# Multi-wall carbon nanotubes/ cyanate ester composites towards the development of novel materials with tailored mechanical, electrical, thermal and RF properties for space antenna reflector applications

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CANEUS 2010 WORKSHOPS
International Collaborative Aerospace Development
Micro Nanotechnologies: From Concepts to Systems

# Contents

# Introduction

## *Facts and Figures*

### Activity Facts:

- **Activity:** ESA contract
- **Duration:** 2007-2009
- **Funding:** ESA-Greek Task Force under the 1$^{st}$ Call for Ideas (2007)
- **ESA Technical Officers:**
  - Peter De Maagt (TEC-EE)
  - Thomas Rohr (TEC-QTM)

### AML/UoP Facts:

- In operation since **1980**
- Part of the Department of Mechanical Engineering and Aeronautics/ University of Patras, Greece
- General field of research: ***MATERIALS & STRUCTURES***
- Focused research topic: science, technology and applications of **COMPOSITE MATERIALS**
- Three major R&D groups: **Materials – NDT/SHM - Design&Analysis**
- Permanent staff: 5 University Professors, 6 PhD holders, 25 Engineers and PhD students
- More than 380 Journal Publications, 500 Conference Presentations and 9 Published Volumes
- Involvement in over **30** EU/ESA or Industry R&D projects


***Enhanced mechanical, electrical and thermal performance*** for Fiber Reinforced Polymers (FRPs) used for space antenna applications is a ***primary requirement*** during their development phase.

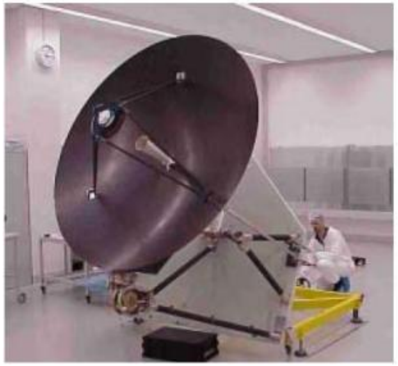
✦

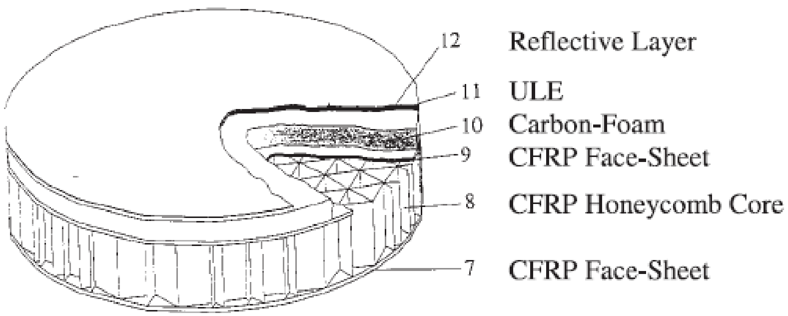
Currently the main requirements (antenna reflector) of low mass, high manufacturing accuracy, enhanced thermo-elastic stability, increased stiffness and high reflectivity are covered by using ***various configurations of carbon reinforcements*** (biaxial, tri-axial, weave etc), ***optimized lay-ups/topologies*** and ***advanced and strictly controlled manufacturing methods***. This approach proved very efficient towards the direction of mass saving and increased stiffness of those structures.

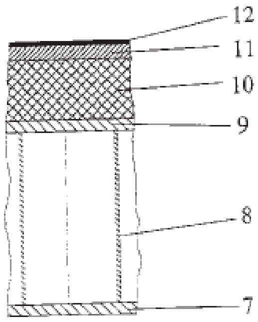
✦

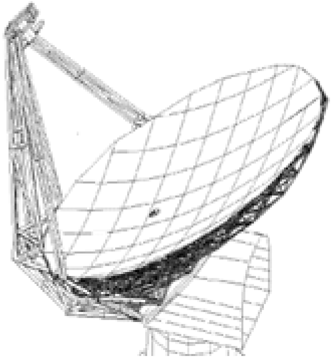
On the other hand the ***inherent anisotropy and the low conductivity*** (thermal/electrical) of all FRPs materials are still creating certain application drawbacks towards mainly the fulfillment of the requirements for ***high reflectivity and good thermo-elastic stability in complex shapes***.

**The objective of this activity was to investigate CNT-modified fiber reinforced polymer materials as a novel material for the manufacturing of space antenna reflectors.**

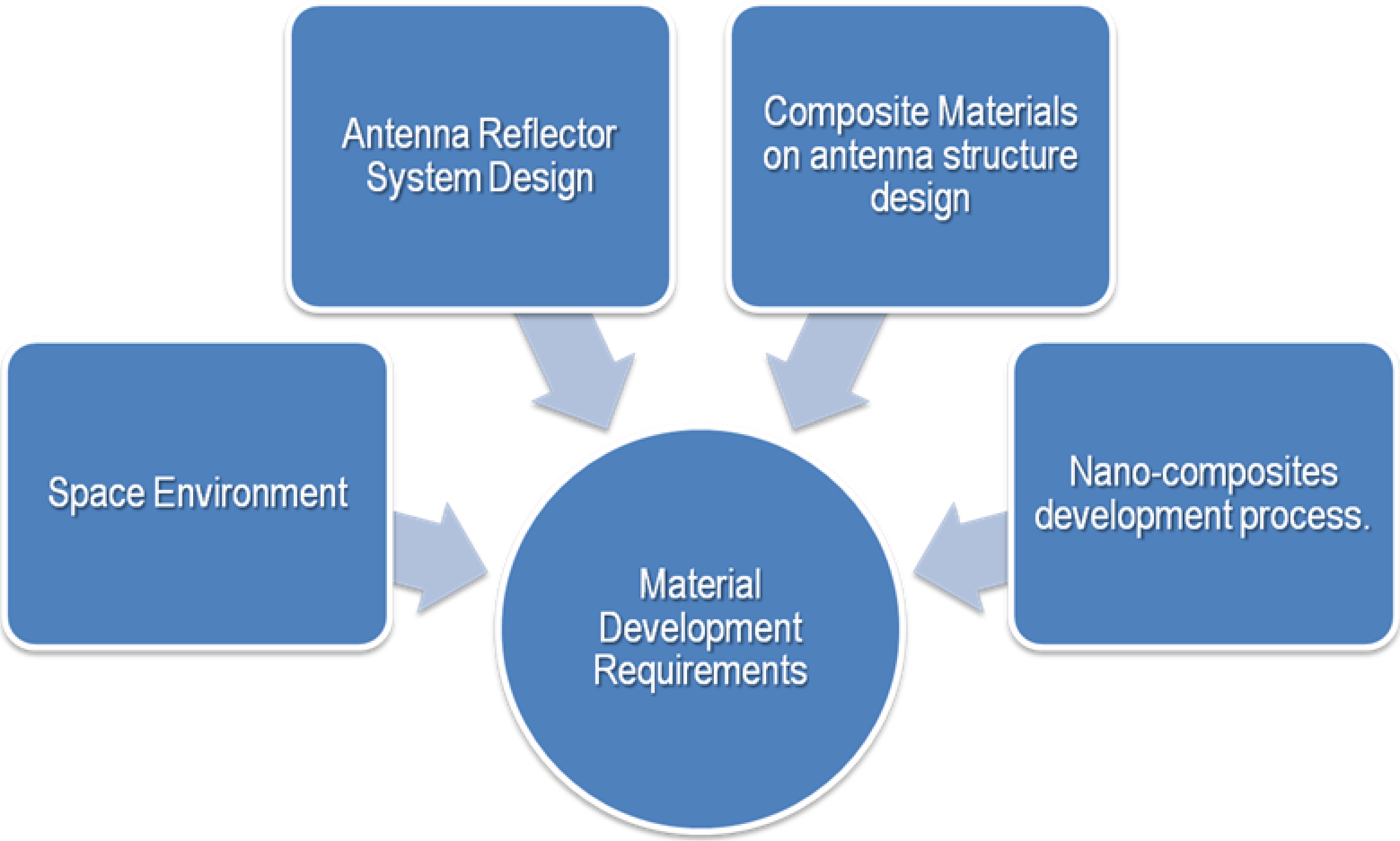




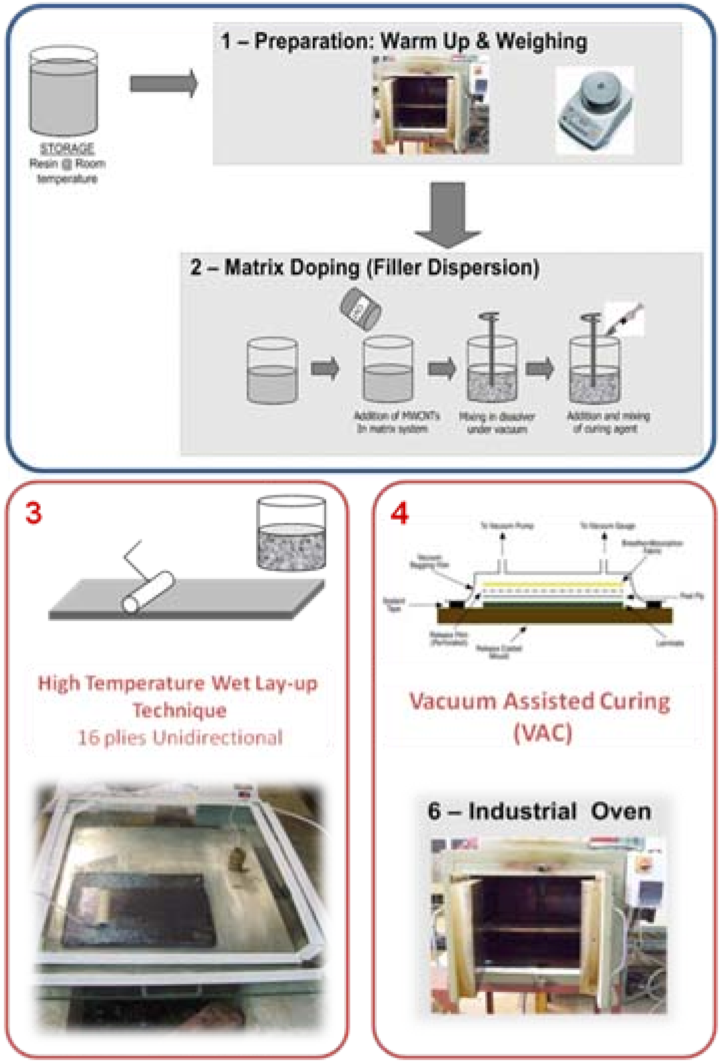
# Material Development



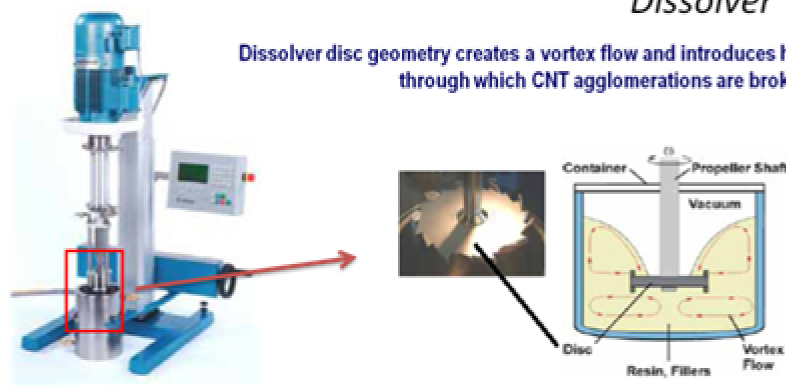
# Material Development



- Matrix: *Cyanate Ester System*
  - PRIMASET® DT-4000 (Lonza, Switcherland)
- Multi-walled Carbon Nanotubes MWCNT
  - Non-Functionalized (ARKEMA, France)
    - (diameter: 10-15 nm, length≥ 500 nm)
  - Amino-Functionalized (Nanocyl, Belgium)
- Carbon Fiber Reinforcement:
  - Unidirectional, aero grade, 140 $gr/m^2$




*Dispersion of MWCNT into the resin system using Dissolver Technology*




The materials

- CFRP-DT-4000 - 16_UD - NEAT
- CFRP-DT-4000 - 16_UD - 0.5% MWCNT
- CFRP-DT-4000 - 16_UD - 1% MWCNT

Additionally

- CFRP-DT-4000 - 16_UD - 0.5% NH2(funct.-)- MWCNT
- CFRP-DT-4000 - 16_UD - 1% NH2(funct.-)-MWCNT

# Material Development



**Apparent Fiber Volume Fraction (Vf)**:

- 46±3 %

**Degree of Cure(DSC)**:

- 92±3 %

**Optical Microscopy**:

- *low void content*

**Ultrasonic Inspection (C-scan)**:

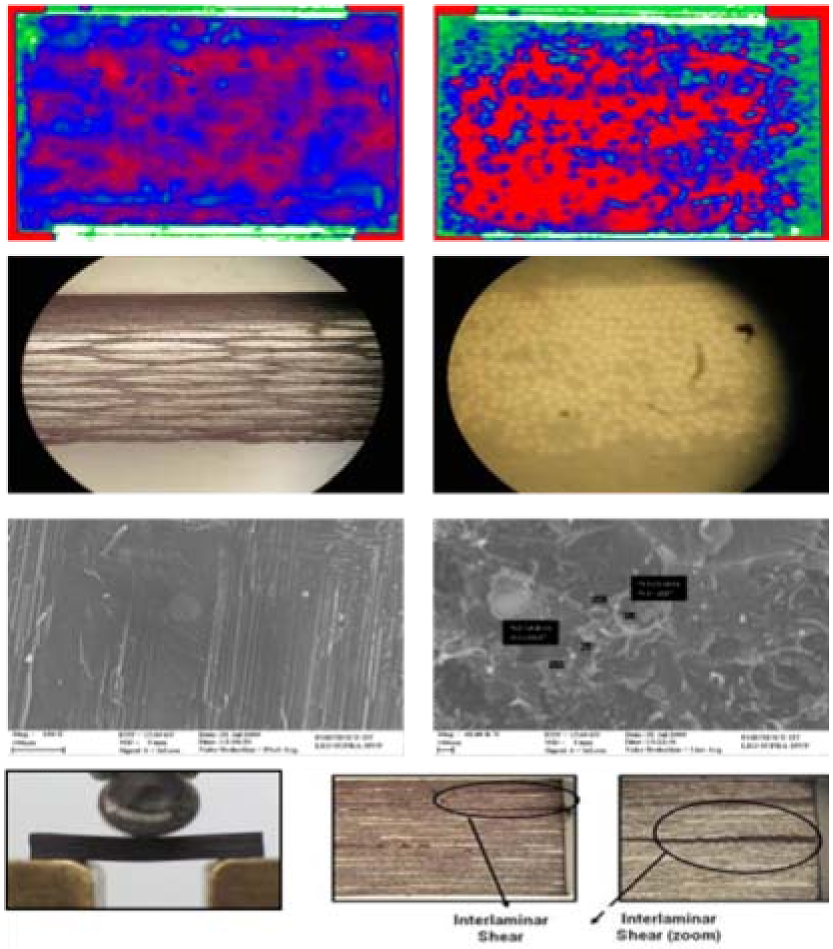
- low void content
- uniform quality of plates

**Scanning Electron Microscopy (SEM)**:

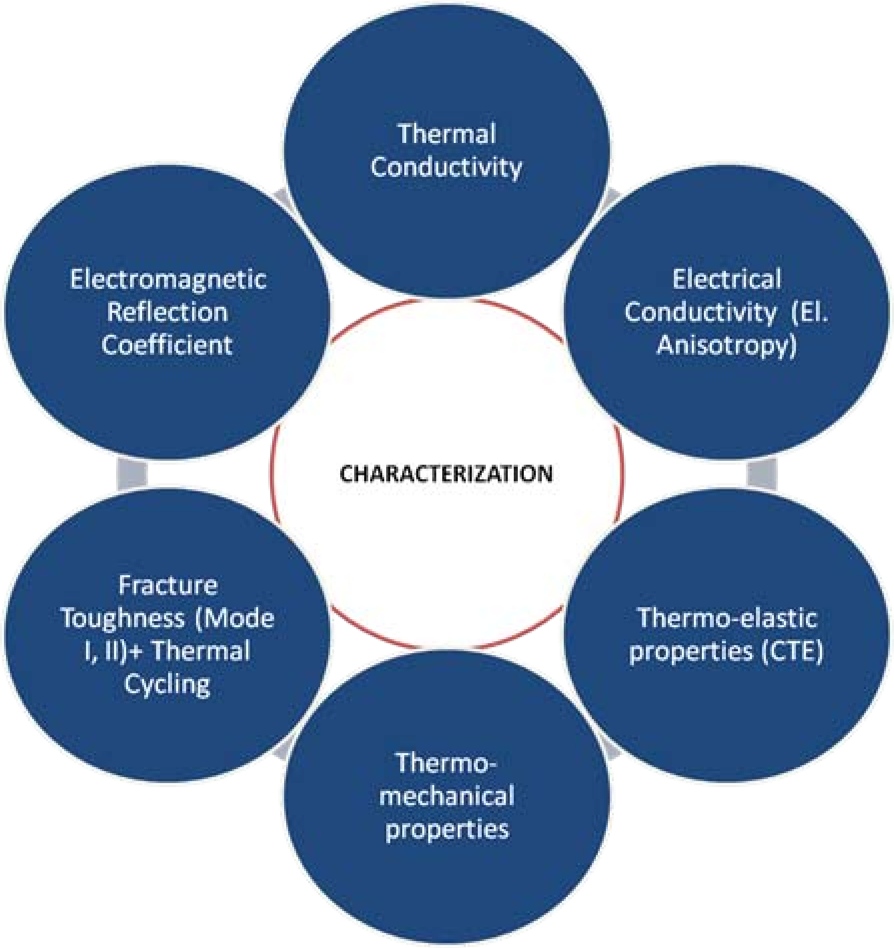
- adequate CNT distribution in CE matrix.

**Short Beam Shear Strength (SBSS/ILSS)**:

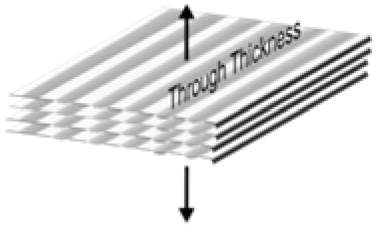
- Low experimental deviation (3%) of Measured Max Strength

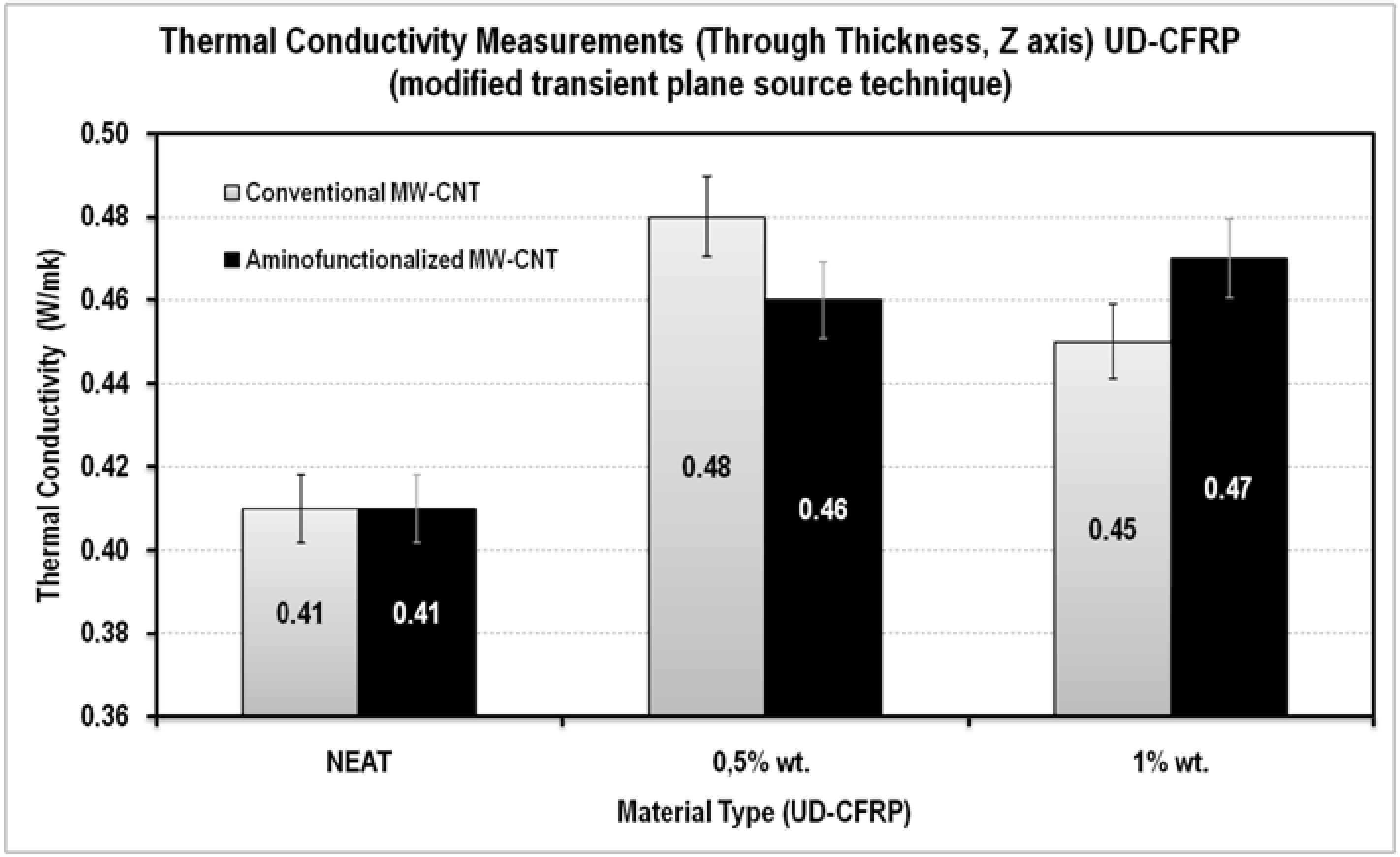


# Material Characterization



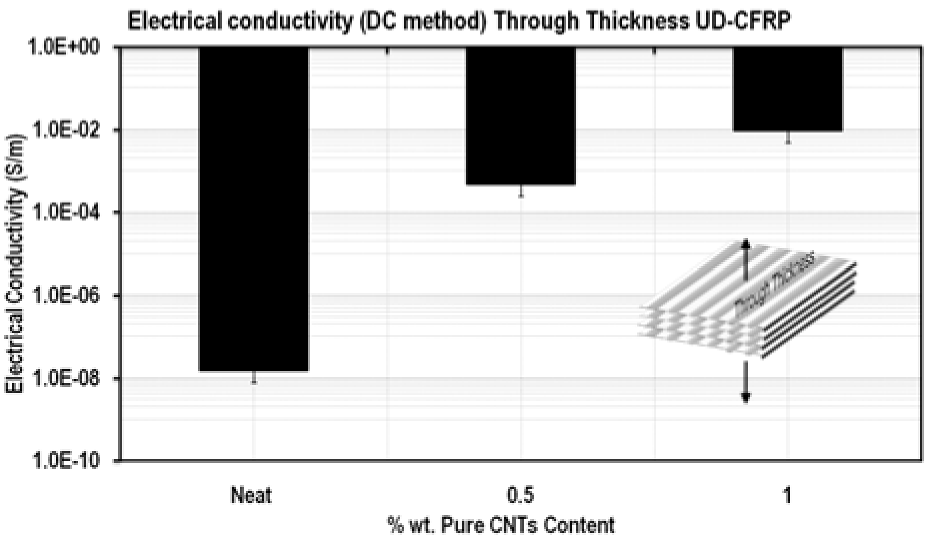
Mathis TCi Thermal Conductivity Analyzer was used. The Mathis TCi is based on the modified transient plane source technique

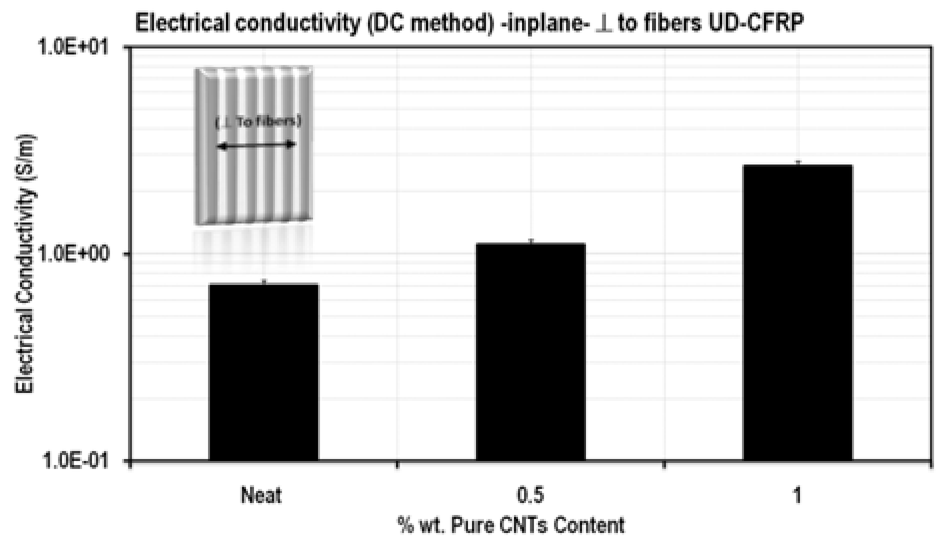


# Material Characterization





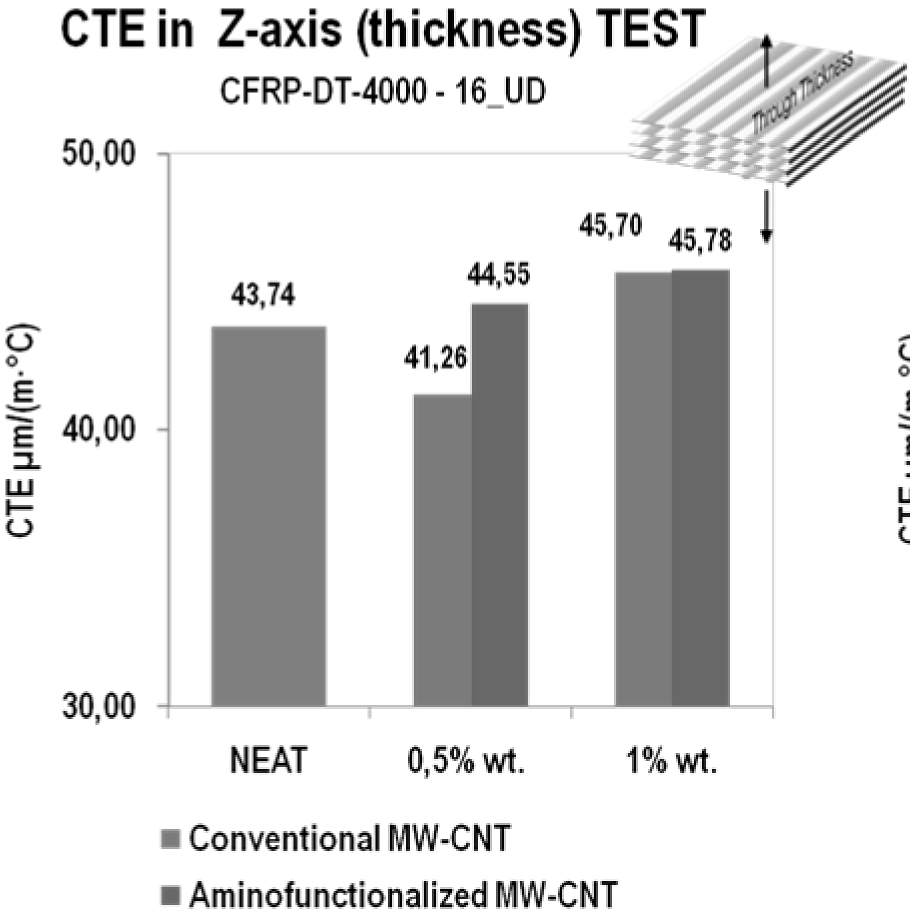



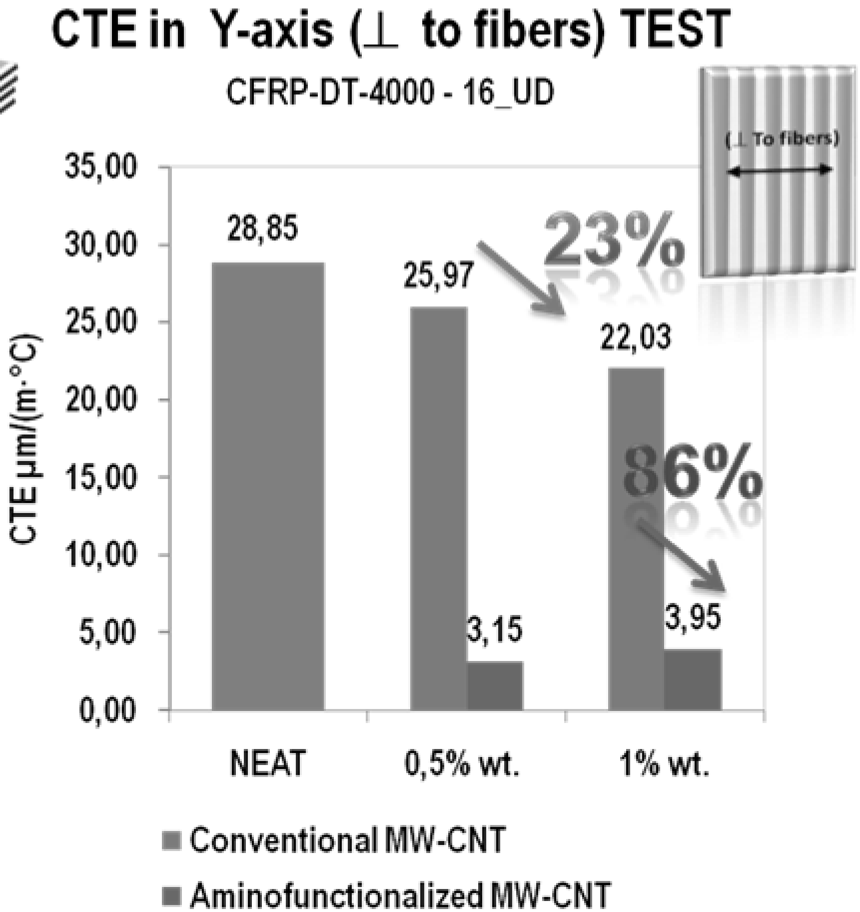

**Through thickness :**

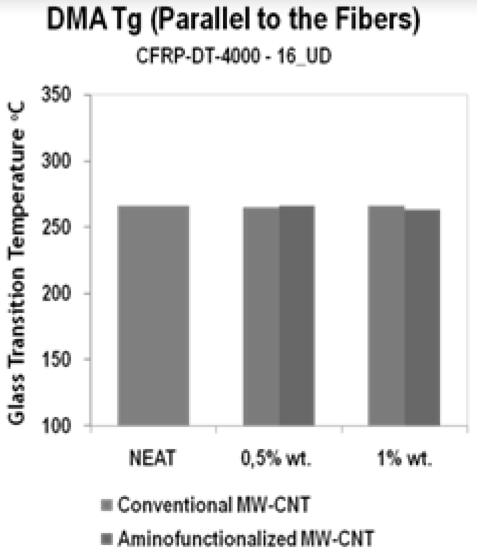
- *5-6 orders of magnitude increase of electrical conductivity*

**In plane ⊥ to fibers :**

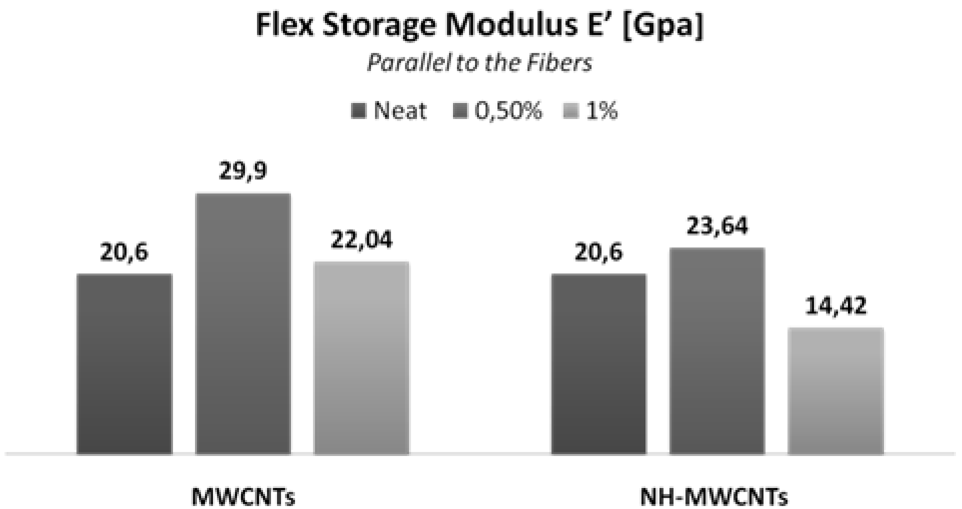
- *1 order of magnitude increase*


CTE in Z-axis (thickness) TEST
CFRP-DT-4000 - 16_UD
Through Thickness
50,00
40,00
30,00
CTE μm/(m·°C)
43,74
41,26
44,55
45,70
45,78
NEAT
0,5% wt.
1% wt.
Conventional MW-CNT
Aminofunctionalized MW-CNT

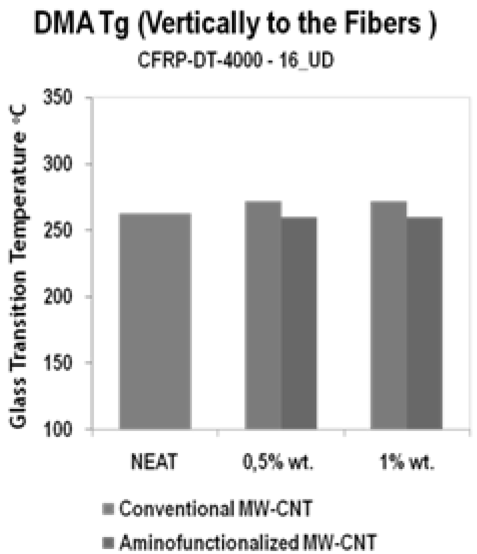

CTE in Y-axis (⊥ to fibers) TEST
CFRP-DT-4000 - 16_UD
(⊥ To fibers)
35,00
30,00
25,00
20,00
15,00
10,00
5,00
0,00
CTE μm/(m·°C)
28,85
25,97
3,15
22,03
3,95
23%
86%
NEAT
0,5% wt.
1% wt.
Conventional MW-CNT
Aminofunctionalized MW-CNT



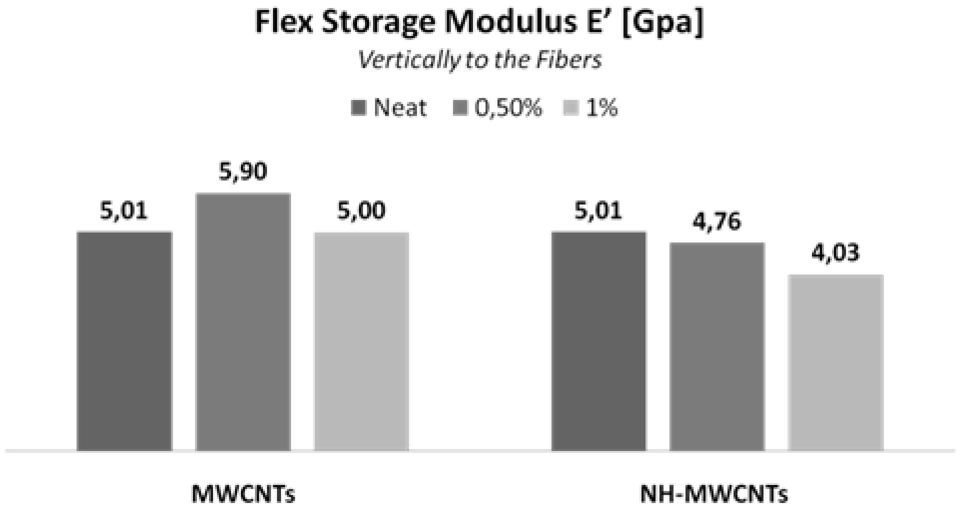
DMA Tg (Parallel to the Fibers)
CFRP-DT-4000 - 16_UD
Glass Transition Temperature °C
350
300
250
200
150
100
NEAT
0,5% wt.
1% wt.
Conventional MW-CNT
Aminofunctionalized MW-CNT

Flex Storage Modulus E' [Gpa]
Parallel to the Fibers
Neat
0,50%
1%
20,6
29,9
22,04
20,6
23,64
14,42
MWCNTs
NH-MWCNTs

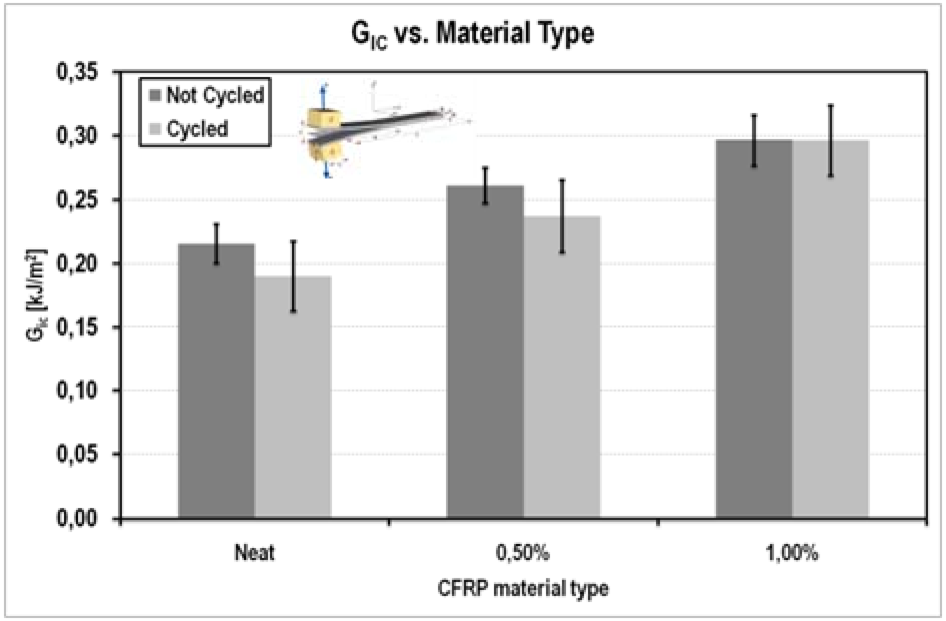
DMA Tg (Vertically to the Fibers )
CFRP-DT-4000 - 16_UD
Glass Transition Temperature °C
350
300
250
200
150
100
NEAT
0,5% wt.
1% wt.
Conventional MW-CNT
Aminofunctionalized MW-CNT

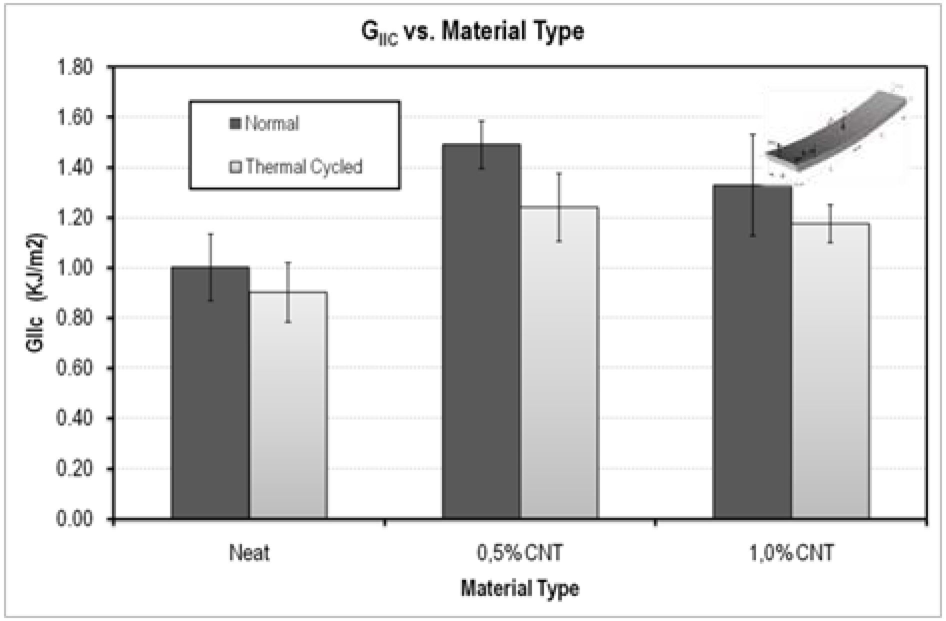



Flex Storage Modulus E' [Gpa]
Vertically to the Fibers
Neat
0,50%
1%
5,01
5,90
5,00
5,01
4,76
4,03
MWCNTs
NH-MWCNTs

# Material Characterization

## *Fracture Toughness*



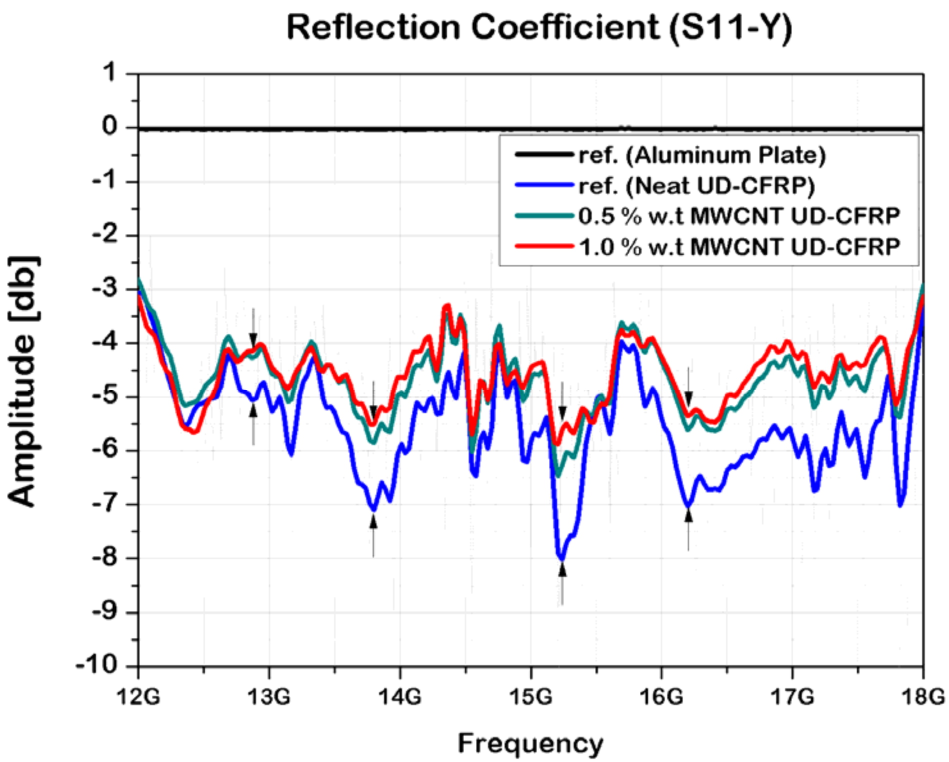



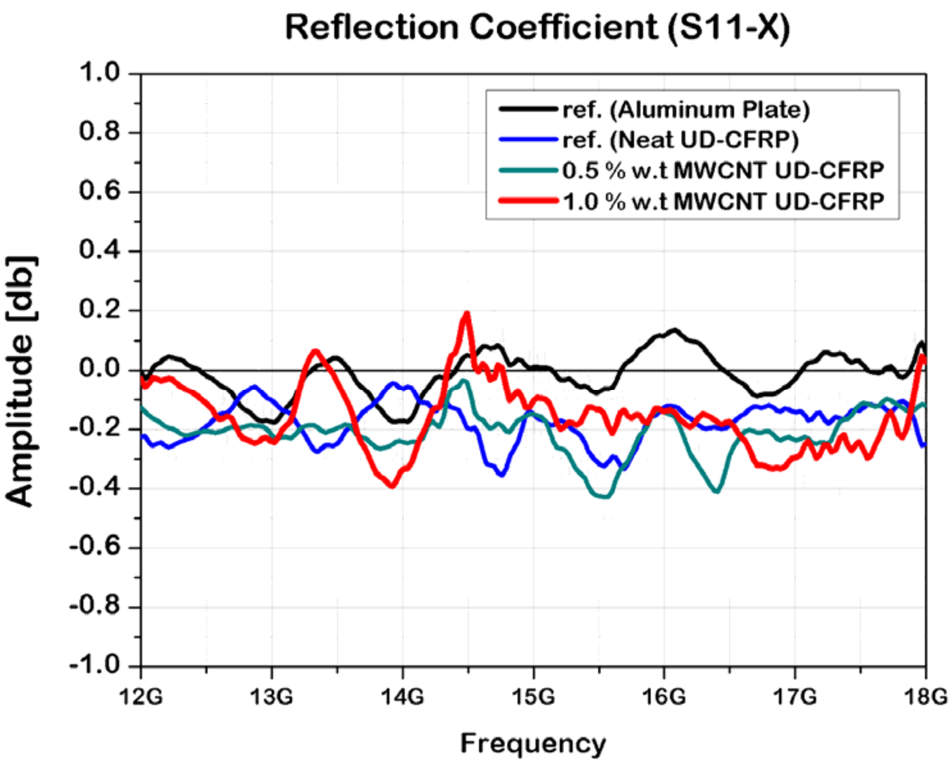

- ***CNT doped CFRP exhibit higher Fracture Toughness Values in both modes (I, II)***
  - *Up to 36% for mode I (1.0 % w.t CNT)*
  - *Up to  49% for Mode II (0.5 % w.t CNT)*
- ***Similar effect also after thermal cycling***

Thermal Cycling: 10 cycles of 160°C (10 minutes) / -170°C (10 minutes)

# Material Characterization

## *Electromagnetic Properties*



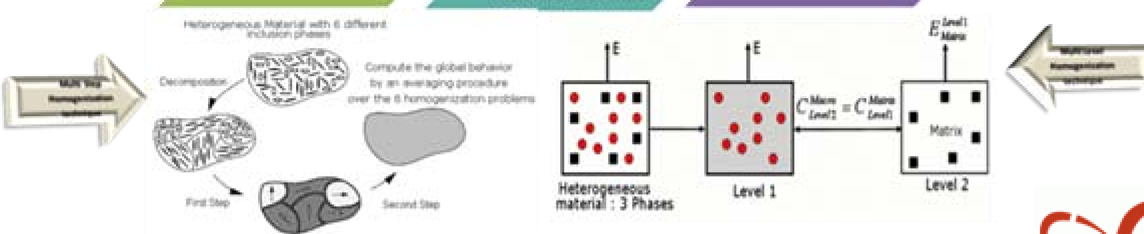



**Investigated material system**
- **Nanocomposite (Nano-reinforced polymer)**

**Modeling methods**
- *Discrete → computational chemistry*
- **Continuum → computational mechanics**
- *Combination of them → multi scale modeling*

**Continuum modeling tools**
- **Mean Field Methods → micromechanical models**
- *Finite Element Methods → finite element models*

**MEF Modeling Approach** → Based on the development of a shapeless material volume. → Use of classical micromechanical models.

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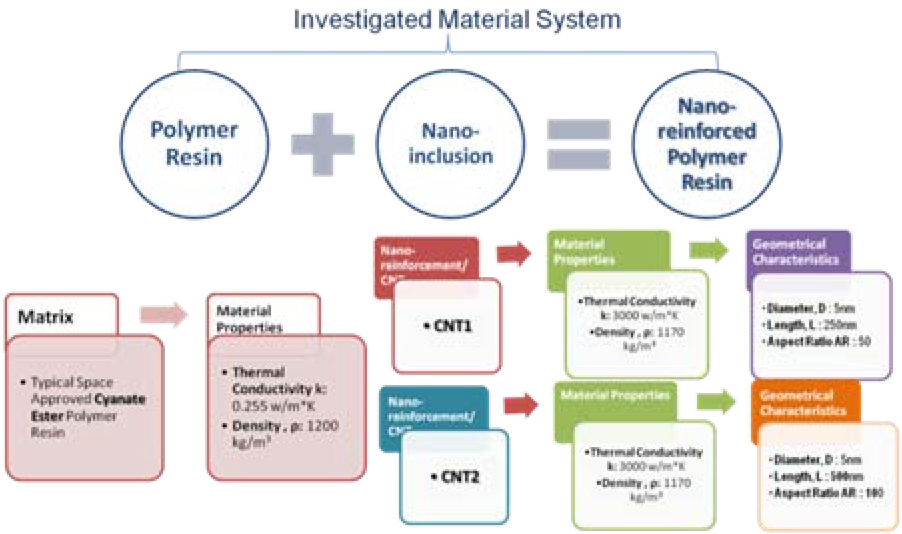
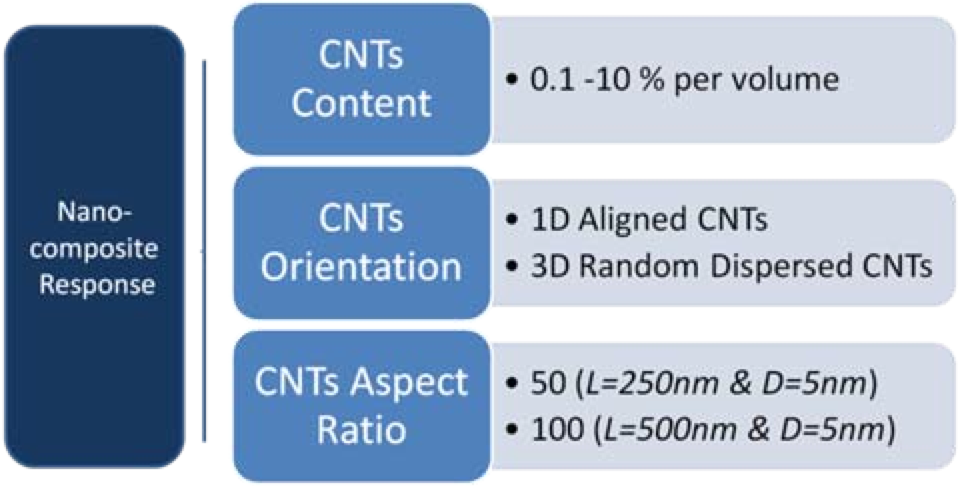
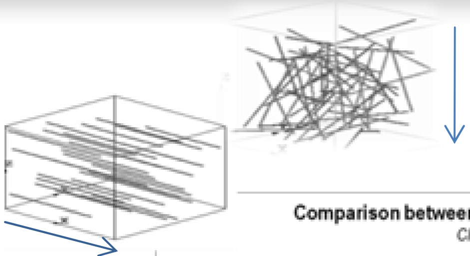
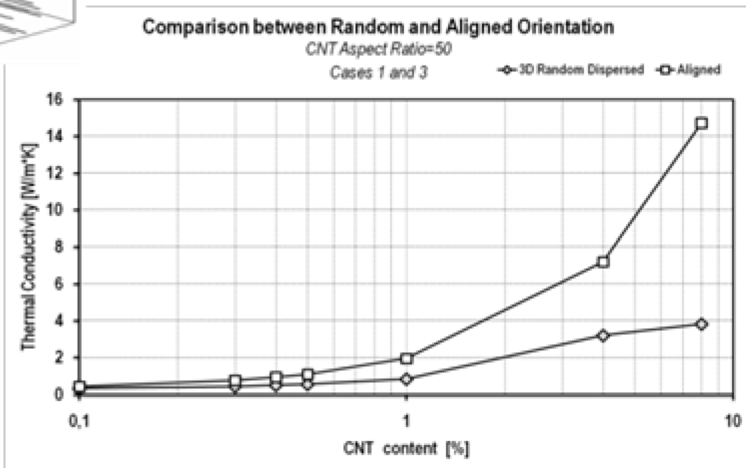
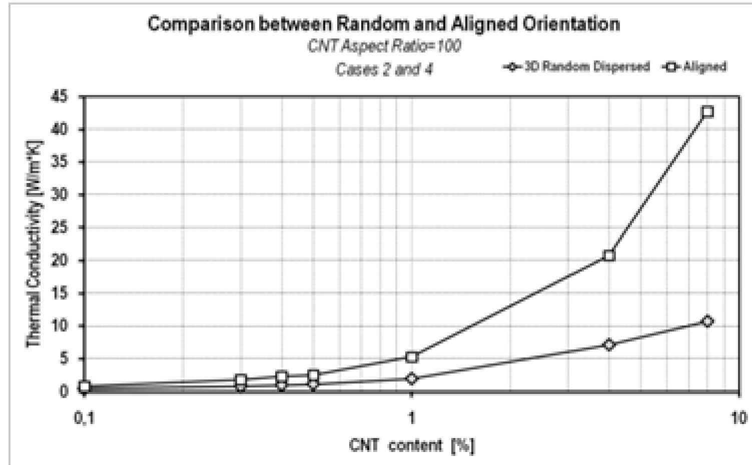
# *Investigated Property ⇨ Thermal Conductivity*








- **CNTs Content:**
  - Higher the content is higher the material's thermal conductivity is achieved.
  - More abrupt increase of thermal conductivity is observed for CNTs contents higher than 1% per volume.
- **CNTs Orientation:**
  - The aligned oriented CNTs leads to higher thermal conductivity values.
- **CNTs Aspect Ratio:**
  - The higher aspect ratio leads to higher the thermal conductivity.
- **MEF modeling approach:**
  - Can provide a first sense of the material system's thermal properties.

# Achievements

**MATERIAL DEVELOPMENT:**

- CNT-Polymers:
  - Feasibility of developing polymers with homogeneous distribution of CNT.
- CNT-CFRP:
  - Development and verification of a setup for high temperature wet lay up
  - Optimization and better understanding of curing parameters
  - Manufacturing of CNT-composites with cyanate ester matrix having reliable quality

**MATERIAL PROPERTIES:**

- CNT-CFRP:
  - Increased fracture resistance (Mode I & II)
  - Resistance to thermal cycling degradation of fracture properties
  - Reduction on CTE ( ⊥ fibers )
  - Increase on Thermal Conductivity, k (~10%) (Through Thickness)
  - One order of magnitude increase on Electrical ( ⊥ fibers )

# Lessons Learned

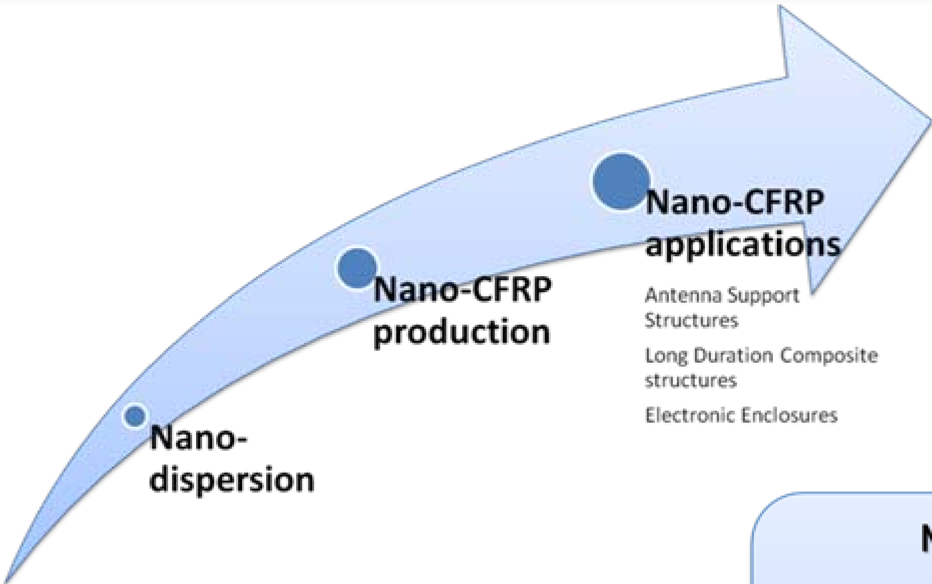
**CNT-POLYMERS:**

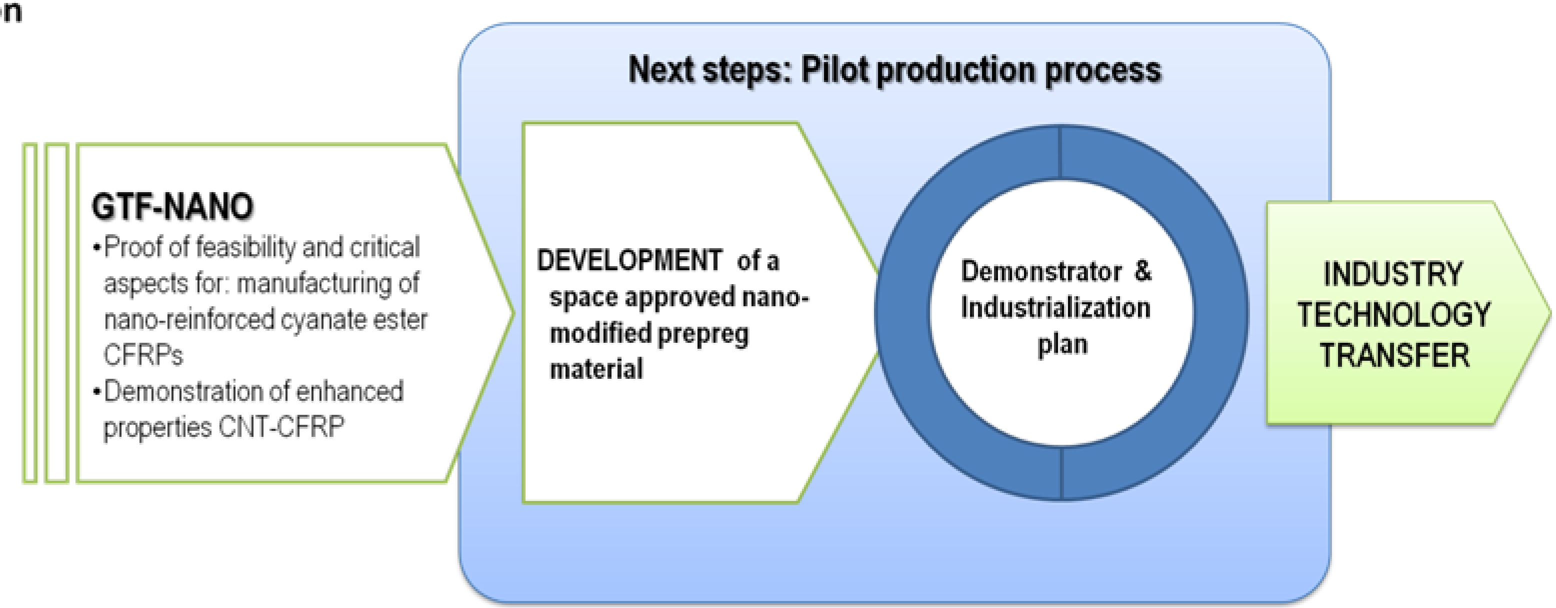
- Each matrix materials has its own special characteristics
  - Cyanate esters: handling, viscosity changes-stability of dispersion
- CNT dispersion key issue controlled by viscosity drop during curing

**CNT-CFRPS:**

- Manufacturing techniques cannot be applied straightforward; adaptation to special properties of the materials is required.
- Composite manufacturing methods require customization in order to develop the CNT-modified composites

# Roadmap


Nano-dispersion
Nano-CFRP production
Nano-CFRP applications
Antenna Support Structures
Long Duration Composite structures
Electronic Enclosures


Next steps: Pilot production process
GTF-NANO
•Proof of feasibility and critical aspects for: manufacturing of nano-reinforced cyanate ester CFRPs
•Demonstration of enhanced properties CNT-CFRP
DEVELOPMENT of a space approved nano-modified prepreg material
Demonstrator & Industrialization plan
INDUSTRY TECHNOLOGY TRANSFER

# Thank you for your attention Questions?

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