



# NANOTECHNOLOGIES FOR COMPOSITE STRUCTURES

## From Nanocomposites To Multifunctional Nano-Enabled Fibre Reinforced Composites For Spacecrafts

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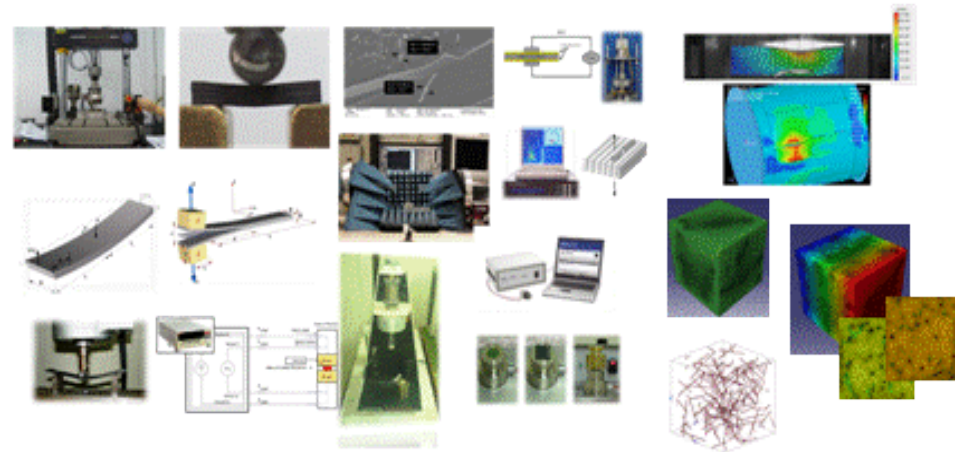
# AML/UoP

- 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**
- Four major R&D groups:
  - **Materials & Processes Development**
  - **Non Destructive Inspection & Structural Health Monitoring**
  - **Design & Analysis of Advanced Structures**
  - **Testing & Materials Characterization**
- More than 380 Journal Publications, 500 Conference Presentations and 9 Published Volumes
- Involvement in over **30** EU/ESA or Industry R&D projects



## AML-UoP

APPLIED MECHANICS LABORATORY  
UNIVERSITY OF PATRAS  
GREECE (HELLAS)



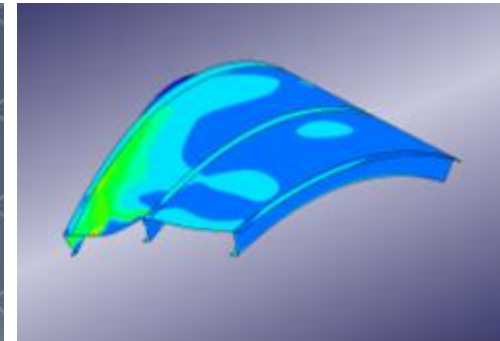
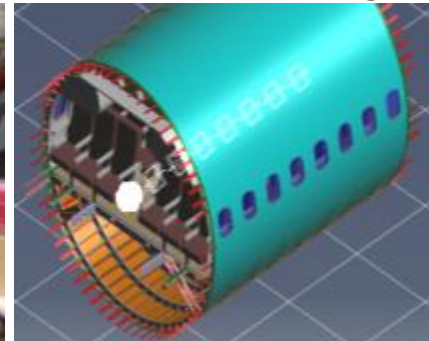
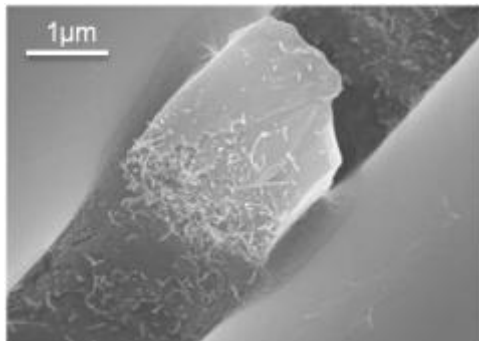
1. ESA-GSTP-(2013-2014) NAFO: Use of Nanocomposite reinforced Foams for Manufacture of Superlightweight Stiff Sandwich Panels
  2. ESA-GTF-(2012-2015) NANO-2: Design, Development, Manufacturing and Process Monitoring for structures of nano-modified multifunctional pre-preg materials targeting near term space applications.
  3. ESA-GSTP-(2011-2013) NACO-2: Non-conventional Matrix / CNT Reinforced Composites for Applications in Space - 2.
  4. EU-FP7-SPACE-(2011-2014) DEORBIT-SAIL: De-Orbiting of Satellites using Solar Sails
  5. ESA-NPI-(2009-2011) MINERVA: Methodology for Innovative Health Monitoring of Aerospace structures using dynamic response measurements and advanced signal process.
  6. ESA-TRP-(2010-2011) NAREMA: Nanotube Reinforced Structural Materials for Spacecraft Applications.
  7. ESA-TRP-(2009-2010) DELAT: Delamination Assessment Tool for Composite Structures.
  8. ESA-GTF-(2008-2009) NANO: Nano-modified fiber reinforced polymers in terms of mechanical, electrical and thermal properties towards the development of new materials for space applications.
  9. ESA-GSTP-(2007-2009) NACO: Non-conventional Matrix / CNT Reinforced Composites for Applications in Space.
  10. ESA-EDU-(2004-2007) YES2: Second Young Engineers Satellite Project. University of Patras YES2 Mechanical Center of Expertise.
- AML/UoP is member of the University of Patras Cube-sat QB50 Team (UPSAT)

# Adamant Composites Ltd.



- Young SME company
- Founded in 2012
- Based in Patras, Greece
- Highly experienced mechanical and aeronautics engineers
- Competences
  - Multi-scale reinforced Composites
  - Composites Processing and Manufacturing
  - Engineering Design and Analysis

[www.adamant-composites.gr](http://www.adamant-composites.gr)



# Overview of presentation

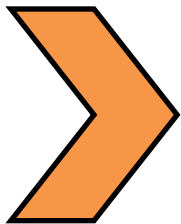
- Systemic approach of nano-reinforcement
- Review of implementation approaches for nano-reinforcement of composites
- Up-scaling strategies towards final structures
- Modeling capabilities for nano-reinforced composites

# Starting point

- Nano-composites have been around already since the '90s (e.g. carbon black)
- CNT gave a boost to research of nano-composites

## *The tipping point*

Nano-modification of FRP matrix



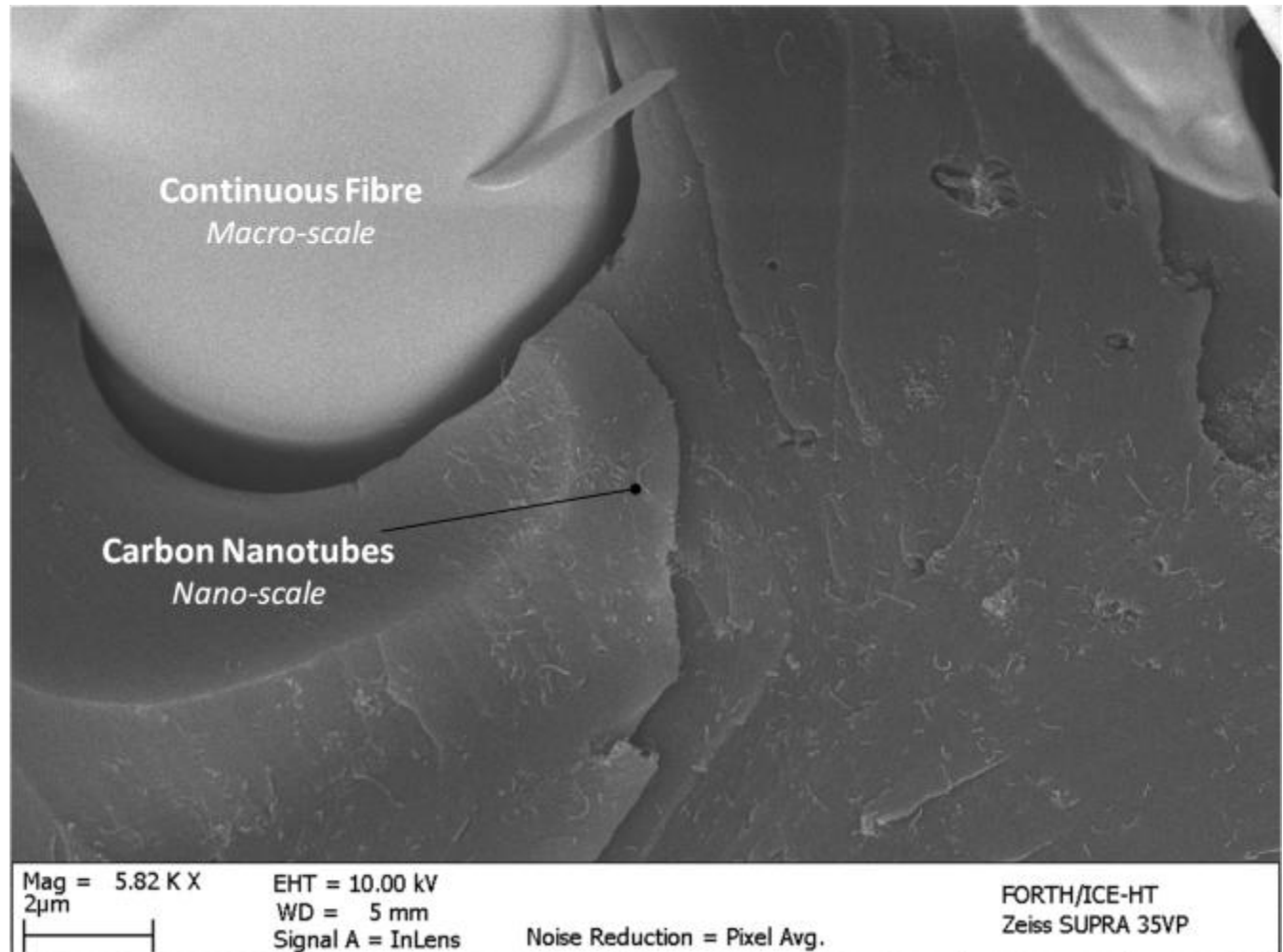
## Multi-Scale Composites

# Multi-Scale Composites

MACRO

MICRO

NANO





- **Nano-augmentation**
  - augment existing or new materials with nanomaterials with significantly enhanced properties for improvement of the structural and functional performance, and therefore reduction of structural weight and cost
- **Nano-engineering**
  - targeted use of different nanomaterials
- **Nano-enabling**
  - Nano-only

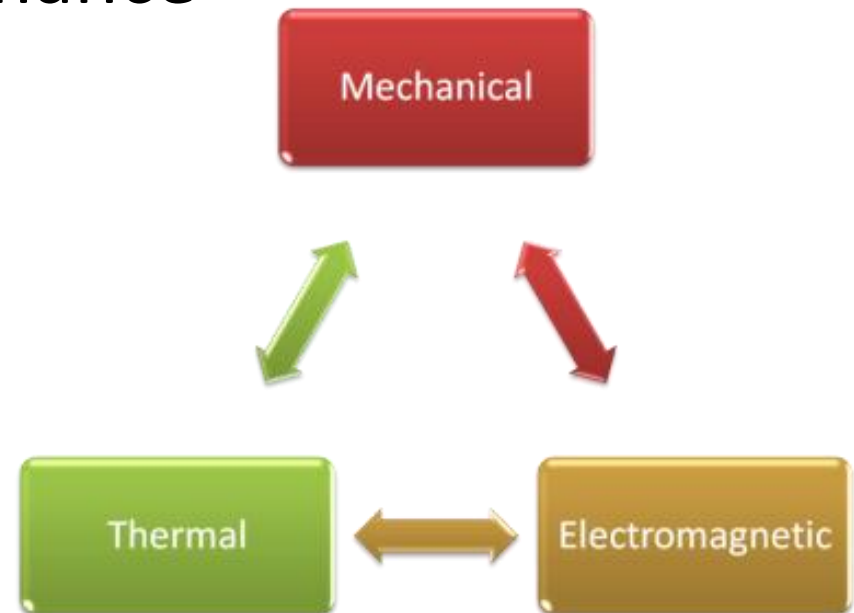


# Background Questions

- Progress has been made, but where do we stand after >10 years?
- What do the end-users see and say?
- Focus is on structural nano-composites

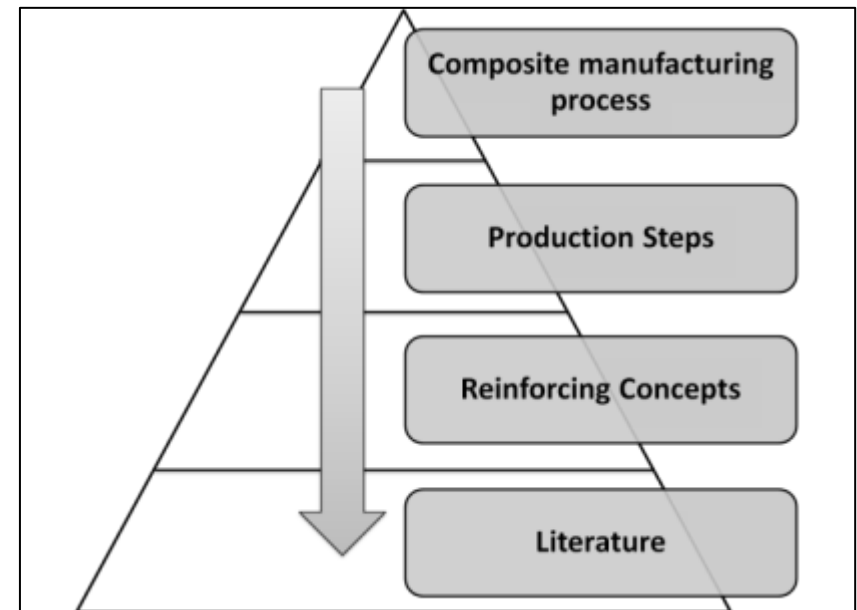
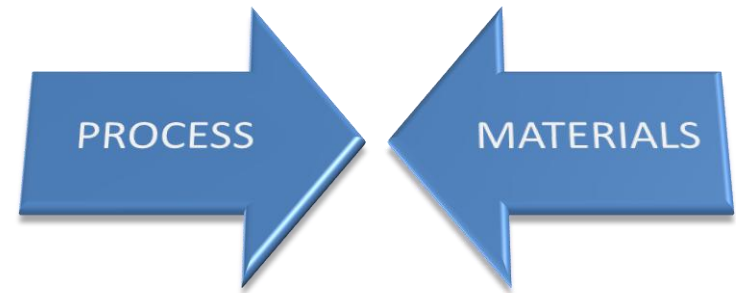
# Framework of presentation

- Structural Composites:  $E > 10\text{GPa}$ ,  $\sigma > 50\text{MPa}$
- Fibrous composites  $\rightarrow$  Manufacturing methods
- Review from the manufacturing perspective
- Multi-functional performance



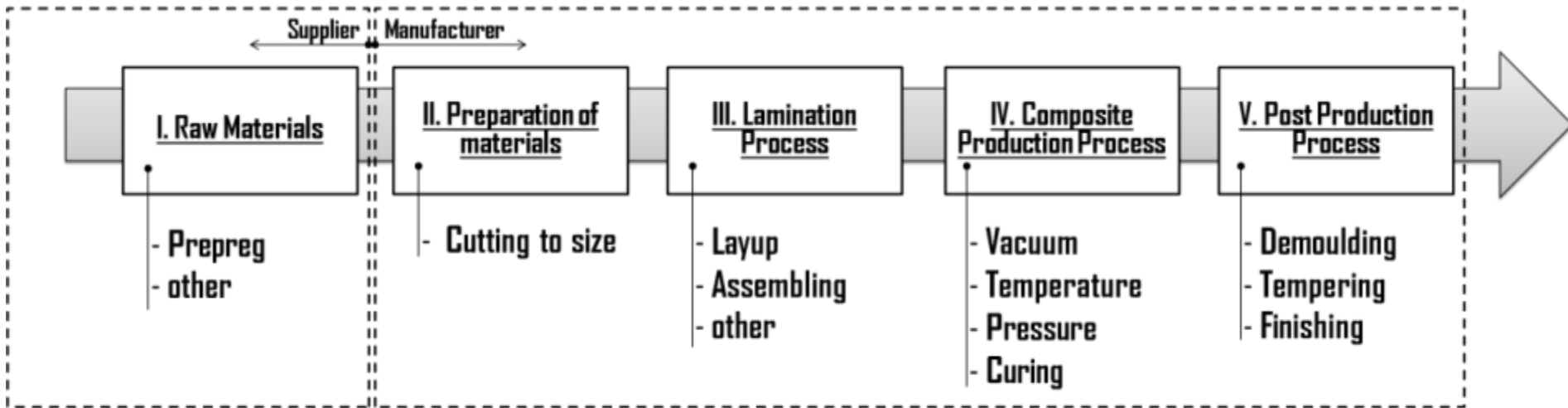
# State-of-the-Art *Approach*

- State-of-the-Art Approach
  - PROCESS
    - AC/prepreg process
    - Infusion-based/RTM processes
  - MATERIAL
    - Nano-materials used in literature for what property ?
      - Electrical
      - Thermal
      - Mechanical
      - Damping
      - Etc.

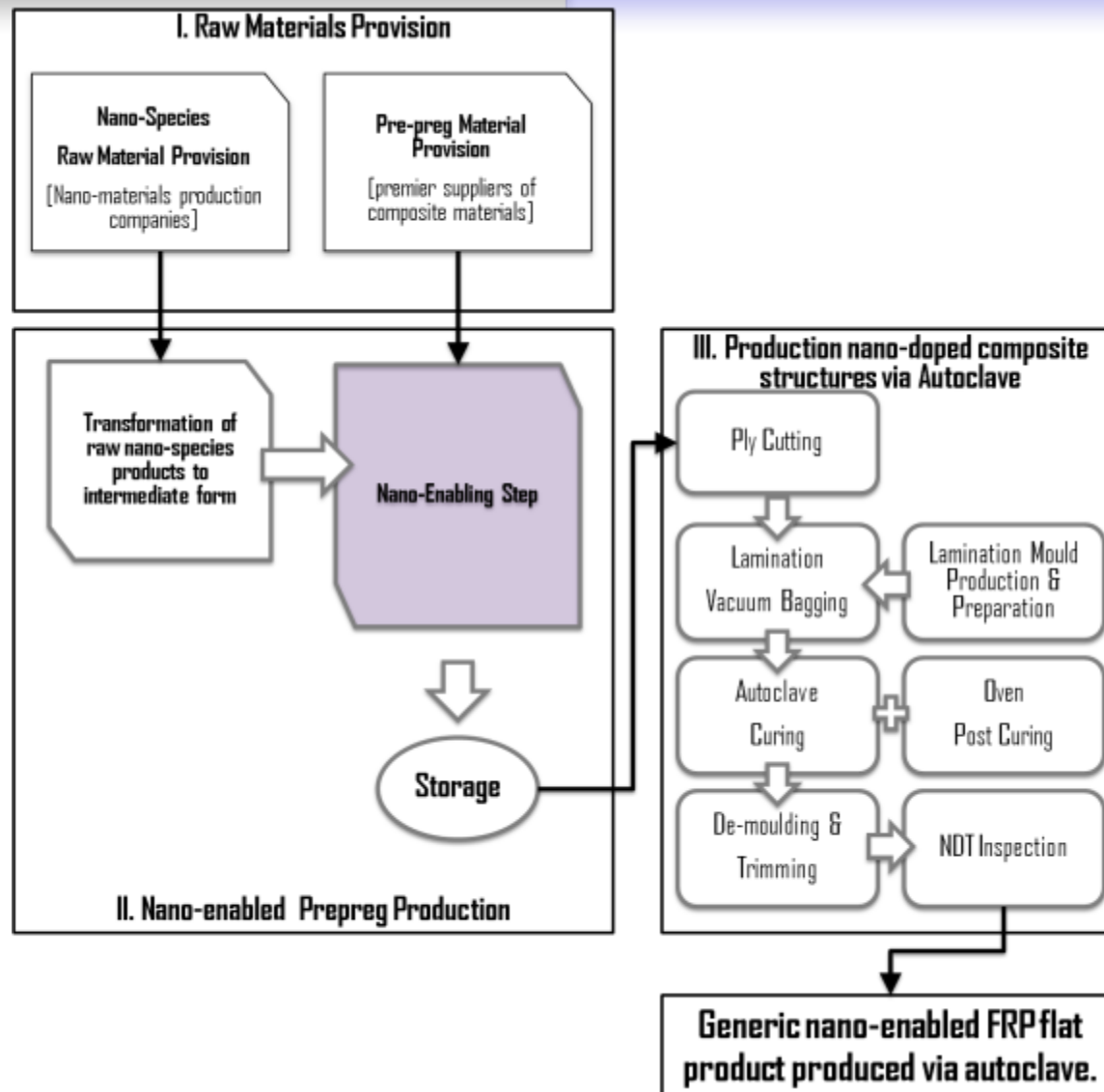


# State-of-the-Art *For Prepreg/Autoclave*

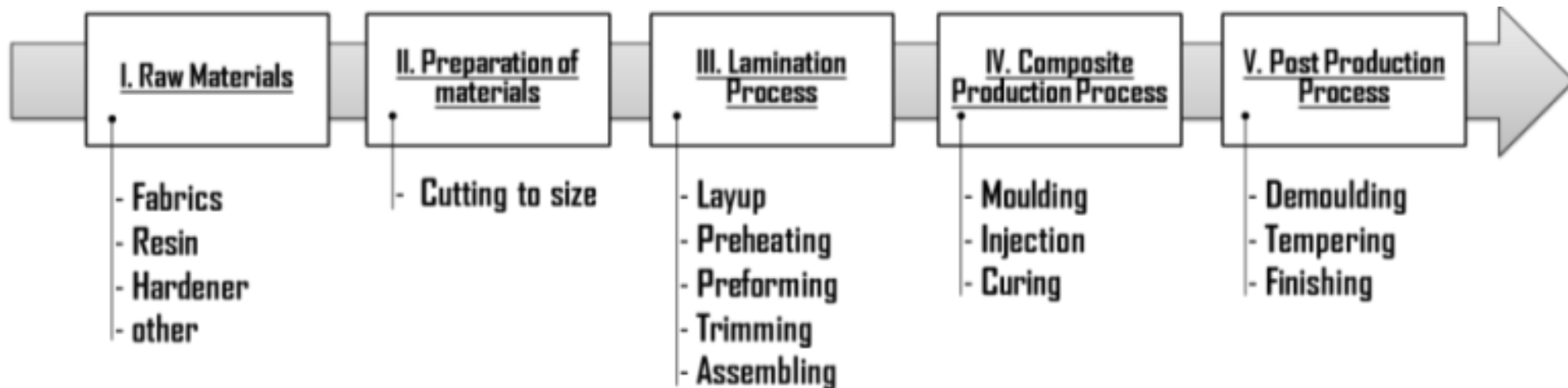
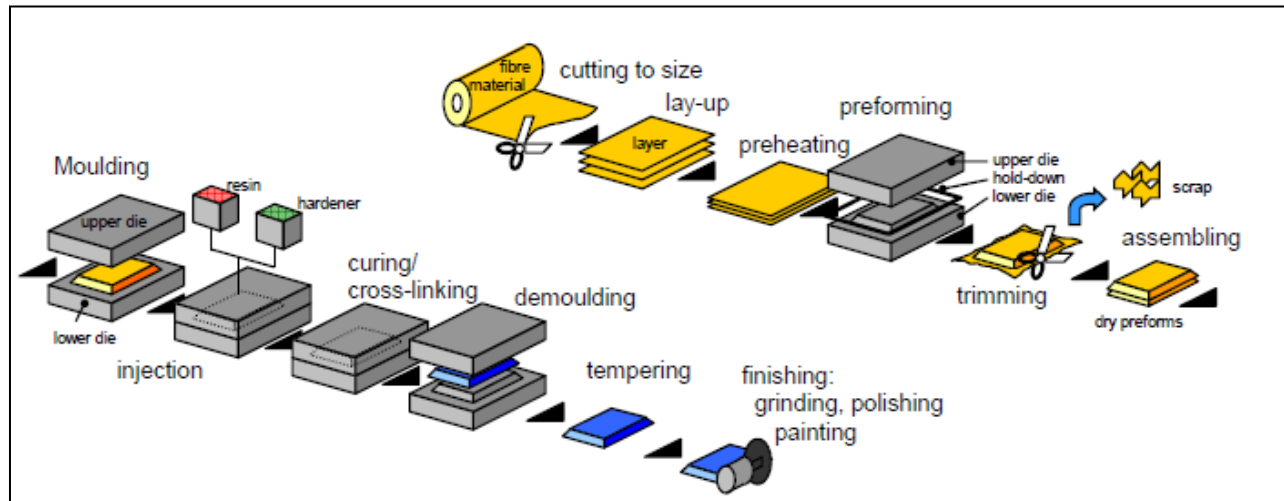
- Prepreg/Autoclave conventional process



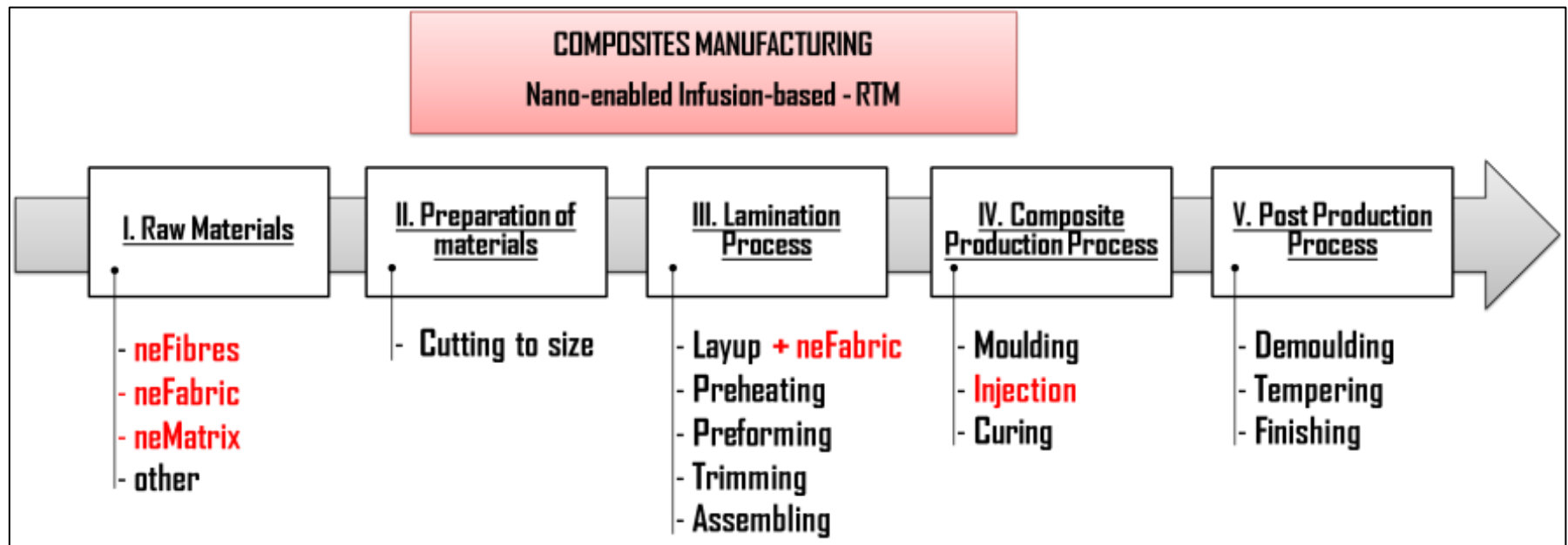
# Beyond the State-of-the-Art *For Prepreg/Autoclave*



# State-of-the-Art *For Resin Transfer Techniques*




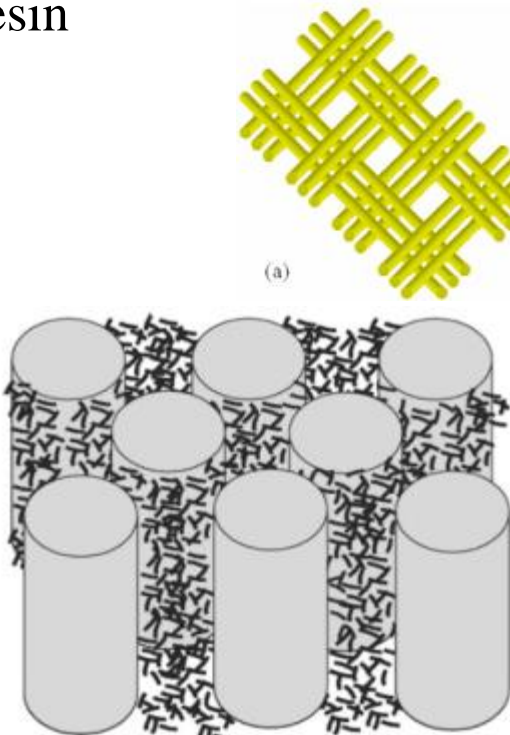
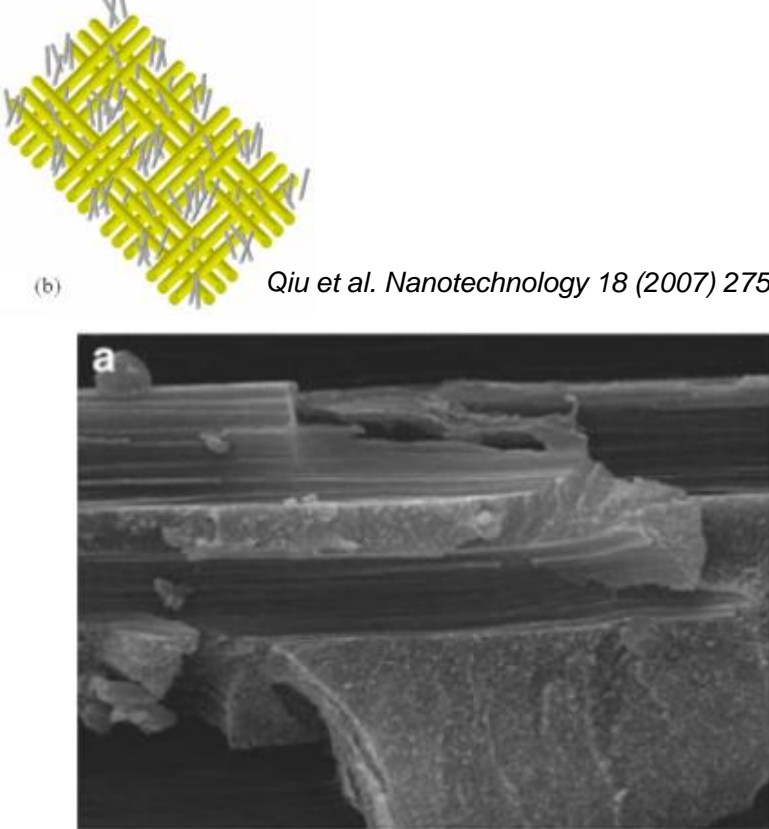
- Nano-Enabled FRPs through Resin Transfer





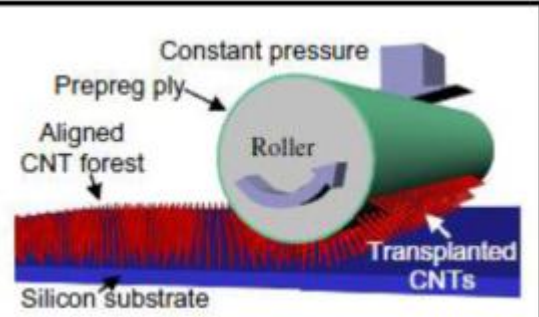
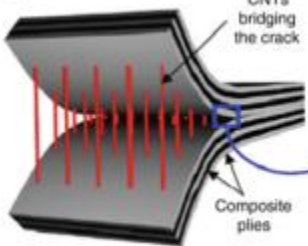
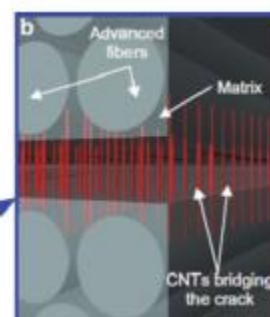
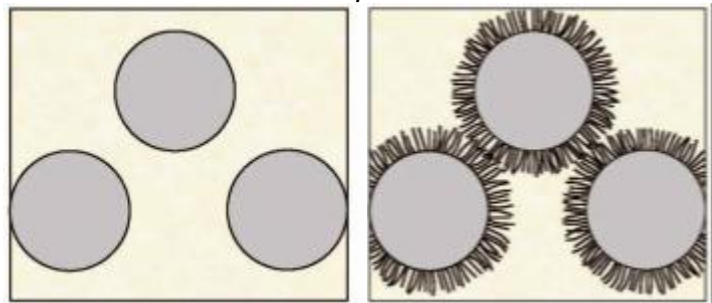
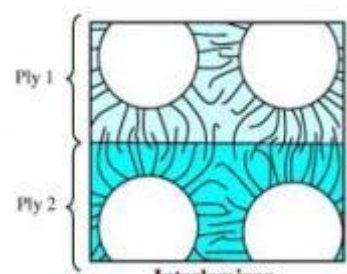
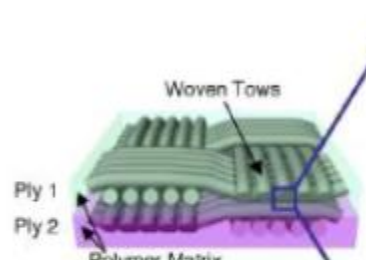
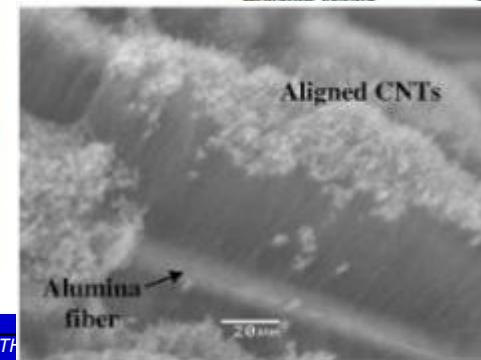
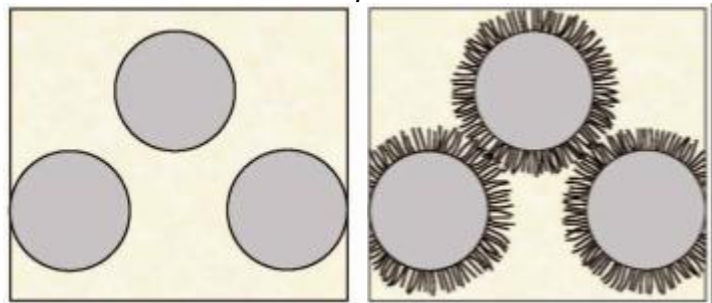
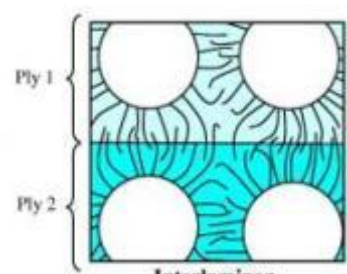
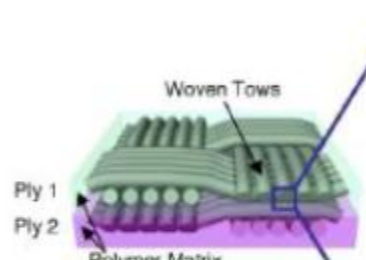
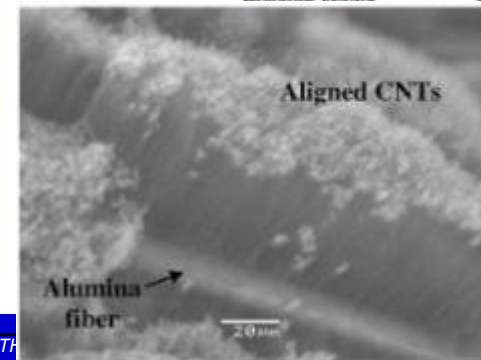
# Approaches for nano-augmentation

## Bulk matrix modification

NANO-AUGMENTING ELEMENT	APPROACH	SCHEMATIC EXPLANATION
<p><b>Matrix</b></p>  <p><i>Vlasveld et al. Polymer 46(23), 10269–10278 (2005)</i></p>	<p>Nano-doped resin</p> 	<p>Preferential orientation through thickness</p>  <p><i>Qiu et al. Nanotechnology 18 (2007) 275708</i></p> <p>25kV - x5000</p> <p>7 μm</p>


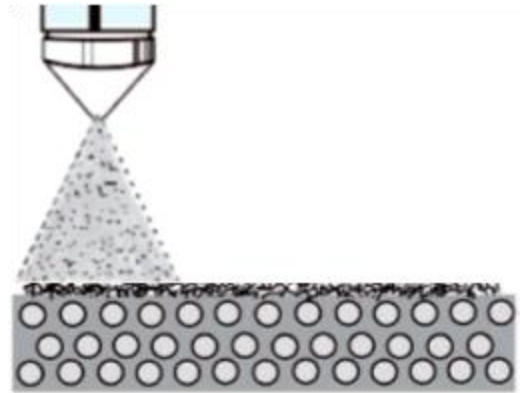
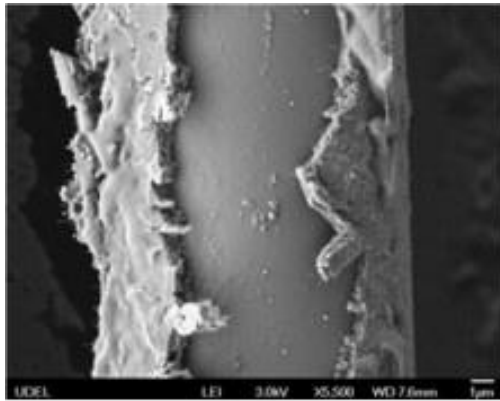
# Approaches for nano-augmentation

## Targeted growth of CNT


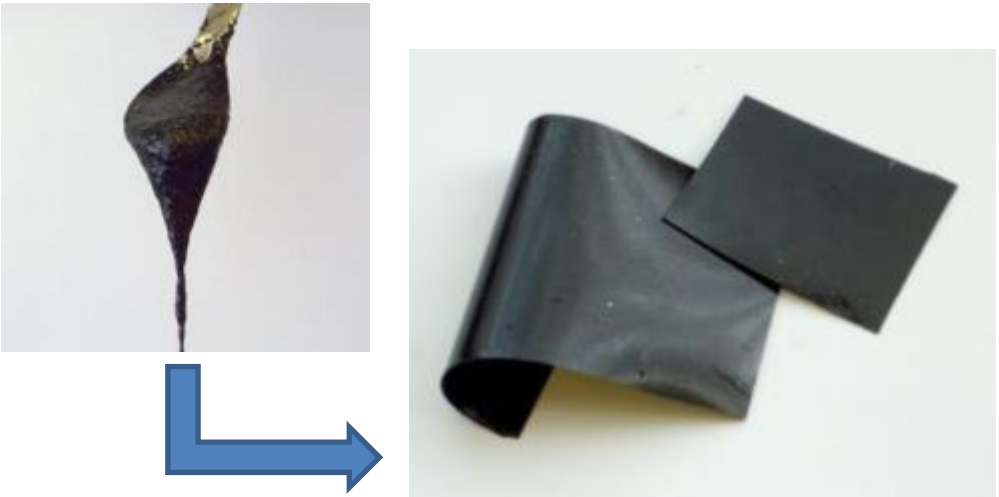
NANO-AUGMENTING ELEMENT	APPROACH	SCHEMATIC EXPLANATION
<p><b>Fabric</b></p> <p>Nano-doped fabric, Nano-reinforcement grown on fabric, Transplanted</p>    <p><i>Garcia et al. Compos. Part A: Appl. Sci. Manuf. 39(6), 1065–1070 (2008).</i></p>	<p><i>Wicks et al. Composites Science and Technology 70 1 (2010) pp. 20-28.</i></p>    	<p><i>Wicks et al. Composites Science and Technology 70 1 (2010) pp. 20-28.</i></p>    

# Approaches for nano-augmentation

## *Other techniques*

NANO-AUGMENTING ELEMENT	APPROACH	SCHEMATIC EXPLANATION
<b>Matrix/ Laminate Interlayer</b>	Nano-doped liquid (resin or solvent), Spray coating or Printing	 
<b>Fabric</b>	Nano-doped fibre sizing	

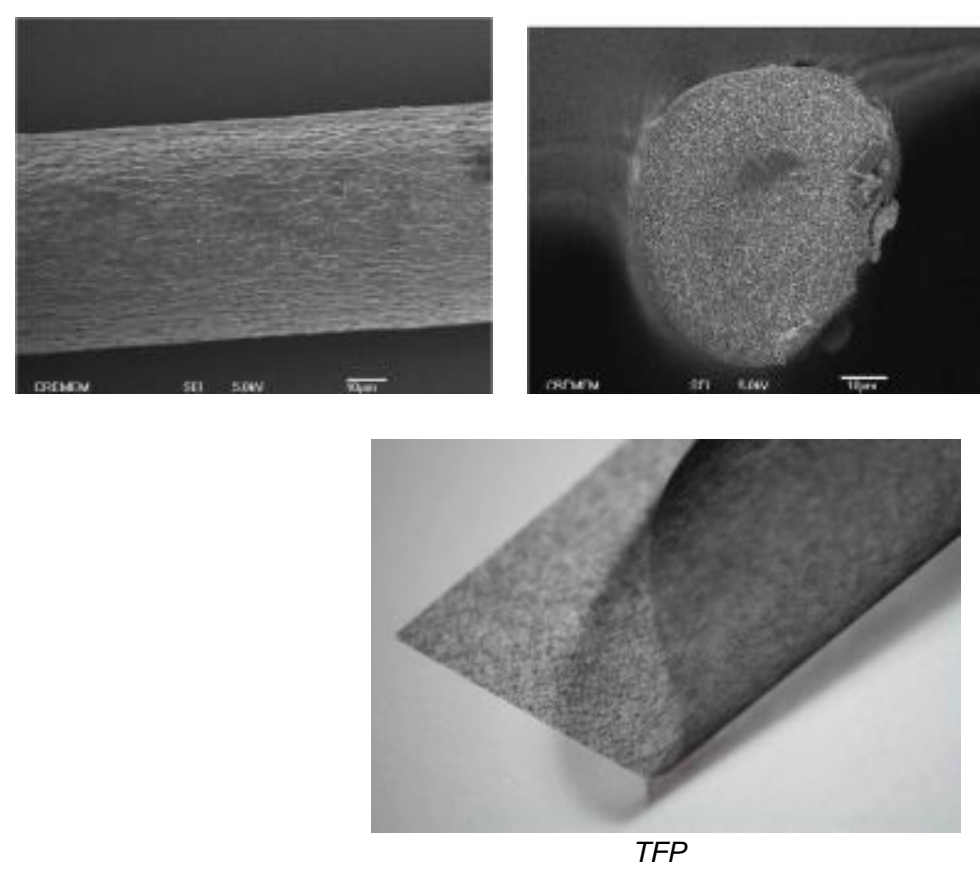
# Approaches for nano-augmentation *Other techniques*

NANO-AUGMENTING ELEMENT	APPROACH	SCHEMATIC EXPLANATION
<b>Matrix/Laminate Interlayer</b>	Nano-filled polymer particles, Dry nano-particles	
<b>Laminate Interlayer</b>	Nano-doped slurry/paste for Filming	

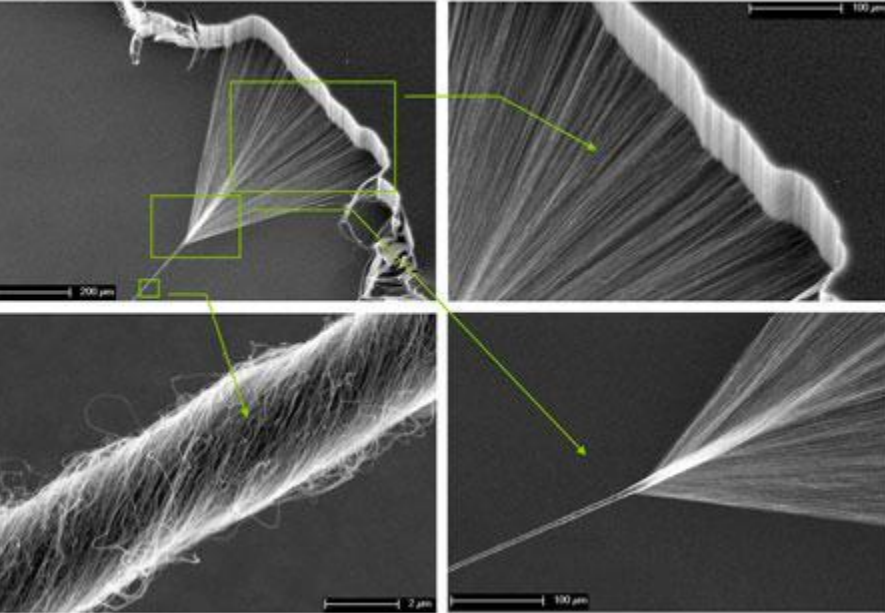


# Approaches for nano-augmentation

## *Nano-augmented fibres*


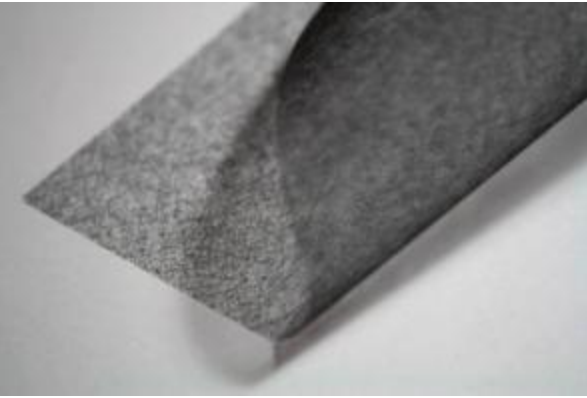

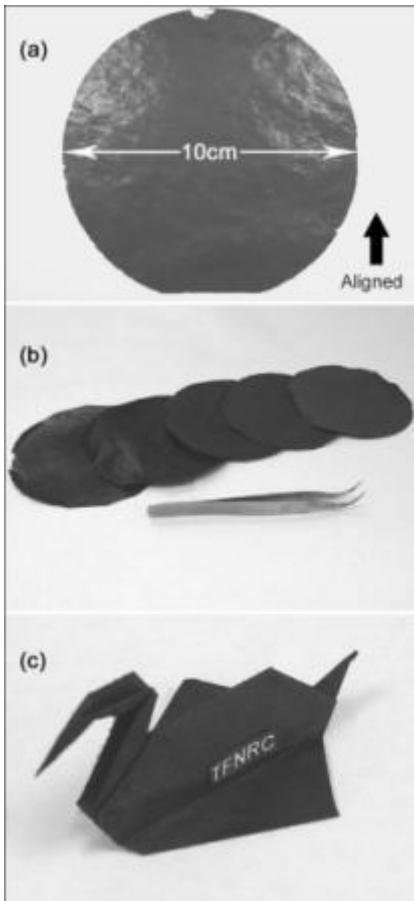
NANO-AUGMENTING ELEMENT	APPROACH	SCHEMATIC EXPLANATION
<b>Laminate Interlayer</b>	Nano-doped polymer fibre in fabric/veil form	 <p>The schematic explanation for the 'Laminate Interlayer' approach includes three images. At the top left is a scanning electron micrograph (SEM) of a single, long, thin fiber with a textured surface, showing a scale bar of 100 μm. To its right is another SEM image of a cross-section of a fiber, revealing a dense, granular internal structure, with a scale bar of 10 μm. Below these is a large SEM image of a fabric or veil form, showing a network of fibers. This image is divided into four quadrants by green lines, with arrows pointing from the top-left quadrant to the other three, indicating a detailed view of the fiber structure. A scale bar of 200 μm is visible in the bottom-left quadrant. At the bottom right is a photograph of a rectangular laminate sample, showing a dark, textured interlayer between two lighter-colored layers, labeled 'TFP'.</p>

Zhang et al. Science, 306 (2004), pp. 1358–1361



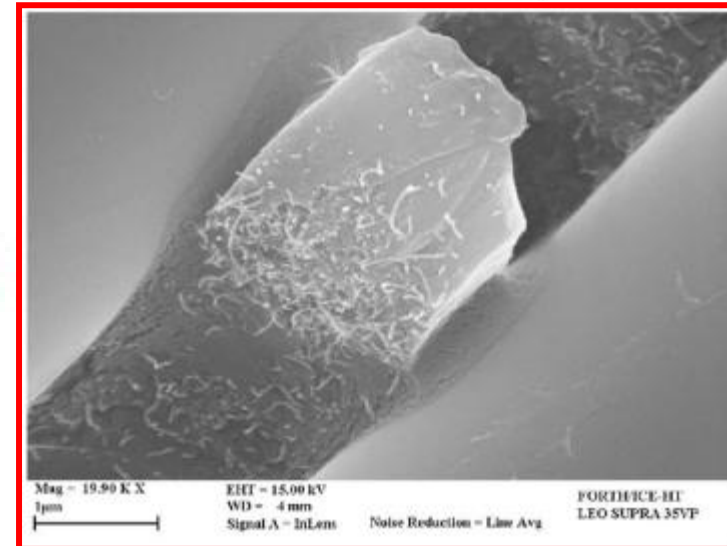
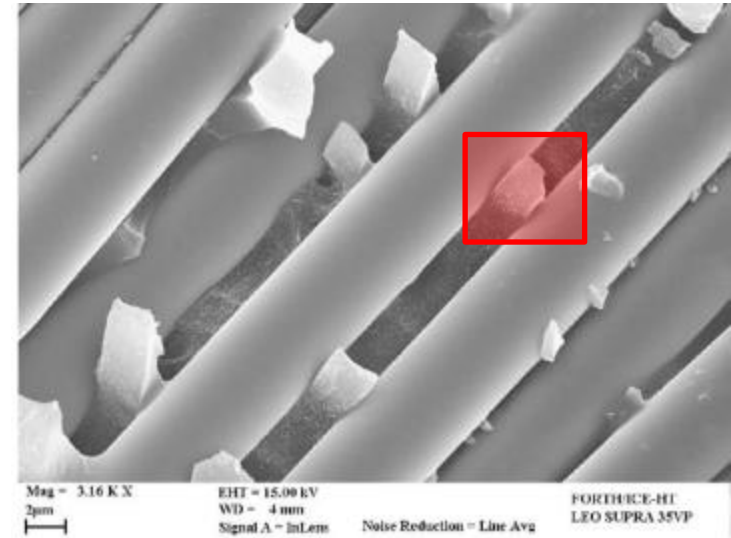
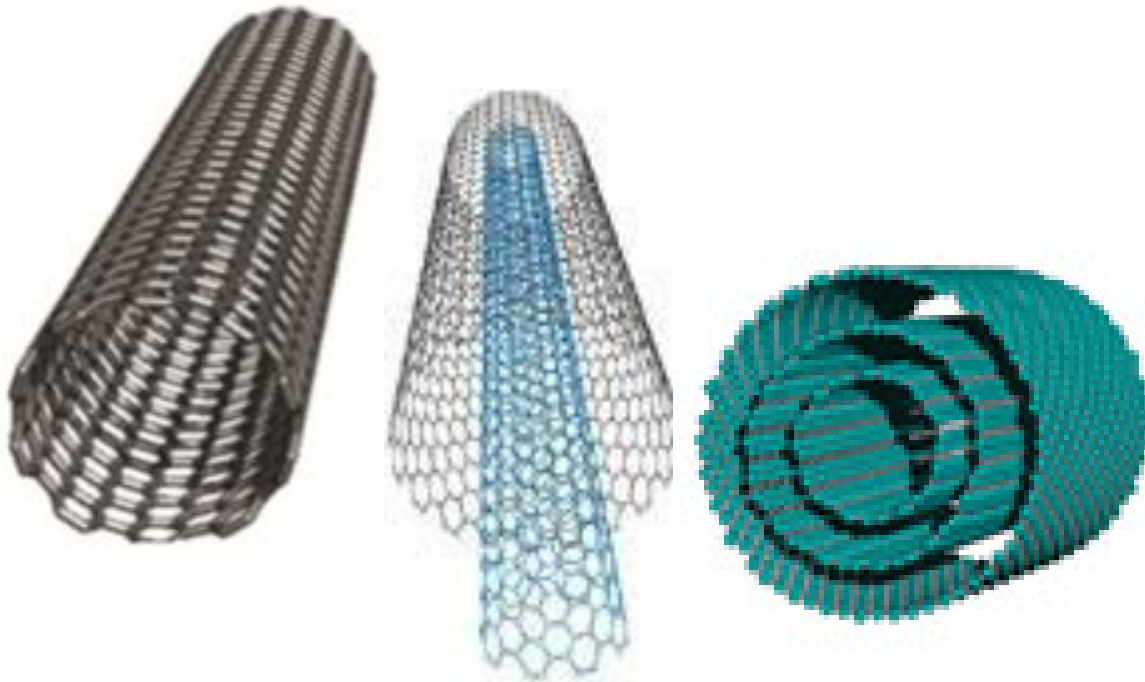
# Approaches for nano-augmentation

## *Nano-augmented fabrics*

NANO-AUGMENTING ELEMENT	APPROACH	SCHEMATIC EXPLANATION
<p data-bbox="86 414 299 578"><b>Fabric / Laminate Interlayer</b></p>  <p data-bbox="338 1313 598 1342"><i>Buckeye composites</i></p>	<p data-bbox="415 414 695 692">3D microstructure/ preform of nano-particles (Buckypaper)</p>  <p data-bbox="1052 821 1120 849"><i>TFP</i></p>  <p data-bbox="908 1313 1207 1342"><i>Florida State University</i></p>	 <p data-bbox="1304 1320 1903 1349"><i>Wang et al. Nanotechnology 2008;19(7):075609</i></p>

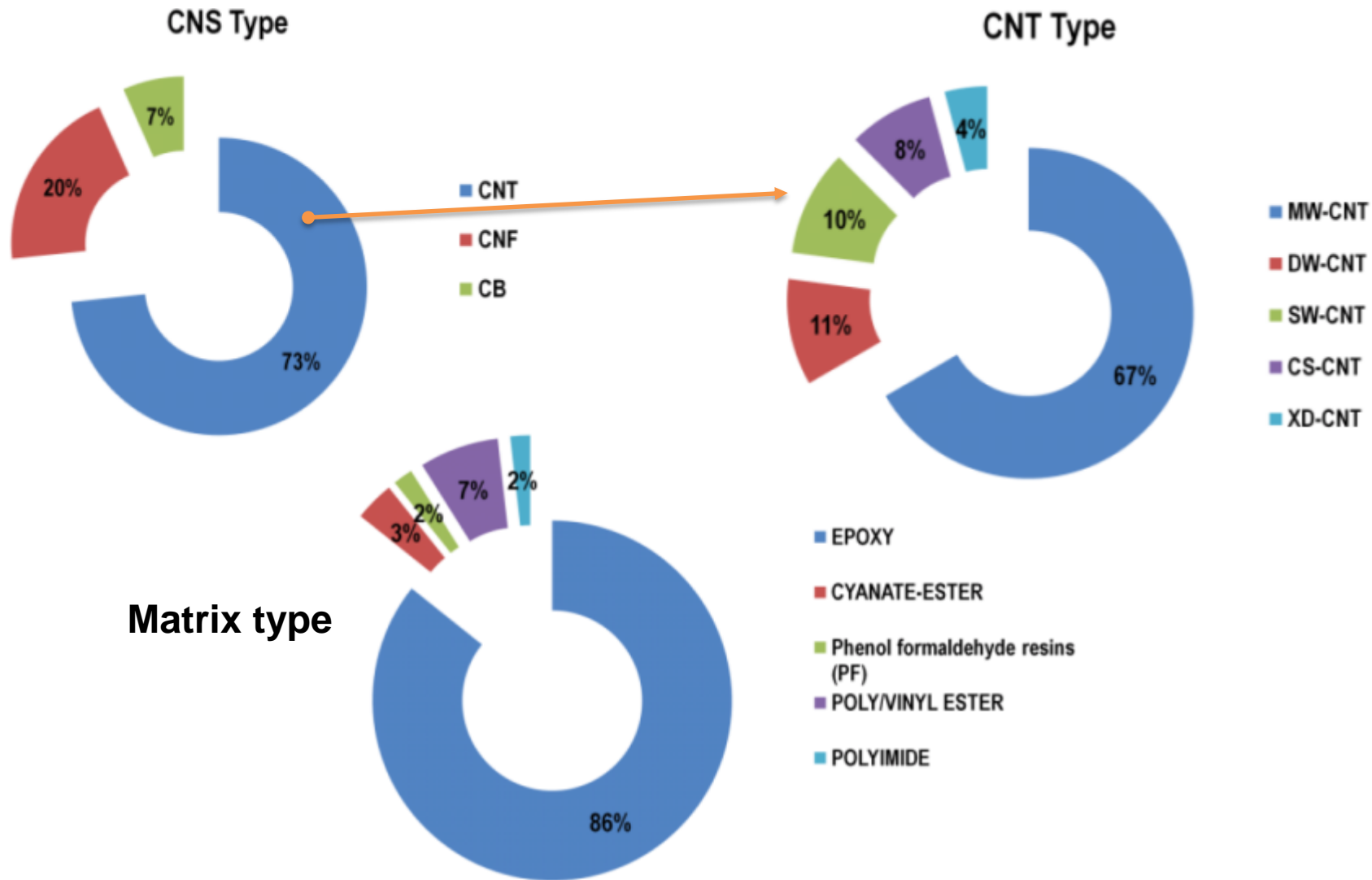
# Scientific Origination

- Carbon Nanotubes
- Other Carbon-based species



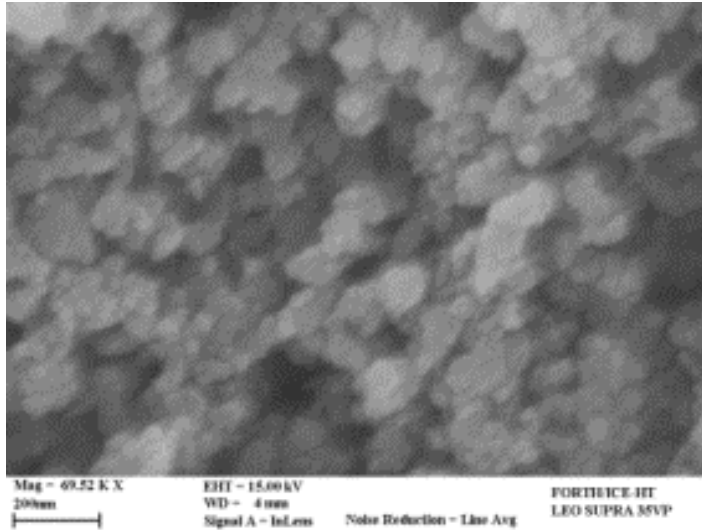


# Former ESA Project *NAREMA* survey

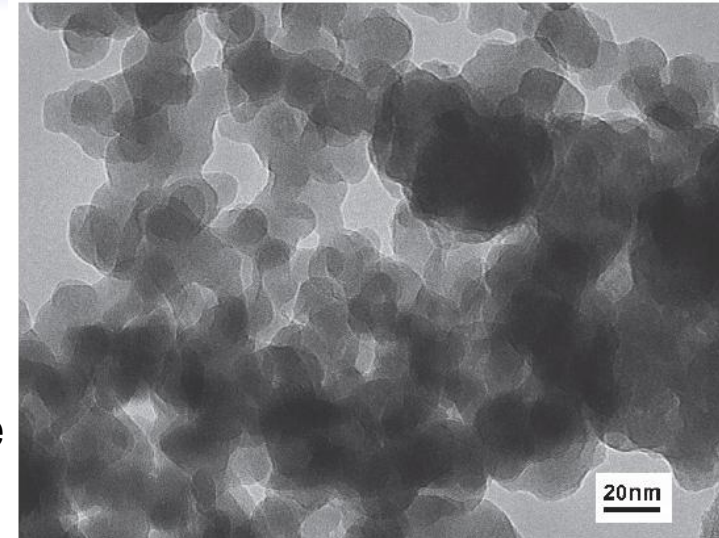


# Extending the nanomaterials palette

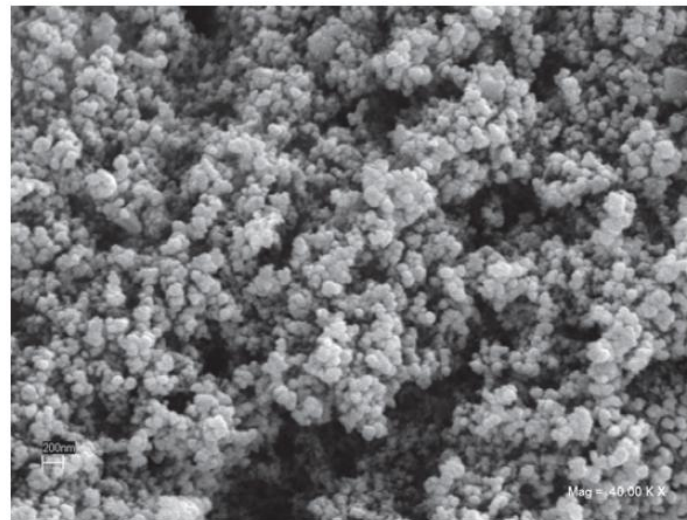
*Towards nano-engineering*



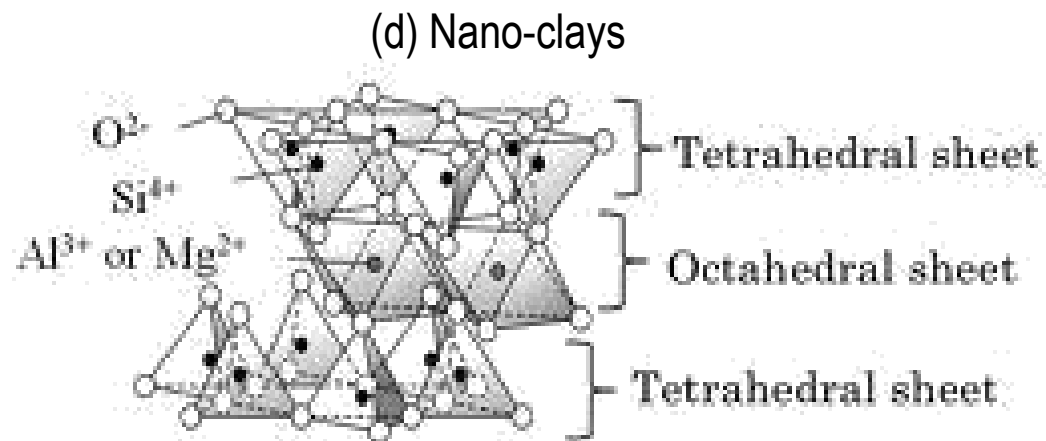
(a) Silicon Carbide



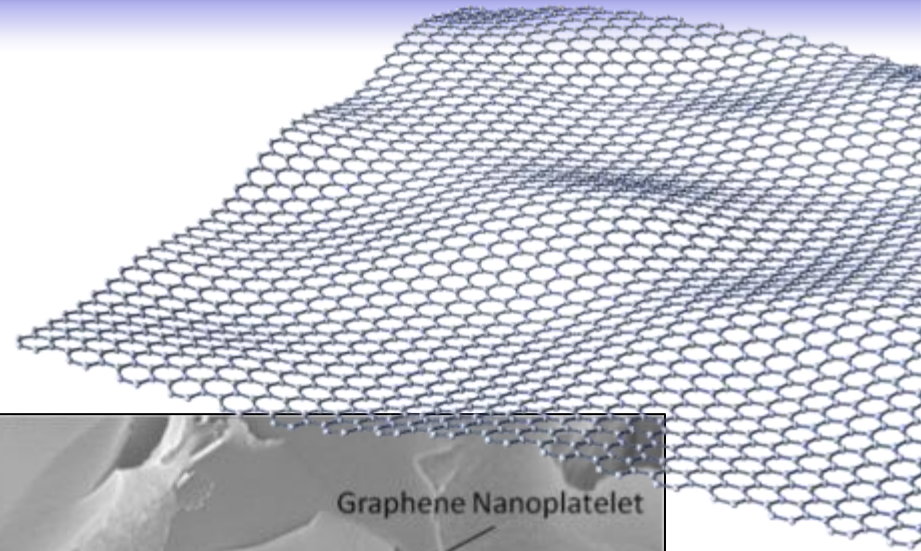
(b) Silicon Oxide



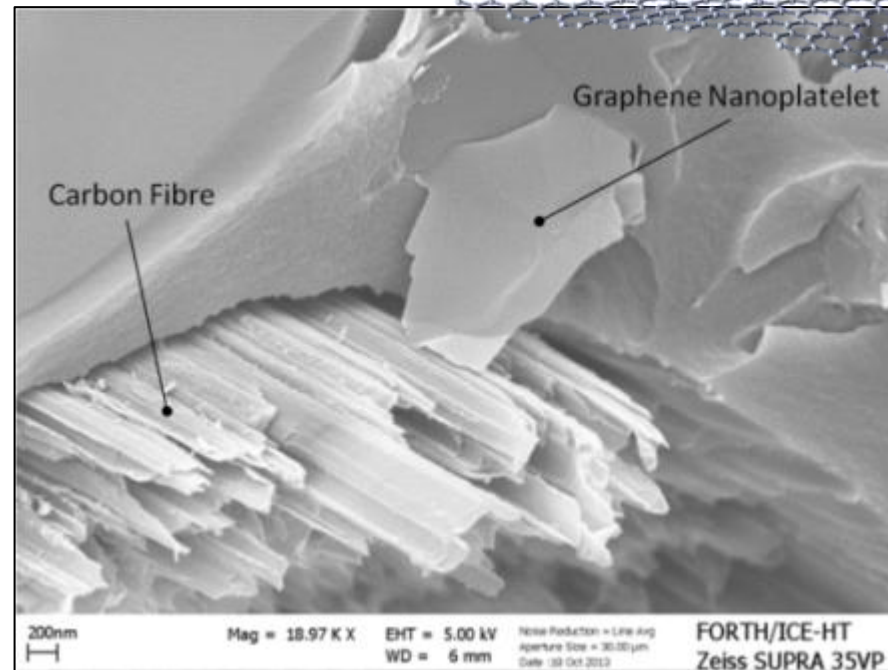
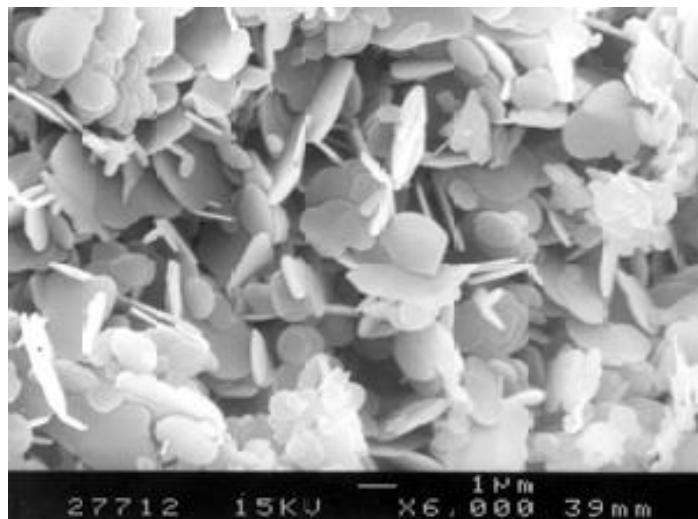
(c) Aluminum Nitride



## Graphene Nano-Platelets (TR-)Graphene Oxide



## Boron Nitride



Courtesy: AML/UoP

# Achieved performance

- Mechanical
  - Increased Fracture and Fatigue resistance
    - e.g. 100%  $G_{ic}$ , 80%  $G_{iic}$
  - Improved damage tolerance
    - e.g. up to 40% CAI
- Electrical
  - Increase in through thickness electrical conductivity
  - Up to 10 [S/m] using CNT
- Thermal
  - Improvement in through thickness conductivity
  - Up to 50% using hybrid nano-formulations



# Products

## *Indicative nano-enabled products for composites*



*Baytubes (Bayer  
Materialscience, D)*



*BuckyShield (Buckeye  
Composites, USA)*



*Raw MWCNT & Epocyl  
(Nanocyl, BE)*



# Implications of nanotechnologies

*For industrial use*

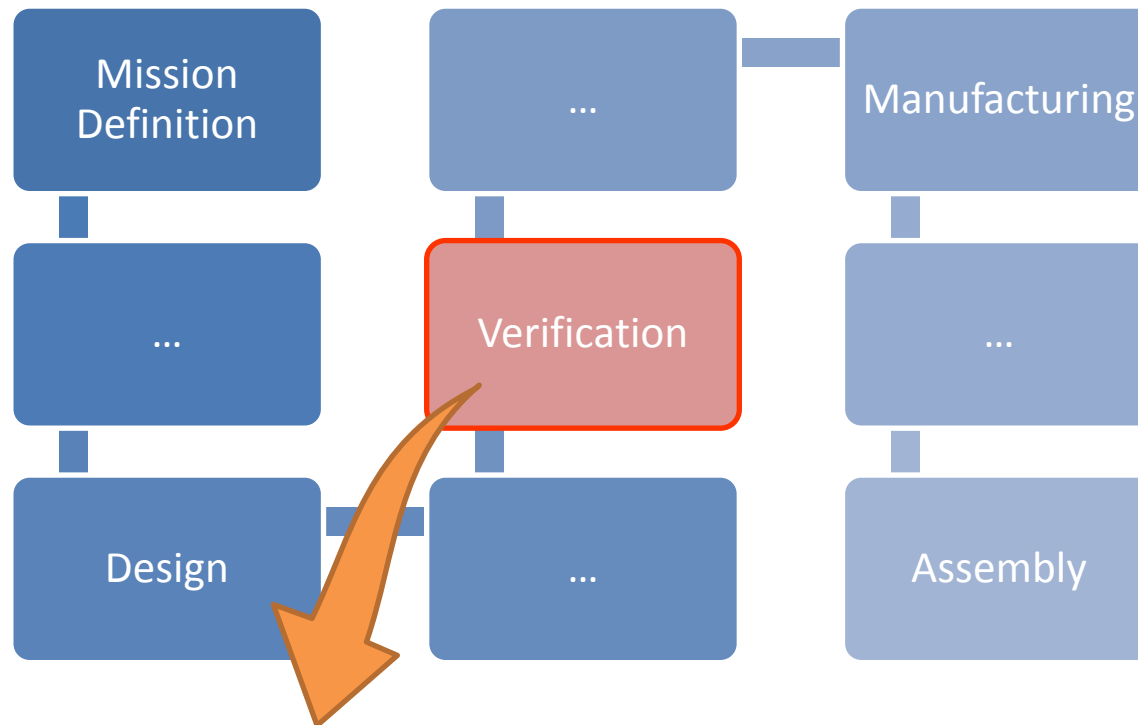
Challenge	Description
<b>Incompatible production scale</b>	<i>The proposed approaches work well at lab scale but investment on new production lines and processes are required to bring these technologies to industrial production.</i>
<b>Compatibility with existing production methods</b>	<i>Many of the proposed technologies require alternations in the supply chain and the production processes or at best special handling conditions</i>
<b>Materials used are very specific</b>	<i>It is very often the case that the results achieved are specific on the materials used and are not transferable to industrially used materials.</i>
<b>Commercial availability and proprietary information</b>	<i>Commercial availability of the materials is limited or restricted for certain products (e.g. resins, fibres).</i>
<b>Quality assurance in industry</b>	<i>Quality assurance measures are not yet defined for such nano-enabling processes and in some cases may violate already established standards.</i>

**Technology adoption drivers:** Performance  
Compatibility

# Why modeling?

## Importance of modelling @NANO-scale

- The road to the launch



Modeling

*"If you cannot model it, you can't fly it"*



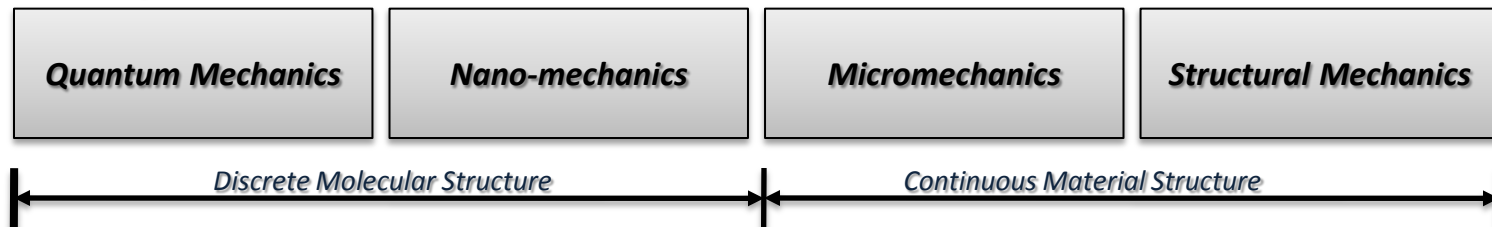
- Based on physical and chemical principles, predict material properties
- Understand trends and capabilities of materials
- To predict the performance of the materials under service conditions
- To design materials according to application needs

# Nano-modeling capabilities *Available approaches*

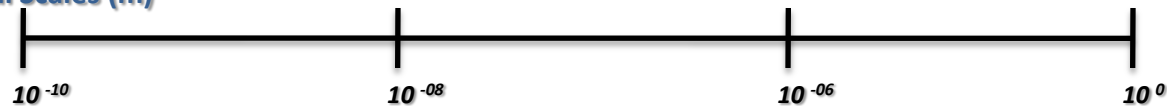
## Modeling Methods



## Modeling Tools



## Spatial Scales (m)

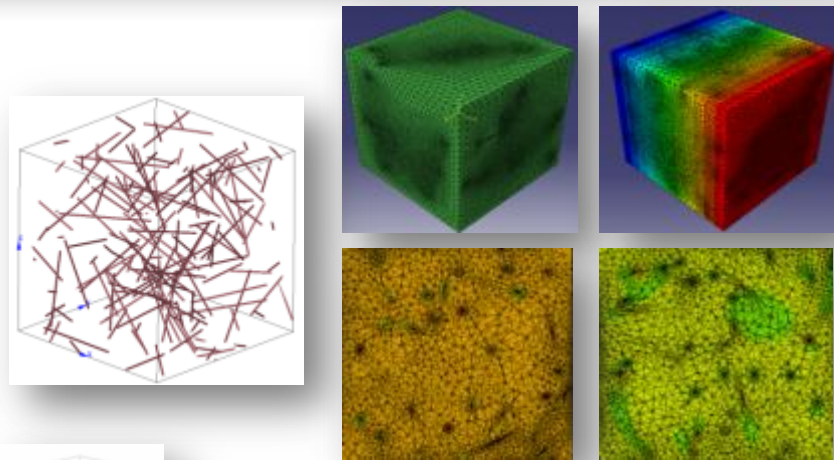


## Time Scales (sec)

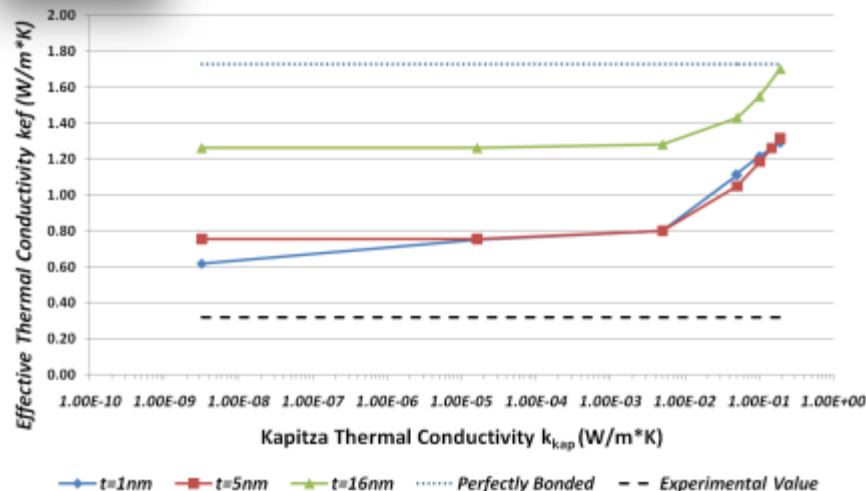


# Nano-modeling capabilities

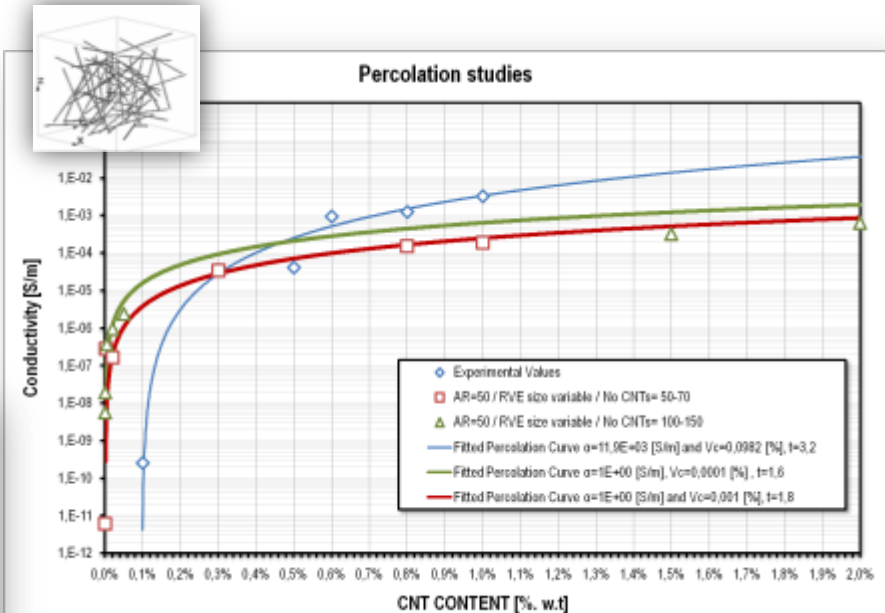
## Electrical and Thermal properties



Interphase's Kapitza Conductivity  $k_{kap}$  & Thickness  $t_{int}$  Influence  
1% CNTs Content CNTs Content

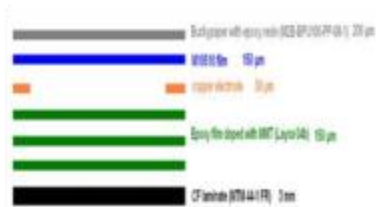


Percolation studies



# Nano-modeling capabilities *Multi-physics problems*

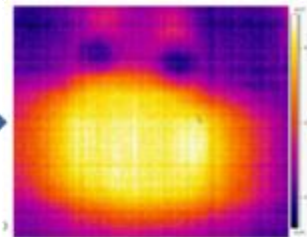
## Experiment



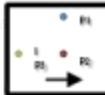
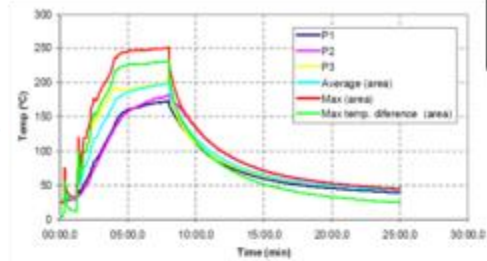
Experimental Layer Set Up



Application of Electrical Power  $P_e$  At RT



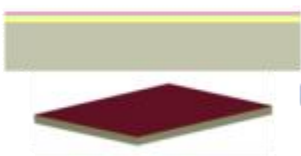
Heat of Top Specimen Surface due to Joule Phenomenon



## 1<sup>st</sup> Modelling Approach

## FEA Model

... LAYER 1\_BP/EPOXY \_Electro-Thermal Conductive  
... LAYER 2\_MY 0510 FILM \_Electrical & Thermal Insulator  
... LAYER 3\_EPOXY/MNT \_Electrical & Thermal Insulator  
... LAYER 4\_CF LAMINATE



Computational Layer Set Up

### Material Model Variables

$\rho, \sigma, k, c_p, \eta, \text{hair}$

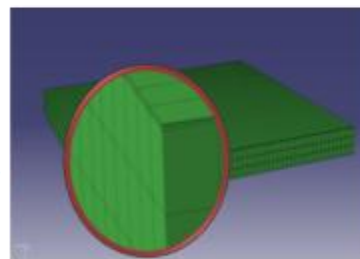
Where:

$\sigma \rightarrow$  derived by the NrPM\_RVE

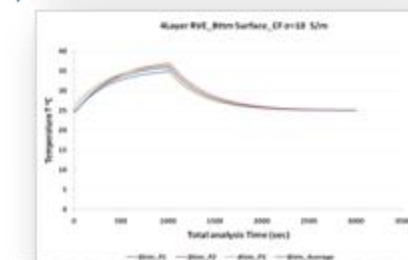
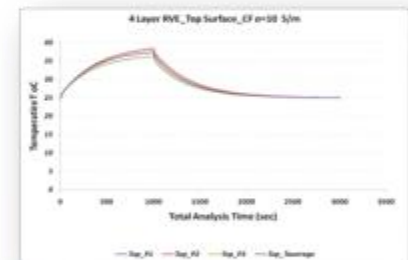
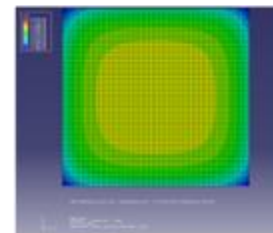
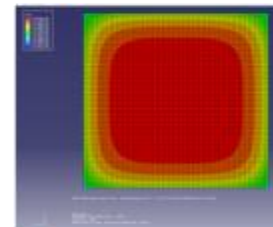
developed for the Electrical Analysis

$k, c_p \rightarrow$  derived by the NrPM\_RVE

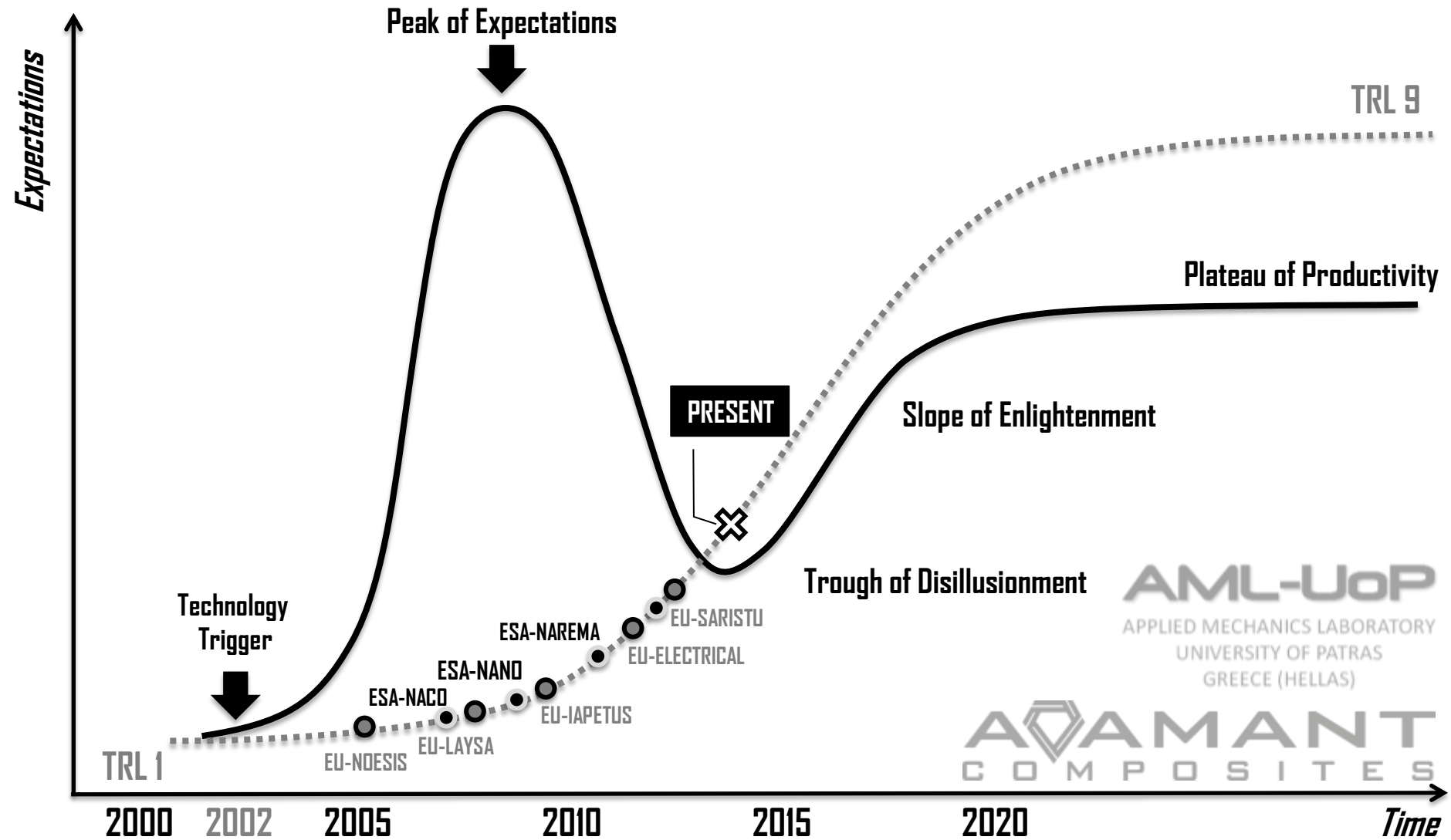
developed for the Thermal Analysis



Application of Electrical Power  $P_e$  At RT



# Estimation of TRL *NANO-ENABLED COMPOSITES HYPE*

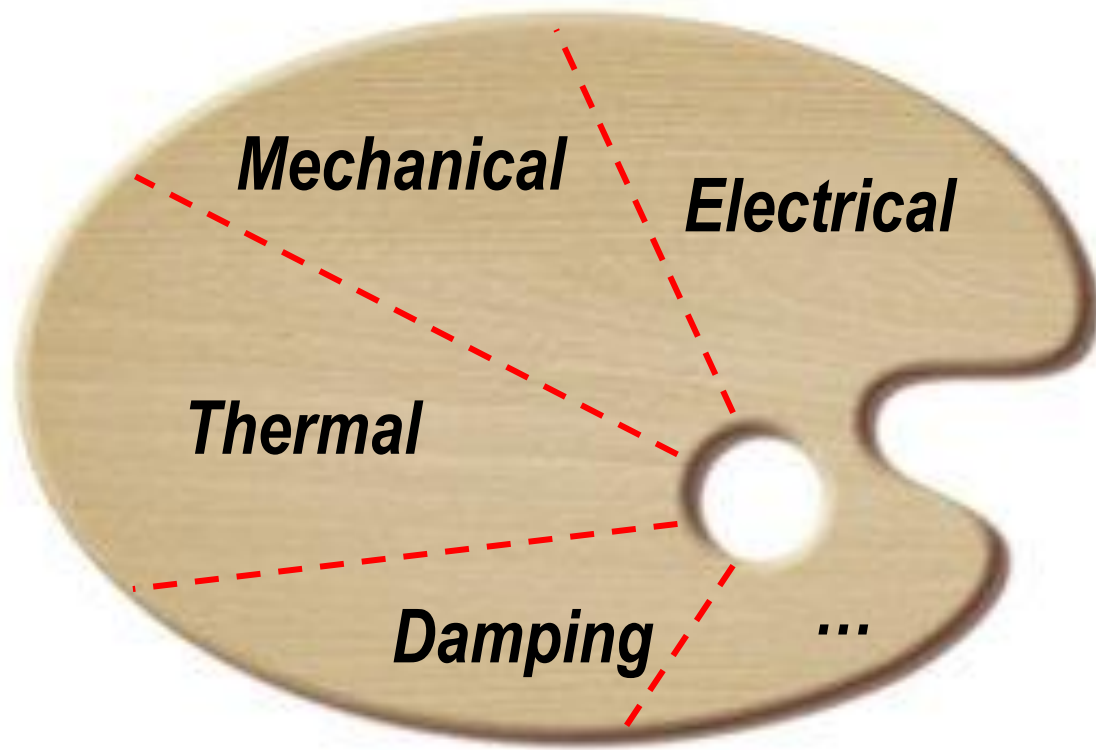


- Targets to be achieved still remain:
  - Enable passive multifunctional utilization
    - Thermal conductivity
    - Electrical conductivity
    - EM compatibility
  - Reduce mass and improve strength
- “Made to Measure” materials



***Made-To-  
Measure  
Philosophy***

# Nano-materials palette *For nano-enabled composites*

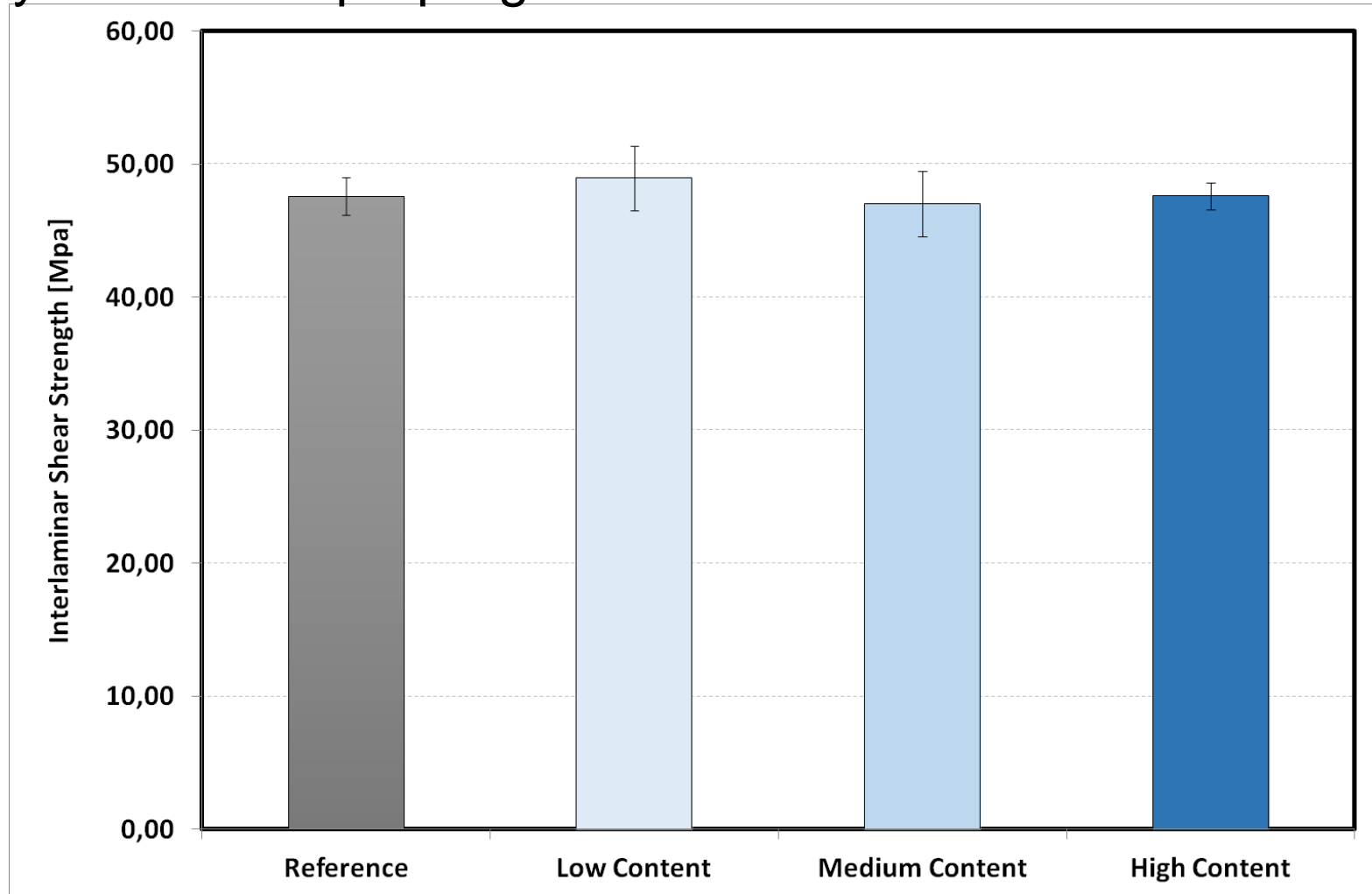




- Applicable to already commercial prepregs
- Develop a suitable nano-formulation
- Introduce the nano-formulation into the material
- Calibration trials for composite processing
- Evaluation of the produced composite's performance
- Given the requirements (input) we develop the nano-formulation and run the evaluation process

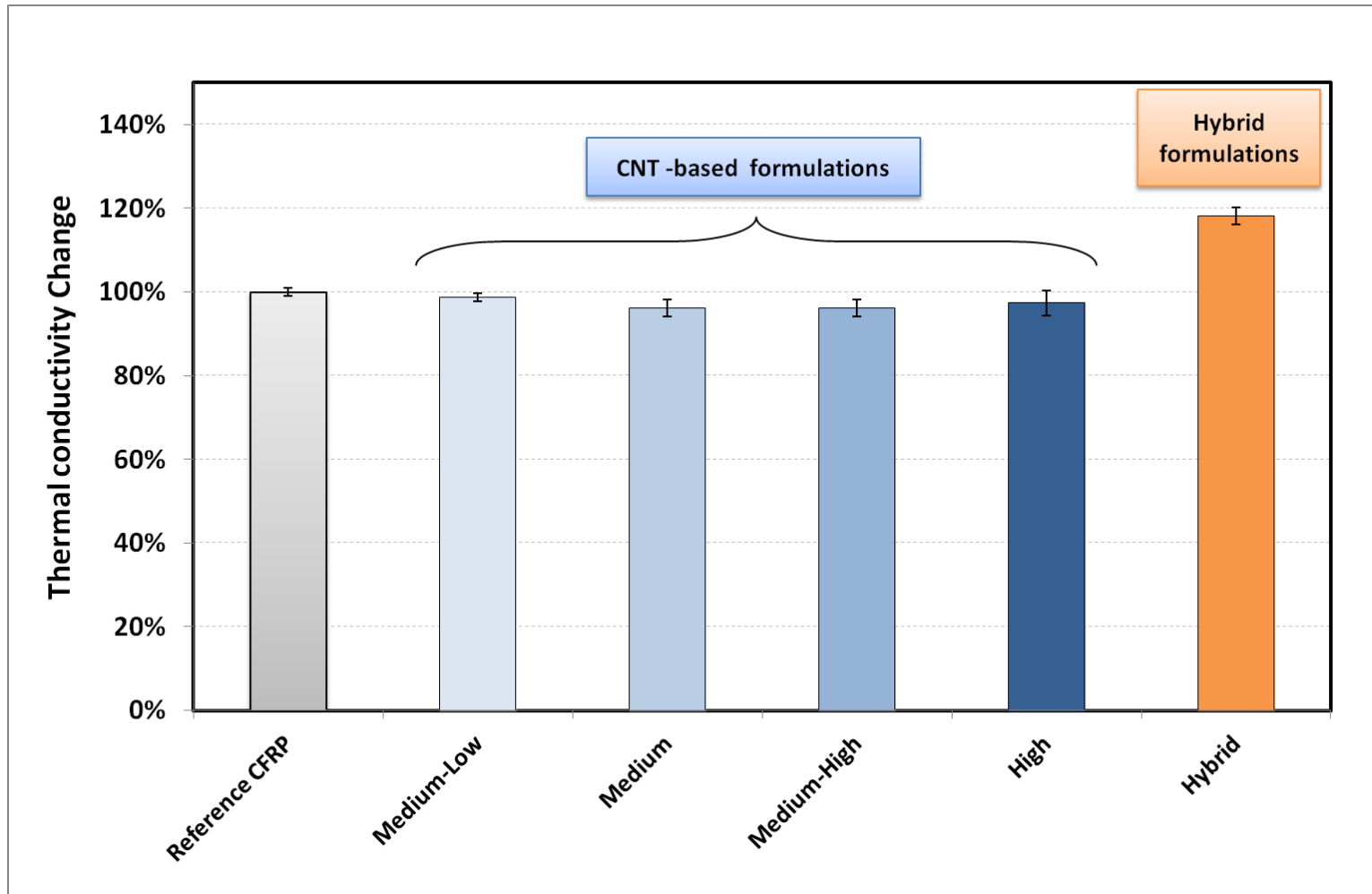
# Achieved performance *Mechanical*

## Cyanate ester prepreg with CNT formulations



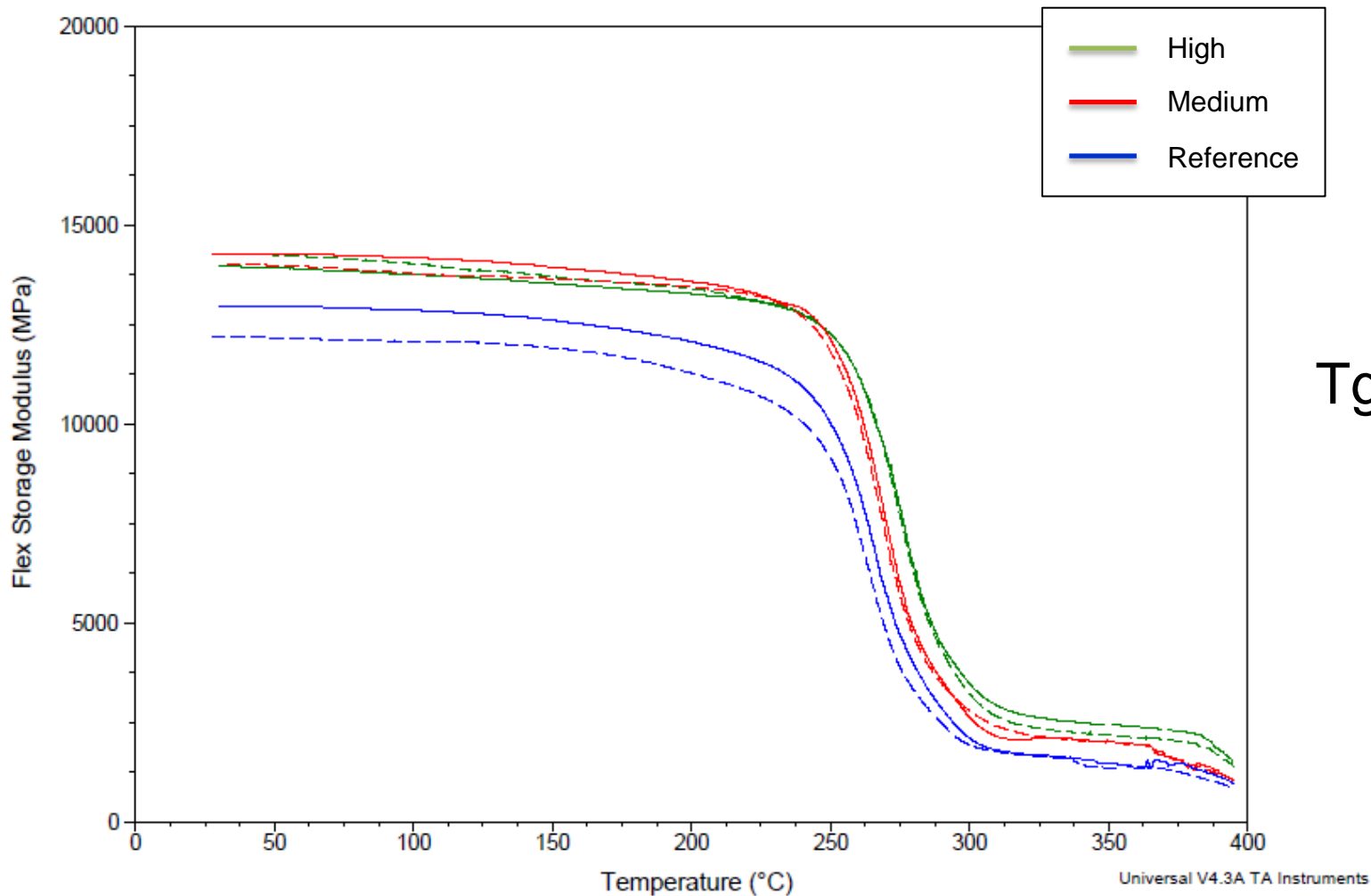
# Achieved performance *Thermal conductivity*

## Cyanate ester prepreg with CNT and Hybrid formulations



# Achieved performance *Dynamic Mechanical Analysis*

## Cyanate ester prepreg with CNT formulations



$T_g > 220^\circ\text{C}$

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# References

1. Mahrholz et al. (2005). *FIBRE-REINFORCED NANOCOMPOSITES FOR SPACECRAFT STRUCTURES*, European Conference on Spacecraft Structures, ESA/ESTEC, Noordwijk (NL), 10 – 12 May 2005.
2. Kostopoulos et al. (2012) *NANOTECHNOLOGIES FOR STRUCTURAL COMPOSITE MATERIALS* Review of latest research developments and open challenges towards application, 8th ESA Micro-Nanotechnology Round Table, ESA/ESTEC, Noordwijk, The Netherlands, 15-18 October 2012.
3. Kostopoulos et al. (2008) *On the use of Resistivity Measurements for Damage Detection of CNT doped CFRPs*, *Journal of Intelligent Materials Structures & Systems* DOI: 10.1177/1045389X08099993
4. Qian et al. (2010) *Carbon nanotube-based hierarchical composites: a review*. *J. Mater. Chem.*, 20, 4751-4762
5. Perreira et al. (2010) *Characterization of carbon nanotube 3D-structures infused with low viscosity epoxy resin system*. *Composite Structures*; 92(9):2252–2257
6. Baltopoulos et al. (2010) *Development of Hybrid Buckypaper (HBP) Structures and multi-functional assessment of composites incorporating HBP*. 14th European Conference on Composite Materials, Budapest, Hungary, 7-10 June 2010.
7. Gao et al. (2010). *Highly conductive polymer composites based on controlled agglomeration of carbon nanotubes*, *Carbon*. Volume 48, Issue 9, Pages 2649–2651
8. Garcia et al. (2008) *Fabrication and multifunctional properties of a hybrid laminate with aligned carbon nanotubes grown In Situ*. *Composites Science and Technology*. Volume 68, Issue 9, Pages 2034–2041
9. <http://www.cnanotechnology.com/en/>, <http://www.arkema.com>, <http://www.microphase.jp/>, <http://www.nabond.com/>, <http://www.nanotechlabs.com/>
10. Poulin et al. (2002) *Films and fibers of oriented single wall nanotubes*. *Carbon* 40 1741–1749
11. Sengupta et al. (2011) *A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites* *Progress in Polymer Science (Oxford)*, 36 (5), pp. 638-670
12. Verdejo et al. (2011) *Graphene filled polymer nanocomposites* *Journal of Materials Chemistry*, 21 (10), pp. 3301-3310.
13. Kostagiannakopoulou et al. (2012) *Study on the synergistic effects of graphene/carbon nanotubes polymer nanocomposites* *Proceedings of SPIE - The International Society for Optical Engineering* 8409. doi: 10.1117/12.923336
14. Karapappas et al. (2009) *Enhanced Fracture Properties of Carbon Reinforced Composites by the Addition of Multi-Wall Carbon Nanotubes*. *Journal of Composite Materials*. vol. 43 no. 9 977-985
15. Garcia et al. (2008) *Joining prepreg composite interfaces with aligned carbon nanotubes*. *Composites: Part A*, 39, 1065–1070.
16. Kostopoulos et al. (2010) *Composites Science and Technology. Impact and after-impact properties of carbon fibre reinforced composites enhanced with multi-wall carbon nanotubes*. Volume 70, Issue 4, Pages 553-563
17. Mannov et al. (2013) *Improvement of compressive strength after impact in fibre reinforced polymer composites by matrix modification with thermally reduced graphene oxide*. *Composites Science and Technology*, Volume 87, Pages 36–41
18. Karapappas et al. (2009) *The effect of silicon carbide nanoparticles on the multifunctionality of epoxy polymers and CFRPs*. *Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series*, Vol. 7493, p. 135
19. Srivastava et al. (2010) *Fatigue and fracture toughness of epoxy nanocomposites*. *JOM*, Volume 62, Issue 2, pp 50-57
20. Liu et al. (2005) *Fracture toughness and water uptake of high-performance epoxy/nanoclay nanocomposites*. *Composites Science and Technology*. Volume 65, Issues 15–16, Pages 2364–2373
21. Goiny et al. (2005) *Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites*. *Composites: Part A*, 36, 1525–1535.
22. Vavouliotis et al. (2013) *Development of multi-functional Aerospace Structures using CNT-modified Composite Prepreg Materials*. 8th International Technical Conference & Forum, SAMPE-SETEC 13, September 11th – 12th 2013, Wuppertal, Germany.
23. ESA-NAREMA: *Nanotube Reinforced Structural Materials for Spacecraft Applications. Final Presentation*, May 8th 2012, ESA/ESTEC.
24. Fiamegkou et al. (2014). *Prediction of the effective thermal conductivity of carbon nanotube-reinforced polymer systems*. *Polymer Composites*, In press, DOI: 10.1002/pc.22859.





# **NANOTECHNOLOGIES FOR COMPOSITE STRUCTURES**

## **From Nanocomposites To Multifunctional Nano-Enabled Fibre Reinforced Composites For Spacecrafts**

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