DEVELOPMENT OF COMPOSITE MATERIALS BASED ON A CARBON NANOTUBES NETWORK FOR SPACE APPLICATIONS

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For few years, carbon nanotubes (CNTs) are added to in various materials. As CNTs have high mechanical, thermal and electrical properties, it is expected to boost by adding CNTs the performances of the matrix material. Usually carbon nanotubes are used as additive to an organic matrix and in small quantities, below 1 wt%. In this work we develop composite materials with high amount of CNT, based on a carbon nanotubes network. The main type of CNT network manufactured and tested is buckypaper obtained by filtration of CNTs dispersed in a liquid solution. Other CNT networks like 3D preformed shape and CNT arrays have been also investigated. The potential improvement brought by adding CNT network to conventional materials has been evaluated using the engineering rules established for composites. Hence, the maximal achievable material properties have been estimated. Using the previously described analysis, the potential of CNT reinforced composite for different space applications have been ranked. The mechanical (mainly for CNT fibre) and thermal driven applications seem the most promising ones, especially if specific properties are considered (due to the low density of CNTs). On the basis of this evaluation and manufacturing technologies available in our consortium, experimental efforts have been put on the optimization of the CNT network mainly for improving its thermal performances. Influence of the CNTs characteristics on the macroscopic buckypaper properties has been evaluated with CNTs of different morphology (MWNT, DWNT), length and functionalization. Several processes for manufacturing the buckypaper have been tried, using different solutions for CNTs dispersion (surfactant, water or ethanol), or applying alternative method like in-situ growth of CNTs on buckypapers. Among different CNT network post-treatment also tried, thermal treatment up to 2800°C has given the greatest improvement on the specific thermal conductivity. Eventually the CNT network is infiltrated by an organic (epoxy) or inorganic (aluminium) matrix to make the composite. 3D shape CNT network gives highly reinforced composite with 30wt% of CNTs. Even if current properties of CNT reinforced composite materials are not yet competitive with reference aerospace materials, improvement potential is large and manufacturing technologies are growing.

I. INTRODUCTION

Carbon nanotubes (CNTs) are new materials, observed for the first time in 1991. Their diameter is few nanometers and their length is usually a few microns (but it can reach several millimeters). Carbon nanotubes are subdivided into several sub-categories according to their morphology, number of walls and chirality. Concerning the number of walls, CNTs are usually categorized as multi-wall (MWNT), single-wall (SWNT) and double-wall (DWNT) carbon nanotubes.

The CNTs have mechanical, thermal and electrical properties orders of magnitude higher than conventional materials. However, their industrial development is impeded by the lack of technologies available to process those tiny tubes into bulk materials. Usually carbon nanotubes are used as an additive to an organic matrix and in small quantities, often less than 1 wt%, to improve matrix performances. While electrical conductivity improvement by this way has now become a successful industrial application, improvement are much weaker concerning mechanical or thermal conductivity[1].

In this work, we develop composite materials with high amount of CNTs, based on a carbon nanotubes network (also designated as CNT skeleton). The project objective is to evaluate the potential of such materials for space applications and then to develop those having the highest potential. The manufacturing strategy is to make first an optimized CNT network and then to infiltrate it with an organic or an inorganic matrix.

II. EVALUATION OF CNTS REINFORCED COMPOSITE IMPACT ON SPACE APPLICATIONS

II.I Predictions of CNT network and composite properties

In a first phase, we have developed a model providing a quantitative prediction of the impact of the carbon nanotube networks on the properties of the composite materials (with an organic or inorganic matrix) in order to compare them with the performances of the materials currently utilized in the aerospace industry. This model is based on classical rules of mixing for fibres. The approach was as follows (see Fig. 1):

Firstly we defined the properties of the "theoretical MICRO-MESO" models (see Fig. 2) based on the performances of the basic constituents: CNT (MWNT and SWNT) and Matrix (epoxy and aluminium). Their main properties used for this model are given at Table 1. These properties are the density, the thermal conductivity (λ), the electrical conductivity (σ), the Young modulus (E) and the yield strength (Y). A length of 1 μm has been considered for CNTs, a diameter of 8 nm for MWNT and 1 nm for SWNT. Coefficient of thermal expansion (CTE) of -12 10^{-6} /°C for CNTs can be found in literature[2], but CTE estimation for macro-materials is not listed here because theoretical models do not integrate the random distribution predictions (2D and 3D) and that the calculated values are therefore incomplete.

Secondly we calculated the properties of the networks of reference on basis of "MICRO-MESO" models in different proportions as a function of network type (see Table 2 for network properties made of MWNT).

Thirdly we assessed the performances of the CNT-based materials: the so-called "MACRO" (see Table 3 for composites made of MWNT infiltrated with epoxy). In the case of continuous-fibre based composites, several architectures are possible depending on whether one is considering a uni-, bi- or tri-directional distribution of the reinforcements. The 3 architectures used here (UD, Fabric and 3D textile) are generally recognised to serve as references for the theoretical models. The transition between these 2 stages is effected by means of the classical laws of mixtures. The proportion of semi-product in the final material is adapted, depending on whether reference is made to fibre, BP (network plan) or 3D layout.

Eventually, it has to be noted that several working hypotheses are taken into consideration during this development as:

- Existing theoretical models for reinforcement with "macro" fibres are valid with nanotubes
- No particle other than nanotubes is present within the composite (residues of catalyst, voids, amorphous carbon)
- No doping or functionalization is taken into account
- Adhesion between matrix and nanotubes is considered as perfect
- Distribution of the nanotubes is homogeneous
- Nanotubes are straight
- All nanotubes have the same characteristics (properties, dimensions)
- Basic theoretical models (mostly linear) are defined for low concentration, especially those concerning short fibres
- All components (CNT, matrices) have intrinsic isotropic properties

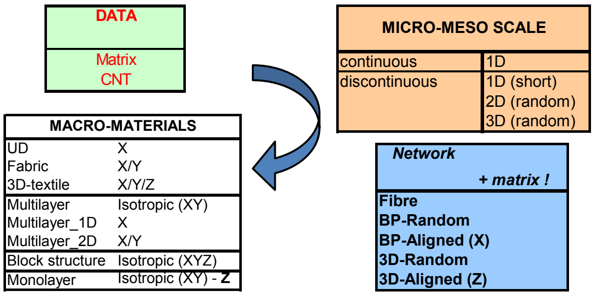


Fig. 1: Overview of the developed approach for material properties assessment

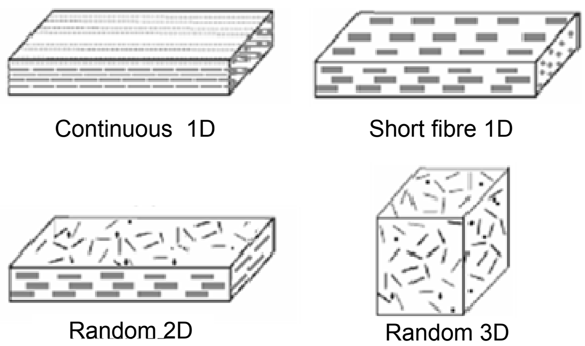


Fig. 2: Schematic representation of the "MICRO-MESO" reference models

	ρ (g/cm^3)	E (GPa)	Y (GPa)	λ (W/mK)	σ (kS/cm)
MWNT	1.73	1280	60	3000	10
SWNT	1.07	1000	200	5780	10
Epoxy	1.15	3	0.1	0.3	1 E-9
Al	2.7	71	0.165	100	155

Table 1: CNTs and matrix (epoxy and aluminium) properties used within our model.

	ρ (g/cm^3)	E (GPa)	Y (GPa)	λ (W/mK)	σ (kS/cm)
Fibre	1.45	84	1.7	96	1.18
BP-random	1.40	38	0.7	24	1.05
BP-aligned	1.41	48	0.9	44	0.91
3D-random	1.35	12	0.2	3	0.26
3D-aligned	1.60	900	42.6	2074	7.07

Table 2: Predictions of CNT network properties (MWNT).

	ρ	E/ ρ	Y/ ρ	λ/ ρ	σ/ ρ
UD	1.33	38	1.7	96	1.18
Fabric	1.33	19	0.38	22	0.27
Multilayer (isotropic)	1.37	25	0.46	16	0.69
Multilayer (1D)	1.38	31	0.60	29	0.59
Block structure	1.35	9	0.15	2.4	0.19
Monolayer	1.60	900	42.6	2074	7.07

Table 3: Predictions of specific properties of EPOXY-MWNT composites.

II.II Space applications

Potential space applications that can benefit of CNT composites or CNT skeleton are identified (leaving aside pure nano-applications like nanotools or nano-electronic ones) are numerous:

- Structural/ Mechanical applications: gossamer mirrors, electrical sails, flywheel, solar sails,
- honeycomb panels, lightweight mirror, high wavelength antennas, tethered satellite, debris protection …
- Thermal applications: heat conducting pads, heat straps, radiator …
- Electronic/Electromagnetic applications: electric sails, thermally insulating electrical materials
- Chemical/surface applications: velcro-like ribbon, hydrogen storage source, cryopump, damping composite, molecular filters
- Other applications: extraction grid for ion source, capacitor, failure detection …

For main identified space application, table 4 gives the main properties (mechanical, thermal, électrrical) of some reference materials, parallel characteristics required by the application (such as flexibility or surface quality), the characteristic dimension required by the application and defines the recommended nature of the CNT network (UD, fabric, monolayer, fibre, etc.). By comparing the properties of the candidate nanotube-based material or materials with the reference aerospace material, we identified thermal applications (heat conducting pads, heat straps, radiator) as having high potential for CNTs reinforced composite.

III. MANUFACTURING OF CNT NETWORK

Parameters defining the different steps of the CNT network manufacturing and potentially impacting the properties of the final product can be found at different levels in the manufacturing process: CNT characteristics, CNT network manufacturing process and post-treatment. CNT networks can be of different nature: buckypapers, forest, 3D, fibre … CNT network manufacturing tests in this work were limited to buckypapers (BP) and also 3D shape network.

III.I Buckypapers

First, to evaluate the influence of the different CNT characteristics on the buckypaper properties (thermal, mechanical and electrical), we have applied the "Design Of Experiment" (DOE) method. CNT parameters are numerous: morphology (number of walls, length, diameter, alignment), purity (nature and concentration of contaminants), functionnalization (physical, plasma, chemical). The CNT factors evaluated with the DOE were: morphology (MW or DW), length (long or short) and functionalization (No functionalization, NH_2 or COOH). Length for long MWNT was ~1.5 µm (NC7000 from Nanocyl), ~0.7 µm for short MWNT (NC3151, NC3152).

Manufacturing of buckypaper (CNT network) was made by classical filtration process assisted by vacuum. CNTs, diluted in a solution containing surfactant (SDS - sodium lauryl sulphate), were dispersed by ultrasonic cycles before the filtration process. Eventually the SDS was removed by water cleaning. Manufacturing from MWNT was done without difficulties (see Fig. 3a), while it was not possible to get some buckypaper samples exploitable for properties measurements from DWNT. Indeed the buckypaper was either broken in small pieces or curled up. This problem seems to be due to DWNT aggregation. The alternative solution found is to mix DWNT with a small percentage of long MWNT. After a few trials with different percentage of MWNT, a mix of DWNT with 25 % of long MWNT (NC7000) has been defined as the best ratio to stabilize the buckypaper. To extract the influence of NC7000 on results for DWNT, the formula [1] has been used:

$$\lambda_{corrected} = \frac{\lambda_{measured} - 0.25\,\lambda_{NC7000}}{0.75} \qquad [1]$$

	ρ (g/cm^3)	**E** (GPa)	**Y** (GPa)	**CTE** (10^{-6}/K)	λ (W/mK)	σ (kS/cm)	**E/ρ**	λ/ρ	σ/ρ	Other required properties / remarks	Dimensions
Honeycomb panel - *Composite candidate: UD/Fabric/Multilayer*											m^2
Epoxy/M40J	1.54	230	2.45		<u>40</u>		**149**	<u>26</u>	<u>High</u>		
Epoxy/K1100	1.8	186		-1.1	<u>300</u>		**103**	<u>166</u>	<u>High</u>		
Lightweight mirror - *Composite candidate: UD/Fabric/Multilayer*										<u>λ/CTE</u>	m^2
Zerodur	2.5	91	0.05	**0.02**	<u>1.6</u>		**36**	0.6			
SiC (Sintered)	3.16	420	0.3	**2**	<u>180</u>		**133**	57			
Be : S65A	2	304	0.207	**11.5**	<u>216</u>	250	**152**	108	125	Toxicity !	
Optical mounting - *Composite candidate: 3D textile or block structure*											dm^3 – m^3
Be, SiC (sintered)											
Fe: Super INVAR	8.13	148	0.27	**0.3**	<u>10</u>	13	**18**	<u>1.2</u>	1.6		
High λ antennas - *Composite candidate: Fabric/Multilayer*											10 m^2
CE/M40J	1.5	204	2.3	**Low**	<u>41.3</u>		**136**	<u>27.5</u>		Roughness !	
Gossamer mirror - *Composite candidate: UD/Fabric/Multilayer with elastomer matrix*										Flexibility	10 – 1000 m^2
Mylar	**1.4**	**3.2**	**0.2**				2.3				
Kapton	**1.4**	**2.5**	**0.23**	<u>20</u>	0.12		1.8	0.08			
Solar Sails - *Composite candidate: UD/Fabric/Multilayer with elastomer matrix*										**Emissivity/ flexibility**	10 – 1000 m^2
Mylar, Kapton											
Teonex	1.4	0.6	0.03	15		10^{-14}	0.4		10^{-14}		
Flywheel - *Composite candidate: CNT fibre*											0.5 m dia.
K1100 Fiber	<u>2.2</u>	965	**3.1**	-1.45	950	8	438	431	3.6		
Electric Sails (tether) - *Composite candidate: CNT fibre*										**Flexibility**	100 km
Coated Kevlar		76	<u>1.38</u>	-4		**High**					
Heat Straps - *Composite candidate: UD/Fabric/Multilayer with elastomer matrix*										<u>Flexibility</u>	0.01-0.1 m^2
Copper	8.9	130		16.5	**400**	588	15	**45**	66		
Radiator - *Composite candidate: UD/Fabric/Multilayer*											0.1-1 m^2
Al: Al 6061 T6	2.7	<u>68</u>	0.27	23.6	**235**	385	<u>25</u>	**87**	142		
Heat conducting pads - *Composite candidate: monolayer*											1-10 cm^2
BeO ceramics	3	380	0.15	9	285	10^{-18}	126	**95**	**0**		
Ion source grids - *Composite candidate: Fabric*											0.1-0.5 m
Molybdenum	10.2	**σ**: 20 kS/cm**;** low **sputtering yield** (0.82*); <u>flexural modulus</u>: 0.32 GPa; <u>CTE</u>: 5.4 10^{-6}/K									
C-C	1.7	**σ**: 4 kS/cm**;** low **sputtering yield** (0.12*)**;** <u>flexural modulus</u>: 0.16 GPa; <u>CTE:</u> -1.5 10^{-6}/K									
Thermally insulating electric material - *Composite candidate: UD/Fabric/Multilayer*										<u>Flexibility / patchwork</u>	0.01 – 1 m
Manganin	8.4	150	0.5	17	**22**	**20**	158	**2.6**	**2.4**		
Constantan	8.9	160	0.5	15	**20**	**20**	169	**2.2**	**2.2**		

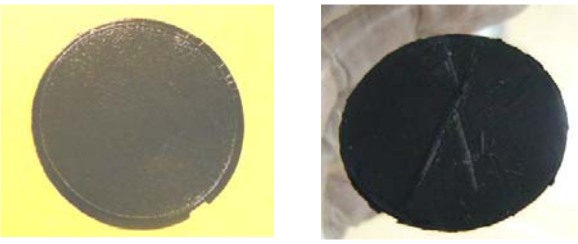
Table 4: Main properties of reference material used for space applications for comparison with CNTs reinforced composites. For each application, main criteria is in bold, secondary criteria is underlined. Recommended nature of CNT network is indicated beside each application in italic. CE: Cyanate Ester. SS: Stainless Steel. * 500eV Ar^+

For all these buckypapers, thermal conductivity has been measured by hot disk method, electrical conductivity by four-points method and mechanical properties with a universal tensile test (INSTRON 4507).

The buckypaper properties are given in Table 6 (see BP with surfactant). The influence of the tested CNT factors have been analysed with the DOE method. It clearly appears that the most influential CNT factor is the morphology in favour of MWNT. The influence of the length is weaker and various in function of the measured property: shorter CNT seems favourable for mechanical properties but long CNT seems better for electrical conductivity. NH2 functionalization has nearly no influence, while COOH functionalization appears favourable (mainly for mechanical properties) except for electrical conductivity. Concerning DWNT, their potential should be better but their trend to aggregate is probably responsible for poor properties results as for manufacturing difficulties.

But the main outcome of the measurement made during the DOE is that the (thermal, mechanical, electrical) properties measured on CNT network (buckypaper) are much lower than predicted values and thus also than current materials used for selected space applications.

Then additional efforts have been put on buckypaper manufacturing, focusing mainly on thermal conductivity improvement. Buckypapers made of Aquacyl (commercial water solution made by Nanocyl from NC7000 and SDS) give similar results to those made of NC7000. Surfactant in CNT network was suspected of being partly responsible for low measured properties. Buckypapers without surfactant have been made using oxidized CNT dispersed in water (see Fig. 4), water/ethanol, acetone or ethanol. For buckypapers made of CNT dispersed in 100% ethanol, evaporation has been assisted by compression/relaxation cycles, giving a thick (0.35 mm) and low density (0.39) buckypaper (see Fig. 3b). But unfortunately no significant improvement of the thermal conductivity has been observed for any of these buckypapers manufactured without surfactant.



(a) (b)

Fig. 3: Buckypapers made of MWNT (a) dispersed in SDS (40 x 0.1 mm^2) and (b) dispersed in ethanol (40 x 0.35 mm^2)

Fig. 4: Buckypapers made of MWNT dispersed in water (without surfactant). Flexibility of these buckypapers is here demonstrated.

Temperature	ρ (g/cm^3)		λ (W/mK)	
	Before	After	Before	After
900 °C	0.67	0.56	2.7	2.6
2000 °C	0.77	0.40	3.5	5.1
2800 °C	0.72	0.54	3.3	7.2

Table 5: Density and thermal conductivity of MWNT buckypapers before and after thermal treatment at 900 °C, 2000 °C and 2800 °C.

Thermal treatment at 900°C of buckypapers (made of MWNT dispersed in SDS) allowed to evacuate contaminants and to decrease density, but had no impact on thermal conductivity (see Table 5). Thermal treatment of buckypapers at high temperature (2000°C and 2800°C) in inert atmosphere has been made in order to get graphitization and to anneal defects. Thermal conductivity of buckypapers made of Aquacyl has been improved by 1.5 at 2000°C or 2800°C (specific value near by 3). The thermal conductivity of 3 buckypapers made of MWNT dispersed in water/ethanol has been improved by more than 2 at 2800°C (specific value near by 3). On one sample the absolute and specific thermal conductivity measured were respectively 8.4 W/mK and 17 W/mK/(g/cm3). Unfortunately, buckypapers became so brittle by this treatment that it has not been possible to use them for mechanical properties measurement or post infiltration.

CNT growth on buckypaper has been also tried to improve performances (see Fig. 7). The experimental conditions for CNT growth on buckypaper inserted with Ni have been optimized. But this allowed only a slight improvement of the thermal conductivity (10%) and the Young modulus (X2), while decreasing mechanical strength (/3).

III.II 3D CNT network development

An original method for manufacturing of 3D CNT network with cylindrical shape has been developed at Nanocyl and optimized during this project. The purpose was to use an empty quartz cylinder open with more or less 5 cm length and 2 cm diameter with CNT catalyst inside. After catalyst introduction inside the cylinder, the two sides were closed with 2 circulars carbon felts (5 mm thickness) with several holes. The quartz cylinder was pushed inside the CNT synthesis reactor which uses CVD (Chemical Vapour Deposition) CNT growth method. Examples of 3D shape CNT network obtained by this method are shown at Fig. 5.

Unfortunately specific thermal conductivity was quite low (~1 W/mK) despite the low density of this product (0.1-0.2 g/cm^3). SEM analysis shows that the microstructure of 3D shape is made of random aggregates and voids (see Fig. 6). Each void could be considered as a weak point (insulating part) in the structure and especially in terms of heat diffusion.

Thermal treatment at 2800°C has also been performed on 3D shape network samples and allowed again to increase by a factor two the thermal conductivity (see table 6). After this thermal treatment, we observed with TEM a densification of the aggregate and CNTs were more coherent. The thermal degradation under oxidative atmosphere (TGA measurement) showed a stability improvement of more than 150°C (maximum weight loss shifted from 498°C to 666°C) after thermal treatment at 2800°C.

Fig. 5: Examples of 3D shape MWNT network

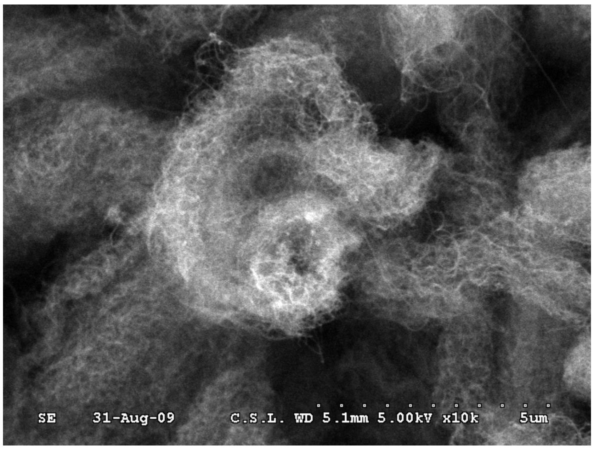
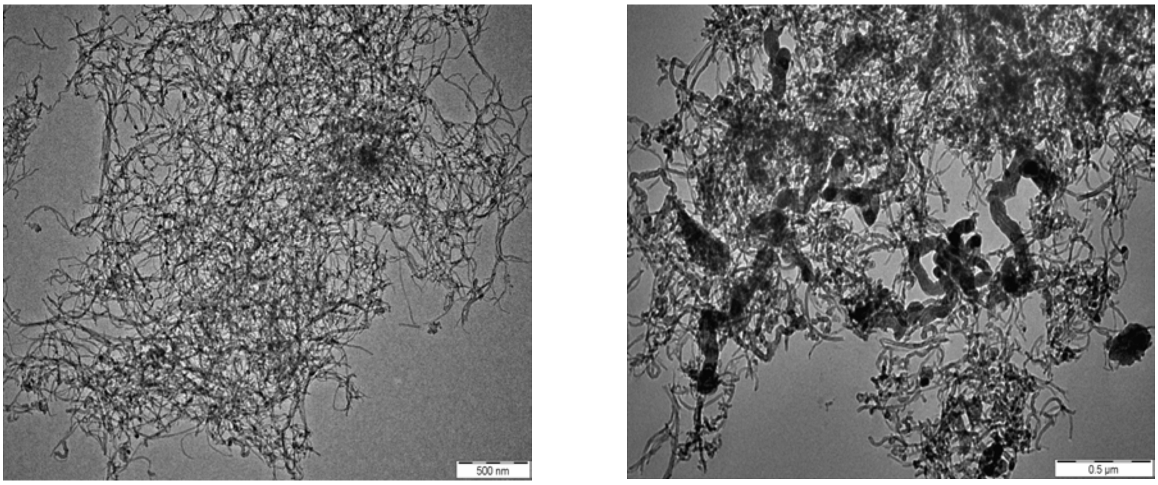


Fig. 6: Scanning electronic microscopy (SEM) on 3D shape CNT network. Aggregate (at centre) and voids are visible on this picture.

	λ (W/mK)	σ (S/cm)	E (GPa)	UTS (MPa)	ρ (g/cm^3)
BP with surfactant (SDS):					
MW_Long (NC7000)	2.7 (4.3)	28 (44)	0.55 (0.9)	5.5 (8.7)	0.63
MW_Short_COOH (NC3151)	3.7 (4.2)	11 (13)	2.7 (3.1)	11.1 (12.8)	0.88
MW_Short_NH2) (NC3152)	2.9 (4.4)	31 (46)	0.69 (1.1)	6.6 (10.4)	0.66
DW_Short* (NC2150)	1.8 (2.3)	13 (16)	0.46 (0.6)	3.6 (4.5)	0.81
DW_Long_NH2* (NC2102)	1.5 (2.5)	14 (25)	0.13 (0.2)	0.3 (0.6)	0.57
DW_Long_COOH* (NC2101)	3.4 (3.1)	21 (19)	2.5 (2.2)	8.3 (7.5)	1.10
Aquacyl	3.6 (4.3)	56 (73) **			0.78
BP without surfactant:					
MW_Short in water/ethanol	3.7 (4.8)				0.78
MW_Long in ethanol	1.7 (4.4)				0.39
BP treated at 2800°C	7.2 (13.5)	49 (91)			0.54
(MWNT in water / ethanol)	Max 8.4 (17)				
BP with CNT growth (40 wt%)	3.6 [+10%]		1.9 [x2]	3.8 [:3]	~1 ***
MW_Long_COOH (NC3101)			Max 6.5	Max 6	
3D shape	0.142 (1.0)				0.14
3D shape treated at 2800°C	0.258 (2.1)				0.12

Table 6: Mean properties for the different CNT network developed in this project. Specific value (divided by density) is given in parenthesis. Highest value obtained on one sample is also given (Max) when this value is much higher than the average value. * Mix of 75% DWNT with 25% MWNT (NC7000). Improvement after treatment (CNT growth) is given in brackets. ** Only one sample measured. *** Density is difficult to evaluate because these buckypapers are not flat.



(a) (b)

Fig. 7: TEM pictures of buckypaper coming from NC7000 (a) before and (b) after CNT growth (49 wt%).

IV INFILTRATION OF CNT NETWORK

IV.I Infiltration with organic matrix (epoxy)

Infiltration of the CNT network with organic matrix has been tested on the different CNT network manufactured: buckypapers, 3D shape and even CNT forest made outside the consortium.

As infiltration was more difficult with space qualified epoxy used for first tests, all CNT networks presented here have been infiltrated with a low viscosity epoxy (90 mPa.s): Araldite BY 158 / Aradur 21 (mix in 100:28 ratio).

Buckypapers were infiltrated by deposition of liquid epoxy on upside and vacuum assistance on downside (see Fig. 8a). Infiltrated buckypapers around 100 µm thickness showed good infiltration homogeneity (measured by EDX), but CNT macro structures with thickness of several centimetres (3D) are much more difficult to infiltrate (limited by the epoxy penetration depth).

Infiltration has also been tested on CNT forests which have been made outside the consortium (University of Cincinatti). These CNT forests had dimensions around 5x5mm^2 and 2 to 4 mm CNT height. Three samples have been measured with the laser flash method (at University of Liège). One sample has been infiltrated by immersion and then compressed. Then this composite sample has been cut and glued with cyanoacrylate to the new dimension required for laser flash. Two other samples are coming from the same CNT array and have been infiltrated by capillarity (see Fig. 8b). Note that the sample with higher CNT concentration gives a higher thermal conductivity (see Table 7).

Infiltration on 3D shape network have been made first by vacuum/relaxation cycles. Eventually composite with high CNT content (30 wt%) from 3D shape CNT network have been infiltrated by a compression method (1500 bar). Thermal conductivity was low for both cases (< 1W/mK), but higher with higher CNT content (see Table 7). 3 samples have been cut out from the same 3D block infiltrated with epoxy. Surface displacements on these 3 samples have been measured in the 3 directions in the temperature range -20°C to 120°C. The average CTE value for these 3 samples in the 3 directions is 51 10^{-6} /°C. As the CTE of the neat resin is 72 10^{-6} /°C, the effect of the CNT on CTE decreasing is really noticeable. For each direction, the CTE is very similar between the 3 samples (see Fig. 10), but seems slightly different between different directions (not completely isotropic material). Moreover the CTE on this composite was similar in the 3 directions after a thermal vacuum cycling test (10 cycles between +80°C and -120°C).

Composite characterization still stays a challenge after thermoset infiltration. Nevertheless, to correlate the relation between CNT/epoxy microstructures with properties require more experiments and bibliography.

(a) (b)

Fig. 8 Infiltration with epoxy of (a) buckypaper assisted by vacuum and (b) CNT forest by capillarity

(a) (b)

Fig. 9: 3D shape CNT network infiltrated with epoxy resin under high pressure (1500 bar)

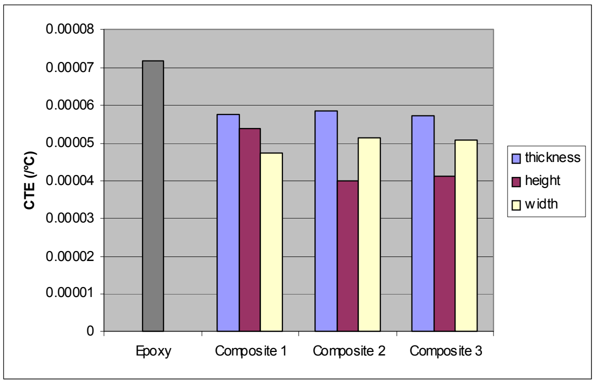


Fig. 10: CTE values measured in the 3 directions of the 3 epoxy composite samples (3D shape block infiltrated at 1500 bar) compared to neat epoxy (in grey)

IV.II Infiltration with inorganic matrix (Aluminium)

For preparation of buckypapers to aluminium infiltration, Ni and Al insertion has been successfully performed by filtration. This method is simpler than electroplating. The buckypapers are composed of oxidised carbon nanotubes only (no surfactant like SDS). Ni insertion in the buckypapers has been performed by simple filtration using oxidized MWNTs (NC7000). Buckypapers have been prepared in water with an electrochemical reduction of nickel ions ($NiSO_4$) already inserted in the buckypapers. Several parameters have been optimised (concentration of $NiSO_4$, combination of filtration and immersion, time of filtration, drying). Concentration of the $NiSO_4$ solution is typically 0.1 M. By this method Ni infiltrated buckypapers have been manufactured in a reproducible way with good flexibility and quite homogeneous distribution of nickel (6% weight, on the average) within the buckypapers.

Direct insertion of Al using $Al(NO_3)_3$ solution has been also demonstrated. It has to be noted that this method is also an alternative way of CNT network infiltration with relatively high Al content (buckypapers infiltrated with Al concentration up to 18wt % have been manufactured).

	ρ (g/cm³)	CNT content (wt%)	λ (W/mK)
3D (high pressure)	1.18	30	0.85
3D (vacuum/relaxation)	1.14	12	0.45
Forest (immersion/ compression)	1.40	5.7	1.14
Forest (capillarity)	1.41	2.1	0.45

Table 7: Properties of composite samples made of 3D and forest CNT network infiltrated with epoxy.

Infiltration of the CNT network with inorganic matrix has been tested firstly by a compression method but buckypapers were too brittle to withstand the infiltration. Moreover it was obvious that there was no affinity between CNTs and aluminium.

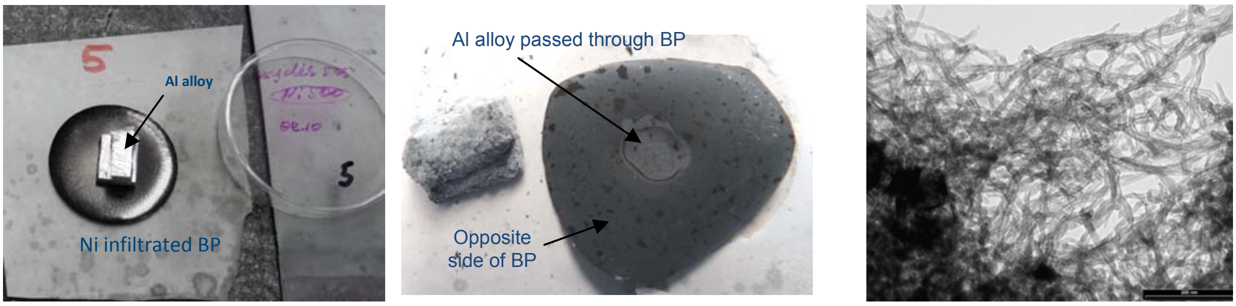
Infiltration tests performed using a simple heating method showed more encouraging results. An interesting result has been obtained on a buckypaper with Ni inserted within: Al was present on the reverse side after the thermal treatment (see Fig 11).

Dissolution of Al alloy composite has shown that (at least a significant part of) CNTs are preserved by the infiltration. SEM-EDX analysis of the cross-section of the buckypaper has shown that Al alloy is present inside the buckypaper. Other tests with Al alloy deposited on Al infiltrated and evacuated buckypapers have also shown infiltration. But these first results require further characterizations and tests to confirm the real nature of the infiltration and Al alloy concentration and homogeneity inside.

V DISCUSSION

The material properties measured during this work are much lower than predicted values (see table 2 and 6). Efforts have been concentrated on CNT network optimization for thermal conductivity and final results were below predictions. Indeed the thermal conductivity of buckypapers treated at 2800°C (~7-8 W/mK) is lower than predicted value for random buckpapers made of MWNT network (22 W/mK). But this difference is much lower if specific values are considered (13 compared to 16). Moreover these measured values correspond to values commonly found in literature[3]. Sometimes values as low as 0.3 W/mK are found for buckypapers made of MWNT[4], while higher values up to 200 W/mK have been reported for buckypapers made of aligned CNTs: SWNT aligned in a magnetic field[5] or made by 'domino pushing' method[6] from MWNT forest.

While thermal conductivity of 3D shape network can seem very low (~0.2 W/mK), specific values measured on 3D shape network treated at 2800°C (~2) is not much lower than expected (2.4).



(a) (b) (c)

Fig. 11: Infiltration test with inorganic matrix (Al alloy) by heating method on Ni inserted buckypaper: (a) before heating, (b) Al alloy is visible at centre of BP opposite side after heating and (c) TEM picture on infiltrated area of the buckypaper after metal dissolution.

The values measured for composite based on CNT forest are much disappointing (~1 W/mK). If back-engineering is performed on basis of the model developed here, the CNT conductivity is evaluated between 15 and 19 W/mK. Indeed much higher conductivity values were expected as the CNT are 100% aligned in this configuration. It's similar to former published results for 1-2 mm length MWNT with ~25 W/mK at room temperature[7], but much lower than for 10-50 µm length MWNT forest[8] with values from 12 to 17 W/mK (~200 W/mK for MWNT taking into account the volume filling fraction of 7–8%).

Heat transport in CNTs is known to be dominated by phonons instead of electrons[9]. As defects are introduced in CNT network, the mean free path of phonons is reduced, thus conductivity decreases. While high thermal conductivity on one single MWNT has been measured[10] around 3000 W/mK, all published measurements on CNT network (even on CNT bundles or forest) are much lower. This is often explained as possibly a result of the effects of tube-tube contacts, the incomplete graphitization of the samples[5] or interfacial thermal resistance between CNTs[11]. Thermal conductivity improvement by a factor ~2 on all the thermally treated networks in this work at 2800°C (while no improvement has been observed at 900°C) confirms the second point.

VI CONCLUSIONS

In conclusion, we can put forward some interesting points achieved and lessons learned during this project.

A model using classical fibre engineering rules has been performed to estimate CNT reinforced material properties; this has guided our choice towards thermal oriented space applications. As predictions of materials properties are often largely overestimated compared to results, it shows that predictions need more complex theoretical modelling and that engineering on CNT materials has to be more developed.

Manufacturing of buckypaper without surfactant has been optimized and some alternative methods for CNT network manufacturing (3D shape, CNT growth on buckypaper, CNT forest) have been tested, but no magic numbers have been reached for the thermal conductivity (~8 W/mK for best buckypaper), only small improvements have been performed.

A composite with high CNT content (wt 30%) has been successfully manufactured from 3D shape CNT network, with a lower coefficient of thermal expansion than neat epoxy and similar values in the 3 directions before and after a thermal vacuum cycling test between 80°C and -120°C.

Toward the end of the project, Al alloy infiltration of buckypaper by a simple heating method and appropriate buckypaper preparation has been observed. CNTs seem to have been preserved, but it requires more characterizations. An interesting perspective to this work could be to continue the development on Al infiltration.

It is clear that the developed CNT network based materials and consequently composite materials developed within this project are not competitive with current aerospace reference materials. Eventually, we can note that composite made of CNT network (non aligned CNTs) have no better thermal properties than composite made by mixing CNTs in a matrix (for the same CNT content). However composite based on aligned CNTs (forest) shows better thermal conductivity improvement but results are still much lower than expected values.

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