Synthesis and characterization of carbon-nanotubes and their application in the aerospace engineering

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Abstract. The unique carbon nanotubes (CN) properties (mechanical, electrical, thermal, etc.) are considered as a key factor for future improvement of technical characteristics of many engineering macro and nano systems [5].

The synthesis, the purification and the characterizations of carbon nanotubes are the primary requirements for a realistic use of it in many engineering sectors. A possible field of application of advanced composite materials, for example, is represented by innovative and recently introduced “Anisogrid Lattice Structures”, realized in the form of a thin-walled shell (cylindrical or conical) with a system of a helical and circumferential ribs (with or without internal and external skin). Using this typology of structures, in principle, it is possible to satisfy high requirements of static resistance and stability in the minimum mass condition (Vasiliev Theory). Further improvements are expected by introducing nanotubes reinforced composites.

This new generation of structures and composite materials find concrete and interesting application in the aerospace technologies.

This paper reports the authors’ studies on the synthesis (arc discharge with inert gas, in water immersion and laser ablation methods), purification (oxidation and chemical etching) and morphological analysis (Optical, SEM, TEM, X-Ray and Chemical) of carbon nanotubes. The methods about the manufacturing of advanced composite materials reinforced with nanotube are discussed. Besides, analytical and FEM analysis showed the performance improvement of a typical space structure (anisogrid lattice shell) with nanotubes composites, as a possible future application in the space technologies.

I Introduction

For the synthesis of carbon nanotubes four different facilities are developed:

- Arc discharge in inert environment (fig. 1) [6][8]
- Arc discharge water immersed (fig. 2) [10]
- Laser ablation CO_2 (fig. 3) [7]
- Laser ablation Nd-Yag (fig. 4) [5].

Using different methodologies, it is possible to obtain different quantity and quality of carbon nanotubes. The requirements imposed for a real use of this new advanced material are:

- High quantity
- High quality (purification and alignment degree)
- Low cost
- Carbon nanotubes morphologies control.

The synthesis process of Carbon Nanotubes is very complex and it is difficult to obtain all the above conditions.

For example, a purification step is always necessary. Instead, the alignment degree in the structural application is less important respect the electronics applications (MEMS/NEMS).

Fig. 1 Arc discharge in inert environment facility

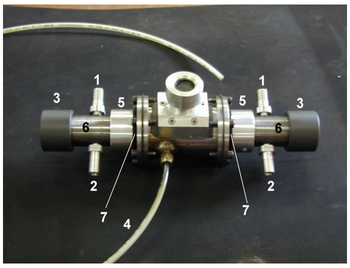


Fig. 2 Arc discharge water immersed facility

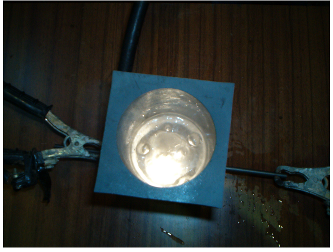


Fig. 3 Laser ablation CO_2 facility

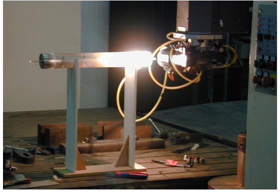
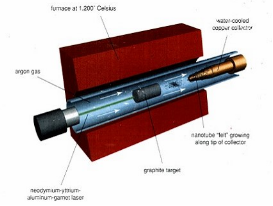


Fig. 4 Laser ablation Nd-Yag facility



II Experimental and Results

A set of experimental test are performed using the above developed facilities. The principal parameters that guide the characteristics (morphologies, quantity, purification and alignment degree) of carbon nanotubes are:

- Inert environment (using helium, argon, deionizzated water)
- Power supply (voltage, amperage, laser power)
- Graphite employed (pure or with catalysts: yttrium, cobalt, nickel).
- Arc and laser stability control.

For each synthesis method, the test are performed using different parameters and conditions. It is necessary to evaluate, with the microscopy analysis (SEM, TEM, EDX, Optical), the difference among different materials produced.
Below, the typical parameters employed are showed:

Arc discharge:

20-30 V
60-100 A
pure o drugged graphite
discharge time: 10-60 sec

Laser ablation CO_2:

power: 900 w
wave length: 10.6 µm
time: 60 secondi

The use of the electronic microscopy requires a particular samples preparation necessary to observe a nanometric elements. The Authors developed the procedures above mentioned [1][2].
To produce high quantity of carbon nanotubes is necessary to give enough energy (with the arc or with the laser spot). Besides, it is requested to perform the processes in inert environment condition, to avoid oxidation phenomena during the synthesis.

Fig. 5 SEM analysis of the material produced with the arc discharge

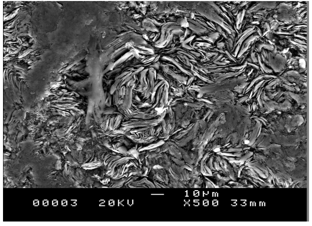


Fig. 6 SEM analysis of the material produced with the arc discharge

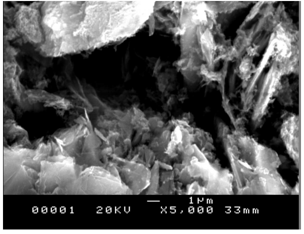


Fig. 7 SEM analysis of the material produced with the arc discharge

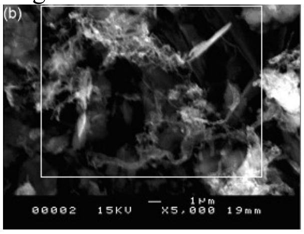


Figure 5÷7 illustrate how it is possible to improve the nanometric materials produced when the used energy increases. The problem is to find the parameters that optimize the processes. By the use of drugged graphite (see EDX analysis in fig. 8) and with a good sustained arc and laser source control, the improvement of the process is very significant (fig. 9÷12). Figs. 9-12 show the high quantity and the high purification degree of the deposited material, with no good alignment degree (using the arc discharge and the laser ablation methods). Only the CVD method gives a intrinsic alignment of the nanotubes, but requires long time to produce it.

Fig. 8 EDX analysis

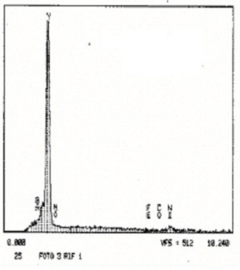


Fig. 9 improvement of the carbon nanotubes produced with the arc discharge

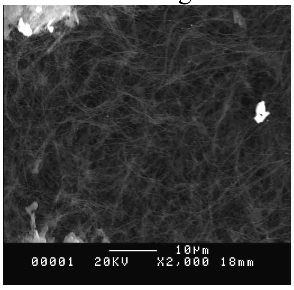


Fig. 10 bundles of carbon nanotubes produced with the arc discharge

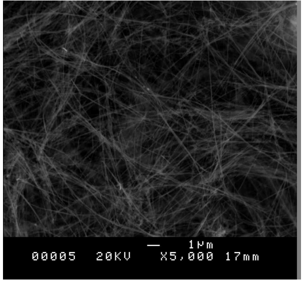


Fig. 11 SEM photo of the target graphite after the laser spot

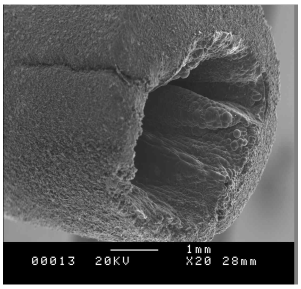
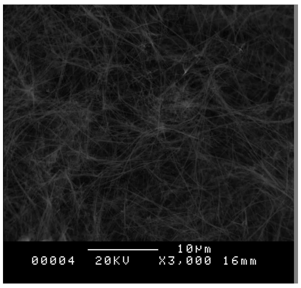


Fig. 12 laser ablation carbon nanotubes deposit



Besides, for a major characterization of the carbon nanotubes, a TEM analysis are performed (fig. 13÷16).

Fig. 13 TEM analysis (50000x)

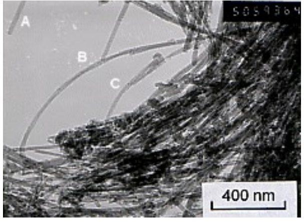


Fig. 14 TEM analysis (100000x)

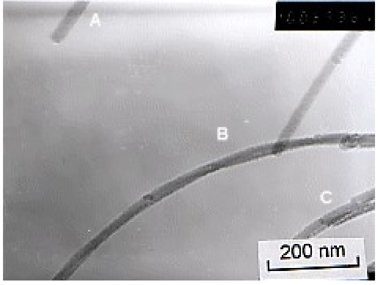


Fig. 15 TEM analysis (30000x)

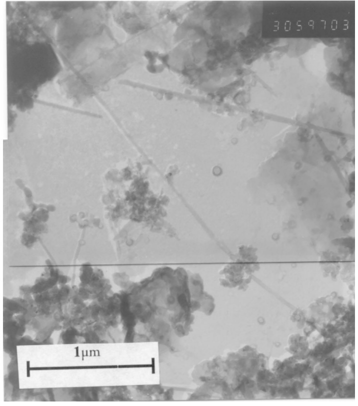


Fig. 16 TEM analysis (20000x)

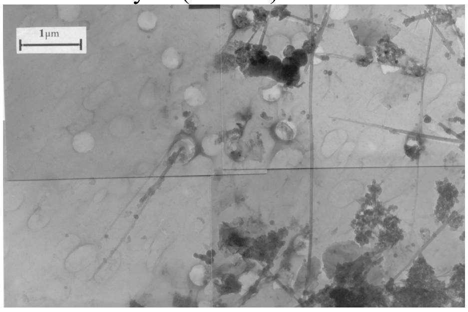
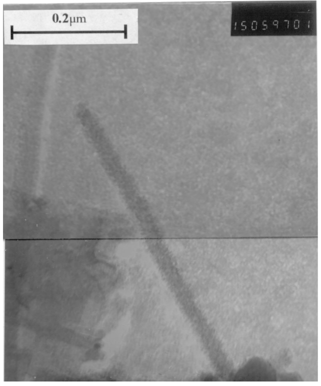


Fig. 17 TEM analysis (150000x)



With the TEM imagines it is possible to evaluate the carbon nanotubes dimensions (medium diameter: 20 nm, length: several microns).
After the synthesis the produced carbon nanotubes are purified with the chemical oxidation: TDA tests (Thermal Differential Analysis) where performed, using 50 mg of raw materials, fluxing

with a slightly oxidizing atmosphere (N_2 90%, O_2 10 %) for 5 hours. Temperature was constantly increased from 20 °C up to a maximum of 780 °C.
The results obtained are characterised by SEM analysis, performed before and after the purification test, figs. 18 and 19 respectively. It is evident (fig. 19) that the mass of amorphous carbon is reduced and dispersed, but a successive treatment of separation of CN by ultrasonic treatment in organic solution is necessary, at least for 30 minutes.

Fig. 18 cathode deposit morphology before purification

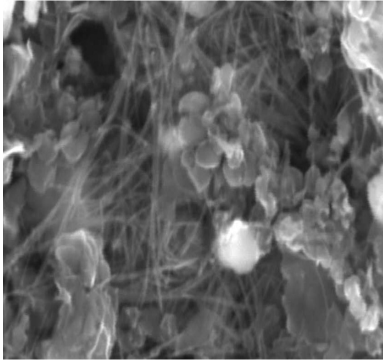
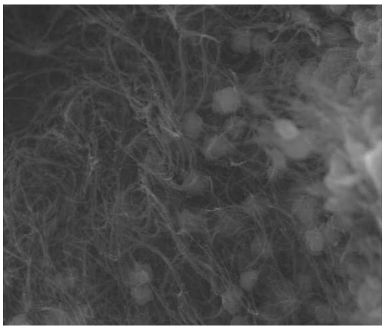


Fig. 19 cathode deposit morphology after purification



The purification by means of ultrasound, with no good control in the time process, gives the “cutting” of the carbon nanotubes.

III Dispersion test of nanometric powders in an epoxy matrix

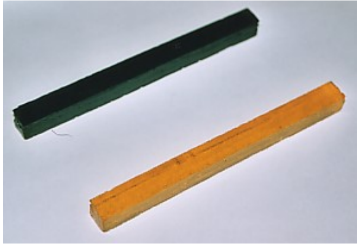
A complex step is the definition of a procedure aimed to the realization of an homogeneous dispersion of a nanometric powder in epoxy resin. Moreover, the adhesion problems related to the interface activity of the resin and the powder and the nanotubes must be solved.

In the present work, adopted procedures are as follows:

- commercial epoxy resin
- curing agent: developed by Chemical Department of “La Sapienza” University - Rome
- nanometric graphite powder with carbon nanotubes addition
- graphite powder granulometry 20 µm.

Total concentration of dispersed powder realised was 10% and 20%.
Samples were realised, dimension 10x10x120 mm (fig. 20)

Fig. 20 specimens for mechanical tests



Curing process adopted:

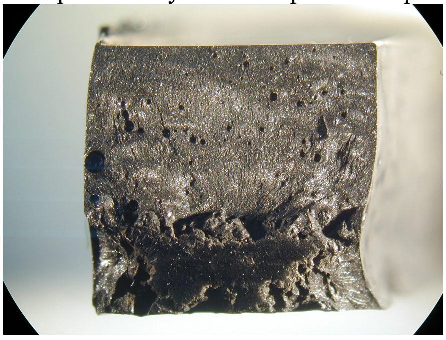
- room temperature x 24 hrs
- furnace curing 80 °C x 3 hrs.

Impact test where finally performed. Following considerations are driven:

1. the reduction of powder granulometry increases the impact resistance properties
2. a good surface finishing improves the mechanical properties.

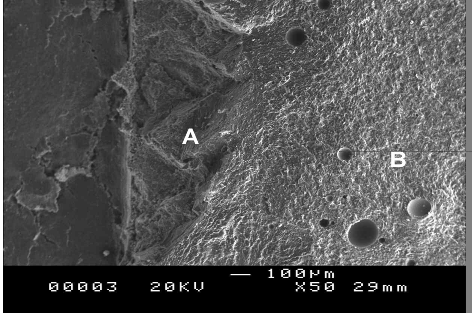
Fig. 21 shows the fracture surface appearance of a sample containing 20 % of powders. The pre-crack length is 2 mm. A brittle behaviour of crack propagation is evidenced.

Fig. 21 optical analysis of composite sample



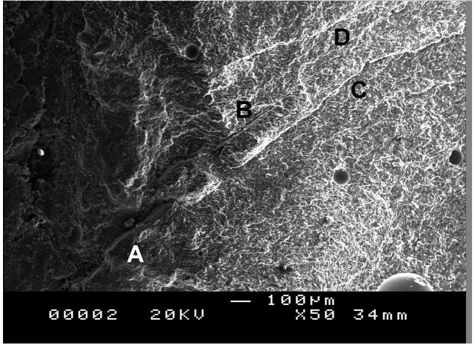
To understand the fracture-mechanic behaviour of the composite, SEM characterizations of fracture surface were performed.
Fig. 22 shows the SEM images of the samples containing 10% of powders.
In the area **A** (crack initiation) and **B** (propagation) there is no presence of preferential directions of crack propagation.

Fig. 22 SEM analysis of fracture surface of composite specimen (10% powder addition)



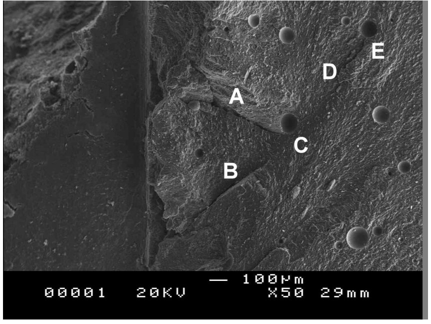
On the contrary, the sample containing 20% powder, preferential directions of crack propagation are observed (fig. 23, area **A**,**B**, **C** and **D**).
The presence of preferential direction is due to the non-uniformity of powders dispersion in the matrix.

Fig. 23 SEM analysis of fracture surface of composite specimen (20% powder addition)



A further observation is that the fracture lines change direction in correspondence of cavities (or voids).
In fig. 24 two fracture lines (**A** & **B**) are deviated by the presence of a void (see points **C** & **D**), and are stopped in point **E**.

Fig. 24 SEM analysis of fracture surface of composite specimen (20% powder addition)

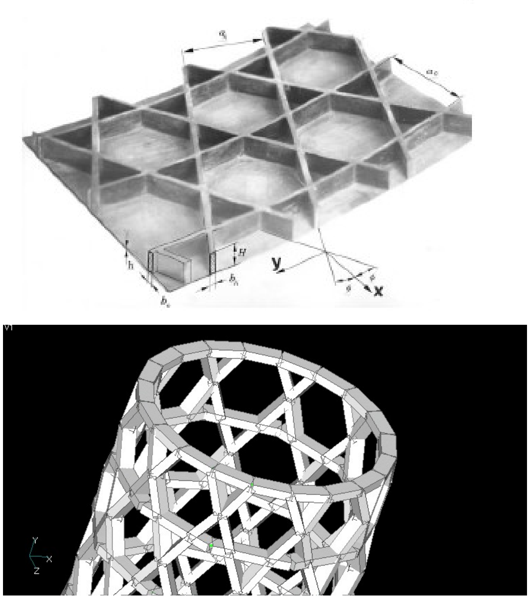


The static test (traction) shows that using a nanometric particles (graphite and carbon nanotubes, 10% in wt) the Young modulus improvement is major of 12 % respect the sample only with resin and agent curing. In theory using only carbon nanotubes (theoretical Young modulus: 1TPa) the mechanical properties of the composite become very interesting [3].

IV The Anisogrid Lattice Strucuters

Anisogrid lattice structures (fig. 25) are characterized by helicoidal ribs, resistant to applied load, and circumferential rib, which ensure stability against buckling [4].

Fig. 25 anisogrid lattice structures



Assuming the radius **R** and height **H** of a cylindrical structure, the applied external compression load **W** and the characteristic of the material, it is possible to determine the dimensions of resistant sections of the ribs (fig. 25) utilizing the theoretical model of Vasiliev, according to the following three constraints;

- Minimum mass of the element
- Static resistance
- Local and global buckling stability.

The Vasiliev model calculates an initial solution of the structural dimensioning, which must be verified by FEM analysis.
Computer programs in MATLAB have been developed by the Authors, which can calculate the geometry of the anisogrid element, when fixed values of the dimensions of the structure are assumed: radius **R**, height **H** and the applied load **W**.
Moreover, a program has been developed, according to Vasilev theory, able to calculate the variation of the geometry of the anisogrid element, when radius **R** and height **H** of the structure are simultaneously varied (fig 26).

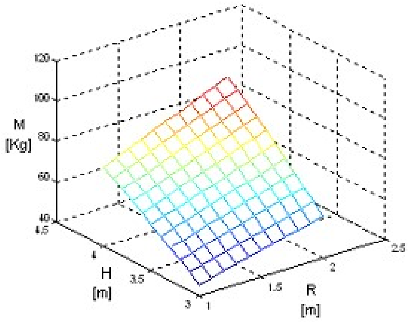
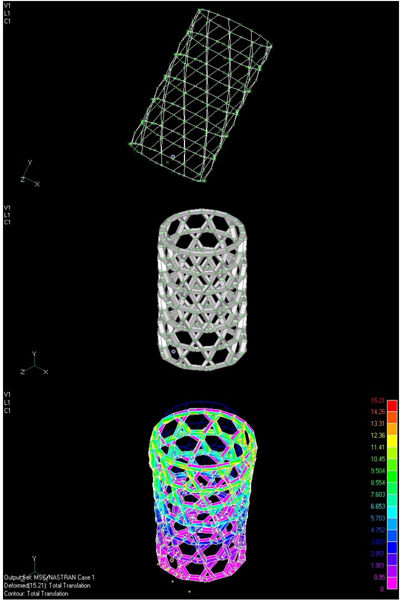


Fig. 26 Structure Mass **M** vs Radius **R** and Length **H**

Following the numerical analysis, FEM analysis (fig. 27) demonstrated that Vasilev model represents a preliminary design. Final dimensions of the structure must be determined by means of FEM analysis, loosing the constraint of minimum mass.

Fig. 27 FEM analysis



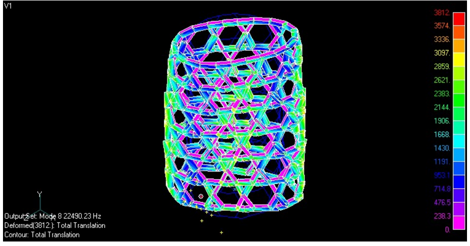
The most complex analysis results the buckling stability, because the Vasiliev model states that, in correspondence of calculated dimensions, the applied load is exactly the buckling load (unitary eigenvalue).

Different distributions of the constraints and of the applied load have been considered, and an eigenvalue 0.98 was reached, using the following configuration:

- The load is uniformly distributed on all the nodes of the FEM model
- The basement of the structure is constrained against translation
- All the remaining nodes of FEM model are constrained against rotation.

Te eigenvalue of 0.98 demonstrates that the buckling stability of a design with minimum mass (Vasiliev model) is verified, when suitable load distribution and constraints are applied.
Besides, also dynamic analysis (rotation and translation frequencies) of the element have been performed (fig. 28).

Fig. 28 dynamic analysis



Finally, the model of Vasiliev is used to evaluate the mass reduction of the structure, when different materials for aerospace applications are considered: a) aluminium alloy Al 2024, b) composite epoxy resin carbon fibres reinforced (Hs/Ep), c) composite epoxy resin reinforced by carbon fibres and by a dispersion of carbon nanotubes, 5% by weight. The Vasiliev model is applied on a cylindrical anisogrid lattice structure (radius **R** = 1.5 m, height **H** = 4 m, applied load **W** = 3 MN) (tab. 1).

tab.1 Structure Mass calculated for different materials [9]

MATERIAL	Al 2024	Hs/Ep	Hs/Ep + 5% CNs
YOUNG'S MODULUS [Pa]	70E9	12E10	16E10
MASS [Kg]	206.3	84.1	69.7

The validation of the structure is performed following the general schema:

- preliminary design
- numerical FEM analysis
- prototype design
- prototype's manufacturing
- test.

After computerised calculation and verification by FEM analysis, a flat prototype of anisogrid lattice structure was realised, with the aim to understand process and practical procedures necessary to future realization of anisogrid elements full scale and characterised by complex geometries, particularly cylindrical.
A preliminary design was calculated (see fig 29) to realise an under-scale prototype, dimensions 21x17 cm.

Successively the mould was prepared (fig. 7.2) by traditional mechanical tooling.
Following materials were utilised for the practical realization of the composite prototype:

- epoxy resin
- curing agent (Triaethylentetramin)
- glass fibres (12000 per single filament)
- nanometric powder (graphite) + carbon nanotubes.

The following curing procedures were adopted:

- room temperature (21 °C) curing x 24 hours
- furnace curing at 80 °C x 3 hrs.

Fig. 29 structure preliminary design

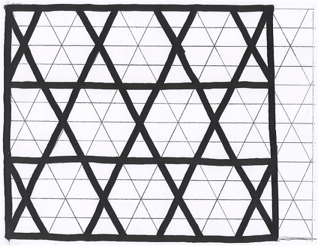


Fig. 30 mould

Fig. 31 flat anisogrid lattice prototype

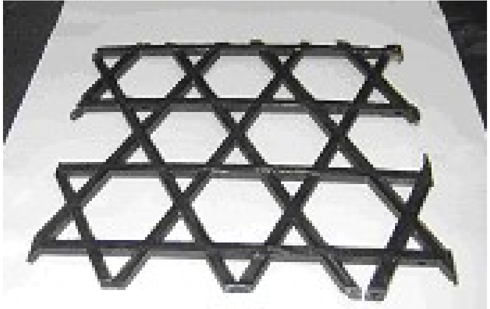
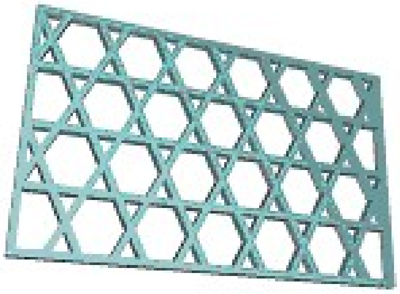


Fig. 31 shows the realized prototype, after some preliminary and successful mechanical tests (vibration and tension tests).
More accurate and detailed investigations are necessary for a complete qualification of the prototype.
The present investigation is looking for procedures which can be used, possibly, during future industrial and automatic production. Therefore, a new CAD design was performed (see figs. 32 & 33), the positive simulacra of the lattice structure was realised by rapid prototyping, the final mould (negative) was obtained in silicon resin.

Fig. 32 CAD design of the anisogrid lattice flat element



Finally, a 3D–CAD model was prepared to be used for rapid prototyping of a positive cylindrical geometry of an anisogrid lattice structure (fig. 34). Final silicon mould (negative) can be easily obtained.

Fig. 33 rapid prototyping positive mould

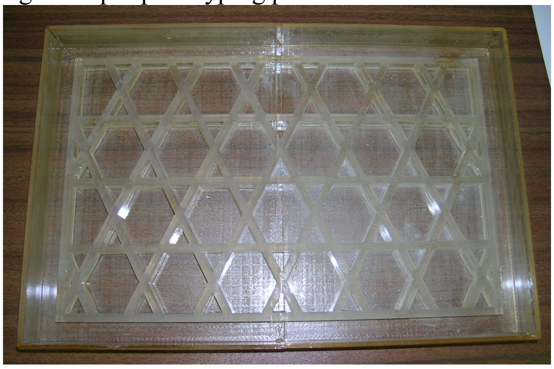


Fig. 34 3D - CAD design of the anisogrid lattice cylindrical element

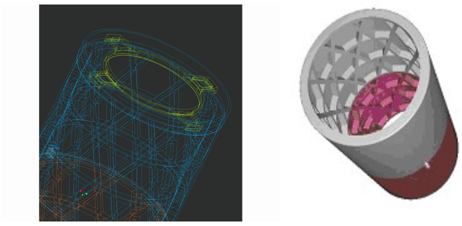


Fig. 35 rapid prototyping positive mould and cylindrical silicon mould preparation

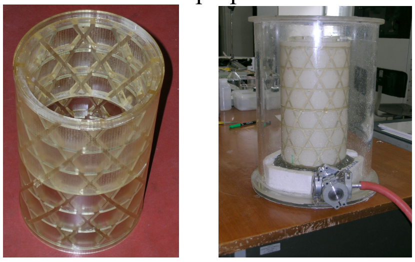


Fig. 36 final silicon mould

The cylindrical prototypes is under construction with the filament windings technologies.

V Conclusions

The different methodologies employed for Carbon Nanotubes synthesis (arc discharge, laser ablation) give different morphologies and purification and alignment degree. This is an important aspect for a real integration of carbon nanotubes in advanced nanotechnologies systems (MEMS, aerospace structures for examples). The purification is a complex procedure, in fact it is very difficult to control the chemical reaction necessary to eliminate the undesired amorphous carbon and to preserve the carbon nanotubes produced. Thus, it is necessary to improve the purification degree of the synthesised nanomaterial.

The utilization of Vasiliev theory allows to design innovate structures, anisogrid lattice, satisfying the requirements of minimum mass in the global and local stability conditions. The load and constraint configuration that satisfy the stability conditions are determined by FEM analysis.

The addition of carbon nanotubes in a composite material (epoxy fibre reinforced polymers) improves the mechanical properties. In particular, the increase of the Young Modulus offers the possibility to further reduce the mass of the structure.

As final results, the combination of both the innovative design of anisogrid lattice structures and the utilization of composite materials containing carbon nanotubes, allows to obtain a strong overall mass reduction of the structural component, maintaining the stability requirements.

Acknowledgement

Special thanks to Dr. Ugo Franzoni (C.S.M. Centro Sviluppo Materiali of Rome) responsible of the Carbon Nanotubes and Anisogrid Lattice Structures Research Program.

Thanks to Debora Montechia, Roberto Procopio, Franco Barulli, Cristiana Angeli and Massimo Sartini for the collaboration.

Thanks to Prof. Gilberto Rinaldi (University of Rome “La Sapienza”) for the collaboration relative the studies of the composite carbon nanotubes reinforced.

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