SYNTHESIS OF CARBON NANOTUBES AND THEIR APPLICATION IN "ANISOGRID LATTICE STRUCTURES"

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ABSTRACT

The unique carbon nanotubes properties (mechanical, electrical, thermal, etc.) are considered as a key factor for future improvement of technical characteristics of many engineering macro and nano systems.
A possible field of application of advanced composite materials 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, it is possible to satisfy high requirements of static resistance and stability (local and global buckling) 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 and laser ablation methods), purification (oxidation and chemical etching) and morphological analysis (Optical, SEM, TEM, X-Ray and Chemical) of carbon nanotubes. The performance of anisogrid lattice shells reinforced with nanotubes composites, simulated by both analytical and FEM analysis, are showed. Besides, manufacturing and test of one anisogrid element prototype are discussed.

Key words: carbon nanotubes, anisogrid lattice structures.

1. Introduction

Macroscopic behaviour of Nanomaterials depends on development and set up of methodologies able to control basic constituents at nanometric dimensions.
The challenge in the worldwide research effort is to develop practical industrial application in medium time.
Carbon Nanotubes (CN) are characterised by intrinsic relevant properties (mechanical, thermal, electric, magnetic) extremely interesting for the development of high tech materials and systems.
The use of CN as reinforcing elements in advanced polymer composites, represents a means to improve performance and reliability of composite structural materials for high-tech applications, including aero-space industry.
Some different and complex process are presently known CN synthesis (arc discharge, laser ablation, chemical deposition, others). Development efforts are considerable, especially with regards to production control and methodologies required for CN purification and functionalising.
Purification process are performed mainly via controlled oxidation at temperature in atmosphere at low O_2 partial pressure or via chemical acid attack, followed by separation under ultrasonic treatment.
Also the procedures and methodologies (SEM + EDS, TEM, Raman etc.) utilised for observation and characterisation of CN production are complex and need a standardization.

Moreover the development of innovative composite material, also the introduction of recent innovative design of light structures is hereby considered.

The new “anisogrid lattice structures” are realised by means of reinforcement elements helicoidal and circumferential, which can reach the local and global buckling stability in the theoretical condition of minimum mass, according to the model of Vasiliev.

The combination of the new anisogrid structures and composites materials reinforced with CN addition, can lead to an extraordinary development of innovative systems with a mix of characteristics (mechanical, thermal, electric, magnetic) never attained up to now.

The activities developed by the authors are described, in the field of synthesis, purification and morphologic characterisation of CN. Problems related with dispersion and bonding of CN in a polymeric epoxy matrix are discussed.

Mechanical properties of the experimental polymer composite reinforced by CN are measured. Based on these results, numerical and FEM analysis of the anisogrid lattice structure are performed and discussed.

Some example of small scale prototype of anisogrid structures, presently under development, are finally shown.

2. Anisogrid Lattice Structures

Anisogrid lattice structures (fig. 2.1) are characterized by helicoidal ribs, resistant to applied load, and circumferential rib, which ensure stability against buckling.

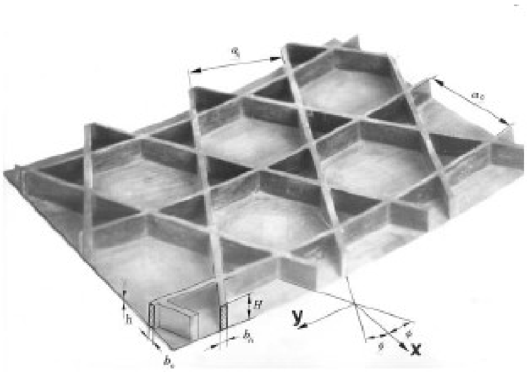

fig. 2.1 anisogrid lattice structures

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. 2.1) 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 programs 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 2.2).

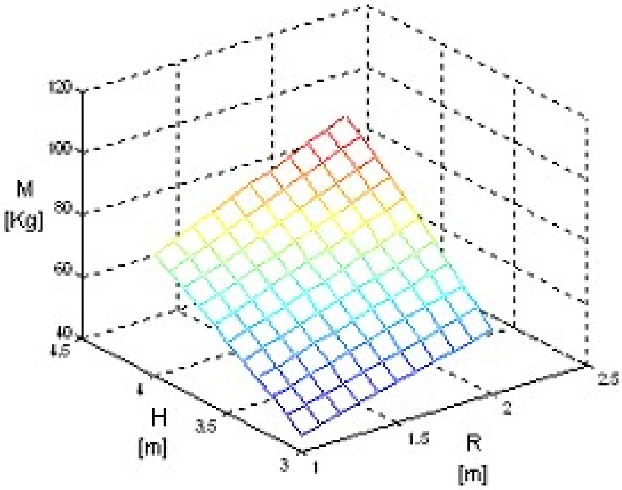

fig. 2.2 Structure Mass **M** vs Radius **R** and Height **H**

Following the numerical analysis, FEM analysis (fig. 2.3) 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.

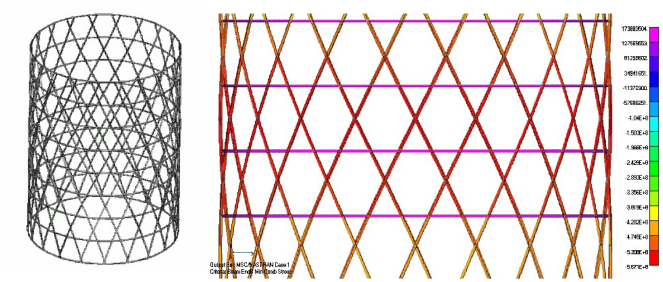

fig. 2.3 FEM analysis

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. 2.4).

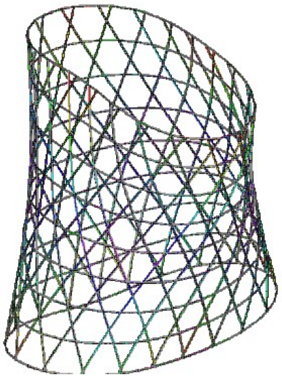

fig. 2.4 dynamic analysis

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. 2.1).

MATERIAL	**Al 2024**	**Hs/Ep**	**Hs/Ep + 5% CNs**
YOUNG'S MODULUS [Pa]	70E9	12E10	16E10
MASS [Kg]	206. 3	84.1	69.7

tab.2.1 Structure Mass calculated for different materials

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

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

3. Synthesis of Carbon Nanotubes

Carbon Nanotubes where synthesized by three different process:

- voltaic arc discharge in inert atmosphere (Helium)
- voltaic arc discharge submerged in water
- CO_2 laser ablation.

Fig. 3.1 shows the equipment for arc discharge in helium.
Fig. 3.2 shows the equipment for submerged arc discharge.

fig. 3.1 arc discharge equipment in inert gas

fig. 3.2 water submerged arc discharge

Pure graphite doped with yttrium was utilised. Normal applied voltage: 20-25 V. Current output: 50-60 A in helium, 60-90 A in water.
The fig. 3.3 shows the equipment utilised for laser ablation (900 W, weave length 10.6 μm, Argon flux: 60 l/min).

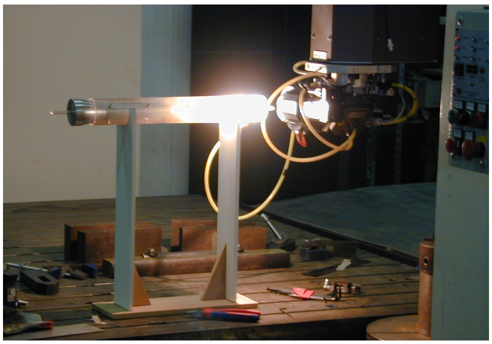

fig. 3.3 laser ablation equipment

The results obtained by arc discharge in helium resulted the most interesting one, with regard to the process productivity and simplification of the operations required for nanotubes purification from reaction products.
Overall production process (synthesis, separation and purification, functionalising) still remains complex, and a full development of possible industrial applications requires a target of Carbon Nanotubes production capacity not yet available.

4. Morphological analysis of Carbon Nanotubes

The procedure applied for the qualification of CN production is described and discussed.
By simple optical microscopy it is possible to perform a first characterization of the obtained product, after the arc discharge application. The surface morphology and of the electrode colour (cathode) offers a means to select the region where the concentration of CN is higher.

The region characterised by grey colour (fig 4.1) is characteristic for the high concentration of CN. More in detail (fig. 4.2) a crystalline aspect determines where the CN concentration is maximum (fig. 4.2 position **B** and **C**).

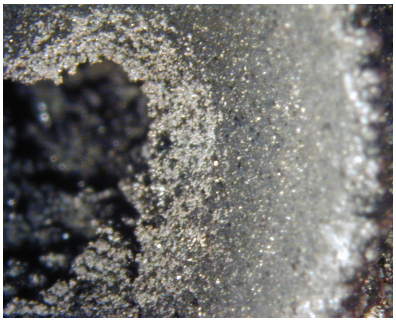

fig. 4.1 optical microscopy analysis, graphite cathode electrode after the arc discharge

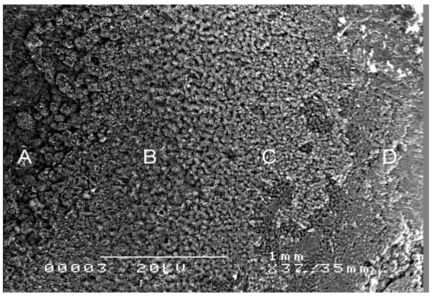

fig. 4.2 SEM imagine of different morphologies of the cathode

By means of electronic microscopy (SEM), finally, it is possible to observe directly the formation of CN bundles and the efficiency of the adopted process methodology. It is possible also to have an indication of the grade of purity attained.
Figs. 4.3, 4.4 and 4.5 shows SEM images of the regions B, C and D, respectively, marked on fig. 4.2 The presence of CN is clearly evidenced by filament structures in figs. 4.3. and 4.4 (regions B and C). The amorphous structures of fig. 4.4 (Region D) evidence practical absence of CN.
The confirmation that the filament structures of figs. 4.3 and 4.4 can be referred to the formation of CN can be obtained only by TEM (Transmission Electron Microscopy) images.
Literature data report that the preparation of CN samples for TEM observation needs not less than 3 hours.
The Authors developed a simple methodology for a rapid preliminary observation of CN, here described:

- positioning of a 100 mesh Ni grid on a filter containing CN powder
- mechanical deposition of powders by compression
- deposition of a C film (metallization).

Figs 4.6 and 4.7 show TEM images (200 KV) of carbon nanotubes, obtained using the described preparation.

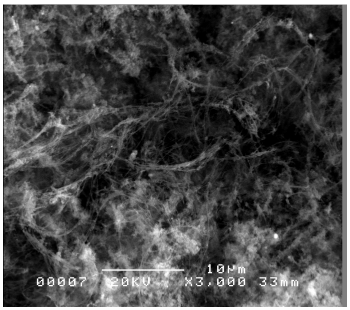

fig. 4.3 region **B,** SEM analysis

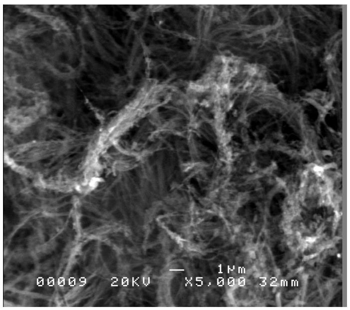

fig. 4.4 region **C,** SEM analysis

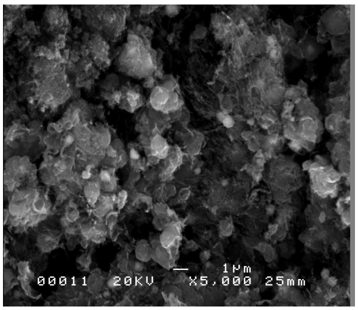

fig. 4.5 region **D,** SEM analysis

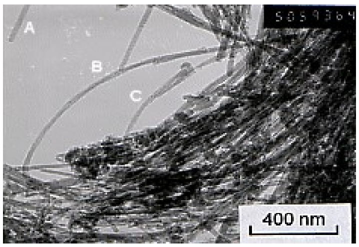

fig. 4.6 STEM imagine of carbon nanotubes bundles (50000x)

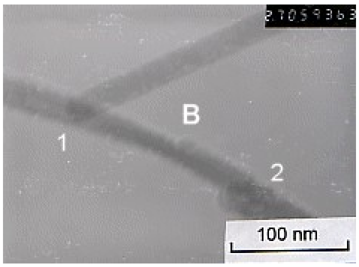

fig. 4.7 STEM imagine of carbon nanotube (270000x)

Finally, EDS analysis can be utilised to evidence the presence of impurity in the final product, typically metals used as catalyst.

Fig. 4.8 shows EDS analysis of the cathode, after arc discharge. The presence of the adopted catalysts (*Ni*, *Y*) is clearly evidenced.

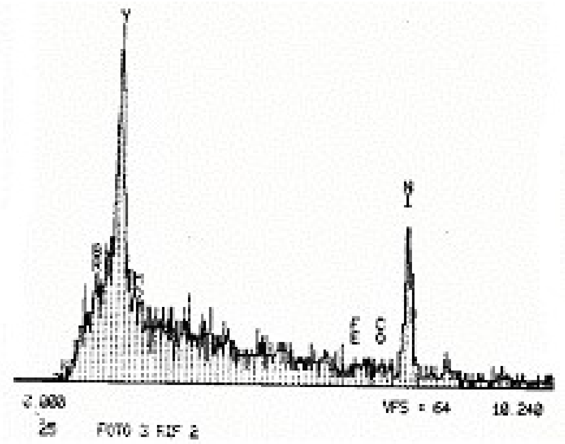

fig. 4.8 EDS analysis of the cathode electrode

5. Carbon Nanotubes Purification

As synthesized, carbon nanotubes must be purified before their utilization, as they appear to be surrounded by a mass of amorphous carbon.

One possible methodology is the partial oxidation by gas fluxing in a controlled atmosphere, at low oxygen partial pressure.

TDA tests (Thermal Differential Analysis) where performed, using 50 mg of materials sampled from the cathode, in correspondence of previously describe grey region, 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.

Results obtained by TDA test are shown in fig. 5.2.

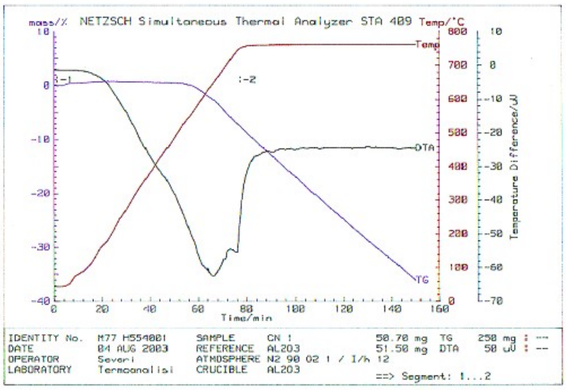

fig. 5.2 DTA – TG test results

In the temperature range 500-600°C there is a reaction of the sample with the atmosphere. The preferential oxidation of amorphous carbon is expected to occur.

Consequently, the purification process was successively performed with a new sample in the TDA apparatus using the following experimental conditions:

- fluxing in (slightly) oxidant atmosphere (N_2 90%, O_2 10%)
- T max = 530 °C
- Time: 2.5 hours.

The results obtained are characterised by SEM analysis, performed before and after the purification test, figs. 5.2 and 5.3 respectively. It is evident (fig. 5.3) 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.

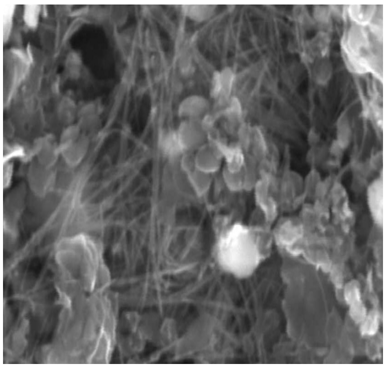

fig. 5.2 cathode deposit morphology before purification

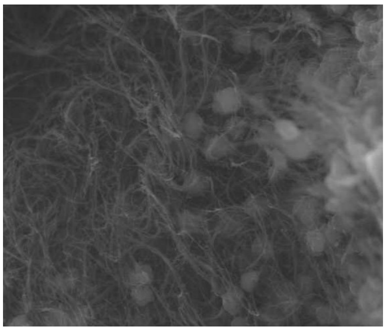

fig. 5.3 cathode deposit morphology after purification

6. 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. 6.1).

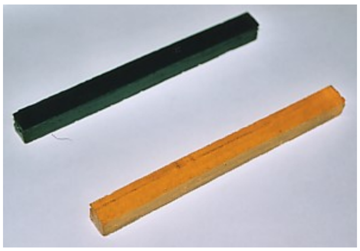

fig. 6.1 specimens for mechanical tests

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. 6.2 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.

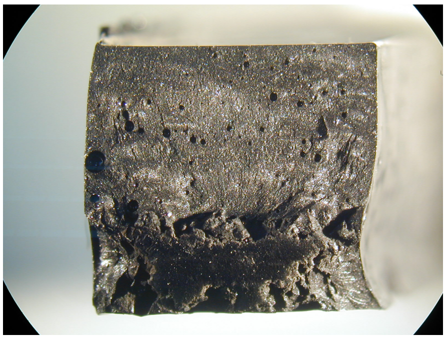

fig. 6.2 optical analysis of composite sample

To understand the fracture-mechanic behaviour of the composite, SEM characterizations of fracture surface were performed.
Fig. 6.3 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.

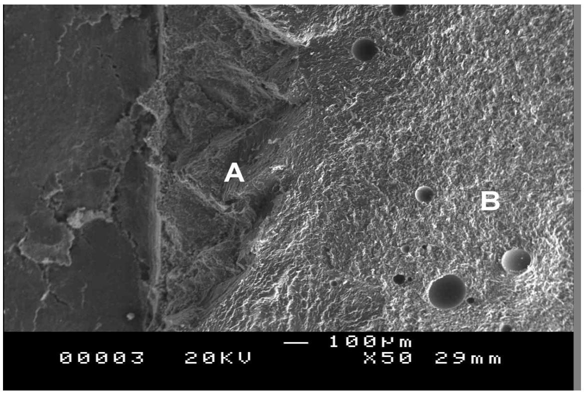

fig. 6.3 SEM analysis of fracture surface of composite specimen (10% powder addition)

On the contrary, the sample containing 20% powder, preferential directions of crack propagations are observed (fig. 6.4, area **A**,**B**, **C** and **D**).
The presence of preferential direction is due to the non-uniformity of powders dispersion in the matrix.

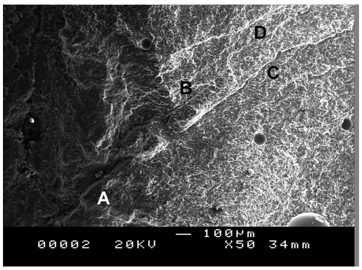

fig. 6.4 SEM analysis of fracture surface of composite specimen (20% powder addition)

A further observation is that the fracture lines change direction in correspondence of cavities (or voids).
In fig. 6.5 two fracture lines (**A** & **B**) are deviated by the presence of a void (see points **C** & **D**), and are stopped in point **E**.

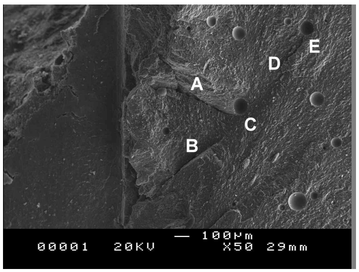

fig. 6.5 SEM analysis of fracture surface of composite specimen (20% powder addition)

7. Production of a flat anisogrid lattice panel

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 7.1) 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.

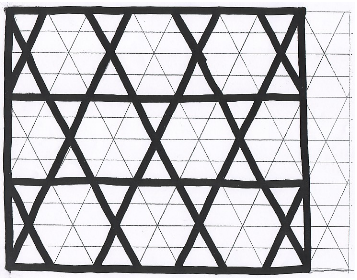

fig. 7.1 structure preliminary design

fig. 7.2 mould

fig. 7.3 flat anisogrid lattice prototype

Fig. 7.3 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. 7.4 & 7.5), the positive simulacra of the lattice structure was realised by rapid prototyping, the final mould (negative) was obtained in silicon resin.

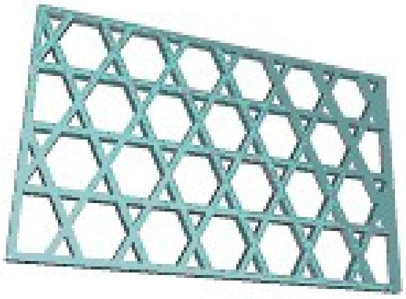

fig. 7.4 CAD design of the anisogrid lattice flat element

Finally, a 3D–CAD model was prepared to be used for rapid prototyping of a positive cylindrical geometry of an anisogrid lattice structure (fig. 7.6). Final silicon mould (negative) can be easily obtained.

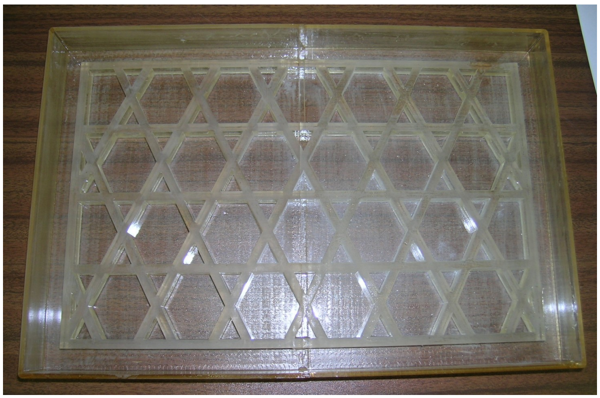

fig. 7.5 rapid prototyping positive mould

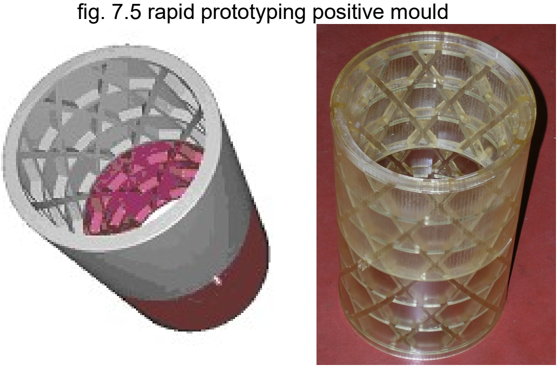

fig. 7.6 3D - CAD design of the anisogrid lattice cylindrical element and rapid prototyping positive mould

8. Conclusions

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.

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