conducted on a composite material made of 4 layers, and the bending test on a composite material made of 2 layers. Epoxy and hardener Epolam 2020 were used as matrix for composite moldings. Typical thermal curing was undertaken, as recommended by the supplier. The composite samples were hand lay-up and pressed in an aluminum mold, demolded then machined allowing molding of type A samples for tensile tests. The composite samples were machined and finished manually on the edges by sanding. The fiber volume fraction (V_f) and the NTC volume fraction (V_{NTC}) of the composites were calculated after ThermoGravimetric Analyses (TGA) according to the standard NF T 46 047 commonly used for carbon black analyses. Electrical tests were conducted on Keithley multimeter.

3. Results and discussions

3.1 CNT characterization.

Before processing, the tapes (see Figure 2a) were coated with a layer of ferrocene with a thickness of 1 µm by air pulverization before being dried at room temperature, evaporating the liquid vector (ethanol). The process conditions for CNT growth depend mainly on 4 parameters which are described in our previous publications [17, 18]. Briefly, promoting CNT growth without degradation of the carbon fibers requires control of i) the area in which the tape is inserted in the flame (h=8.1 mm distance from the extremity of the torch and the exposed surface of the tape), ii) the flows and ratio between acetylene and oxygen (Q = 0.9 l/min and R = 1.54), iii) the flame scanning speed (V = 0.5 m/min), iv) the distance of penetration of the deflector in the flame (d = 6 mm). The extreme temperature of the tapes when scanned by the flame was evaluated by the pyrometer at 800 – 900 °C. In each test, we treated 400 mm length of tape on each face (see Figure 2b).

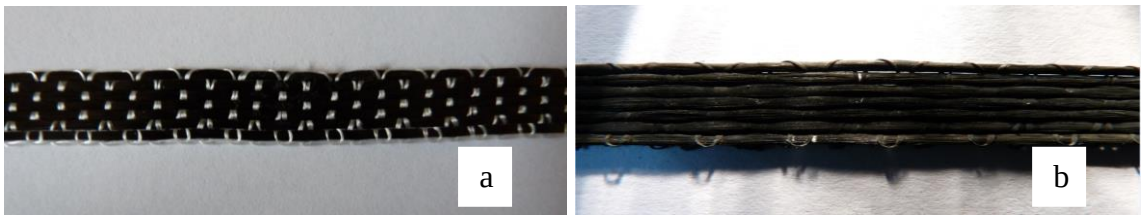

Figure 2 a-b: Carbon tape before and after treatment.

Figures 3 and 4 show very precisely the CNT forest obtained after treating the tapes. Their length is more than 50 µm. At the extremity of a few CNTs we observe small white spots that are representative of catalyst particles after growth.

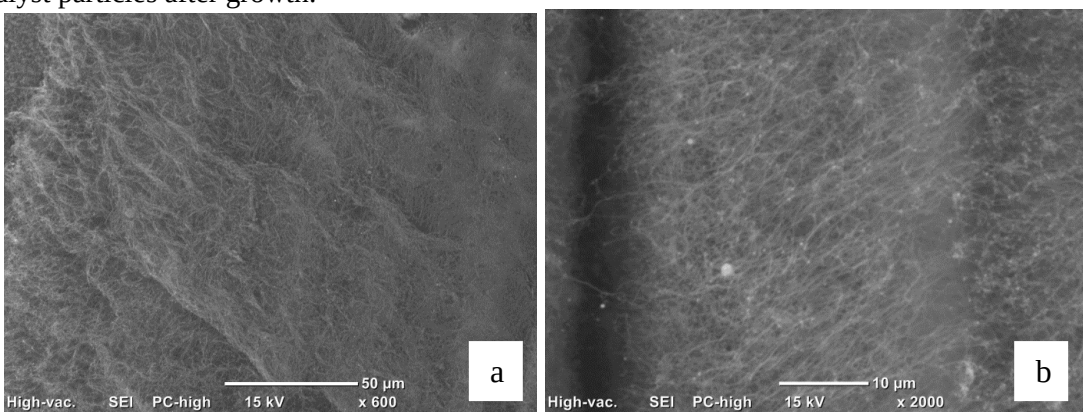

Figure 3 a- b: CNT forest coating the fibers whose presence we guess under the CF layer.

Excerpt from ISBN 978-3-00-053387-7

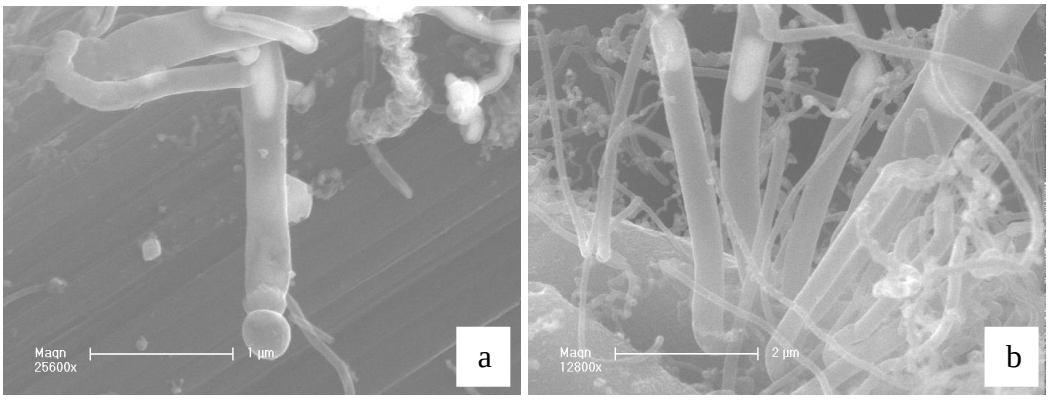

Figure 4 a-b: HR SEM examination of CNTs.

HR SEM examinations allow identification of at least two families of CNTs; Straight and hollow CNTs where we distinguish metallic particles by transparency inside the tube (white spots on Figures 2a and b) and CNTs that are thinner and tortuous where the particles are situated at the extremity of the CNTs (Figure 2 b). This reveals two growth mechanisms. While both are based on "tip growth", they lead to different CNT structures. The diameters, internal structures and terminations of the tubes were determined using TEM images as shown in Figures 5 a and b.

The TEM images (Figures 5 a and b) reveal two main kinds of MWCNTs:

- a: straight and hollow MWCNTs whose internal diameters vary from 30 to 240 nm with a wall thickness between 12 to 28 nm made up of 34 to 80 carbon layers respectively.
- b: compartmentalized MWCNTs, as presented on the photo, known as "bamboo" like structures. External diameters, 20 to 150 nm, are thinner than the other species. The size of the compartment is evidently proportional to particle size as seen at the extremity of the tube presented. Assumptions of "bamboo" like structure growth mechanisms were reported by Yuan and al. and Wang and al. [20, 21].

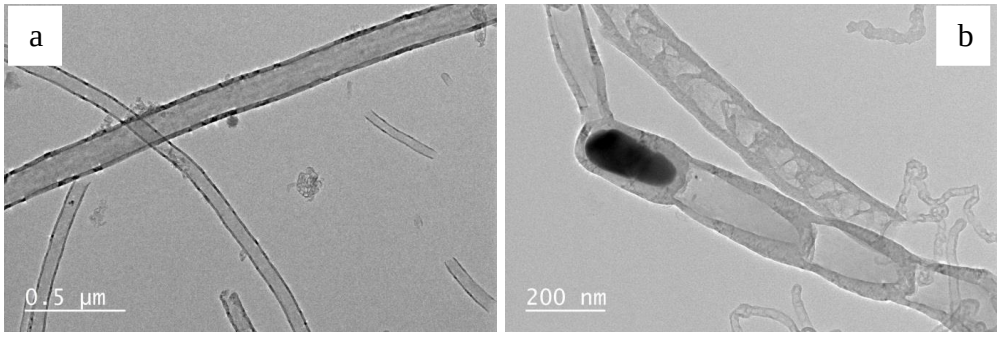

Figure 5 a-b: MWCNTs examined by TEM.

CNT crystallinity was determined using Raman spectrometry. Six different areas of a piece of tape, rich in CNTs, were scanned between 250 cm^{-1} and 3800 cm^{-1} for 180 s. The analysis focused on two peaks appearing at roughly 1350 (Band D) and 1580 cm^{-1} (band G). The D band is representative of the degree of disorder present in the carbon structure, while the G band is characteristic of the vibrations in the plane of an ideal sp^2 connection. The means and standard deviations are expressed in Table I. Overall CNTs obtained are of quite average quality with many defects. Nevertheless, this quality is in the high part of the mean observed for most MWCNTs. The table I shows also the synthesis of the CNT characterizations carried out in the framework of this research.

Excerpt from ISBN 978-3-00-053387-7

Catalyst	CNT density	CNT quality	Particle diameter in nm	Termination	I_D/I_G	Growth mode
Ferrocene	High	Straight and Bamboo	50 - 300	Encapsulated particles	0.66	Tip growth

Table I: Synthesis of characterizations of MWCNTs

3.2 Characterization of the composite material

The tests were carried out on two kinds of samples:

- Composite reference (tapes molded as shown in Figure 2a)
- Composite reinforced with carbon fiber treated CNTs.

To compare the mechanical performances of the composites, we needed to determine the fiber and CNT volume fractions. These values are presented in Table II below. A constant observation was carried out after TGA tests, and showed that the fiber volume fraction of the composite reference was always greater than the composite treated. Taking into account that the samples were molded in the same mold and had the same thickness, we concluded that this phenomenon could be accounted for by degradation and volatilization of superficial fibers scanned by the flame, generating a 10 % loss of fiber volume fraction. Microscopy examinations revealed a porosity level that is quite the same for both kinds of composites, close to 5 % in accordance with the classical values obtained for hand lay-up processing.

Specimen	Resin % w/w	% NTC	Fiber weight fraction	Fiber volume fraction
Ref 4 layers (tensile)	38.6%	0%	57.7%	**46.2%**
Ref 4 layers (tensile)	46.4%	2.20%	47.9%	**36.6%**
CF-NTC 2 layers (bending)	45 %	0 %	52,3 %	**42 %**
CF-NTC 2 layers (bending)	52 %	2,2 %	42.3 %	**33 %**

Table II: Weight and volume fractions of resins, fibers and CNTs.

It should be noted that the architectured CF-CNT reinforcements were directly molded without any subsequent cleaning or sizing. All the mechanical results are presented in Table III.

Properties	Tensile tests		Variation	Flexural test		Variation
	Reference	CF – CNTs		Reference	CF - CNTs	
Thickness h mm	1.5 ±0.14	1.38 ±0.04	-8%	0.74 ±0.05	0.74 ±0.05	
Width b mm	10.1 ±0.11	9.8 ±0.36		10.1 ±0.1	10.1 ±0.1	
Strength at break σ MPa	1 692 ±136	1 282 ±82	-24%	1 208 ±97	1355 ±91	+12%
Young Modulus E MPa	110 800 ± 6 794	120 675 ±7 101	+ 9%	80 420 ±4 001	93 175 ±2 769	+16%
Elongation at break ε %	1.50 ±0.14	1.05 ±0.03	- 30%	1.6 ±0.13	1.6 ±0.15	

Table III: Synthesis of mechanical properties on composite materials.

From these results we can advance many findings:

- A significant improvement of the Young moduli in tension and bending is provided by CNT treatment,
- Contrasting results for strength and elongation at break for tensile and flexural tests, a substantial

Excerpt from ISBN 978-3-00-053387-7

decrease in these properties recorded during the tensile tests and a consequent increase inbending,
- The failure mode of tensile specimens was quite different between reference and CF-CNT composites. The reference broke distinctly in tension, characterized by a transversal failure of the fibers, while the CF-CNTs broke according to a "longitudinal splitting", marking a lack of cohesion between fibers and resin.
- The CF-CNT specimens contain 10% fewer reinforcement volume fractions

We could explain these tendencies as follows. Most importantly, the stress mode is quite different, as the tension mode stresses the fibers only in the direction of the strength, while the flexural mode stresses the material in compression, tension and interlaminar shear when the L/h ratio is short. To reduce shear strength inside the specimen, the L/h ratio was taken superior to 40. All failures occurred visibly in tension during flexural tests due to breakage of the tautest layer. The difference in strength at break and moduli between bending and tensile tests could be due to the fiber volume fractions which were lower for 2 layers composites (see table II).

Figures 7 a-b show a fractographic MEB examination after CF-CNT specimen bending failure. They highlight on the one hand a debonding between CNTs and fibers (fig. 6a) and on the other hand good wettability of the CNTs by the resin. CNT orientation is markedly oriented in the fiber directions, probably following resin impregnation during the hand lay-up process.

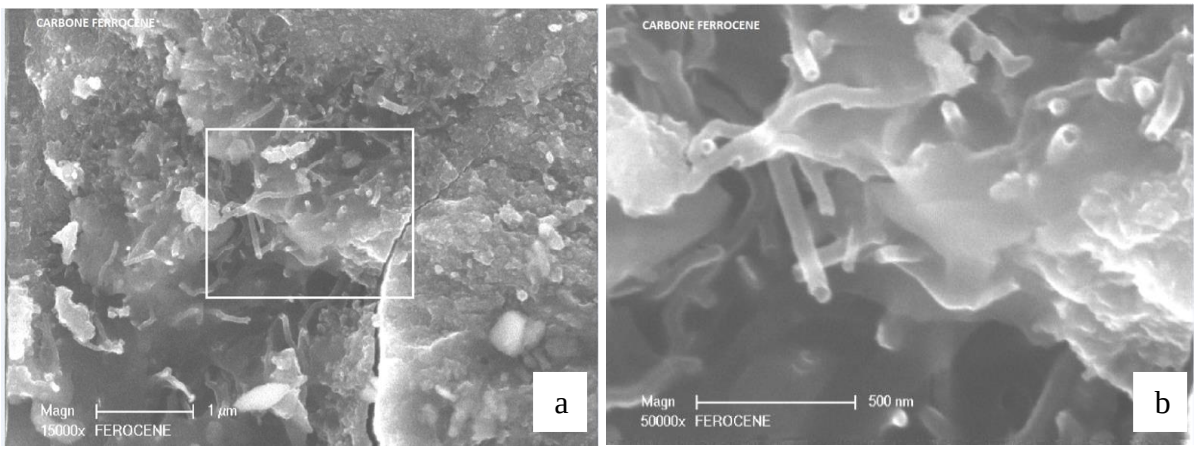

Figure 6 a-b: Details showing architectured CF-CNT composite materials.

Both measured tensile and flexural moduli increased when the fibers were treated with CNTs, revealing the positive effect of CNTs. This effect was checked using the theoretical classical mechanics of composite materials. However, it is evident that compatibility between fibers, CNTs and epoxy resin must be improved. Some tests using specific CNT sizing agents were carried out, involving a marked increase in Young modulus but not improving strength at break, even in presence of sizing. The "longitudinal splitting" mode was confirmed in any case. Undoubtedly, the choice of an efficient sizing product and process remains a challenge for global improvement of mechanical properties.

Concerning electrical properties, only longitudinal conductivity tests were carried out on composite specimens 10 mm wide, 0.74 mm thick and 110 mm long. Their extremities were very lightly sanded in order to reveal fibers and CNTs at the surface and obtain an electric contact for measurements. To improve this contact, a silver resin was applied on the sanded surface. The values are summarized in Table IV.

Excerpt from ISBN 978-3-00-053387-7

Composite specimen	Electrical resistivity in Ω	Variation %
Carbon reference	27.5	
CF-CNTs	7.4	-73.1%

Table IV: Electrical resistance of composite materials

We thus observed an improvement in electrical conductivity of 73 % which is considerable without optimization. Among the numerous tests we conducted, a maximum decrease of 8 in resistivity was measured.

4 Conclusions

In these works we have demonstrated the ability to produce CNTs on carbon fiber tapes using a simple oxyacetylene flame method. The analyses showed that CNT quality is quite good and that two main CNT species grew: straight and hollow and bamboo-like, for the other. The former exhibits the best mechanical and electrical properties. Two kinds of termination were also found. These structures seem very dependent on the flame. The best quality was observed in the center of the tape, the warmest zone, while the otheron the edges of the tapes, the coldest zone. The composite specimens were molded without any difficulties, as the composite seemed to be properly manufactured. However, the TGA analyses showed that flame scanning is probably damaging for the exposed fibers. Effectively, the treated tape fiber volume fraction is always 10% less than the reference tape. Despite this deterioration, the mechanical tests carried out showed a significant improvement in bending strength and moduli. The effect of CNTs was less marked in tensile strength, probably due to lack of sizing, compatibilizer between epoxy resin and CNTs and fibers leading to undesirable failures. Electrical conductivity was also improved, multiplying this property by 4 to 8 when fibers were treated CNTs.
Future works will consist in improving deposition and increasing CNT quantity on fibers, for example by separating and flattening the strand before flame scanning. Unfortunately, we have not yet carried out shear tests due to the fineness of the specimens. These results will be presented in future papers.

Acknowledgments

These works were partially funded by Conectus Alsace in the framework of the “Nanograft” Project.

References

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley C60: buckminsterfullerene, Nature, 318, 162-163, 1985
[2] S. Iijima, Helical microtubules of graphitic carbon, 354, 6348, 56-58, 1991
[3] S. Iijima, T. Ichihasi, Single-shell carbon nanotubes of 1-nm diameter, Nature, 363, 603, 1993
[4] M.S. Dresselhaus, G. Dresselhaus, P. Avouris, Carbon Nanotubes, Synthesis, Structure, Properties and Applications, Topics in applied Physics, 80, Springer-Verlag, 2001
[5] H. Dai, Carbon nanotubes: opportunities and challenges, Surface Science, 500, 218-241, 2002
[6] H. Qian, A. Bismarck, E. Greenhalgh, CNT grafted silica fibres : Characterising the interface at the single fibre level, Composites science and technology, 70, 393-399, 2010
[7] H. Qian, A. Bismarck, E. Greenhalgh, CNT grafted carbon fibres : A study of wetting and fibre fragmentation, Composites Part A, 41, 1107-1114, 2010
[8] Q. Zhang, J. Liu, Ryan Sager, L. Dai, J. Baur, Hierarchical composites of carbon nanotubes on carbon fiber: Influence of growth condition on fiber tensile properties, Composites Science and Technology, 69, 594-601, 2009
[9] International Publication Number WO2012 037042A1, B. K. Malet, T. Shah, Glass substrate having caborn nanotubes grown thereon and methods for production thereof, 2010
[10] International Publication Number WO2012 040004, B. K. Malet, T. Shah, Carbon fiber substrates having caborn nanotubes grown thereon and methods for production thereof, 2010
[11] International Publication Number WO2012087526, H. C. Malecki, J. P. Loebach, T. K. Shah, M. R. Alberding, J. K. Braine, J. A. Larue, Apparatus and method for the production of carbon nanotubes on a continuously moving substrate, 2010

Excerpt from ISBN 978-3-00-053387-7

[12] Steven Storck, Harry Malecki, Tushar Shah, Marc Zupan, Improvements in interlaminar strength: A carbon nanotube approach, Composites: Part B 42, 508–1516, 2011
[13] L. Yuan, T. Li, K. Saito Growth mechanism of CNT in methane diffusion flames, carbon, 41, 1889-1896, 2003
[14] M. J. Height, J. B. Howard, J. W. Tester, J. B. Vander Sande, Flame synthesis of single walled carbon nanotubes, Carbon, 42, 2295-2307, 2004

[15] T. C. Liu, Y. Y. Li, Synthesis of carbon nanocapsules and carbon nanotubes by an acetylene flame method, Carbon, 44, 2045-2050, 2006
[16] B. Hall, C. Zhuao, Y. A. Levandis, H. Richter, Influence of the fuel structure on the flame synthesis of carbon nanomaterials, Carbon, 49, 3412-3423, 2011
[17] J.B. Donnet, H. Oulanti, T. Le Huu, Mechanism growth of multiwalled CNT on carbon black, Diamond and related material,17, 1506-1512, 2008
[18] H. Oulanti, F. Laurent, T. LeHuu, B. Durand, J.B. Donnet, Growth of carbon nanotubes on carbon fibers using the combustion flame oxy-acetylene method, Carbon (2015), 95, 261-267.
[19] J.B. Donnet, B. Durand, T. Lehuu, F. Laurent, Method for Preparing an Elongate Material Provided with Grafted Carbon Nanostructures, and Associated Device and Products, 2013. FR1350228, EP2014050406, WO2014108511 A2.
[20] L. Yuan, T. Li, K. Saito, Growth mechanism of CNT in methane diffusion flames, Carbon, 41, 1889-1896, 2003
[21] X. Wang, W. Hu, Y. Liu, C. Long, Y. Xu, S. Zhou, D. Zhu, L. Dai, Bamboo-like carbon nanotubes produced by pyrolysis of iron(II) phthalocyanine, carbon, 39, 1533–1536, 2001

Excerpt from ISBN 978-3-00-053387-7